THE CHEMISTRY OF SELECTIVE OXIDATION OF SULFUR COMPOUNDS AND ITS RELATION TO FUEL DESULFURIZATION

Thesis by

Amir Attar

In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1977

(Submitted July 9, 1976)

Dedication

This thesis is dedicated to Ilana, my wife, and to Eyal and Ron, my two sons.

ACKNOWLEDGMENTS

I wish to thank my advisor, Dr. William H. Corcoran, for his support in all the phases of this work.

The financial support of the National Science Foundation is gratefully acknowledged.

The construction of the experimental system would have been impossible without the help of George Griffith, Ray Reed, Chico Nakawatase, Zig Jenner and Eric Siegel.

Different aspects of the experimental work were done by Robert Forgey, Russell Bone, John Horn, Alex Brooks, Paul Goodson, Dale Shultz, Mike Porter and Mike Huster. Their ready help and understanding is greatly appreciated.

Glenn Wood who worked with me many long nights in the computing center deserves special thanks.

I wish to thank Russell Bone, who spent with me hours correcting English mistakes, and Ruth Stratton who typed the thesis. Their help made this work readable.

It was a great pleasure knowing the Caltech community and working with so many nice people.

ABSTRACT

An alternative method to desulfurize fossil fuel is proposed. There are two steps in the method: 1) Selective oxidation of the sulfur compound to the corresponding sulfoxide (I) and sulfone (II),

$$S \xrightarrow{[O]} \underset{I}{SO} \xrightarrow{[O]} \underset{II}{SO_2}$$

2) Pyrolysis of the product to a hydrocarbon and sulfur dioxide,

$$SO_2 \xrightarrow{\Delta} \text{Hydrocarbon} + SO_2$$

The critical step is the selective oxidation of the sulfur compound to I and II. This oxidation was carried out by peroxides that were formed <u>in situ</u> when a hydrocarbon solution of the sulfide was oxidized with molecular oxygen in the presence of a catalyst like HBr, at 140-160°C. Butyl sulfide was used as a model sulfur compound and toluene and Tetralin in bromobenzene were used to simulate the organic medium. The most important results are:

1. In the absence of HBr the oxidation proceeds to the sulfoxide only, but when HBr is present also sulfone is found.
2. HBr increases the rate of oxidation of the hydrocarbon and the reactivity of free radicals. The butyl radical is attacked about 14 times more rapidly in the presence of HBr.
3. Denote:

$$S_{UM} = [\text{sulfoxide}] + [\text{sulfone}]$$

$$\psi_{MPR} = \frac{S_{UM}}{\Sigma(\text{oxidation products of sulfides} \neq \text{sulfoxide, sulfone})}$$

Let the subscript o indicate the absence of catalyst and 1 the presence of catalyst. Then

I $\psi_{MPR_o} > \psi_{MPR_1}$ when $S_{UM} < 10^{-5}$ mole/liter

II ψ_{MPR_o} decreases when S_{UM} increases.

ψ_{MPR_1} increases when S_{UM} increases.

III For a given [HBr], conditions can be found for which $\psi_{MPR_o} = \psi_{MPR_1}$ and $S_{UM_o} = S_{UM_1}$, e.g., when [HBr] = $6.4 \cdot 10^{-4}$ mole/liter $S_{UM_o} = S_{UM_1} = 1.8 \cdot 10^{-3}$ mole/liter, and $\psi_{MPR_o} = \psi_{MPR_1} = 15.5$ is achieved after 65 min. (When [HBr] = 0, 300 min are required to reach the same conditions.)

4. Denote D(R–H) the smallest bond energy from all hydrogens in the system. Then a) the oxidation of the sulfur compounds is less selective the larger D(R–H) is, more products are found and intense oxidation of the butyl radical is observed; b) the oxidation potential of the medium is larger when D(R–H) is larger; c) more hydrocarbon is oxidized when D(R–H) is smaller.

5. When protic solvent is added, e.g., 1-octanol, the selectivity to sulfoxide increases and fewer products of free radical oxidation of the sulfide are found. However, no sulfone was detected when 1-octanol was present. The octanol stabilizes the sulfoxide by hydrogen bonding with an estimated energy of -1.55 kcal/mole.

Table of Contents

List of Tables

List of Figures

LIST OF ABBREVIATIONS

1. A list of the abbreviations of the species names is given in Table 7.1, page 118.
2. A list of the abbreviations of names of the methods of qualitative analysis is given in Table 5.3, page 79.
3. A list of the abbreviations of names of the methods of quantitative analysis is given in Table 5.4, page 81.

Abbreviation	Meaning
BUS	butyl sulfide
CATSC	The chemical system Hydrocarbon-O_2-Catalyst-Sulfur compound.
DBS	dibutyl sulfide
DBT	dibenzothiophene
D(R–H)	The smallest bond energy of all the carbon-hydrogen bonds of a molecule.
EXP	experiment
FG	functional group
FGD	functional group's distribution
FR	free radicals
HA	hydrogen abstraction, except for Chapter 3, where it denotes a protic molecule.
MO	molecular oxygen
NOCAT	the system Hydrocarbon-Oxygen-Sulfur compound
NOSC	the system Hydrocarbon-Oxygen-HBr
OCTOL	1-octanol
SC	sulfur compound
TRLN	Tetralin

Nomenclature

Symbol	Meaning
A	frequency factor
$C_{e\ HBr}$	equilibrium concentration of HBr
$C_{e\ O_2}$	equilibrium concentration of O_2
c_i	concentration of the i^{th} component
$\bar{c}_j$	concentration of the j^{th} functional group
c_o	initial concentration
D	diffusivity
D_{O_2}	diffusivity of oxygen
E	activation energy
H	enthalpy of formation
H_i	enthalpy of formation of the i^{th} molecule
H_R	enthalpy of reaction
H_S	enthalpy of formation of the system per unit volume
M	molecular weight
M_S	ratio of rate of mass transfer from the gas to the rate of fastest reaction.
P	concentrations of oxidizers
P_j	partial pressure of component j
R	gas constant
$S^{\dagger}$	entropy of formation of activated complex
$[S]_{per}$	concentration of sulfur compounds that were oxidized by a peroxide molecule
$[S]_{oxidized}$	total concentration of oxidized sulfur compound

T	absolute temperature
V	volume of reaction, except in Eq. 5.3 where it means the specific volume of the solvent
W_o	total rate of initiation
x	association factor
h_j	enthalpy of formation of the j^{th} group
k	reaction rate constant
k_c	overall rate of oxidation of sulfide
k_f	overall rate of oxidation of sulfoxide
k_{io}	frequency factor of the i^{th} reaction
k_e	mass transfer coefficient
m	number of functional groups in the system
n_{ji}	number of times that the j^{th} functional group appears in the i^{th} component
t	time
$t_{0.99}$	the time that is required to achieve 99% of the equilibrium value of a concentration
α	coefficient of proportion in Polayni equation, $E = \alpha\Delta H$
μ	viscosity
ρ	density

Notes

1. Δ denotes difference
2. ΔH_B, ΔH_H, and ΔH_o are defined on p. 182
3. ψ denotes selectivity. All selectivities are defined on pp. 163 and 165.
4. $\sim$ under a variable denotes a vector.

Chapter 1

INTRODUCTION

Desulfurization of fossil fuels has become a major issue in the world's economics and politics. It is not surprising, therefore, that many investigators are currently examining the technology and science of desulfurization.

One of the major contributors to the problem known as the "energy crisis" is the lack of desulfurization technology. Because of air pollution regulations and the lack in the United States of low-sulfur fuel, the huge U.S. energy market looked for other sources of fuel abroad. However, high sulfur fuel in the form of coal does exist in the United States and it would be possible to use it, if it could be desulfurized first.

The function of science and technology is to provide a process which will convert high-sulfur fuel into a clean energy source.

The task of desulfurizing fuel is different in many ways from the classic problems the chemical industry has faced, for example, the scale of the problem and of its solution. No desulfurization process should be considered before the impact of its nationwide use on the steel and transportation industries is studied. The energy-efficiency of a process, i.e., how much of the input energy will be lost in order to achieve desulfurization, is important, as is the disposal of the refuse. The above-mentioned technological questions are still without solutions.

One way to approach desulfurization is presented here, as well as exploratory experiments on one special system.

1.1 Desulfurization by Selective Oxidation*

Current desulfurization processes can be classified into two categories: 1) processes for the desulfurization of gaseous combustion products; and 2) processes for the desulfurization of dense fuel prior to combustion.

Many processes have been proposed for desulfurization of gaseous combustion products; however, in the mind of the author, gas-phase desulfurization cannot be more than a temporary solution. The concentration of SO_2 in the combustion products is small, and the resistance to SO_2 mass transfer is in the gas phase. The particular solution or solid used to scrub it is of secondary importance only. The penalty for gas-phase desulfurization is paid in the form of large capital investments in huge processing units and in large operation costs. The only method practiced commercially to desulfurize liquid fuel prior to combustion is hydrodesulfurization.

Hydrodesulfurization of fuels is widely practiced and much literature is available on the process (H-10, S-5, S-7, M-5). Work is currently done on hydrodesulfurization by many research groups. However, the basic facts about hydrodesulfurization have remained unchanged in the last forty years:

---

*Different aspects of desulfurization were reviewed by the author in previous reports and therefore will not be detailed here. The industrial processes for hydrodesulfurization of oil were reviewed in 1972(A-1). A comparison of desulfurization by hydrogenation and by selective oxidation was made in 1973 (A-2, A-6). The area of organic sulfur compounds in coal was reviewed in 1976 (A-3).

1. Hydrodesulfurization is a process which needs hydrogen. The only large-scale commercial process to obtain H_2 is from fossil fuels, and its cost is continuously on the rise.
2. Hydrodesulfurization needs high pressures and temperatures, and therefore ties up large amounts of capital in huge processing equipment.
3. Many peripheral processes are required which add to the cost of hydrodesulfurization and reduce its energy efficiency.
4. The selectivity of hydrodesulfurization is poor when thiophenes are desulfurized. High pressures and temperatures are required and considerable amount of H_2 is used to saturate aromatics.

In Figure 1.1 the scheme of a general hydrodesulfurization process is demonstrated.

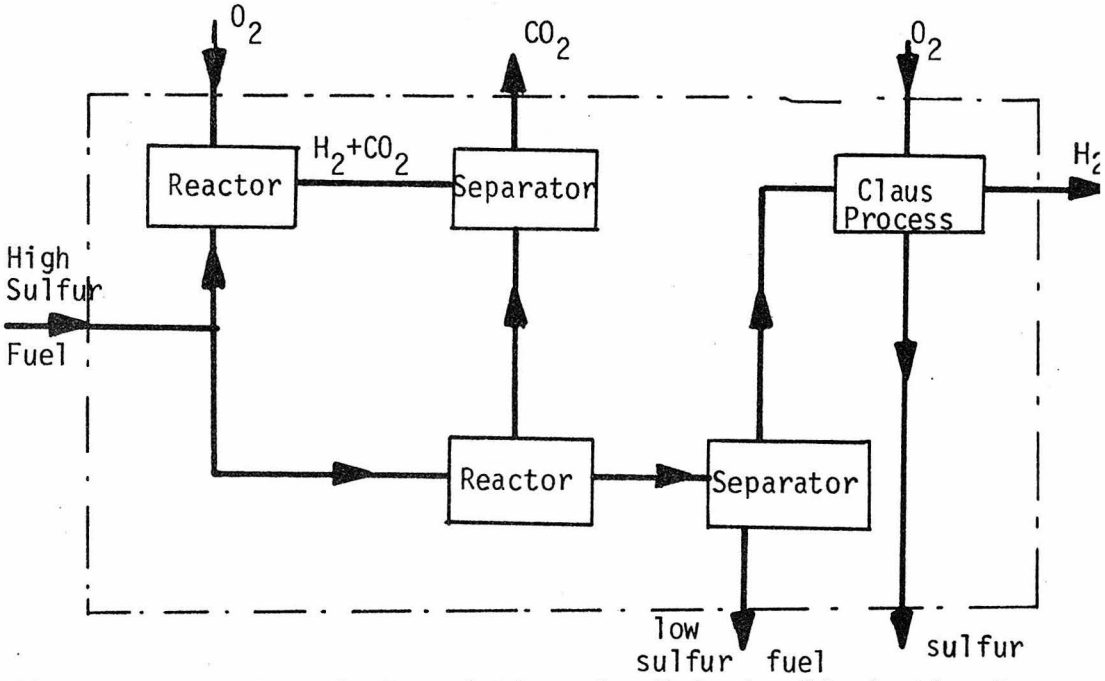


Figure 1.1. Schematic Description of a Hydrodesulfurization Process

Many high-pressure and high-temperature processing stages are used between the feed and the final product; however, this staging increases the capital investment and the cost of operation.

The next question that may be asked is whether the same end products can be obtained in a more efficient way. Hydrogen was required as an intermediate because it can selectively attack the sulfur-to-carbon bond, C—S,which is very similar to the carbon-to-carbon bond, C—C. The C—S bond can, however, be cleaved thermally if the sulfur is oxidized first to the corresponding sulfoxide (I) and sulfone (II)

$$S \xrightarrow{[O]} \underset{I}{SO} \xrightarrow{[O]} \underset{II}{SO_2} \qquad (1.1)$$

$$SO_2 \xrightarrow{\Delta} \text{hydrocarbon} + SO_2 \qquad (1.2)$$

A second scheme for desulfurization based on reactions 1.1 and 1.2 is given in Figure 2:

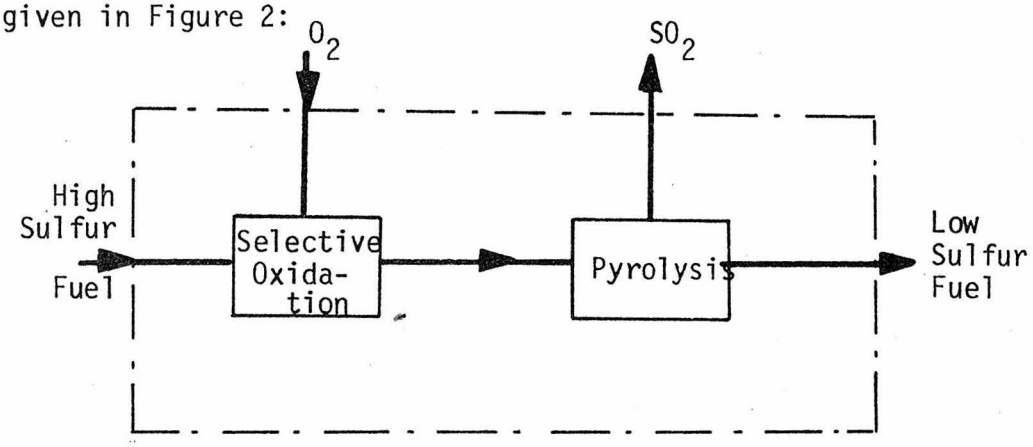


Figure 1.2. Schematic Description of a Process for Desulfurization by Selective Oxidation.

Several differences are noted between Figures 1 and 2:

1. The sulfur outlet of hydrodesulfurization is elementary sulfur, while a gaseous SO_2 is produced when selective oxidation is used.

2. Fewer steps are required in scheme 2 (although the method to accomplish selective oxidation was not specified.)

3. CO_2 and H_2O are produced in scheme 1. No such products are recognized in scheme 2, provided that the oxidation is truly selective. Hydroxyl and carbonyl groups, as well as olefinic groups will be formed in the desulfurized fuel as a result of poor selectivity.

The comparison of the two schemes shows that if a sufficiently selective oxidation process can be devised, desulfurization of fossil fuels might be done in a much cheaper and more efficient way than by hydrogenation.

The goal of this present work was to probe how selective oxidation of sulfur compounds can be achieved.

1.2 The Proposed Method to Achieve Selective Oxidation of Sulfur Compounds

Selective oxidation of sulfur compounds to the corresponding sulfoxides and sulfones can be achieved by hydroperoxides and by other peroxy species. (A detailed literature review is given in Chapter 3.) Hydroperoxides and other peroxy compounds are intermediates in the oxidation of hydrocarbons. (A detailed literature review is given in Chapter 2.) If these two facts are coupled, the following scheme for selective oxidation of sulfur compounds emerges: 1) oxidize the hydrocarbon medium

to the extent that a sufficiently large concentration of peroxides is formed; 2) the peroxides that are formed in the medium will selectively oxidize the sulfur compounds to the sulfoxides and sulfones.

The next question is how to effect selective oxidation of the hydrocarbon to maximize the concentration of the intermediate peroxides. The concentration of the peroxides in an organic solvent is controlled for each hydrocarbon by the relative rates of formation and of annihilation of the peroxide. The general scheme of oxidation in excess of oxygen is:

$$\text{Initiation:} \quad 2RH + O_2 \xrightarrow{k_0} 2R\cdot + H_2O_2 \tag{1.3}$$

$$\text{Propagation:} \quad \begin{cases} R\cdot + O_2 \xrightarrow{k_1} RO_2\cdot & \text{fast} \quad (1.4) \\ RO_2\cdot + RH \xrightarrow{k_2} RO_2H + R\cdot & \text{rate limiting} \quad (1.5) \end{cases}$$

$$\text{Termination:} \quad 2RO_2\cdot \xrightarrow{k_6} ROH + R'C{=}O + O_2 \tag{1.6}$$

The hydroperoxide RO_2H decomposes and provides additional means of branching:

$$RO_2H \xrightarrow{k_3} RO\cdot + \cdot OH \tag{1.7}$$

The radicals RO· and ·OH abstract hydrogens and enhance the conversion:

$$RO\cdot + RH \xrightarrow{k_8} ROH + R\cdot \tag{1.8}$$

$$\cdot OH + RH \xrightarrow{k_9} H_2O + R\cdot \tag{1.9}$$

R· is an unspecified organic radical.

The concentration of the hydroperoxide in the system is determined essentially by the rate of the decomposition reaction (1.7) and the rate of reaction (1.5) which controls the rate of conversion of the hydrocarbon. When excess hydrocarbon and oxygen are present, the temperature determines the relative rates of reactions (1.5) and (1.7), and thus the concentration of the hydroperoxide is controlled by the temperature.

If the rate of reactions (1.5) and (1.7) is expressed in the Arrhenius form, then:

$$k_2 = k_{20}\, e^{-E_2/RT} \tag{1.10}$$

$$k_3 = k_{30}\, e^{-E_3/RT} \tag{1.11}$$

where k_i is the rate constant, k_{io} and E_i are the frequency factor and the activation energy, respectively, R is the gas constant, and T is the absolute temperature.

The sensitivity of the rate constant to the temperature is given by:

$$\frac{\partial \ln k}{\partial T} = \frac{E}{RT^2} \tag{1.12}$$

Equation (1.12) shows that the sensitivity of the rate constant to the temperature is determined at each temperature, by the value of the activation energy. Values of the Arrhenius parameters of reactions (1.5) and (1.7) are given in Table 1.1.

Table 1.1 Arrhenius Parameters for the Abstraction of Hydrogen by a Peroxy Radical and for the Decomposition of Hydroperoxides

Hydrogen	Methyl	Primary	Second.	Tert.	Tetralyl	Ref.
D(R-H)	102.5	96.9	93.2	90.0	$\sim$83.5[h]	K-4
log k_{20}	8.8	8.7	8.2	8.2	5.75[e]	K-4
E_2	10.3	7.5	5.1	4.7	8.3[e]	K-4
log k_{30} gas		13.4[a]	15.2[b]	13.7[c]		K-5
E_3		13.7[a]	40.0[b]	37.8[c]		K-5
log k_{30} liquid		10.0[f]	12.0[g]		11.1[d]	
E_3		26.9[f]	31.7[g]		29.0[d]	

[a]Values for ethyl radicals
[b]Values for i-propyl radicals
[c]Values for t-butyl radicals
[d]Ref. (T-1)
[e]Ref. (H-6)
[f]Values for octyl radicals in white oil, Ref. (T-1)
[g]Values for isodecyl radicals in white oil, Ref. (T-2)
[h]Estimated in this work, see Section 7.10.

The data of Table 1.1 show that the rate of decomposition of the hydroperoxides has much larger activation energy than the rate of hydrogen abstraction, and is therefore much more sensitive to the temperature. Therefore, if the oxidation is carried out at lower temperatures, the half life of the hydroperoxides will be significantly increased. However, the rate determining step, reaction (1-5), will be even slower.

The natural deduction from the previous discussion is the following: If the oxidation is carried out at a sufficiently low temperature and the rate of the hydrogen abstraction stage is catalyzed, it will be possible to obtain relatively large concentrations of hydroperoxides, and thus to oxidize selectively the sulfur compounds that are present.

HBr was reported in the literature to be a good catalyst for the hydrogen abstraction step, even at low temperatures (150-230°C) (R-1). Full discussion of the role of HBr is given in Section 2.5. The mechanism of the enhancement of the hydrogen abstraction by HBr is

$$RO_2\cdot + HBr \xrightarrow{k_{10}} RO_2H + Br\cdot \qquad (1.13)$$

$$Br\cdot + RH \xrightarrow{k_{11}} HBr + R\cdot \qquad (1.14)$$

$$R\cdot + O_2 \xrightarrow{k_2} RO_2 \qquad (1.4)$$

The result of the sequence of reactions (1.13) and (1.14) is the same as that of (1.5); however, the rate of propagation is much larger.

The previous discussion leads to the following conclusion: in order to oxidize the sulfur compound selectively, oxidize in a hydrocarbon at low temperature and in the presence of a catalyst for the hydrogen abstraction step. In this work this concept was probed as a potential method for the selective oxidation of sulfur compounds.

1.3 The Goals of the Work

The main goals were: 1) verify experimentally if selective oxidation of sulfur compounds can be accomplished by low temperature oxidation in the presence of a catalyst to the hydrogen abstraction step.

2) Derive kinetic data on the oxidation for selected systems and use it to study i) the mechanism of the reaction; ii) the effect of the catalyst; iii) the variation of the kinetics with the hydrocarbon medium; iv) the effect of the solvents on the oxidation.

1.4 Scope of the Work

Nine experiments are described. The details of these experiments and their results are given in Chapter 6. Discussion of results is given in Chapter 7. In Table 1.2 the most important parameters of the initial conditions of the experiments are summarized.

1.5 Main Results

Detailed discussion of the results is given in Chapter 7, so only a brief summary of the most important conclusions is given here.

1.5.1 The Effect of the Catalyst

Tables 7.3 and 7.4 show the rate data of the elementary steps of the catalyzed oxidation of Tetralin and of the uncatalyzed oxidation of butyl sulfide in Tetralin. The data indicate that ν , the ratio of the propagation step in the presence of a catalyst and in its absence is:

$$\nu = \frac{k_{11}[RH][Br\cdot]}{k_2[RH][RO_2\cdot]} \simeq 10$$

The increased rate of oxidation as measured by the rate of formation of ketone is first order with the concentration of the HBr.

Table 1.2 Initial Conditions of the Experiments

Experiment No.	Hydrocarbon (RH)	RH Conc. mole/lit	Sulfur Compound (SC)	SC Conc. mole/lit	Temperature °C	HBr Conc. mole/lit 10^3	O_2 Conc. mole/lit 10^3	Solvent (SOL)	SOL Conc. mole/lit
1	Tetralin	5.039	-	-	140	1.34	5.6	Bromo-benzene	2.130
2	-	-	Butyl Sulfide	0.1423	140	1.1	5.6	"	9.281
3	Tetralin	5.514	"	0.1424	140	-	5.7	"	2.130
4	"	5.395	"	0.2784	140	0.64	6.0	"	2.081
5	"	5.614	"	0.1424	140	1.0	5.6	"	2.130
6	Toluene	2.177	"	0.1424	136.5	0.9	5.6	"	7.078
7	Tetralin	5.002	"	0.1292	140	1.2	5.5	1-Octanol	1.882
8	"	5.514	Dibenzo-thiophene	0.1292	160	1.2	6.4	Bromo-benzene	2.130
9	"	5.002	"	0.1292	160	1.2	6.4	1-Octanol	1.889

1.5.2 The Results of the Use of HBr

The main results of the use of HBr are:

1. Increased rate of oxidation. The rate constant of ketone formation is about 5.3 times larger when the oxidation is catalyzed by HBr.

2. Formation in the solution of compounds with larger oxidation potential than the compounds produced when HBr is absent. The oxidation potential that is required to oxidize sulfoxides to sulfones is larger than that required to oxidize the sulfides to the sulfoxides. Sulfones are found when HBr is present, but are not found when HBr is absent.

3. The activity of free radicals is increased about 100 times by $1.3 \cdot 10^{-3}$ mole/liter HBr. The increased activity of the radicals shows as an increase in the side chain reactions of the sulfide, e.g., the formation of about 100 times more of α-keto butyl sulfoxide (COSO) than the amount that is formed when HBr is absent. The ratio of the concentrations of COSO remained about constant for the first two hours. The addition of only $0.64 \cdot 10^{-3}$ mole/liter HBr doubled the activity of the free radicals, and hence increased the concentration of species like COSO by a factor of 2-3 only. This shows that the dominant mechanism of the oxidation of the sulfide is a complex function of the concentration of HBr.

4. Change in the selectivity of the reaction. Define:

$$[S]_{per} = [\text{sulfoxide}] + [\text{sulfone}] \tag{1.15}$$

and

$$\psi_{MPR} = \frac{[S]_{per}}{[S]_{oxidized} - [S]_{per}} \qquad (1.16)$$

where $[S]_{per}$ is the molar concentration of sulfur compounds that were produced by a reaction with at least one peroxide molecule, $[S]_{oxidized}$ is the total number of moles of sulfide that were oxidized, ψ_{MPR} is the "mechanistic selectivity" which defines the ratio of moles of sulfur which were oxidized by a homolytic reaction with the peroxides and that reacted by a free radical reaction.

A plot of $[S]_{per}$ vs ψ_{MPR} for the uncatalyzed oxidation defines a region in which, by the use of HBr, better selectivity and larger conversion to sulfoxides and sulfones can be obtained. Whether such conditions will be realized depends on the concentration of HBr and on the residence time in the reactor. When [HBr] = $6.4 \cdot 10^{-4}$ mole/liter, better ψ_{MPR} and larger $[S]_{per}$ were obtained after 65 min. (Comparable ψ_{MPR} and $[S]_{per}$ conditions were obtained in the uncatalyzed reaction after about 310 min.) When (HBr] = $1.34 \cdot 10^{-3}$ mole/liter the equivalence point was not reached in five and a half hours.

5. Sulfoxides oxidize HBr to Br_2 and water. This process takes place in ionic mechanisms and is considerably accelerated when water separates as a suspension in the solution.

A list of estimated rate constants for the reactions of Br containing species is given in Table 7.3.

1.5.3 The Effect of the Hydrocarbon Medium

The hydrocarbon medium serves both as a solvent and as the

source of radical R· . The oxidation potential of the solution and the reactivity of the radicals depends on the structure of R· . The tolyl radical is very unstable and therefore less selective than the tetralyl radical. Many more products of free radical side chain reactions are found when toluene is used instead of Tetralin. Moreover, less stable R· forms less stable RO_2· radicals and oxidizers with a larger oxidation potential. Therefore, in toluene, the sulfoxide and the sulfone are oxidized to more advanced oxidation products than when the hydrocarbon medium is Tetralin. The reactivity of R· is measured by the energy of the bond R–H. The rate of hydrogen abstraction of all the common aromatic hydrocarbons is between that of toluene and Tetralin.* Therefore, one may infer that when a mixed medium is used the rates and selectivities which can be expected are between those found for Tetralin and those for toluene. The initial rate of formation of COSO in toluene is 7.5 times that in Tetralin. However, the initial rates of formation of sulfoxides is approximately the same, so when small conversions are considered one may expect the same yield of sulfoxides in any aryl hydrocarbon, but different concentrations of products of free radicals attack on the side chain.

1.5.4 The Effect of the Solvent Proticity

Protic solvents stabilize the sulfoxides by formation of the complex[–S–O–HO–R]and solvate the free radical RO_2· . Therefore, large concentrations of sulfoxides and fewer products of reactions of free

*The difference in energy of the R–H bond between tetralin and toluene was estimated in this work to be about 1.5 kcal/mole.

radicals are found when the hydrocarbon is modified by a protic solvent, e.g., octyl alcohol. The energy of solvation of butyl sulfoxide by octyl alcohol was estimated to be -1.55 kcal/mole, which is smaller than the energy of solvation of dimethyl sulfoxide by phenol (-6.5 kcal/mole) but larger than the "heat of mixing" of water and dimethyl sulfoxide (at 0.1 M), -0.36 kcal/mole.

1.5.5 Loss of Heating Value Due to the Oxidation

Experimental measurements have indicated that the loss of heating value due to the oxidation was less than the experimental error in the calorimetric measurement that was used (1-1.5%). Estimates of the loss of heating value, based on the computer simulation of the reaction, have shown that a loss of about 1-2 cal/gram (or 1-2 kcal/liter) occurred. The results are encouraging, since a loss of such a small magnitude for 25% conversion of the sulfide was not anticipated.

Chapter 2

INTRODUCTION TO THE AUTOCATALYTIC OXIDATION OF HYDROCARBONS WITH MOLECULAR OXYGEN

A considerable amount of literature is available on the liquid phase oxidation of hydrocarbons, therefore the discussion will be limited to the homogeneous, liquid-phase oxidation of hydrocarbons by molecular oxygen in the absence of salts of transition metals. Furthermore, only the reactions that take place at low temperatures (below 200°C) and with oxygen pressure of one atmosphere or less will be described.

The material was collected from several books and review articles (E-1, S-3, I-1, I-2, G-3). Many other papers were used which will not be referenced specifically. The reactions of peroxides, hydroperoxides and the properties of peroxy compounds have recently been described in a three-volume manuscript edited by Swern (S-4).

Oxidation of hydrocarbons by molecular oxygen proceeds via a free radical mechanism (FRM). In a FRM there are three types of reactions: (1) reactions in which more FR are produced than with the initial reactants; such reactions are termed "initiation" or "branching" reactions; (2) reactions in which the number of free radicals is the same in the reactants and in the products; such reactions are termed "propagation" or "transfer" reactions; (3) reactions in which the number of FR de-decreases; such reactions are termed "termination" reactions.

2.1 Initiation Reactions

Two kinds of initiation reactions can be distinguished: (1) decomposition of unstable compounds ("initiators"), and (2) hydrogen abstraction

by molecular oxygen. Typical unstable initiators are azo and peroxy compounds. Typical initiation reactions are:

$$(CH_3)_2\overset{CN}{\underset{}{C}}-N=N-\overset{CN}{\underset{}{C}}(CH_3)_2 \rightarrow 2(CH_3)_2\overset{CN}{\underset{}{C}}\cdot \qquad (2.1)$$

Two radicals are obtained from each azoisobutyronitrile molecule. Initiation via peroxides can be by a first or by a second order reaction, or by both. First order decompositions of hydrogen peroxide yields two·OH radicals:

$$H_2O_2 \rightarrow 2HO\cdot \qquad (2.2)$$

Second order decomposition of t-butyl hydroperoxide (I) yields an alkoxy and a peroxy radical, and a water molecule is eliminated:

$$2(CH_3)_3\,COOH \rightarrow (CH_3)_3CO\cdot + (CH_3)_3CO_2\cdot + H_2O \qquad (2.3)$$

The first order decomposition yields an alkoxy and a hydroxy radical:

$$(CH_3)_3\,COOH \rightarrow (CH_3)_3CO\cdot + \cdot OH \qquad (2.4)$$

Several generalizations can be made on the decomposition reactions of peroxide:

1. Peroxide decomposition reactions have a large activation energy (28-45 kcal/mole), and therefore the rate of initiation changes very rapidly with temperature. Values of typical activation energies for initiators are given in Table 2.1.

Table 2.1 Activation Energies for the Dissociation of Initiators

Name	Structure	Activation Energy kcal/mole
Hydrogen peroxide	HO–OH	48
t-Butyl hydroperoxide	t-BuO–O–H	42
t-Butyl peroxide	t-BuO–O–Bu–t	37
t-Butyl perbenzoate	t–BuO–OC(=O) ph	34
Benzoyl peroxide	ph C(=O)–O–C(=O) ph	30
Acetyl peroxide	CH_3 C(=O)–O–C(=O)CH_3	30-32

2. The structure of the organic ligand strongly influences the rate of decomposition of the peroxide and its activation energy. Electron repelling groups and resonance with π bonds stabilize the products of the decomposition of the peroxides. The peroxides of this group are relatively more stable.

Peroxides are intermediates in oxidation reactions with molecular oxygen (MO). MO can abstract a hydrogen atom and form a hydroperoxy radical (I) and a FR (II) (reaction (2.5)). The hydroperoxy radical reacts with a second molecule of hydrocarbon producing hydrogen peroxide and another FR (reaction 2.6).

$$\underset{}{RH} + O_2 \rightarrow \underset{I}{HO_2\cdot} + \underset{II}{R\cdot} \qquad (2.5)$$

$$HO_2\cdot + RH \rightarrow H_2O_2 + R\cdot \qquad (2.6)$$

At temperatures below 90°C the H_2O_2 is stable; however, it may decompose at higher temperatures and cause further branching.

The rate of initiation with molecular oxygen is strongly dependent on the bond energy of the hydrogens. Larger rates of initiation are observed when smaller bond energies exist. Bond energies for classes of hydrogens are given in Table 2.2:

Table 2.2 R-H Bond Dissociation Energies

Structure	Bond Energy kcal/mole	Structure	Bond Energy kcal/mole
CH_3–H	103	Ph CH_2–H	85
n–C_3H_7–H	99	RC(=O)–H	86
i–C_3H_7–H	94	CH_3S–H	88
t–C_4H_9–H	90	CH_3pH–H	85
CH_2=CH–H	105	phO–H	88
C_6H_5–H	103	phNH–H	80
CH_3=CH–CH_2–H	85	ROO–H	90

Larger rates of production of peroxide are observed when the FR that is formed is more stable. π bonds or n electrons in α position to the abstracted hydrogen enhance the rate of hydrogen abstraction with MO.

The general form of the initiation reactions with peroxide R–O–O–R' are:

$$R–O–O–R' \rightarrow RO\cdot + R'O\cdot \qquad (2.7)$$

$$RO\cdot + R''H \rightarrow ROH + R''\cdot \qquad (2.8)$$

Initiation with molecular oxygen can be written as:

$$2RH + O_2 \rightarrow 2R\cdot + H_2O_2 \qquad (2.9)$$

2.2 Propagation Reactions

Propagation is a chain reaction, with at least two steps. The FR that is formed in the initiation step reacts very rapidly with molecular oxygen producing a peroxy radical:

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad \text{fast} \qquad (2.10)$$

The peroxy radical abstracts a hydrogen and forms a new FR and a hydroperoxide molecule:

$$RO_2\cdot + RH \rightarrow RO_2H + R\cdot \qquad (2.11)$$

The chain is completed by the last step, because R· can react with MO (2.10), thus the chain propagates; the result of the chain is the production of a hydroperoxide molecule from a hydrocarbon and an oxygen molecule. Since (2.11) is considerably slower than (4.10), the rate of oxidation is determined by the rate of hydrogen abstraction by the peroxy radicals.

Several generalizations may be made:

1. Larger rates of hydrogen abstractions (HA) are obtained when the heat of reaction of the HA is larger. Thus, larger rates of oxidation are obtained for hydrocarbons with hydrogens with smaller carbon to hydrogen bond dissociation energy. The relative rates of the HA reactions for primary, secondary, and tertiary hydrogens is approximately

1:30:300. Allylic, benzylic, thiotic and aminic radicals react more rapidly.

2. Hydrogens or carbons which are connected to oxygen, e.g., in alcohols, ethers or aldehydes, can be easily abstracted because the free radical that is produced can resonate with the n electrons of the oxygen. Therefore, partially oxidized hydrocarbon continues to oxidize much more rapidly than the parent hydrocarbon.

3. The bond energy of the hydrogens of hydroperoxides is smaller than that of alcohol, so hydrogen abstraction by $RO_2\cdot$ is more selective than HA by $RO\cdot$.

The free radicals can isomerize either before or after reacting with oxygen. A full discussion of such reactions is beyond the scope of this thesis, and the reader is referred to Vol. I of reference (S-5). A short discussion of the secondary oxidation reactions is given in Section 2.4.2. Typical rate constants for the HA reaction are given in Table 2.3.

Table 2.3 Rate Constants for the Hydrogen Abstraction Reactions

Hydrocarbon RH	Peroxy Radical $RO_2\cdot$	Temp. °C	Rate Const. lit/mole/sec
Tetralin	cumyl	30	1.65
Tetralin	tetralyl	30	6.4
cyclohexene	cyclohexenyl	40	3.7
ethylbenzene	1-phenethyl	30	1.3
isopropylbenzene	α-cumyl	30	0.18
octene-1	octenyl	25	0.03
benzaldehyde	benzoyl	5	1900
decanol	hydroxy-decyl	5	720
phenol	polyperoxyntyryl	65	$5\cdot10^3$
2,6-Di-t-butylphenol	polyperoxyntyryl	65	$5\cdot10^3$
diphenylamine	polyperoxystyryl	65	$20\cdot10^3$

2.3 Termination Reactions

Termination can occur by the recombination of two FR. Usually the most important termination reaction is that between the two most abundant FRs. If the partial pressure of O_2 is greater than 100 torr, $RO_2\cdot$ will be the most abundant radical because reaction (2.10) is very fast. Thus, the dominant termination reaction will be the recombination of two $RO_2\cdot$ radicals. Such a reaction can produce a peroxide molecule:

$$2RO_2\cdot \rightarrow RO_2R + O_2 \qquad (2.12)$$

or other non-radical products, like an alcohol and a ketone molecule:

$$2RO_2\cdot \rightarrow ROH + R'C{=}O + O_2 \qquad (2.13)$$

The particular products will depend on the structure of the organic radical.

Typically, termination reactions will have zero or negligible activation energy, and a large frequency factor. So, the rate of termination has a weak temperature dependence. However, large changes in the temperature affect the rate of HA reactions by the peroxy radicals and the rates of their isomerization and decomposition.

Selected average values of the rate of termination reactions by recombination of peroxy radicals are given in Table 2.4.

Table 2.4 Rate Constants for the Recombination of Peroxy Radicals

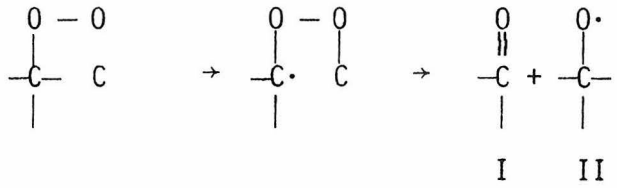
Alkylperoxy radicals	$2k_t$ (ℓ/mole/sec) at 30°C	
primary, $RCH_2O_2\cdot$	$2\text{-}4 \cdot 10^8$	
secondary, $R_2CHO_2\cdot$	$20\text{-}40 \cdot 10^6$	benzylic
	$1\text{-}10 \cdot 10^6$	allylic
	$6\text{-}8 \cdot 10^6$	cyclic
tertiary $R_3CO_2\cdot$	$0.1\text{-}60 \cdot 10^4$	
$HO_2\cdot$	$1.2 \cdot 10^9$	

2.4 The Effect of Oxidation Products on the Reaction

Primary oxidation products influence both the rate and the selectivity of the oxidation. The oxidation potential of oxidation products is larger than that of molecular oxygen, so the hydrogen abstraction becomes less selective to the most labile hydrogens. In the presence of oxidation products, all the hydrogens become prone to abstraction. Furthermore, the overall rate of oxidation increases, since the decomposition of the primary products is in most cases a branching reaction.

2.4.1 Elementary Reactions of Hydroperoxides and Peroxy Radicals

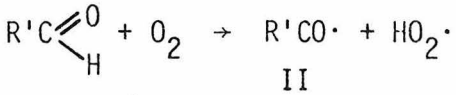
Peroxy radicals can react in two important ways: 1) abstract a hydrogen from another molecule and form a hydroperoxide; this reaction is important at temperatures below 200°C and when hydrogens with a small bond energy are present. 2) decompose with a rupture of a C—C bond. An aldehyde or ketone (I) molecule is produced plus an alkoxy radical (II):



(2.14)

I II

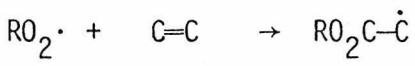
When I is an aldehyde, it branches according to:



(2.15)

II

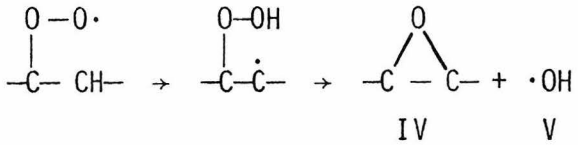
The alkoxy radical, II, abstracts a hydrogen from a hydrocarbon molecule much more readily than does the peroxy radical. Decomposition of the radical to an olefin and a hydroperoxy radical becomes important at higher temperatures (450-500°C). In the presence of olefins, the peroxy radicals can add to the double bond.



(2.16)

III

The addition reaction is reversible. The peroxide radical III can either absorb O_2 or add to another olefin molecule; polyperoxide is formed. III can also decompose to an epoxide molecule, IV, and a hydroxy radical V,



(2.17)

IV V

Polyperoxide formation occurs in solution only. Epoxide formation is important in the gas phase at high temperatures (above 300°C).

Typical values for the frequency factors and the activation

energies of some of the reactions are given in Table 2.5:

Table 2.5 Kinetic Data for Homogeneous Processes

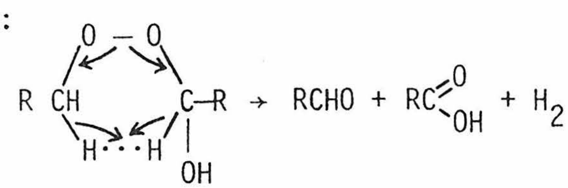
Reaction	log A*	E kcal/mole
$RO_2\cdot \rightarrow$ aldehyde + $R'O\cdot$	13	20
$RO_2\cdot \rightarrow C\overset{O}{-}C + \cdot OH$	11	15
$RO_2\cdot \rightarrow C = C + HO_2\cdot$	9	33
$RO_2\cdot \rightarrow R\cdot + O_2$	14.5	29
$RO_2\cdot + RH \rightarrow RO_2H + R\cdot$	8	12
$RO_2\cdot + C{=}C \rightarrow$	8.5	5-7
$R\cdot + O_2 \rightarrow RO_2\cdot$	8.5	3
$R\cdot + O_2 \rightarrow C{=}C + HO_2\cdot$	9.2	4
$RO_2H \rightarrow RO\cdot + \cdot OH$	15	43

*A is in sec^{-1} or lit/sec/mole

Once sufficient primary hydroperoxide and aldehyde molecules are formed in the system, the hydroperoxide can add to the carbonyl double bond:

$$RCH_2OOH + RCHO \rightarrow \underset{VI}{RCH_2OO\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}R} \qquad (2.18)$$

The adduct VI can decompose to an aldehyde, an acid and a hydrogen molecule:

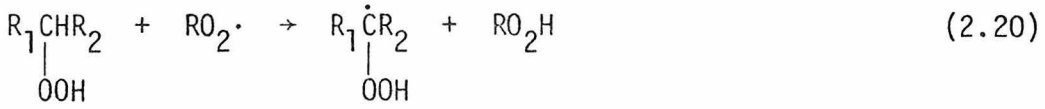


VI

(2.19)

The VI oxidation potential of VI is very large. In the presence of acid, VI decomposes to an ester by ionic mechanism.

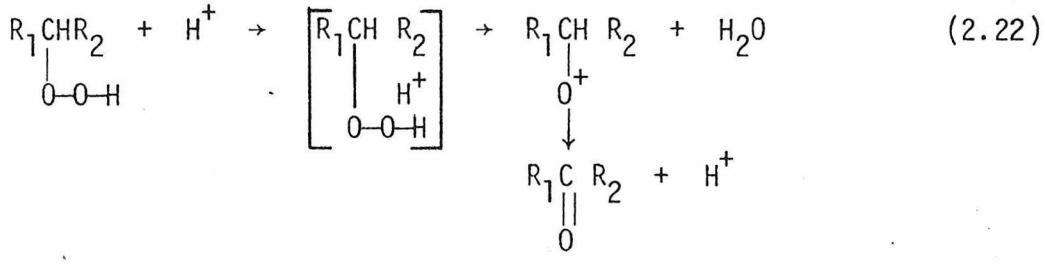
Secondary hydroperoxides react with peroxy radicals; ketones and hydroxy radicals are formed:



(2.20)

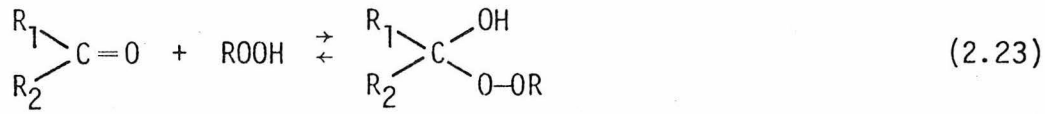
(2.21)

Acids catalyze the decomposition of secondary hydroperoxides to ketones and water.



(2.22)

The ketones react with another hydroperoxide molecule forming a molecule of hydroxy peroxide (VII):



(2.23)

VII

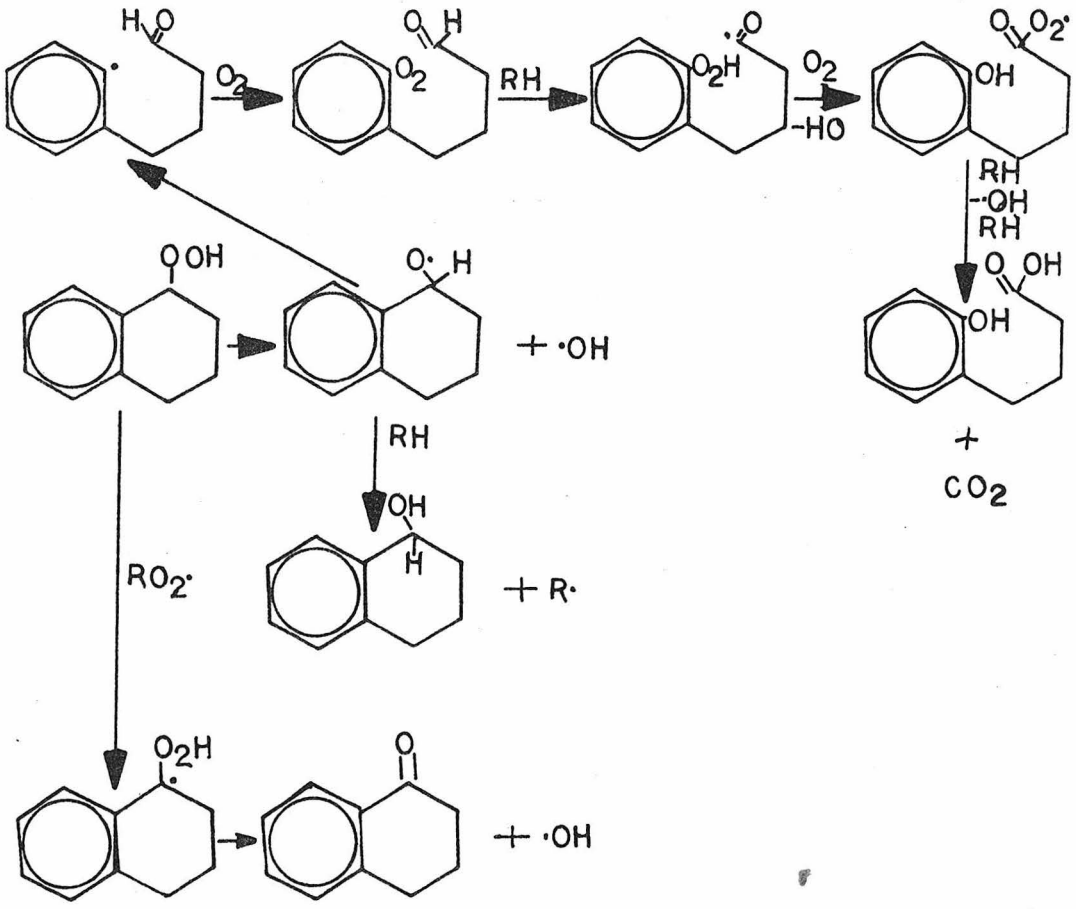
VII is a very strong oxidizer.

Peroxy radicals with a special structure can rearrange. A C–C bond is broken and the HC structure is changed. Tertiary peroxy radicals

and α-phenyl peroxy radicals are two important examples of this class of reactions:

$$(CH_3)_3C{-}O{-}OH \rightarrow (CH_3)_3C{-}O\cdot \begin{cases} \nearrow (CH_3)_3COH \\ \searrow (CH_3)_2C{=}O + CH_3\cdot \end{cases} \qquad (2.24)$$

The decomposition of tetralyl hydroperoxide is an interesting example of such a decomposition:



(2.25)

The reactions of peroxides and peroxy radicals with sulfur compounds are discussed in Chapter 3.

2.4.2 Oxidation of Secondary Alcohols and Ketones

Alcohols and ketones are relatively stable compounds and may accumulate in the reaction system. However, the oxygen in the molecule activates the α and β hydrogens, so that their abstraction becomes a very facile reaction. Therefore, as long as the concentration of alcohols and ketones remains small, they will accumulate, but when their concentration increases, they will start to play an active role in the oxidation. The most important reactions that may take place are listed below. Examples were taken from the oxidation of cyclohexanol and cyclohexanone.

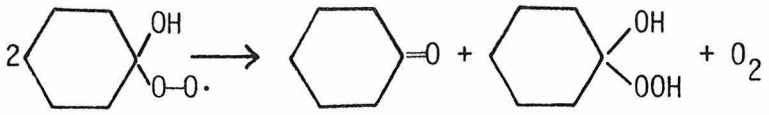
Oxidation of Secondary Alcohols

1. The oxidation is initiated by molecular oxygen by reaction 2.9. For cyclohexanol the Arrhenius form of the rate constant is $k_{03} = 8.3 \exp(-16000/RT)$ $lit^2/mole^2/sec$.

2. Oxygen absorption is rapid. The HA propagation reaction (2.11) proceeds exclusively to the hydrogens on the carbon α to the oxygen. Arrhenius form of the rate of propagation for cyclohexanol is

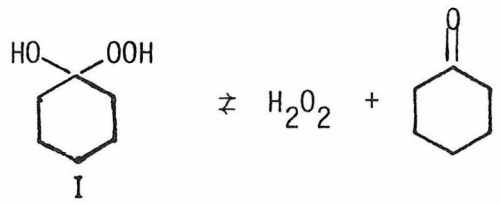
$$k_2 = 1.1 \cdot 10^7 \exp(-11900/RT) \text{ lit/mole/sec}$$

3. Termination takes place exclusively via 2.13, however, because of the presence of the hydroxyl, it is slightly modified. For cyclohexanol it is:



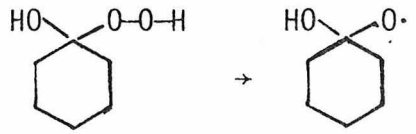
(2.26)

The rate constant is $k_6 = 5 \cdot 10^6 \exp(-2200/RT)$ lit/mole/sec. The hydroperoxy alcohol (I) is in equilibrium with H_2O_2 and cyclohexanone.



(2.27)

I is a strong oxidizer and can cause branching:



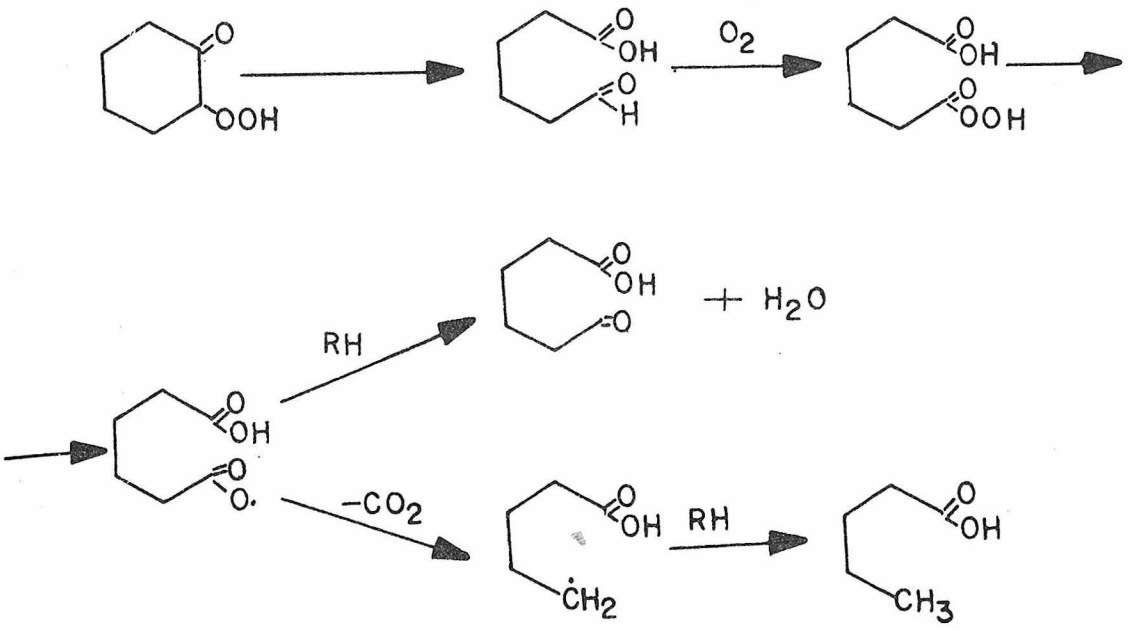
(2.28)

The rate constant is $k_{35} = 2.2 \cdot 10^4 \exp(-16200/RT)\ sec^{-1}$. The decomposition is much faster in the presence of transition metals, acids or on surfaces. The rate of decomposition via reaction (2.28) is very large; accumulation of I can result in an explosion.

Oxidation of Ketones

The main products of the oxidation of ketones are α-ketohydroperoxides, lactones and mono and dibasic acids. Initiation is by abstraction of the β hydrogens. The activation energy for the abstraction of hydrogens β to the keto-oxygen is approximately the same as that for the hydrocarbon, in other words, the carbonyl group does not significantly change the bond energy of the neighboring hydrogens. Once some α-ketohydroperoxide is formed, it becomes the major source of free radicals. The rate constant for the decomposition of α-hydroperoxycyclohexanone is $k_i = 6.0 \cdot 10^7 \exp(-20400/RT)\ sec^{-1}$.

Typical chain reactions which yield mono (II) and dibasic (III) acids proceed according to:



(2.29)

The peroxy acid (IV) is a very strong oxidizer and can very rapidly oxidize nucleophiles like sulfur or nitrogen compounds.

2.5 Oxidation of a Hydrocarbon in the Presence of a Homogeneous Catalyst

The rate data of Table 2.5 clearly indicate that the rate limiting step in the propagation is the hydrogen abstraction, reaction (2.11). The rate of oxidation will therefore be enhanced by any catalyst that can abstract hydrogen at a larger rate than $RO_2\cdot$. One such catalyst is HBr.

In the presence of HBr, the following sequence of reactions takes place:

$$RO_2\cdot + HBr \rightarrow RO_2H + Br\cdot \qquad (2.30)$$

$$Br\cdot + RH \rightarrow HBr + R\cdot \qquad (2.31)$$

The net result of reactions (2.30) and (2.31) is reaction (2.11), however much larger rates may be obtained, provided that the HBr

concentration is not too small.

HBr enhances the rate of initiation by the reaction:

$$HBr + O_2 \rightleftarrows HO_2\cdot + Br\cdot \qquad (2.32)$$

Reaction (2.32) is reversible, so in the presence of excessive peroxy or hydroperoxy radical termination may occur. The rate of the forward reaction (2.32) is given by $k = 3.16 \cdot 10^{14}\exp(37700/RT)$ (R-2) and that of the reverse reaction by $k = 3.63 \cdot 10^{14}\exp(-2750/RT)$. The contribution of reaction (2.32) to the rate of initiation in systems with a weak hydrogen-carbon bond, or systems which contain oxidation products, may be negligible; however, it may be important in the initial stages of the oxidation.

The rate of hydrogen abstraction by Br· (2.31) is smaller than that by ·OH, and therefore Br· is more selective than the hydroxy or alkoxy radicals. Thus specific isomers can be obtained by oxidizing hydrocarbons in the presence of HBr·. Rust and Vaughan (R-1) obtained stable hydroperoxides from branched hydrocarbons, e.g., t-butyl hydroperoxide from isobutane and ketones from hydrocarbons with secondary hydrogens. They concluded that the hydrogen with the smallest bond energy will be abstrated by the Br· . Barnett et al. (B-12) examined the oxidation of toluene in the presence of HBr and Lin and Kehat (L-2) investigated the oxidation of toluene and benzene in the presence of HBr, HCl and water. All the studies indicate that the Br· is selective to the hydrogen with the smallest bond energy; and therefore

oxidation will take place at this site.

The presence of HBr will affect the oxidation of hydrocarbons in the following ways:

1. Catalyze the propagation by reaction (2.30).

2. Catalyze the initiation by reaction (2.32).

3. Cause termination in a special range of parameters, via reactions (2.33), (2.34) or (2.35):

$$HO_2\cdot + Br\cdot \rightarrow HBr + O_2 \qquad (2.33)$$

$$RO_2\cdot + Br\cdot \rightarrow \text{olefin} + O_2 + HBr \qquad (2.34)$$

$$R\cdot + Br\cdot \rightarrow RBr \qquad (2.35)$$

4. Decompose the hydroperoxide to ketone via an ionic mechanism:

$$RO_2H + HBr \rightarrow R'C{=}O + HBr + H_2O \qquad (2.36)$$

5. Inhibit the oxidation when the ratio of HBr/O_2 is too large by competing with the propagation reaction (2.10):

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (2.10)$$

$$R\cdot + HBr \rightarrow RH + Br\cdot \qquad (2.37)$$

For a given hydrocarbon, with a given hydrogen-carbon bond energy, a region of the parameters T, $[O_2]/[HBr]$ and $[RH]/[HBr]$ can be defined, in which catalysis will be observed.

6. Dehydrate alcohols by an ionic mechanism:

$$ROH \xrightarrow{[HBr]} REN + H_2O \qquad (2.38)$$

where REN is an olefin. Reaction 2.38 complicates the oxidation because oxidation of olefins is much more rapid than oxidation of paraffins.

Chapter 3

OXIDATION OF ORGANIC SULFUR COMPOUNDS BY PEROXIDES

Oxidation of organic sulfur compounds (SC) was investigated by many researchers. The work was reviewed by Behrman and Edwards (B-2), Barnard et al. (B-3) and by Davies (D-5). More recently, Curci and Edwards (C-1) reviewed the oxidation of nucleophiles by peroxides, and the effect of the solvent on the oxidation of sulfur compounds. The oxidation of thiols (mercaptans) was reviewed very recently by Capozzi and Modena (C-2). Oxidation of thiols will not be discussed here because no work has been done on thiols in this study.

3.1 Literature Survey of the Rate Data on the Oxidation of Sulfur Compounds by Peroxides

The data that have been published on the oxidation of SC by peroxides are summarized in Tables 3.1 and 3.2. Only low-conversion oxidation was covered. Data on the oxidation of sulfides in less well defined systems have been omitted; so were data on systems where inorganic salts were included (e.g.,(D-2)). Oxidation of sulfides which contain double bonds and oxidation of sulfides in solvents with double bonds were also not included.

3.2 Chemistry and Mechanism of Oxidation of Sulfur Compounds by Peroxides

Curci and Edwards (C-1) have recently reviewed the mechanism of oxidation of sulfur compounds. Therefore only generalizations and conclusions are given here.

Table 3.1 Rate Constants for the Oxidation of Sulfur Compounds by Peracids

Sulfur Compound	Acid	Solvent	Temperature °C	Rate*	k**	E kcal/mole	log A	Ref.
Tetramethylene	peracetic	toluene	-70	2nd 1:1	4			F-1
Di-n-butyl sulfide	"	"	-70	2nd 1:1	3.2			F-1
Di-sec butyl sulfide	"	"	-70	2nd 1:1	1.47			F-1
Di-t-butyl sulfide	"	"	-70	2nd 1:1	0.83	8.6	9.164	F-1
Di-t-butyl sulfide	"	"	-50	2nd 1:1	5.65	8.6	9.164	F-1
phenyl methyl sulfide	"	"	-49	2nd 1:1	0.097	9.6	8.338	F-1
" " "	"	"	-39.1	2nd 1:1	0.24	9.6	8.338	F-1
" " "	"	"	-30.0	2nd 1:1	0.53	9.6	8.338	F-1
" " "	"	"	-20.0	2nd 1:1	1.7	9.6	8.338	F-1
Di phenyl sulfide	"	benzene + 10 N acetic acid	0	2nd 1:1	0.268	9.6	7.166	F-1
" "	"	"	10	2nd 1:1	0.483	9.6	7.166	F-1
" "	"	"	20	2nd 1:1	0.880	9.6	7.166	F-1
Di benzothiophene	"	benzene	15	2nd 1:1	0.0049	14.7	8.572	F-1
"	"	"	30	2nd 1:1	0.0091	14.7	8.572	F-1
"	"	"	40	2nd 1:1	0.0168	14.7	8.572	F-1

Table 3.1 - Continued

Sulfur Compound	Acid	Solvent	Temperature	Rate*	k**	E kcal/mole	$\log_{10}A$	Ref.
di benzothiophene	peracetic	benzene	50	2nd 1:1	0.0357	14.7	8.572	F-1
"	"	"	60	2nd 1:1	0.0694	14.7	8.572	F-1
"	"	benzene + 10N acetic acid	15	2nd 1:1	0.00433	14.8	5.8596	F-1
"	"	"	30	2nd 1:1	0.0157	14.8	5.8596	F-1
"	"	"	40	2nd 1:1	0.0329	14.8	5.8596	F-1
"	"	"	50	2nd 1:1	0.0725	14.8	5.8596	F-1
"	"	"	60	2nd 1:1	0.142	14.8	5.8596	F-1
benzothiophene	"	benzene	40	2nd 1:1	0.0026		5.8596	F-1
"	"	benzene + 10N acetic acid	40	2nd 1:1	0.0017		5.8596	F-1
thiophene	"	"	40	2nd 1:1	$6 \cdot 10^{-5}$		5.8596	F-1
tetramethylthiophene	"	"	40	2nd 1:1	0.0368			F-1
2,5 dimethylthiophene	"	"	40	2nd 1:1	0.00186			F-1
2 methylthiophene	"	"	40	2nd 1:1	$4.1 \cdot 10^{-4}$			F-1
3 methylthiophene	"	"	40	2nd 1:1	$3.4 \cdot 10^{-4}$			F-1

Table 3.1 - Continued

Sulfur Compound	Acid	Solvent	Temperature	Rate* Law	k**	E kcal/mole	$\log_{10}A$	Ref.
p-p' dichlorobenzyl sulfide	p-methoxy perbenzoic	toluene	-65	2nd 1:1	0.61	6.6	6.6881	0-1
"	"	"	-55	2nd 1:1	1.32	6.6	6.6881	0-1
"	"	"	-45	2nd 1:1	2.44	6.6	6.6881	0-1
"	"	i-propyl alcohol	-35	2nd 1:1	0.19	9.9	8.382	0-1
"	"	"	-25	2nd 1:1	0.44	9.9	8.382	0-1
"	"	"	-15	2nd 1:1	0.95	9.9	8.382	0-1
"	peroxybenzoic	toluene	-65	2nd 1:1	1.29	5.2	5.646	0-1
"	"	"	-55	2nd 1:1	2.50	5.2	5.646	0-1
"	"	"	-45	2nd 1:1	4.17	5.2	5.646	0-1
"	perbenzoic	i-propyl alcohol	-40	2nd 1:1	0.15	9.6	8.2516	0-1
"	"	"	-30	2nd 1:1	0.38	9.6	8.2516	0-1
"	"	"	-20	2nd 1:1	0.79	9.6	8.2516	0-1
"	p-methyl perbenzoic	"	-40	2nd 1:1	0.11	11.3	9.5979	0-1
"	"	"	-30	2nd 1:1	0.29	11.3	9.5979	0-1
"	"	"	-20	2nd 1:1	0.70	11.3	9.5979	0-1

Table 3.1 - Continued

Sulfur Compound	Acid	Solvent	Temperature °C	Rate* Law	k**	E kcal/mole	$\log_{10}^{*}A$	Ref.
p,p' dichlorobenzyl sulfide	p-chloro-perbenzoic	i-propyl alcohol	-45	2nd 1:1	0.17	9.6	8.4687	O-1
"	"	"	-35	2nd 1:1	0.45	9.6	8.4687	O-1
"	"	"	-25	2nd 1:1	0.89	9.6	8.4687	O-1
"	p-nitro-perbenzoic	"	-55	2nd 1:1	0.43	6.9	6.5578	O-1
"	"	"	-45	2nd 1:1	0.88	6.9	6.5578	O-1
	"	"	-35	2nd 1:1	1.60	6.9	6.5578	O-1
3 methoxythio-naphthene	perbenzoic	CH_2Cl_2	30		0.61			K-1
3 methylthio-naphthene	"	"	30		0.112			K-1
thionaphthene	"	"	30		0.0057			K-1
"	"	dioxane-H_2O	25		0.004			G-1
3 methoxythionaph-thene sulfoxide	"	CH_2Cl_2	30		0.08			K-1
3 methylthionaph-thene sulfoxide	"	"	30		0.032			K-1
thianaphthene sulfoxide	"	"	30		0.050			K-1
"	"	dioxane-H_2O	25		0.0029			G-1

Table 3.1 - Continued

Sulfur Compound	Acid	Solvent	Temperature °C	Rate** Law	k*	E kcal/mole	$\log^{*}_{10}A$	Ref.
diphenyl sulfide	perbenzoic	dioxane-H_2O	25		5.0			G-1
diphenyl sulfoxide	"	"	25		0.0032			G-1
dibenzothiophene	"	"	25		0.0396			G-1
dibenzothiophene sulfoxide	"	"	25		0.0037			G-1

* Overall order, then order with respect to the sulfide and the oxidizer, respectively.

** For first order: sec^{-1}. For second order: lit/mole/sec.

\+ From different supplier. Used as received.

Table 3.2 Rate Constants for the Oxidation of Sulfur Compounds by Hydroperoxides and Peroxides

Sulfur Compound	Peroxide	Solvent	Temperature °C	Rate** Law	k*	E kcal/mole	$\log_{10}^{*}A$	Ref.
dibenzothiophene	t-butyl hydroperoxide	acetic acid	40	2nd 1:1	5×10^{-6}			F-1
"	H_2O_2	H_2O, acetic acid, and white oil	100	1st 1:0	9.4×10^{-2}			H-1
dibenzothiophene sulfoxide	H_2O_2	"	100	1st 1:0	0.13			H-1
dibenzothiophene	H_2O_2	white oil, H_2O, and acetic acid	50	1st 1:0	6.2	13.04	8.078	H-1
"	"	"	75	1st 1:0	6.2	13.04	8.078	H-1
"	"	"	85	1st 1:0	6.2	13.04	8.078	H-1
"	"	"	100	1st 1:0	6.2	13.04	8.078	H-1
cyclohexyl methyl sulfide	t-butyl hydroperoxide	t-butanol	50	2nd 1:1	1.43×10^{-5}	17.5		B-4
"	"	n-butanol	50	2nd 1:1	1.71×10^{-4}	15.0		B-4
"	"	methanol	50	2nd 1:1	2.2×10^{-4}	14.1		B-4
"	"	ethylene glycol	50	2nd 1:1	2.3×10^{-3}	12.7		B-4
"	cyclohexene hydroperoxide	t-butanol	50	2nd 1:1	1.19×10^{-4}	15.1		B-4
"	"	methanol	50	2nd 1:1	1.65×10^{-3}	12.6		B-4
"	"	ethylene glycol	50	2nd 1:1	1.27×10^{-2}	11.0		B-4

Table 3.2 - Continued

Sulfur Compound	Peroxide	Solvent	Temperature °C	Rate** Law	k*	E kcal/mole	$\log^{*}_{10}A$	Ref.
cyclohexyl methyl sulfide	cyclohexene hydroperoxide	benzene	50	3rd 1:2		10.9		B-5
"	"	cyclohexene	50	2,9 0.9:2		8.5		B-5
"	t-butyl hydro-peroxide	benzene	50	2,7 0:7:2		6.5		B-5
"	"	cyclohexane	50	2,4 0:4:2				B-5
"	"	cyclohexane	50	2,4,5,0:45:2				B-5
"	" + air	benzene	50	2,3,0.9:1:4		13.4		B-5
p,p' dichlorobenzyl sulfide	H_2O_2	i-propyl alcohol	30.2	2nd 1:1	3.1×10^{-5}	17.2	7.9476	O-2
"	"	"	39.8	2nd 1:1	7.6×10^{-5}	17.2	7.9476	O-2
"	"	"	49.8	2nd 1:1	1.91×10^{-4}	17.2	7.9476	O-2
"	"	ethyl alcohol	49.8	2nd 1:1	2.02×10^{-4}			O-2
"	"	acetonitril	49.8	2nd 1:1	1.8×10^{-5}			O-2
"	"	propionitril	49.8	2nd 1:1	0.7×10^{-5}			O-2
"	"	di isopropyl ether	49.8	2nd 1:1	1.6×10^{-5}			O-2
cyclohexyl methyl sulfide	t-butyl peroxide	t-butanol	50	2nd 1:1	9.4×10^{-6}	17.7		H-2

Table 3.2 - Continued

Sulfur Compound	Peroxide	Solvent	Temperature °C	Rate** Law	k*	E kcal/mole	$\log^{*}_{10}A$	Ref.
cyclohexyl methyl sulfide	cyclohexyl peroxide	t-butanol	50	2nd 1:1	7.9×10^{-5}	15.5		H-2
"	"	methanol	50	2nd 1:1	1.01×10^{-3}	13.1		H-2
"	t-butyl peroxide	methanol	50	2nd 1:1	1.58×10^{-4}	14.4		H-2
p-nitrophenylene methyl	H_2O_2	94% C_2H_5OH; 6% H_2O; 0.1N $HClO_4$	25	2nd 1:1	3.2×10^{-4}	14.4		M-1
diphenyl sulfide	H_2O_2	"	25	2nd 1:1	3.8×10^{-4}	14.4		M-1
m-chlorophenylene methyl sulfide	"	"	25	2nd 1:1	1.41×10^{-4}	14.4		M-1
phenyl benzyl sulfide	"	"	25	2nd 1:1	2.04×10^{-3}	13.5		M-1
p-chlorophenylene methyl sulfide	"	"	25	2nd 1:1	2.27×10^{-3}	13.5		M-1
phenyl methyl sulfide	"	"	25	2nd 1:1	3.73×10^{-3}	13.2	7.253	M-1
m-methyl phenylene methyl sulfide	"	"	25	2nd 1:1	4.38×10^{-3}			M-1
p-methyl phenylene methyl sulfide	"	"	25	2nd 1:1	6.34×10^{-3}			M-1
p-methoxy phenylene methyl sulfide	"	"	25	2nd 1:1	7.84×10^{-3}			M-1

Table 3.2 - Continued

Sulfur Compound	Peroxide	Solvent	Temperature °C	Rate** Law	k*	E kcal/mole	$\log^{*}_{10}A$	Ref.
benzyl methyl sulfide	H_2O_2	94% C_2H_5OH; 6% H_2O; 0.1N $HClO_4$	25	2nd 1:1	$3.73\ 10^{-3}$	13.2	7.253	M-1
di-n-butyl sulfide	"	"	25	2nd 1:1	$2.03\ 10^{-2}$			M-1
thioxane	"	H_2O	0	2nd 1:1	$3.2\ 10^{-4}$	13.5		D-2
"	"	"	25	2nd 1:1	$2.58\ 10^{-3}$	13.5		D-2
"	"	"	34.2	2nd 1:1	$5.32\ 10^{-3}$	13.5		D-2
"	"	D_2O	9.7	2nd 1:1	$4.5\ 10^{-4}$	13.5		D-2
"	"	"	25	2nd 1:1	$1.54\ 10^{-3}$	13.5		D-2
"	t-butyl hydroperoxide	H_2O	25	2nd 1:1	$1.35\ 10^{-4}$	14.1		D-2
"	"	"	45.9	2nd 1:1	$6.42\ 10^{-4}$	14.1		D-2
"	"	$H_2O + HClO_4$	25	2nd 1:1	$1.91\ 10^{-3}$			D-2
"	"	D_2O	25	2nd 1:1	$9.6\ 10^{-5}$			D-2
"	"	$D_2O + HClO_4$	25	2nd 1:1	$2.03\ 10^{-3}$			D-2
"	H_2O_2	dioxane	25	3rd 1:2	$4.07\ 10^{-6}$	16.3	-6.77	D-2
"	"	"	45.9	3rd 1:2	$2.46\ 10^{-6}$			D-2
"	"	acetic acid	25	2nd 1:1	$2.43\ 10^{-2}$			D-2

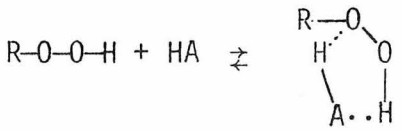
Table 3.2 - Continued

Sulfur Compound	Peroxide	Solvent	Temperature C°	Rate** Law	k*	E kcal/mole	$\log^{*}_{10}A$	Ref.
Thioxane	H_2O_2	t-butanol	25	2nd 1:1	9.45×10^{-6}	19.3	-4.808	D-2
"	"	"	45.9	2nd 1:1	4.0×10^{-5}	19.3	-4.808	D-2
"	"	methanol	25	2nd 1:1	6.16×10^{-5}	15.1	-6.338	D-2
"	"	"	45.9	2nd 1:1	3.27×10^{-4}	15.1	-6.338	D-2
"	"	ethylene glycol	25	2nd 1:1	4.96×10^{-4}	14.2	-6.120	D-2
"	"	"	49.5	2nd 1:1	2.38×10^{-3}	14.2	-6.120	D-2
"	"	D_2O	25	2nd 1:1	1.54×10^{-3}	13.5	-6.120	D-2
"	"	H_2O	25	2nd 1:1	2.58×10^{-3}	13.5	-5.901	D-2
"	"	N-methyl acetamide	25	2nd 1:1	2.2×10^{-6}	19.3	-4.808	D-2
"	"	"	45.9	2nd 1:1	1.87×10^{-5}	19.3	-4.808	D-2

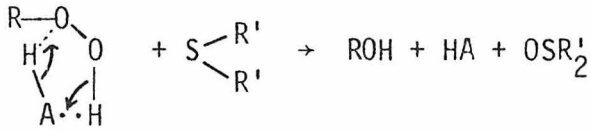
*For first order reaction sec^{-1}. For second order reaction mole/lit/sec.

**First the overall rate dependence, then the dependence on the sulfur compound and the peroxide, respectively.

1. Sulfur compounds are oxidized by a cyclic peroxy complex which contains a hydroperoxide molecule and a protic molecule (HA).



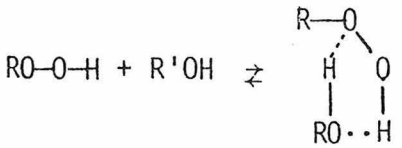
(3.1)



(3.2)

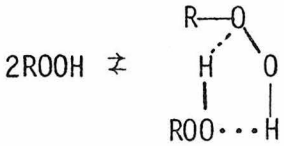
This mechanism was first proposed by Overberger and Cummins (O-1 and O-2). Many other studies confirmed its validity, e.g. (B-2), (B-3).

If excess protic solvent is available in the solution, then the solvent will form a complex with the hydroperoxide molecule, e.g., in alcoholic media:



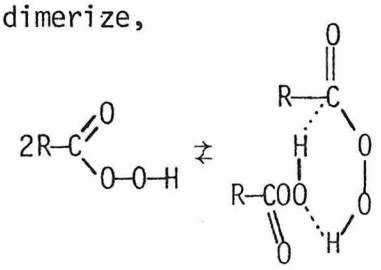
(3.3)

In aprotic solvent the hydroperoxide will dimerize:



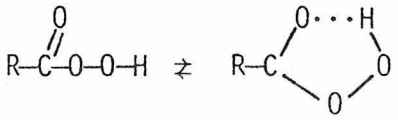
(3.4)

The chemistry of hydroperoxides was reviewed by Hiatt (H-3). Peracids may either dimerize,



(3.5)

or form an intramolecular complex,



(3.6)

The chemistry of peracids was reviewed by Swern (S-1). The mechanism of oxidation of sulfur compounds by peracids was discussed by Modena and Miola (M-1).

2. The solvent determines the rate equation as follows: A) In protic solvent the rate equation will be first order in each of the peroxide and the sulfur compounds, since the complex which actually oxidizes the sulfur compound contains only one peroxide molecule and one solvent molecule (B-5). B) In aprotic solvent, the rate equation will be second order in the peroxide, and first order in the sulfur compound. The second order dependence on the peroxide indicates that the peroxide dimer is the specie which actually does the oxidation (B-5, B-6). C) The rate equation will usually be first order with respect to the peroxy acid, since the function of the cyclic complex can be performed by the intramolecular complex.

3. In this study, it has been observed that oxidation of sulfur compounds in a nonprotic medium results in many more products than oxidation in a protic medium. A possible explanation is that the peroxidic dimer has a larger oxidation potential than complex of peroxides with nonprotic molecules.

4. The rate of oxidation of sulfur compounds, with sulfur in the α-position to π electrons, is a few orders of magnitude smaller than

that of compounds in which strong n-π electron interaction is impossible (F-1, B-4, B-5).

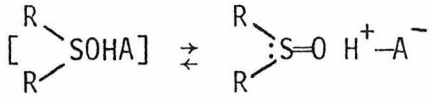
5. Acids catalyze the rate of oxidation but salts do not affect it (D-2, C-1).

6. Peroxides attack the sulfur atom faster than they attack olefinic bonds (B-6, B-7, B-8, B-9, B-10, H-2).

7. At temperatures below 70°C the rate of oxidation of sulfur compounds does not change due to the presence of air or of free radical inhibitors (B-4, B-5, O-1, O-2). Such behavior is consistent with the assumed mechanism, which does not include free radicals. However, free radicals react with the sulfur at higher temperatures (see part II).

8. The protic nature of the solvent affects the free energy of the oxidation both by altering the mechanism of oxidation and by interacting with the sulfoxide (D-3). Since sulfoxides are weak bases they can form complexes with protic solvent. The complex has low free energy and thus causes the rate of oxidation of sulfides to sulfoxides to increase and of sulfoxides to sulfones to decrease:

(3.7)



(3.8)

Reaction (3.8) shows that protic solvent affects the n-electrons of the sulfur in a similar way to a π bond in α position. The reduction in the availability of electrons on the sulfur causes the rate of oxidation to decrease.

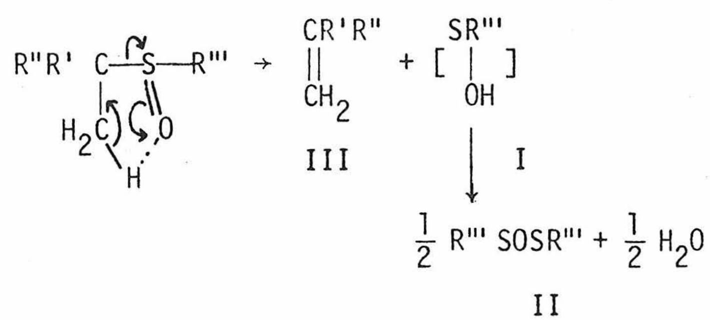
9. The rate of oxidation of aliphatic sulfides to the corresponding sulfoxides is much larger than the rate of oxidation of the sulfoxides to the sulfones. Stronger oxidizers are required to oxidize the sulfoxides to the sulfones than to oxidize the sulfides to the sulfoxide (S-2, H-4, H-5). The rate of oxidation of aryl sulfides and condensed thiophenes to the corresponding sulfoxides and sulfones is much smaller than that for aliphatic sulfides. The ratio of the rates of oxidation of aryl sulfoxides to sulfones and that of oxidation of the aryl sulfides to the sulfoxides is about one, but occasionally it is greater than one (G-1).

10. Sulfoxides were found to inhibit the oxidation of hydrocarbons (D-4, C-3, B-11) and to decompose peroxides. Inhibition can be due to several processes; the important ones are: A. oxidation of the sulfoxide to sulfone by the peroxides:

$$RO_2H + OS\langle \rightarrow ROH + O_2S\langle \qquad (3.9)$$

The consumption of peroxides by this reaction reduces the rate of branching and therefore the rate of oxidation.

B. A reaction between decomposition products of the sulfoxide and oxygen or peroxides (B-11):



(3.10)

The sulfenic acid (I) dimerizes to the thiolsulphinate II, which then reacts rapidly with oxidizers to form thiolsulphonates III (C-2):

$$R'''SOSR''' + RO_2H \rightarrow R'''SO_2SR''' + ROH\cdot \qquad (3.11)$$

The olefinic fragment (III) may react with oxygen or peroxide and cause additional inhibition.

11. Peroxy radicals at temperatures above 70°C may oxidize sulfur compounds in two ways:

A. By direct radical attack on the n electrons of the sulfur:

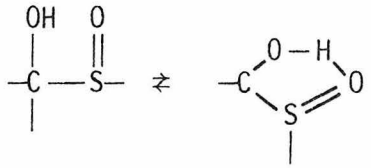
$$RO_2\cdot + :S\!\!\diagup\!\!\diagdown \rightarrow RO\cdot + OS\!\!\diagup\!\!\diagdown \qquad (3.12)$$

B. By attack on the α or β hydrogens:

$$RO_2\cdot + \underset{\displaystyle H}{\underset{|}{C}}\!-\!\ddot{S}\!- \rightarrow RO_2H + -\dot{C}\!-\!\ddot{S}- \qquad (3.13)$$

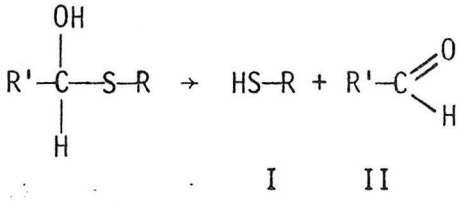
(I)

The presence of the sulfur greatly stabilizes radical I. Radical I absorbs oxygen very rapidly and reacts in a similar way to other organic radicals (see Chapter 2). The result is the production of α and β hydroxy-sulfides and α and β keto-sulfides. Sulfoxides react with peroxy radicals in the same way to produce α and β hydroxy-sulfoxides and α and β keto-sulfoxides. It is believed that the α hydroxy sulfoxide is the most stable specie because of the possibility of intramolecular cylic complex, II, which stabilizes the molecule via hydrogen bonding:



(3.14)

12. α-hydroxy sulfides decompose to the corresponding mercaptan (I) and aldehyde (II) [B-3]:

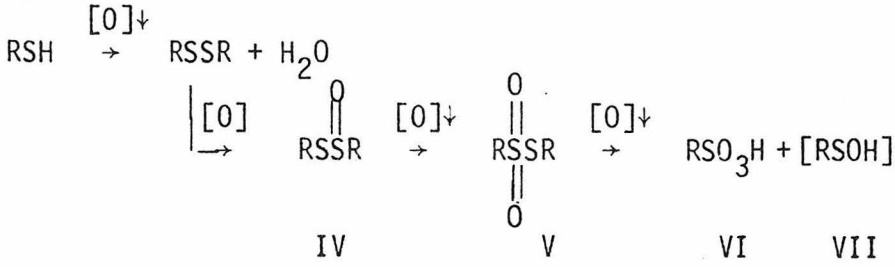


(3.15)

I II

Further oxidation will convert the aldehyde to the acid, and the mercaptan will react according to the following sequence:

I III



(3.16)

IV V VI VII

The disulfide (III) is easily oxidized to the thiasulfoxide IV. IV is oxidized to the thiasulfone V; V is oxidized to the sulfonic acid VI and to the sulfinic acid VII. VII is unstable, and will either rearrange and decompose or absorb a molecule of oxygen and become sulfonic acid (C-2).

13. The reactions of HBr with sulfides and sulfoxides are complex and depend significantly on the temperature and on the solvent. The following is a list of reactions that were quoted in the literature for a system which contains aliphatic sulfides, sulfoxides, HBr and Br_2.

1. Formation of sulfonium ion (R-4):

$$R\text{—}S\text{—}R + HBr \rightarrow [RSRH^+]\ Br^- \qquad (3.17)$$

2. Cleavage of the C—S bond (very slow (R-3):

$$CH_3\text{—}S\text{—}CH_3 + HBr \rightarrow CH_3SH + CH_3Br \qquad (3.18)$$

Note that Br is incorporated into the organic structure.

3. Adduct formation with Br_2 (R-3):

$$R\text{—}S\text{—}R + Br_2 \rightarrow R\ SBr_2R \qquad (3.19)$$

In the presence of water, hydrolysis occurs and sulfoxide is formed:

$$RSBr_2R + H_2O \rightleftarrows R\overset{\overset{O}{\|}}{S}R + 2HBr \qquad (3.20)$$

The kinetics of this reaction were studied in detail by Miotti et al. (M-4) who examined several aryl-methyl sulfides at 25°C and in a mixed organic-aqueous medium. Under these conditions they state that the reaction is "practically irreversible". The reaction with iodine is reversible (H-8). However, several authors have used the reverse

reaction as a method to determine sulfoxide by titrating the bromine which is liberated (A-8, p. 33)

$$R\text{—}SO\text{—}R' + 2HBr \rightarrow RSR' + Br_2 + H_2O \qquad (3.21)$$

but reduction with HI was generally performed as an analytical method. The conclusion is that at room temperature Br_2 would probably oxidize sulfides but at higher temperatures the reverse reaction may become more important.

A particularly interesting case is the behavior in a system which contains water dispersed in aprotic solvent. The solubility of HBr in water is very large, and it tends to be extracted to the aqueous phase. Sulfoxides are surface-active materials and concentrate on the interphase between the water and the organic medium. Since the sulfides are soluble essentially only in the organic medium and have no surface activity, they will remain evenly distributed in the bulk of the organic solvent. Since large concentrations of sulfoxide and HBr are realized on the boundary of the two phases, reaction (13.21) will dominate and the sulfoxide will be reduced back to the sulfide.

Chapter 4

THERMODYNAMIC ANALYSIS AND THE LOSS OF HEATING VALUE DUE TO OXIDATION

Two kinds of thermodynamic analysis were made:

1. Calculations of the equilibrium composition that the system will try to reach.

2. Calculation of the enthalpy losses due to oxidation.

The results of the calculations of the equilibrium concentrations have a limited value because under the conditions of the reaction, the system was far from equilibrium. However, conclusions may be derived on the general trends of the reactions The method for calculating the equilibrium composition was detailed by Attar (A-6, p. 20); so only a brief discussion of the results will be given.

A general method for calculating enthalpy changes is discussed first and then applied to the calculation of the heat loss due to the co-oxidation of Tetralin and butyl sulfide. The actual use of the method is demonstrated in Chapter 7, where the loss of heating value as a function of the reaction time and of the sulfide conversion was calculated and plotted.

4.1 Calculation of the Equilibrium Concentration

A variation of the steepest-descent method of White et al (W-6) was used. A detailed description of the method and of the modifications that were made was given in a previous report (A-6). The main results are:

1. In the presence of limited amounts of oxygen, the large organic molecules tend to crack to carbon and hydrogen.

2. The oxygen ends essentially as water, although small amounts of CO and CO_2 are also formed.

3. The sulfur ends as H_2S.

4. The HBr does not change.

Small perturbations in the values of the free energy or of the temperature did not affect the equilibrium composition.

At temperatures higher than 500°C, organic reactants may reach equilibrium; indeed it is known that H_2, C, and H_2S are formed when hydrocarbons are heated or pyrolized unaerobically. However, at temperatures below 200°C, the kinetics of the reactions controls.

4.2 The Trade-Off of Energy vs. Desulfurization

The penalty for the conversion of the sulfur compounds to the corresponding sulfoxides and sulfones is the loss of heating value of the fuel due to its oxidation. We therefore want to know how much heating value is lost for a given conversion of the sulfur compound. The product distribution is controlled by the kinetics of the reaction, but since the enthalpy of the system depends on its composition, once the composition is known, it is possible to evaluate the enthalpy loss for a given conversion.

The method is first discussed for a general system and then applied to the analysis of the oxidation of sulfur compound in a hydrocarbon medium.

4.2.1 A Method for the Evaluation of Enthalpy Changes due to a Complex Reaction

The classical method for the evaluation of enthalpy changes of a chemical system requires detailed knowledge of the chemical composition and the corresponding thermodynamic data. Such information is difficult to derive for a complex mixture and therefore is rarely available. A very good estimate of the enthalpy change can be obtained, however, if the chemical functional group distribution (FGD) of the system is known. The FGD can be obtained experimentally much more easily than the detailed composition of the system. Furthermore, thermodynamic data for specific compounds are not required.

The following assumptions are used in the derivation: 1) The system is isothermic and isobaric. 2) The reactants and the products are ideal mixtures. 3) The enthalpy of a molecule is the sum of the enthalpies of the functional groups that make it.

Let there be in the system m functional groups and let the j^{th} group appear n_{ji} times in the i^{th} component. Denote the specific enthalpy of the j^{th} group h_j, then the enthalpy of the molecule, H_i, will be

$$H_i = \sum_{j=1}^{m} h_j n_{ji} \tag{4.1}$$

If the concentration of the i^{th} component is C_i, then the enthalpy of the system per unit volume, H_s, is

$$H_s = \sum_{i}^{n} C_i H_i = \sum_{i}^{n} C_i \sum_{j}^{m} h_j n_{ji} = \sum_{i}^{n} \sum_{j}^{m} h_j n_{ji} C_i = \sum_{j}^{m} h_j \bar{c}_j \tag{4.2}$$

$\bar{c}_j$ denotes the concentration of the j^{th} functional group in the system. When the concentration vector changes, the enthalpy will change by ΔH_R. When all the concentrations and specific enthalpies are known the change in the enthalpy can be calculated from:

$$\Delta H_R = \sum_i^n C_i \sum_j^m h_j n_{ji}\Big|_{final} - \sum_i^n C_i \sum_j^m h_j n_{ji}\Big|_{initial}$$

$$= \sum_i^n (C_{i\ final} - C_{i\ initial}) H_i \qquad (4.3)$$

But when only the FGD is known, ΔH_R can be calculated from

$$\Delta H_R = \sum_j^m h_j \bar{c}_j\Big|_{final} - \sum_j^m h_j \bar{c}_j\Big|_{initial} =$$

$$= \sum_j^m h_j (\bar{c}_{j\ final} - \bar{c}_{j\ initial}) \qquad (4.4)$$

The two methods are equivalent provided that the group additivity rule for the enthalpy of formation holds.

The proposed method has two major advantages:

1. The functional group distribution can be determined experimentally much more readily than the exact composition of numerous components.

2. Only the m functional groups that actually change need to be considered.

4.2.2 Application to a Reacting System

Consider a system in which a chemical reaction takes place. Denote the chemical composition vector $\underset{\sim}{C}(t)$ (n elements), and the FGD vector

$\underset{\sim}{\bar{c}}(t)$ (m elements). If the system is modeled by the set of differential equations

$$\dot{\underset{\sim}{c}} = f(\underset{\sim}{c}, t, \underset{\sim}{c}_0) \tag{4.5}$$

then by integrating the initial value problem (4.5), one obtains $\underset{\sim}{c}(t)$. $\underset{\sim}{\bar{c}}(t)$ is uniquely determined by $\underset{\sim}{c}(t)$ and can be readily calculated from it. Substitution of $\bar{c}(t)$ in equations (4.4) give:

$$\Delta H_R(t) = \sum_j^m h_j(\bar{c}_j(t) - \bar{c}_j(0)) = \underset{\sim}{h} \cdot (\underset{\sim}{\bar{c}}(t) - \underset{\sim}{\bar{c}}(0)) \tag{4.6}$$

ΔH_R can be plotted vs. the time and vs. the conversion of a particular component, vs. the production of a particular functional group, or vs. any other desirable parameter. A diagram for the energy of the system results. In Chapter 7 such graphs are presented in which the enthalpy loss due to the oxidation was plotted vs. the reaction time and vs. the sulfide conversion.

4.2.3 Case Study: The Enthalpy Loss in the Co-oxidation of Tetralin and Dibutyl-Sulfide

1. Definition of the Problem:

Derive an algorithm to evaluate the loss of heating value of a mixture of Tetralin (TRLN) and dibutyl sulfide (DBS) due to oxidation.

2. Definition of the Initial Condition:

Let the initial condition of the system be: 5.059 mole/liter TRLN and 0.1424 mole/liter DBS. Let the reaction be isothermal at 140°C and the oxygen concentration of $5.34 \cdot 10^{-3}$mole/liter.

3. Definition of the Course of the Oxidation

Let us assume that a model with N reactions can describe the system. The major products of the reaction according to the model are: tetratone (CO), tetralol (ROH), 1,2-dihydronaphthalene (REN), tetralyl hydroperoxide (RO_2H), tetralin di-ketone (DICO), water (H_2O), hydrogen peroxide (H_2O_2), butyl sulfoxide (SO), butyl sulfone (SO_2), α-keto-butyl sulfoxide (COSO), α-ketobutyl sulfide (COS) and α-hydroxy butyl sulfoxide (SOOH). Note that the carbon structure of neither the TRLN nor the DBS was broken.

4. Analysis of the Functional Group Distribution and the Enthalpy Loss

The analysis can be simplified if the molecules that did not react would be neglected. The following subscripts are introduced: 1 for TRLN, 2 for CO, 3 for ROH, 4 for REN, 5 for RO_2H, 6 for DICO, 7 for H_2O, 8 for H_2O_2, 10 for DBS (or S), 11 for SO, 12 for SO_2, 13 for COSO, 14 for COS, and 15 for SOOH. Since the solutions are assumed to be ideal, their volumes do not change due to the reaction. The decrease in the concentration of TRLN is therefore given by

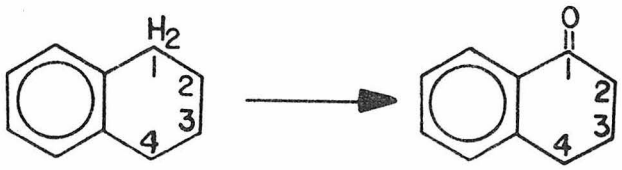
$$\Delta C_1 = \sum_{2}^{6} C_i \tag{4.7}$$

The decrease in the concentration of the sulfide is

$$\Delta C_{10} = \sum_{11}^{15} C_i \tag{4.8}$$

Only the groups that change in the reaction need be considered in the calculation. For example, one molecule of Tetralin (I) reacted to produce one molecule of tetralone. The net change in enthalpy is

the enthalpy of a carbonyl group minus the enthalpy of a methylene group.



I II

Note that the mechanism of the reactions does not influence the thermodynamic calculation. Only the final products do. The nomenclature of reference (B-14) is used, the data for the enthalpies of formation were taken from the tables in reference (B-14, p. 178-215). The results are summarized in Table 4.1. Only the FG that changed were considered, so in the case of Tetralin or its derivatives, only the carbons at positions 1, 2, and 4 were considered. In the case of butyl sulfide and its derivatives, only the sulfur and the two α carbon atoms were considered. The sum of the enthalpies of formation for the groups that changed was denoted $\Delta \sum_j h_j n_{ji}$. The difference between $\Delta \sum_j h_j n_{ji}$ and its value for the original hydrocarbon was denoted ΔH_i. To calculate the heat loss at any desired composition, equations (4.3) or (4.4) were used. Plots of the loss of heating value as a function of time and sulfide conversion are given in Chapter 7.

Table 4.1 The Change in the Functional Groups in the Co-Oxidation of Tetralin and Butyl Sulfide at 140°C and the Enthalpy of Formation of the Oxidation Products (Nomenclature and data taken from Ref. (B-14) and Table 7.1)

Group	Enthalpy of Formation	CO	ROH	REN	RO_2H	DICO	SO	SO_2	COSO	COS	SOOH	RH TRLN	S BUS
C-Cb$(H)_2$C	-3.96	1	1	1	1							2	
C-$(C)_2(H)_2$	-4.13	1	1		1	1						1	
C-Cb,O,C,H	-8.90		1		1								
O-C,H	-37.4		1								1		
Cd-Cb,H	7.46			1									
Cd-C,H	9.18			1									
CO-C,Cb	-36.9	1				2							
O-O,C	-4.07				1								
O-O,H	-15.6				1								
*C-C,(SO),H_2	7.72						2		1		1		
SO-C_2	-13.25						1		1		1		
C-C$(SO_2)H_2$	-7.83							2					
SO_2-C_2	-68.42							1					
CO-S,C	-30.91									1			

Table 4.1 (continued)

Group	Enthalpy of Formation	CO	ROH	REN	RO_2H	DICO	SO	SO_2	COSO	COS	SOOH	RH TRLN	S BUS
*C-(OH),(SO),C,H	5.64										1		
*CO-C,SO	-18.39								1				
C-C(H)$_2$S	-4.81										1		2
S-C$_2$	12.57										1		1
H_2O	-56.90												
H_2O_2	-31.30												
$\Delta\sum_j h_i n_{ij}$		-44.99	-54.39	12.68	-36.66	-77.93	2.19	-84.08	-23.92	-23.15	0.11	-12.05	2.95
**ΔH_i kcal/mole		-32.94	-42.34	24.73	-24.61	-65.88	-0.76	-87.03	-26.87	-26.10	-2.84	0	0

*Estimated by the author.

**ΔH_i is the change in the enthalpy due to the formation of one molecule of oxidation product.

Chapter 5

EXPERIMENTAL

The experimental work had three goals: 1) to establish whether catalysis of the hydrogen-abstraction step enhances the oxidation of the sulfur compounds, 2) to find the type of sulfur compounds which are produced and to infer from it the oxidation mechanism, and 3) to find limited amounts of kinetics data for selected systems.

The work was exploratory. Therefore the qualitative answers were regarded as important as the quantitative ones.

In the discussion of the experimental work there are four parts:

1) An elaboration on the choice of the experimental system.
2) Description of the chemical reactor and the experimental procedure.
3) Description of the analytical instruments and analytical procedures.
4) Estimation of the possible mass transfer in the reactor.

5.1 On the Choice of the Experimental System

Choice of the experimental system involved type of reactor and analytical methods, the chemical system, and the range of parameters to be examined.

5.1.1 The Reactor

A batch reactor was chosen because long reaction periods were anticipated and because it can be easily designed to minimize the surface/volume ratio and thus minimize surface effects.

In practice, oxygen and HBr were bubbled through the liquid solution of the hydrocarbon; however, because the rate of oxidation was rather slow, the liquid assumed rapid equilibrium with the gas and therefore

modeling of the system as a batch reactor holds. (See also Section 5.4).

5.1.2 The Chemical System

Two approaches to the choice of the chemical system were possible: 1) work on oil fraction; 2) work on model sulfur compounds in a medium which simulates oil.

Work on oil would provide information on the oxidation of a real fuel; however, it would have only limited value in the understanding of the mechanism of the reaction and to extrapolation of the data beyond the region that was empirically tested. Enormous analytical difficulties were anticipated for work with oil.

Work with model compounds allowed the determination of the mechanism of reaction of a single sulfur compound or of a homolog group. The analytical problems were simpler and the system was much better defined. Extrapolation of the work on model sulfur compounds to actual fuel, however, might be difficult.

The latter approach was chosen because it is more basic and may provide information on the mechanism of a class of reactions.

The choice of four chemical components was required: the sulfur compound, the hydrocarbon carrier, the solvent, and the catalyst.

5.1.2.1 The Choice of Sulfur Compound

Di-n-butyl sulfide (DBS) and di-benzothiophene (DBT) were chosen for the preliminary study. The criteria for the choice were:

1. DBT and DBS resemble chemically the largest two groups of sulfur compounds that were found in gas oil and heavy crudes.

2. Limited amounts of data were available on the rate of oxidation of DBT and DBS by organic peroxides.

3. DBT and DBS as well as some of their oxidation products are available commercially.

4. DBT and DBS have a symmetric structure. A smaller number of products are possible with symmetric structures and therefore easier analytical problems were anticipated.

The two major differences between the behavior toward oxidation of DBS and DBT are: that the sulfur in DBS is connected to two electron releasing groups which tend to increase its nucleophility. The sulfur in DBT is connected to two aromatic rings. The π electrons resonate with the n-electrons of the sulfur and cause a reduction in the electron density. The oxidation potential which is required to oxidize DBT is much larger than that for DBS ($E_{1/2}$(DBT) =-2.432 V in DMF vs. Ag/AgCl electrode (G-2); $E_{1/2}$(DBS) = 0.77 V in 0.1 N HCl in CH_3OH vs. Ag/AgCl electrode (D-5).

The second major difference is that DBS contains aliphatic hydrogens, which can be abstracted much more readily than the aromatic hydrogens of DBT. As a result, one may expect the selectivity to be larger when DBT is oxidized compared with that when DBS is oxidized.

5.1.2.2 The Choice of the Hydrocarbon Medium and Solvent

The hydrocarbon medium serves two functions: It is a source of free radicals, R, and is a solvent for the reagents and products.

In order to be able to infer from the results the behavior of an oil, a hydrocarbon with a benzene ring was desired, because most of the

molecules of a heavy oil contain at least one. No clear criterion is available by which to evaluate the adequacy of alternative hydrocarbons to simulate fuel. The criterion that was adopted was the relative rate of hydrogen abstraction, because the hydrogen abstraction was the rate limiting step of the oxidation for hydrocarbons. Two hydrocarbons were chosen with extreme reactivities toward hydrogen abstraction. The idea was that the reactivity of fuel will be an intermediate value between the two. The two hydrocarbons that were used were toluene and Tetralin; and the relative reactivity of the two toward hydrogen abstraction is 1:300 (H-6). The reactivity of all the common hydrocarbons is between the reactivity of these two.

The properties of the hydrocarbons were modified by adding solvents with different proticity, e.g., bromobenzene (non-protic) and 1-octanol (protic). Bromobenzene and O-dichlorobenzene are inert to oxidation below 200°C, because they do not have active hydrogens. The reactivity of the solvent will be seen when the hydrocarbon is non-reactive, as with toluene. However, if the hydrocarbon is much more reactive than the solvent, the reactions of the solvent will be of marginal importance.

5.1.2.3 The Choice of the Catalyst

The properties of the desired catalyst are reactivity toward hydrogen abstraction and specificity to the hydrogen abstraction step.

In order to eliminate complications from mass transfer and surface effects, a homogeneous catalyst was preferable. Because information on the reactivity and specificity of HBr was available (see Section 2.5),

it was chosen to start with. HBr is a reactive catalyst for hydrogen abstraction; however, it also catalyzes the decomposition of peroxides, produces olefin by dehydration of alcohols, and isomerizes alkyl benzenes. The Br radicals form Br_2 which is even more reactive than HBr and further complicates the system. HBr can reduce sulfoxides to bivalent sulfur, and in this way counteract the goal of obtaining oxidized sulfur compounds. The dangerous properties of HBr and its high corrosivity complicated the work and imposed safety constraints on the operation.

HBr proved a useful catalyst to demonstrate the principle of the thesis; however, a more specific one is recommended for future studies.

5.2 The Reactor and the Experimental Procedure

5.2.1 Mechanical Design of the Experimental System

Figure 5.1 is a flow diagram of the experimental system. A detailed description is given only for the non-standard items.

The reactor was constructed from a standard 500 ml 3-necked pyrex flask to which two additional 24/40 ground glass points were symmetrically connected. Figure 5.2 shows the reactor. The central joint was a ground joint 34/40 into which a pyrex stirrer with Teflon blades was connected (Corning type 28-52). The other four necks were used for 1) a liquid sampling device (Fig. 5.3), 2) gas bubbler composed of a standard 20 mm porous sintered glass type M through which the oxygen-catalyst mixture was dispersed, 3) a thermowell in which a thermistor (YSI Part No. 44004) and a copper-constantan 24G thermocouple were inserted, 4) a reflax condenser. The gas that came from the condenser was passed through a gas-sampling valve and vented. Gas samples were analyzed by GC for selected experiments.

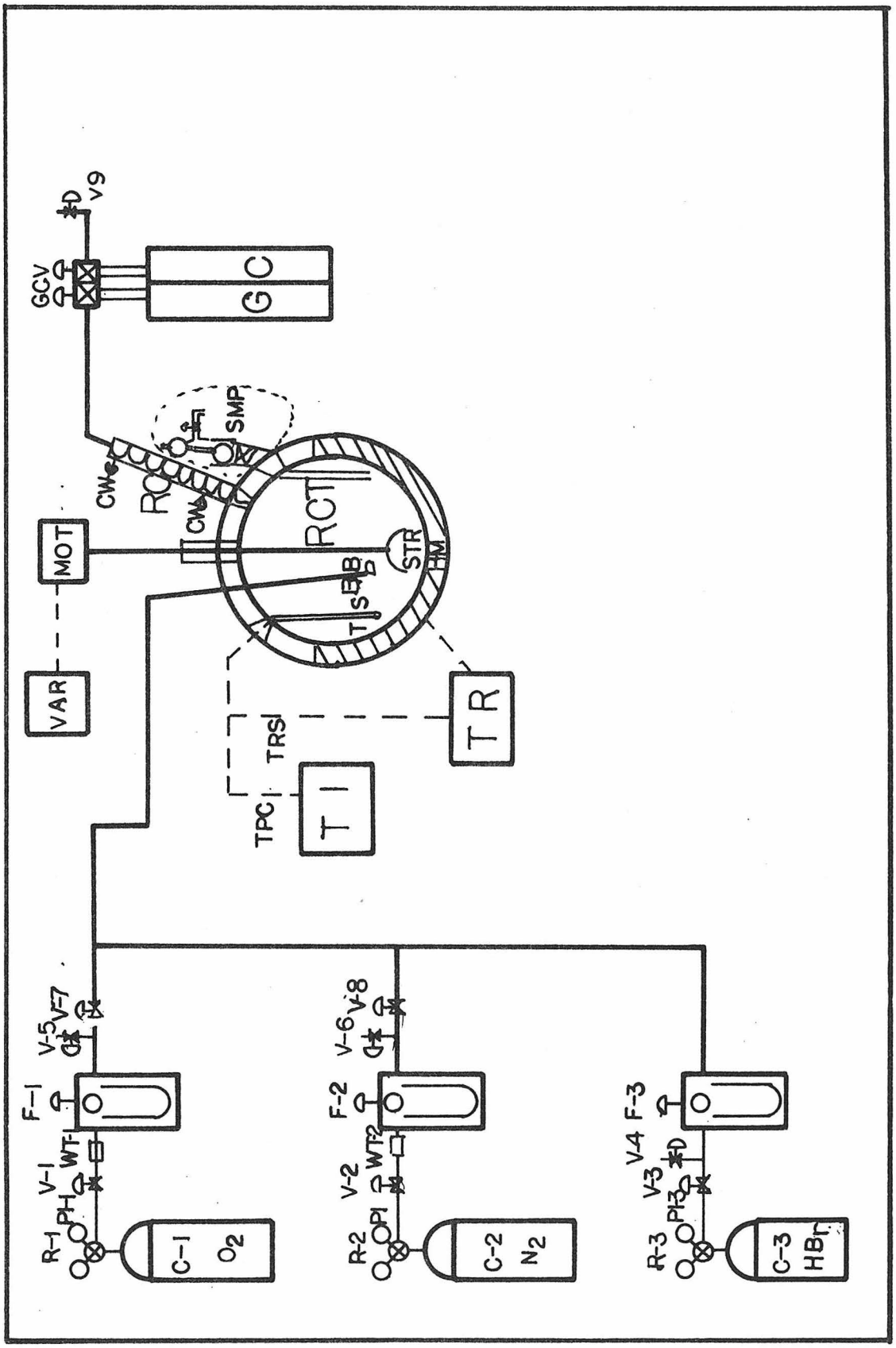


Figure 5.1 Schematic Flow Diagram of the Experimental System. The nomenclature is detailed in Table 5.1.

Table 5.1

List of Major Parts

Designation	Function	Material	Remarks
BB	Gas bubbler	Sintered Glass	Medium porosity 20 mmϕ
C-1	Oxygen cylinder		
C-2	Nitrogen cylinder		
C-3	HBr cylinder		
CW	Coding water line	tygon	
F-1	Oxygen flowmeter	SS316	See Figure 5.4
F-2	Nitrogen flowmeter	Brass	
F-3	HBr flowmeter	Monel	
GC	Gas chromatograph		Carl, Basic
GCV	Gas chromatograph sampling valve	SS316	Carl, 8 ports
HM	Heating mantel		Glass Col 500W, 500 ml
MOT	Motor		1/10 HP
PI-1	Oxygen pressure indicator		Matheson PN-63-3115
PI-2	Nitrogen pressure indicator		Matheson PN-63-3115
PI-3	HBr pressure indicator	Monel	Matheson PN-63-3312
R-1	Oxygen pressure regulator		Matheson 8-350
R-2	Nitrogen pressure regulator		Matheson 8-850
R-3	HBr pressure regulator		Matheson B15-330
RCT	Reactor	Pyrex	500 ml

Table 5.1 (cont'd)

Designation	Function		Remarks
SMP	Sampling device	Pyrex	See Figure 5.3
STR	Stirrer	Pyrex, Teflon	Glass, Corning Model 7272
TI	Temperature indicator		Bailey Instr. Model BAT-7
TS	Temperature sensing probe	Glass	
TR	Temperature regulator		Versa-Term, Model 2156
TRC	Thermocouple (ion-constantan)		
TRS	Thermistor		YSP, Model 44004
V-1	O_2 Regulator valve	Brass	
V-2	N_2 Regulator valve	Brass	
V-3	HBr Regulator valve	Brass	
V-4	HBr Vent valve	Monel	Swagelok, M-1GS4
V-5	O_2 Vent toggle valve	Brass	Swagelok, B-OG52
V-6	N_2 Vent toggle valve	Brass	Swagelok, B-OG52
V-7	O_2 Flow toggle valve	Brass	Swagelok, B-OG52
V-8	N_2 Flow toggle valve	Brass	Swagelok, B-OG52
V-9	Outlet gas back pressure valve	Monel	Swagelok, M-2JR
WT-1	Water trap	Brass	MS 5Å
WT-2	Water trap	Brass	MS 5Å

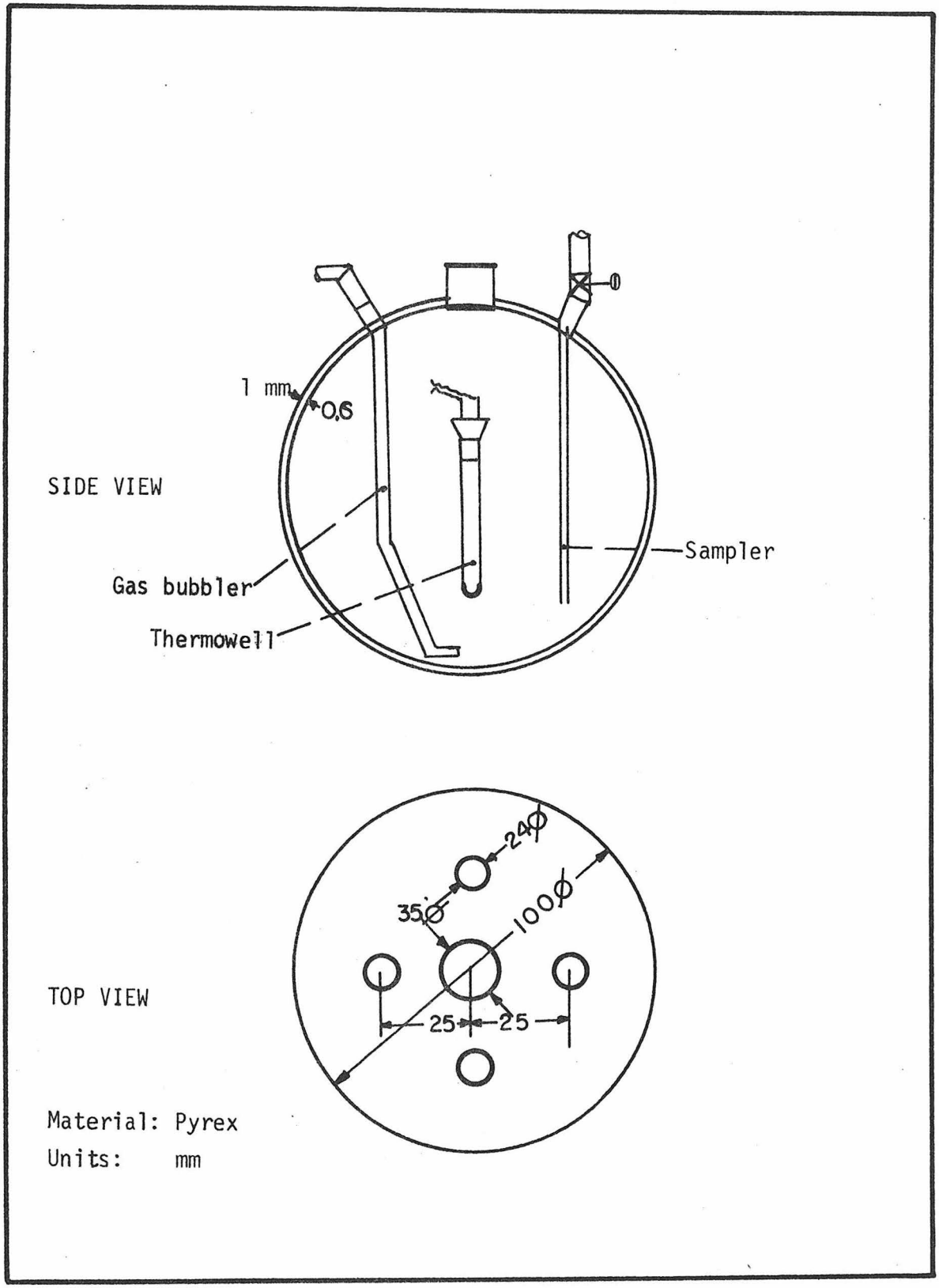


Figure 5.2. Reactor for Liquid Phase Oxidation of Hydrocarbons

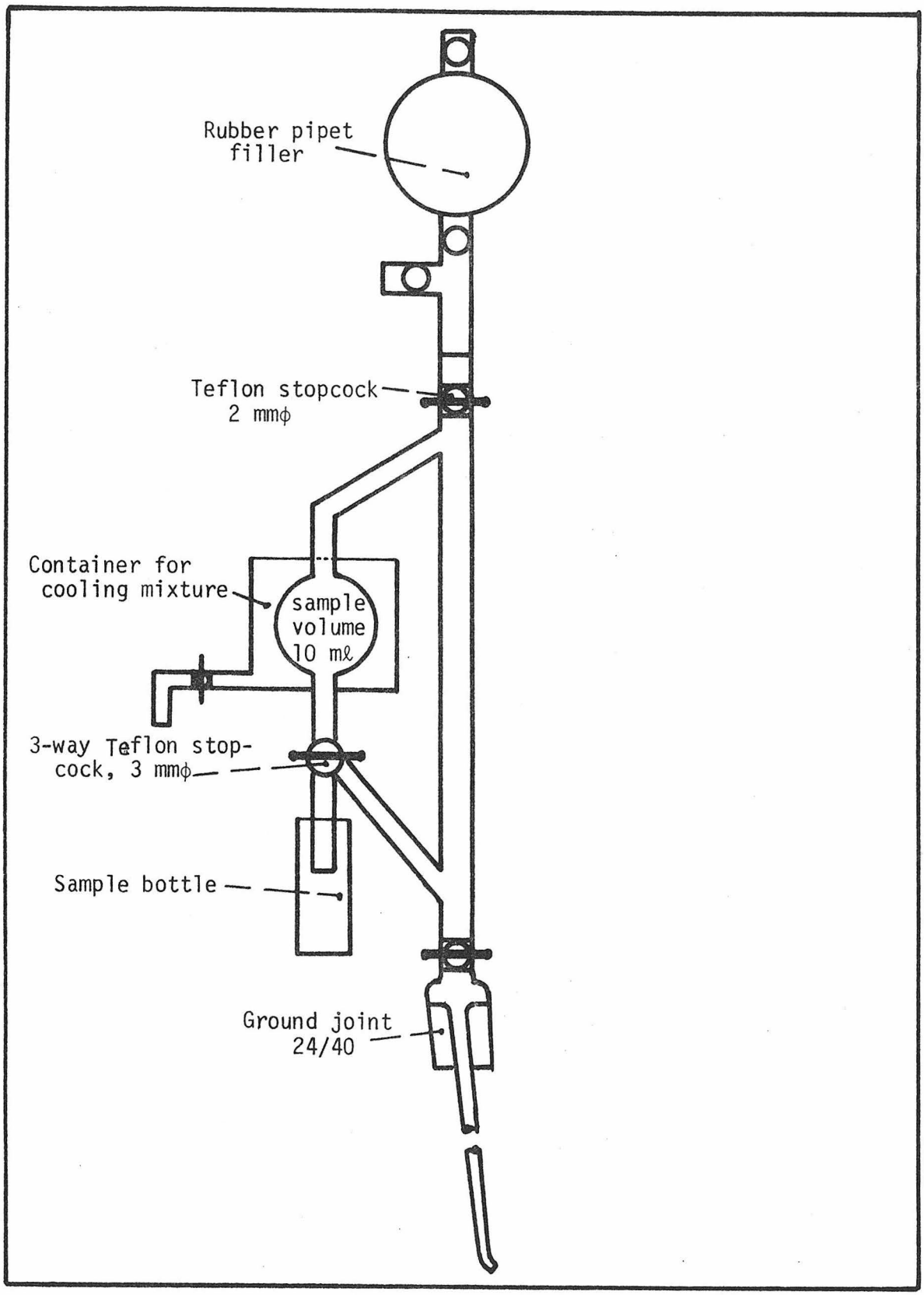


Figure 5.3 Sampling Device for Liquid Samples

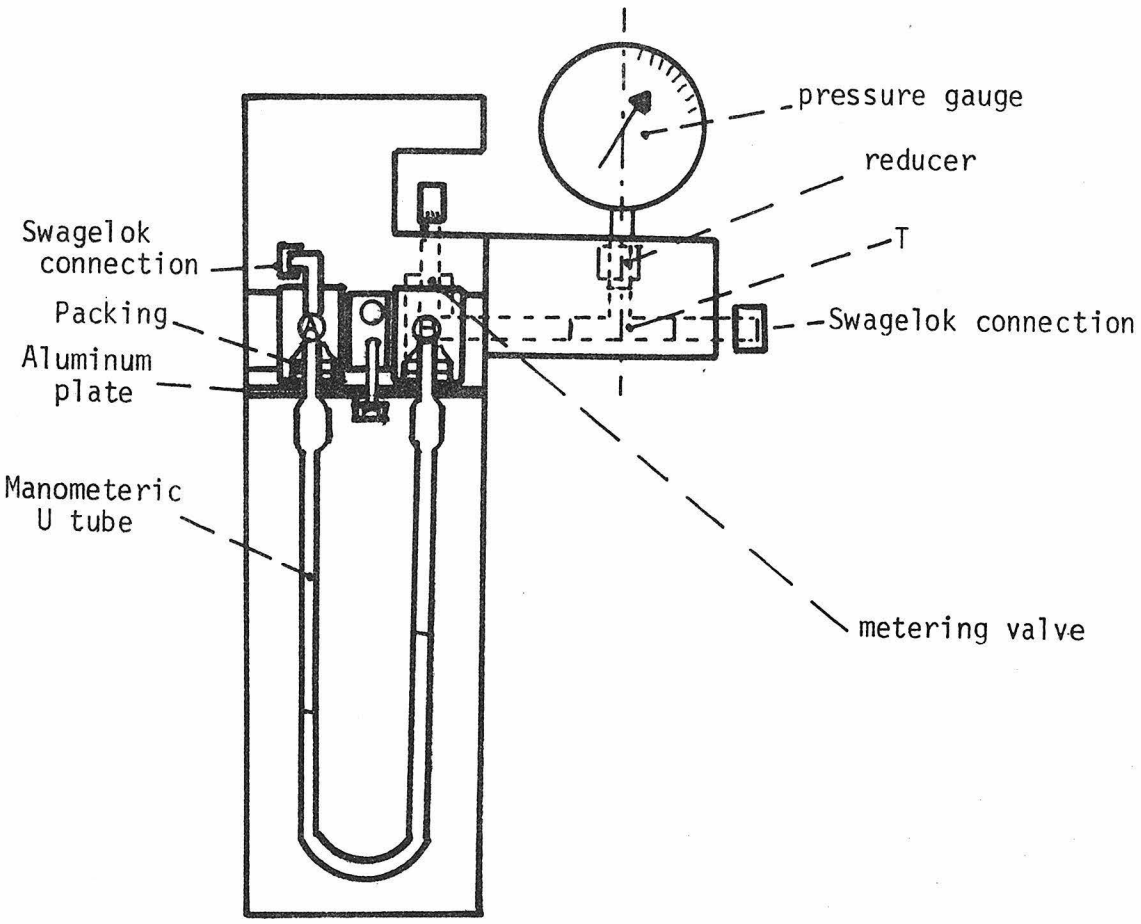


Figure 5.4 A fixed-bed pressure drop volumetric flowmeter. The manometeric pressure difference is proportional to the volumetric flow rate. Used to measure accurately flow rates of the order of 10 ml/hr. Leads A and B are connected by a tube packed with glass beads 0.00095" through which the gas flows.

The reactor was heated with a Glass-Col 500 ml mantle and controlled with a Versa-therm controller, Model No. 2156. The temperature was monitored with an electronic thermometer, Bailey Inst. Model Bat 7.

Oxygen, hydrogen bromide and nitrogen were fed to the reactor from cylinders of compressed gas. The pressure was regulated with standard gas regulators. The rate of flow was monitored with a flowmeter which was specially designed for this purpose. Figure 5.4 shows one of the flowmeters. The rate of flow was measured by monitoring the pressure drop that it created across a fixed bed of small glass beads. The range of flow measurement was determined by the length of the bed of beads, the length of the manometer tubes, and the density of the fluid in them.

5.2.2 Experimental Procedure

Each experiment was conducted as follows:

1. All glass and Teflon parts which came in contact with the reacting solution were deactivated. (The deactivation procedure is described in Appendix B). This deactivation resulted in the etherification of the active OH groups on the glass surface. It was found necessary to repeat the treatment after every three experiments.
2. The reaction components were purified (Appendix B) and stored under nitrogen.
3. The reactants were mixed in the reactor, under nitrogen atmosphere and a sample of the cold mixture was taken.
4. The mixture was heated to the desired temperature while HBr and nitrogen at the desired rates were flowing through. The N_2 rate

was adjusted to be the same as the desired oxygen flow during the oxidation.

5. One to two hours after the mixture reached temperature, a sample of the hot liquid was withdrawn and the nitrogen flow was switched to oxygen at the same rate. The moment of turning on the oxygen was denoted time 0.
6. Samples were withdrawn every fifteen minutes in the first two hours, and every thirty minutes in the following three and a half hours.
7. The reaction was stopped after five and a half hours by turning off the heat, the oxygen, and the HBr flow. The reactor was cooled in an ice bath to about 60°C and the solution was vacuum pumped out into a specially designed cold container.
8. The UV absorbance of the samples was measured at the desired wavelengths immediately after the reaction, using the first sample as a reference.
9. The samples were analyzed qualitatively and quantitatively in the following days.

5.3 Methods of Chemical Analysis

The discussion of the qualitative methods is separated from that of the quantitative ones.

5.3.1 Methods of Qualitative Analysis

One of the biggest problems that has been encountered was the qualitative analysis of the reaction products. The difficulty was due to 1) the complexity of the multicomponent mixtures involved 2) the

availability of small and dilute samples only, 3) the low conversion that was used, and 4) the low sensitivity of the equipment used for qualitative analysis (e.g., IR and NMR).

Traditionally, qualitative analysis is done using IR, NMR, MS and UV techniques. However, in order to utilize these techniques, a relatively large amount of a pure material is required. Separation and purification was done by chromatography; however, except for a few of the major components, it was impossible to isolate sufficient amounts of pure components to carry on a meaningful analysis.

First, the non-standard methods are described, and then a list of standard techniques is given.

5.3.1.1 IR Techniques

IR analysis gives information on the functional groups that are in the sample. A compilation of the IR absorption bands of sulfur functional groups is given in Table 5.2 (L-1):

Table 5.2 IR Absorption Bands for Sulfur Functional Groups

Group	Band, cm^{-1}
$-\overset{}{\underset{}{S}}=O$	1060-1040
$-\overset{O}{\overset{\|\|}{S}}-O^{1+}$	1090
$-\overset{O}{\overset{\|\|}{S}}-OR$	1135-1125
$RO-\overset{O}{\overset{\|\|}{S}}-OR$	1215-1150
$-SO_2-$	1160-1140, 1300-1350
$-O-SO_2-$	1200-1145, 1350-1300
$-O-SO_2-O-$	1230-1150, 1440-1350
SO_3H, SO_3^-	1210-1150, 1060-1030, and 650
$-SO_2-SR$	1150-1110, 1350-1330
Aryl sulfides	732-710
Primary sulfides	660-630
Secondary sulfides	630-600
Tertiary sulfides	600-570

Perkin-Elmer IR equipment with two kinds of cells from Barnes Engineering Company was used:

1. NaCl cell, Model 0003-504 for water free samples.
2. BaF_2 cell, Model 0004-035 for moist samples.

The BaF_2 windows allow only modest sensitivity because they absorb up to 70% of the light. They are not useful for wavenumbers smaller than 950 cm^{-1}.

5.3.1.2 GC-MS Computer

GC is a powerful separation technique, and MS is an excellent identification method for organic compounds. When the two methods are combined, it is often possible to identify components of mixtures which cannot be done in any other way. The output from a GC column is fed into a mass spectrometer after most of the carrier gas is separated. MS scans are taken at the desired frequency, and the results are stored on a tape. At the end of the chromatogram, the data are retrieved from the tape and analyzed as required. In this study the method was used for the identification of three kinds of components: 1) bromine containing compounds, 2) sulfur containing compounds and 3) hydrocarbon oxidation products.

The method for the identification of Br compounds was developed in this study. The method of Ref. G-4 for identifying sulfur compounds was attempted. Identification of hydrocarbon products is a standard technique, and will not be detailed here.

Identification of Bromine Compounds

The identification of bromine compounds was based on two facts: 1) bromine is present in nature in two isotopes, Br^{79} and Br^{81}, with a

relative abundance of 100:98, respectively; 2) organic bromine compounds form a Br^+ ion.

To identify a bromine compound, three signals are simultaneously monitored as a function of time: the total current of ions, the ion current due to m/e = 79 and that due to m/e = 81. Whenever a peak was seen in the total ion current, the size of the signals from the m/e = 79 and the m/e = 81 were compared. When their value was the same, it was assumed that that component contained bromine. Bromobenzene and its impurity,bromoethyl benzene were clearly identified by this method. Butyl bromide was also seen, but no tetralyl bromide was found. Only m/e below 250 was scanned.

Identification of the Sulfur Compounds

MS of bivalent sulfur compounds shows a peak at m/e = 47, which corresponds to $H_2C = SH^+$ (S-6), and at m/e = 45, which corresponds to CHS^+ (G-4). However, fragments with the former m/e are common to many organic compounds, and the abundance of the latter is rather small and not sufficiently specific unless a high-resolution spectrometer is used. The natural abundance of sulfur isotopes is S^{34}/S^{32} = 4.4/100, so if the total concentration of sulfur compound is small, the m/e = m/e + 2 peak cannot be seen.

Tetra and hexavalent organosulfur compounds were in such small concentration, and so poorly resolved, that none were seen where they were expected. Obviously, the MS is less sensitive to sulfur than the FPD, or the oxidized compounds did not reach the ion source because they

adsorbed to a surface in the duct between the GC and the MS.

The GC-MS was carried out on the home-made unit of the Chemistry Department, and on a Finnigan Model 3200El unit at the Jet Propulsion Laboratory. The standard techniques that were used for qualitative analysis are listed in Table 5.3.

5.3.2 Methods of Quantitative Analysis

Most of the quantitative analysis was done by gas chromatography. The methods that were developed in this study are detailed in Table 5.4.

Other methods that were used are liquid chromatography, polarography, titrametry and calorimetry. Standard determination of the heat of combustion was done using a Parr Adiabatic Calorimeter. The non-standard methods are described briefly in the following sections.

5.3.2.1 Determination of H_2O_2 and Hydroperoxides by Polarography (POL-1)

The method of Willits et al. (W-1) was used with a small modification. Platinum wire was used as an anode instead of a mercury pool. The solvent used was 0.3 LiCl in 50:50 C_6H_6: CH_3OH. A 1 ml sample was diluted with nine ml solvent and the polarogram was recorded from 0 to -2V. $E_{1/2}$ for hydrogen peroxide is -0.2V and for tetralyl hydroperoxide -0.75V. Each mole/liter of the original sample creates $4.0064 \cdot 10^3$ μa current, both for the H_2O_2 and the tetralyl hydroperoxide. The methods of Drushel (D-1) were used for the analysis of sulfur compounds by polarography.

Table 5.3 Methods of Qualitative Analysis

No.	Method and Equipment	Notation	Application	Ref.
1	Comparison of retention times or volumes. Hewlett-Packard Mod. 5700	GC-RT	Identification of compounds by comparing them to known compounds.	M-3, E-3
2	Comparison of retention times on columns with different polarity.	GC-RPOL	Identifying homolog members when some of the homologs are available.	E-3
3	Liquid chromatography. Spectra Physics Mod. 3500B	LC	Identifying compounds by their retention volume.	K-3
4	Mass spectrometry of separated compounds at the outlet of a GC (Homemade, Chemistry Dept, Caltech).	GC-MS	Identifying minor components which could be separated easily from the major ones	Sect. 5.3.1.2
5	Mass spectrometry. DuPont Mod.21-4926	MS	Identifying a compound and its structure.	S-6
6	Nuclear Magnetic Resonance. Varian A-60.	NMR	Identifying a compound by the NMR chemical shift of its hydrogens or carbons.	S-6
7	Infrared spectroscopy Perkin-Elmer Model 257	IR	Identifying the chemical functional groups in a compound by the absorption of IR light.	S-6
8	Ultraviolet spectrometry Carry Model 14M	UV	Identifying the unsaturated functional groups by absorption of UV light.	S-6
9	Polarography, Sargent, Model IV	POL	Identifying functional groups which can go redox reactions (to support identification by other methods).	Z-1 D-3

Table 5.3 - continued

No.	Method	Notation	Application	Ref.
10	Wet Chemistry	WC	Many chemicals or groups can be identified by their reactions with specific chemicals. The reagents differ from one problem to another.	

Note: The prefix R prior to the notation means that the analysis was done on a sample which was concentrated by vacuum distillation. The prefix S means analysis of a component which has been separated from the mixture.

Table 5.4 Methods of Analysis by Gas Chromatography

Separation of; and Notation	COLUMN						CONDITIONS	
	Length (ft)	Diameter (in.)	Support	Support size mesh	Stationary Phase	Stationary Phase %	Temp. Program °C	Carrier Flow ml/min
1,4 Dihydronaphthalene from Tetralin GC-1	6	1/8	Gas Chrom Q	80/100	DEGS	10	120	N_2 19
Tetralone and tetralol from Tetralin GC-2	6	1/8	Gas Chrom Q	80/100	DEGS	10	200	N_2 19
Sulfur Containing Oxidation products of Butyl Sulfide GC-3	6	1/8	Gas Chrom Q	80/100	DEGS	10	60-200°C @ 10°C°/ min.	N_2 19
Sulfur Containing Oxidation products of Butyl Sulfide GC-4	3	1/8	Chromosorb W	60/80	Carbowax 20M	20	80-200°C @ 4°C/ min.	N_2 38
Butyl Sulfide, tetrolin and oxidation products GC-5	3	1/8	Chromosorb W	60/80	Carbowax 20M	20	160	N_2 15
Butyl Sulfide, toluene and bromobenzene GC-6	3	1/8	Chromosorb W	60/80	Carbowax 20M	18	110	He 50
Butyl sulfide, oxidation products GC-7	6	1/8	Gas Chrom Q	80/100	DEGS	10	60-200°C @ 8°/min.	N_2 19
Tetralin, octanol oxidation products of Butyl Sulfide GC-8	6	1/8	Gas Chrom Q	80/100	DEGS	10	8 min @ 70°C at 10°/min to 200°C	N_2 17

Table 5.4 - continued

Separation of; and notation	COLUMN						CONDITIONS	
	Length (ft)	Diameter (in.)	Support	Support size mesh	Stationary Phase	Station-ary Phase %	Temp. Program °C	Carrier Flow ml/min
Tetralin, DBT, GC-9	3	1/8	Gas Chrom. Z	60/80	Carbowax 20M	20	215	He 30
Toluene, DBT, O-Dichlorobenzene	2	1/8	Gas Chrom. Q	80/100	OV-1	1	100-180° @ 15°C/ min	N_2 20

5.3.2.2 Acidometric Titration of Organic Acids

The method is applicable to the determination of dilute ($C < 10^{-3}$ mol/lit) organic acids. The potential of a glass electrode is monitored vs. a double-junction reference electrode. Saturated LiCl in CH_3OH is used in the outer junction cell.

1-2 ml organic solution is dissolved in 10 ml isopropanol and 5 ml 0.3 M LiCl solution in 70:30 volume ratio of a mixture of 95% C_2H_5OH, 5% i-C_3H_7OH and water are added. 0.01 NaOH in H_2O is used to titrate the acid. The titration should be done very slowly in a well mixed cell, because the reactions of higher molecular weight acids are slow. Radiometer automatic titrator was used for these measurements.

5.3.2.3 Liquid Chromatography

Reverse-phase isocratic liquid chromatography was used for verification of the determination of tetralone and tetralyl hydroperoxide. 70% CH_3OH in H_2O was used and the absorbance was monitored at 254 nm and at 310 nm. Spectra Physics liquid chromatograph Model 3500B, equipped with Perkins-Elmer detector LC-55 was used for these determinations.

5.3.3 Analytical Procedure

The following qualitative analysis measurements were made on samples from all the experiments:

1. IR and R-IR
2. WC for elementary sulfur
3. GC-RT and GC-RPOL.

On selected experiments GC-MS, MS, NMR and R-NMR, UV and POL were made. The following quantitative measurements were made on the samples of all

the experiments: UV at 310 and 475 nm and often at other wavelengths in the visible range and GC measurements for sulfur compounds and for the hydrocarbon products. The determination of most of the samples was made more than twice. Selected samples were analyzed by polarography, titrametry, and calorimetry. The results of the analysis are given in Chapter 6.

5.4 Estimation of the Possible Mass Transfer in the Reactor

In kinetics measurements it is required that the observed rate of change of concentrations be controlled by the rate of reaction and not by the rate of mass transfer. The dimensionless number M_s gives the ratio of the rate of mass transfer per unit volume to the rate of the fastest oxidation step.

$$M_s = \frac{k_\ell A[O_2]}{V k_2[O_2][R\cdot]} \tag{5.1}$$

where k_ℓ is the mass transfer coefficient, A the total area for mass transfer, V the volume of the solution, k_2 the rate of constant for the fastest oxidation reaction, $[O_2]$ an estimate of the oxygen concentration in the solution, and $[R\cdot]$ is an estimate of the free radical concentration in the solution. k_ℓ was estimated from equation (5.2) (C-5):

$$k_\ell = 0.31(g\frac{\mu}{\rho})^{1/3}\left(\frac{D_{O_2}}{\mu}\right)^{2/3} \tag{5.2}$$

where μ and ρ are the viscosity and the diffusivity of the solvent and D_{O_2} is the diffusivity of oxygen in it. μ was calculated as if the mixture were ideal. ρ was estimated from a nomograph (P-1).

D_{O_2} was estimated from the formula of Wilke and Chang (W-2):

$$D = 7.4 \cdot 10^{-8} \frac{T(xM)^{1/2}}{\mu V^{0.6}} \qquad (5.3)$$

where M is the molecular weight of the solvent, T the absolute temperature, μ the viscosity cp, V the molecular volume of the solvent, and x the association factor of the solvent. $x = 1$ for non-protic materials. The values that were obtained are: $\rho = 0.9$ gm/cm^3, $\mu = 2 \cdot 10^{-2}$ poise, $D_{O_2} = 9.2 \cdot 10^{-4}$ cm^2/sec^2. Substitution in (5.2) yields $k_\ell = 0.106$ mole/cm/sec. The dispenser produced bubbles approximately 0.7 mm, the total area for mass transfer was approximately 10.8 cm^2. The volume of the liquid was approximately 300 cm^3. Had the oxygen been in equilibrium with the gas phase, the oxygen concentration would be about $6 \cdot 10^{-3}$ mole/liter. The concentration of R· is approximately 10^{-10} mole/liter when there is sulfur compound in the solution, and 10^{-7} when there is no sulfur compound. (These values were estimated by the computer integration procedure, see Chapter 7). k_2 is approximately $7 \cdot 10^6$ liter/mole/sec. The smallest value of M_s is approximately:

$$M_s = \frac{0.106 \cdot 10.8 \cdot 6 \cdot 10^{-3}}{300 \cdot 7 \cdot 10^6 \cdot 6 \cdot 10^{-3} \cdot 10^{-10}} = 5.45 \ . \qquad (5.4)$$

Mass transfer of oxygen is possible at a much larger rate than the rate of oxygen consumption; therefore, one may assume that the solution is in equilibrium with the oxygen in the gas phase; and that the reactor is a batch reactor with a constant oxygen concentration.

Chapter 6

EXPERIMENTAL RESULTS

The results of nine experiments are given in this chapter. The analysis and discussion of the results are made in Chapter 7.

For each of the experiments three kinds of data are listed:

1. the experimental conditions,
2. qualitative results, and
3. quantitative results.

When standard qualitative or quantitative analysis techniques were used, no details are given. Methods which were developed for this study are discussed in Chapter 5 or Appendix A. Experimental errors are possible in the characterization of the experimental conditions, in the qualitative or in the quantitative analysis. The experimental conditions are known and were controlled with an error smaller than:

1. 0.5% in the weights of the hydrocarbon and the solvent,
2. 0.03% in the weights of the sulfur compound,
3. 0.2°C in the temperature. The large error was due to cooling down of the reactor content when a sample was withdrawn.
4. 5 mm Hg (estimate) in the pressure,
5. 20 sec in the time (period of sampling),
6. 10 mm in the HBr partial pressure,
7. 70 mm Hg in the O_2 partial pressure for the first 30 min of the experiment, and 30 mm Hg after that.

The identification of a chemical compound is rarely certain. When known and standard material is available for comparison, the chances for a

correct identification are relatively large; however, when a standard is not available, or when the compound is not pure or is a minor component of a complex mixture, the certainty of the identification decreases. Most of the sulfur containing products are minor components of a complex mixture, and no standard is available for comparison. The preparation of such standards involves considerable handling of α and β halosulfides, which are very dangerous poisons, similar to mustard gas. Because of lack of adequate facilities the compounds were not synthesized independently. Synthesis of standards was done when it was not too dangerous (e.g., butyl sulfonic acid and 1,2-dihydronaphthalene).

In the tables which detail the qualitative results, the last column gives the author's relative confidence in the certainty of the identification in a scale from 0 to 100.

The quantitative analysis of sulfur compounds by gas-chromatography has been detailed by the author in two papers, which have been submitted for publication (A-4,A-5). Systematic errors of up to 25% are possible for the sulfur compounds for which calibration standards were not available. The error in GC data with an FID detector was usually below 3% for non-routine analysis and less than 1% for routine analysis. Such an accuracy was not sufficient for the major components, e.g., the hydrocarbon and the solvent. The total consumption of hydrocarbon was of the order of the 1% possible error of the analysis. Thus material balance on the hydrocarbon-derived species was impossible. However, the major products of the oxidation of the hydrocarbon were determined

and provide a measure of the oxidation. The accuracy of polarographic and tetrametric methods is estimated as 20 and 2%, respectively.

In the tables of the quantitative results, the method which was used for the determination is written under the component name. The time interval between the end of the experiment and the analysis affect the quantitative results. The solutions that are formed keep reacting even when frozen. Therefore only a limited number of reliable determinations can be made on each sample. The result of the analysis of the reaction product is markedly different from that of the last sample, although the time difference between them is small. The product changes faster than the sample, even under nitrogen atmosphere because it was kept in a large bottle with a smaller surface/volume ratio.

6.1 Experiment 1

6.1.1 Experimental Conditions

Hydrocarbon:	Tetralin	218 grams
Sulfur compound:	None	-
Solvent:	Bromobenzene	100 grams
Oxidizer:	Oxygen (O_2), P_{o_2} = 591 mm Hg, C_{eO_2} = 5.3×10^{-3} mol/lit	
Catalyst:	Hydrogen bromide (HBr), P_{HBr} = 149 mm Hg, C_{eHB_r} = 1.3×10^{-3} mol/lit	
Total Pressure:	739.8 mm Hg	
Temperature:	140 ± 0.2 °C	
Duration of run:	336 min	

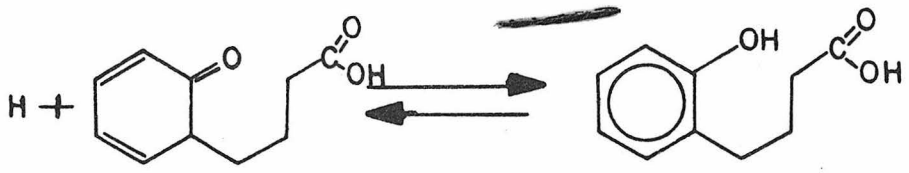
6.1.2 Qualitative Results of Experiment 1

Table 6.1 Qualitative Results of Experiment 1

Compound	Method	Support Evidence	Confidence of the Identification and Notes	
Tetralone	GC-RT	IR,POL,VV	100	compared with synthetic material
Tetralol	GC-RT	IR,NMR	100	compared with synthetic material
1,2-Dihydronaphthalene	GC-RT	IR	90	compared with synthetic material
Tetralyl hydroperoxide	POL	WC	100	iodometric method
Hydrogen peroxide	POL		90	
Water			100	

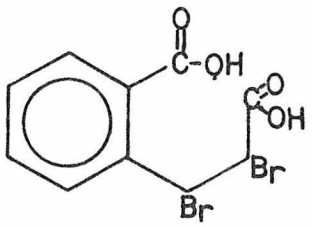
Comments on the Qualitative Analysis

1. Pale yellow color developed during the oxidation (λ_{max} = 475 mm). It was possible to extract some of the colored material by an aqueous 2N NaOH solution. Its quantity was very small, however, for identification. At least two components were found in it using MS. One compound had two Br atoms; the material had shown a strong OH absorbance band in the IR.By comparison with the literature (R-3) it is believed that the compounds are γ-O-phenoxybutyric acid (I) which exists in equilibrium with its phenol (II).



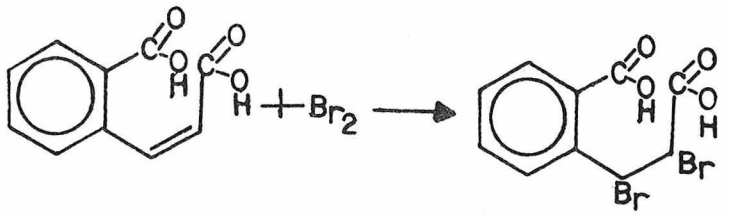
I II

The yellow color is due to the phenol-quinone equilibria



III

III is the result of the reaction of Br_2 with the olefin-acidic product, IV, of the oxidation of 1,2-dihydrohaphthalene. Br_2 is the dominant termination product of Br·.



IV III

Low eV MS of the solid residue (Appendix A) gives two strong peaks at m/e = 223 and at m/e = 297. Both contain Br and may correspond to III which lost CO_2 or two H_2O molecules.

2. Standard iodometric methods had shown very small color indication of the presence of peroxide in the product. The polarographic method of Willits et al. (W-1) had shown the presence of hydroperoxide and hydrogen peroxide ($E_{1/2}$ = -0.73 volts and $E_{1/2}$ = -0.2 volts, respectively, using DME and P_t electrodes). However, as the concentration of tetralone increases, its half wave decreases due to the hydroperoxide (for tetralone $E_{1/2}$ = -1.2 volts).

3. The water that was formed made the material turbid. The turbidity increased when the samples were cooled.

6.1.3 Quantitative Results of Experiment 1

Table 6.2 Quantitative Results of Experiment 1

The method of analysis of each specie is written under the component name.

Sample No.	Time (min)	Tetralin mol/lit GC-1	1,2-Dihydro-naphthalene mol/lit $\times 10^2$ GC-1	Tetralone mol/lit $\times 10^2$ GC-1	Hydrogen peroxide mol/lit $\times 10^4$ POL-1
0	0	5.109	0.034	0.00	-
1	15	5.014		0.212	0.0
2	30	5.059	0.186	0.352	0.028
3	45		0.138	0.490	0.075
4	60	4.943	0.239	0.426	0.262
5	75	4.925		0.640	0.175
6	90	4.995	0.211	0.750	0.175
7	105	4.891	0.270	0.780	0.150
8	120		0.71	1.26	0.412
9	150		0.62	1.18	0.524
10	180	4.750	1.63	1.30	0.599
11	210	4.750	1.34	1.55	0.849
12	240	4.950	1.98	1.56	1.20
13	270	4.440	1.96	1.77	1.27
14	300		1.53	2.10	1.57
15	330	4.260	1.71	2.23	1.55
product	336		2.76	2.20	1.64

Comments on the Quantitative Analysis

1. The concentration of tetralyl hydroperoxide was 0.00, $8.24 \cdot 10^{-5}$, and $9.0 \cdot 10^{-5}$ mole/liter at times 0, 15 and 30 min, respectively. The tetralone that is formed did not allow the determination of hydroperoxide after 30 min.

2. Approximately 10^{-5}mole of acid was formed (about $3.3 \cdot 10^{-5}$ mole/liter). The acid was very weak and exhibited very slow rate of reaction with base. Potentiometric titration in organic media (Section 5.3.2.2) was used for its determination. The heat of combustion of the first sample was 8504.5 cal/gram and that of the product was 8483.1 cal/gram.

6.2 Experiment 2

6.2.1 Experimental Conditions

Hydrocarbon:	None	-
Sulfur compound:	Dibutyl sulfide	6.23 grams
Solvent:	Bromobenzene	436 grams
Oxidizer:	Oxygen (O_2), P_{O_2} = 619 mm Hg, C_{eO_2} = $5.6 \cdot 10^{-3}$mol/lit	
Catalyst:	Hydrogen bromide (HBr), P_{HBr}= 120 mm Hg, C_{eHBr}= $1.1 \cdot 10^{-3}$mol/lit	
Total pressure:	738.8 mm Hg	
Temperature:	140 ± 0.5 °C	
Duration of run:	334 min	

6.2.2 Qualitative Results of Experiment 2

Table 6.3 Qualitative Results of Experiment 2

Compound	Method	Support Evidence	Confidence of the Identification and Notes
Butyl sulfoxide	GC-RT	GC-RPOL,S-NMR IR	100
Butyl sulfone	GC-RT	GC-RPOL	85
α-ketobutyl sulfoxide	GC-RPOL	IR,R-IR	80
α-ketobutyl sulfide	GC-RPOL	IR,R-IR	70
α-hydroxy butyl sulfide	GC-RPOL	IR,S-IR	70
Butyl disulfide	GC-RT		40 Because of the low confidence, it was denoted A in Table 6-5.

Comments on the Qualitative Analysis

1. Intense brown-yellow color was formed in the reaction. See comment 1 in 6.1 for the explanation.

2. Several new bands in the IR region were formed, their list and explanation are given in Tab.e 6.4 below.

Table 6.4 New IR Bands Formed in Experiment 2

Band cm^{-1}	Observation	Interpretation
2860, 2920, 2945	small intensity	consumption of oliphatic hydrogens
1715, 1750	most prominent	formation of C=O groups
1420, 1360, 1218	small intensity	SO_2, RO–S–OR (?)
1230-1130, 1420-1350	seen in R–IR	–O–SO_2–O– (?)
1050-1070	R–IR	

3. Twenty-five new sulfur-containing compounds were detected in the product by the sulfur-specific FPD. The concentration of seven of them is estimated to be above 10^{-6} mole/liter.

4. Comments 3, Section 6.1.2 are applicable.

6.2.3 Quantitative Results for Experiment 2

Table 6.5 Quantitative Results for Major Components, Experiment 2

The concentrations were multiplied by 10^{+6} throughout. All sulfur compounds were determined by method GC-4.

Sample No.	Time (min)	Butyl Sulfoxide mol/lit	Butyl Sulfone mol/lit	-Keto Butyl Sulfide mol/lit	α-Hydroxy Butyl Sulfide mol/lit	α-Hydroxy Butyl Sulfoxide mol/lit	A mol/lit	B mol/lit
0	0	8.8						2.3
1	15	8.8					0.68	2.3
2	30	14.8					2.22	2.3
3	45	19.0		0.68			2.70	2.3
4	60	56.0		2.76			6.20	3.96
5	75	82.0		5.40	2.7		7.00	2.8
6	90	106	0.68	15.0	4.6		9.20	3.36
7	105	190	1.54	18.6	5.8		4.6	2.02
8	120	304	2.76	28.0	9.2	1.34	4.6	2.3
9	135	544	12.6	54.0	19.0	3.90	5.8	3.16
10	176	2686	21.0	158.	25.0	3.90	6.2	3.48
11	206	5880	31.6	118.	19.0	3.40	6.2	2.6
12	235	5361	48.0	490.	38.0	10.4	7.8	3.36
13	265	6399	54.0	1040.	47.0	14.8	11.0	3.7
14	300	9793	89.0	1053.	64.0	16.0	14.8	9.2

Comments on the Quantitative Analysis

1. The calibration curve for butyl sulfoxide was used in the quantitation of all the sulfur compounds except for the butyl sulfone. Because of differences in the response factors for different sulfur functional

groups, the set of results for each component may have a systematic error of up to 25%. The differences in the response factor for oxidized sulfur compounds were discussed in reference (S-8).

6.3 Experiment 3

6.3.1 Experimental Conditions

Hydrocarbon:	Tetralin	218 grams
Sulfur compound:	Dibutyl sulfide	6.23 grams
Solvent:	Bromobenzene	100 grams
Oxidizer:	Oxygen (O_2), P_{O_2} = 629 mm Hg, $C_{eO_2} = 5.7\times10^{-3}$ mol/lit	
Catalyst:	Hydrogen bromide (HBr), P_{HBr} = 0.0 mm Hg, C_{eHBr} = 0.0 mol/lit	
Total pressure:	629 mm Hg	
Temperature:	140 ± 0.3 °C	
Duration of Run:	345 min	

6.3.2 Qualitative Results for Experiment 3

Table 6.6 Qualitative Results of Experiment 3

Compound	Method	Support Evidence	Confidence of the Identification and Notes
Butyl sulfoxide	GC-RT	GC-RPOL, S-NMR, IR	100
α-Keto butyl sulfide	GC-RPOL	IR, R-IR	70
α-Hydroxy butyl sulfoxide	GC-RPOL	IR, R-IR	80
Tetralone	GC-RT	IR, UV, POL	100

Comments on the Qualitative Analysis

1. Pale yellow color was formed in the reaction. See comment 1 in Section 6.1.2.

6.3.3 Quantitative Results for Experiment 3

Table 6.7 Quantitative Results for Major Components, Experiment 3

Method of determination for each component appears under its name.

Sample No.	Time (min)	Tetralin mol/liter GC-8	Butyl Sulfoxide mol/lit $\times 10^3$ GC-4	-Hydroxy Butyl Sulfoxide mol/lit $\times 10^6$ GC-4	-Keto Butyl Sulfide mol/lit $\times 10^5$ GC-4
0	0	5.514	0.4		0.54
1	15	5.577	2.1		0.74
2	30	5.482	4.6		4.9
3	45		6.8		1.18
4	60	5.444	12.	6.8	1.78
5	85	5.698	17.	10.	4.2
6	110	5.723		13.	6.8
7	140	5.720	19.5	60.	20.
8	190	5.420		60.	40.
9	230	5.616	19.0	210.	79.
10	270	5.467	18.0	1700.	98.
11	310	5.583	18.0	1100.	120.
12	340	5.227	16.0	960.	99.
P	345		19.0	2000.	280.

Comments on the Quantitative Analysis

1. Comment 1 in Section 6.2.3 is applicable.

6.4 Experiment 4

6.4.1 Experimental Conditions

Hydrocarbon:	Tetralin	218 grams
Sulfur compound:	Dibutyl sulfide	12.46 grams
Solvent:	Bromobenzene	100 grams
Oxidizer:	Oxygen (O_2), P_{O_2}=669 mm Hg, C_{eO_2} = 6×10^{-3}mol/lit	
Catalyst:	Hydrogen bromide (HBr), P_{HBr}= 71 mm Hg, C_{eHBr}= 6.4×10^{-4}mol/lit	
Total pressure:	739.8 mm Hg.	
Temperature:	140 0.3 °C	
Duration of run:	341 min	

6.4.2 Qualitative Results for Experiment 4

Table 6.8 Qualitative Results of Experiment 4

Compound	Method	Support Evidence	Confidence of the Identification and Notes
Butyl sulfoxide	GC-RT	GC-RPOL,S-NMR, IR	100
Butyl sulfone	GC-RT	GC-RPOL	85
α-Hydroxy butyl sulfoxide	GC-RPOL	GC-RPOL,R-IR	80
α-Keto butyl sulfide	GC-RPOL	IR,R-IR	70
α-Hydroxy butyl sulfide	GC-RPOL	IR,R-IR	70
α-Keto butyl sulfoxide	GC-RPOL	IR,R-IR	70
Butyl disulfide	GC-RT		50
Butyraldehyde	GC-MS		90

Comments on the Qualitative Analysis.

1. IR bands were found which can be due to $-SO_2-S-$ and to $-O-SO_2-O-$ as detailed in comment 2 , Section 6.2.2.

2. IR examination of the GAS above the liquid shows: 1) absorption band at 1640 cm^{-1}; absorption at this wavenumber is due to double bond, possibly 1-butene; 2) absorption band at 3400-3500 cm^{-1}, due to hydroxyl, possibly butyl alcohol; 3) absorption band at 1740 cm^{-1}, possibly due to butyl aldehyde. Butyraldehyde was found also in the liquid solution by GC-MS. Butyraldehyde is produced by the decomposition of α-hydroxy-sulfide.

After a day in the freezer the only bands left were for -OH and for double bond (much larger in size than in the original sample).

3. Mass spectrometric examination of the gas phase above the reactor shows: a) The presence of very small amounts of hydrogen (H_2) (Confidence: 60%).

b) A strong molecular ion at m/e = 90, possibly due to butyl mercaptan. An ion at 92 about 5% in height of the ion at 90, supports the identification of butyl mercaptan because the isotopic ratio of S^{34} to S^{32} is 4.4 to 100. Furthermore, fragments at 90-34 = 56, and at 34 are found. The ion at 34 may be due to H_2S^+. Mercaptans are known to lose H_2S (S-6).

c) Comment 1, Section 6.1.2 is applicable.

6.4.3 Quantitative Results for Experiment 4

The data are presented in Tables 6.9 and 6.10. The components that

start to be important after 100 min are given in Table 6.8.

Table 6.9 Quantitative Results for Major Components, Experiment 4
The concentration of all the components was multipied by 10^{+4}. The method of determination for each component is written under the component name.

Sample No.	Time (min)	Tetralol mol/lit GC-2	Tetralone mol/lit GC-2	Butyl Sulfoxide mol/lit GC-3	Butyl Sulfone mol/lit GC-3	-Hydroxy Butyl Sulfoxide mol/lit GC-3	-Keto Butyl Sulfide mol/lit GC-3
0	0			0.026		2.1	
1	6			0.28	0.33	1.5	
2	12					3.0	
3	18			2.15	1.0		
4	24						
5	30			3.7	0.8		
6	36					2.5	
7	42			4.5	0.96	2.1	
8	48						
9	54			4.7	2.1		
10	60		0.179			1.0	0.1
11	90			23.	6.0		0.2
12	120	4.45	2.06	32.	10.	1.7	1.55
13	150	2.66	4.06	59.	16.	0.6	3.4
14	180	6.39	3.98	82.	24.	0.7	5.5
15	210	8.00	4.96	86.	27.	0.88	14.2
16	240	8.21	3.33	95.5	27.	1.2	22.2
17	270	8.31	3.68	96.	21.	1.0	25.0
18	300	7.48	1.66	100.	17.	1.2	25.3
19	330	9.28	2.9	83.	11.	1.0	25.0

The heat of combustion of sample 0 was 8687.9 cal/gram and that of sample 19 was 8594.0 cal/gram.

Table 6.10 Quantitative Results, Experiment 4. Components that are produced after a long time. Method of determination for each component appears under its name. RT is retention time in the GC, using method GC-3; the concentrations were multiplied by 10^4 throughout.

Sample No.	Time (min)	A' mol/lit RT=840-850 sec	B' mol/lit RT=980-1000 sec	B" mol/lit RT=1000-1030 sec	α-Hydroxy Butyl Sulfide* mol/lit RT=1425-1435 sec	α-Keto Butyl Sulfoxide mol/lit RT=1715-1750 sec
12	120	0.18	0.7		0.8	
13	150	0.34	2.5	0.34	0.9	
14	180	0.34	7.0	0.78	1.9	0.79
15	210	2.6	16.3	1.8	1.6	0.53
16	240	5.6	26.5	4.3	1.2	1.20
17	270	9.5	34.0	6.7	1.45	1.36
18	300	13.5	36.5	7.6	1.2	1.95
19	330	14.0	34.5	12.3	0.42	2.6

*In the first 120 min it increases gradually from about 10^{-5} mole/liter to approximately $8 \cdot 10^{-5}$ mole/liter.

Comments on the Quantitative Analysis

1. Comment 1, Section 6.2.3 is applicable.

6.5 Experiment 5

6.5.1 Experimental Conditions

Hydrocarbon:	Tetralin	218 grams
Sulfur compound:	Dibutyl sulfide	6.23 grams
Solvent:	Bromobenzene	100 grams
Oxidizer:	Oxygen (O_2), P_{O_2}=626 mm Hg, $C_{eO_2}=5.6\times10^{-3}$ mol/lit	
Catalyst:	Hydrogen bromide (HBr), P_{HBr}=114 mm Hg, $C_{eHBr}=1.0\times10^{-3}$ mol/lit	
Total pressure:	739.3 mm Hg	
Temperature:	140 ± 0.3°C	
Duration of run:	375 min	

6.5.2 Qualitative Results for Experiment 5

Table 6.11 Qualitative Results, Experiment 5

Compound	Method	Support Evidence	Confidence of the Identification	and Notes
Sulfur (elementary)	WC	yellow color	60	Acetone-KOH , Ref. (U-1)
Butyl Sulfoxide	GC-RT	IR,S-NMR, GC-RPOL	100	
Butyl Sulfone	GC-RT	GC-RPOL	100	
Butyl Sulfonic Acid	WC	S-NMR	60	
α-Hydroxy Butyl Sulfoxide	GC-RPOL	IR,R-IR	80	
α-Keto Butyl Sulfide	GC-RPOL	IR,R-IR	70	
α-Keto Butyl Sulfoxide	GC-RPOL	IR,R-IR	70	

Table 6.11 (continued)

Compound	Method	Support Evidence	Confidence of the Identification and Notes
Butyl Disulfide	GC-RT		50
α-Hydroxy Butyl Sulfide	GC-RPOL	IR	
Tetralol	GC-MS	IR	100
Tetralin Diketone	GC-MS	IR	80
Butyl Bromide	GC-MS		100 See Section 5.3.1.2
Butanone	GC-MS	IR	100
3-O-phenyl Propionic Acid	GC-MS	IR	70

Comments on the Qualitative Results

1. Comments 1, 2, and 3, Section 6.1.2 are applicable.
2. Comments 1, 2, and 3, Section 6.2.2 are applicable.
3. Butyl bromide was identified by GC-MS (see 5.3.1.2 for the details of the method.) No other Br-containing compounds which boil below 200°C were found. However, MS analysis of crystalline solid that was obtained by method WC-1 contained two BR atoms/molecule.

6.5.3 Quantitative Results, Experiment 5

The concentration of the compounds which become significant above 10^{-4} mole/liter only after 120 minutes are given in Table 6.13.

Method of determination for each component appears under its name. RT is the retention time in seconds.

Sample No.	Time (min)	Butyl Sulfide mol/lit RT = 247 GC-5	Butyl Sulfoxide $\times 10^{5}$ mol/lit RT = 1274 GC-4	Butyl Sulfone $\times 10^{5}$ mol/lit RT = 1305 GC-4	α-Keto Butyl Sulfide $\times 10^{-6}$ mol/lit RT = 1145 GC-4	α-Keto Butyl Sulfoxide $\times 10^{3}$ mol/lit RT = 1936 GC-4	α-Hydroxy Butyl Sulfoxide $\times 10^{4}$ mol/lit RT = 2320 GC-4
0	0	0.1424	2.2		6.68	1.92	1.36
1	15	0.1463	7.8		6.27	1.90	2.72
2	30	0.1439	12.4		9.35	2.72	4.2
3	45	0.1366	2.8		4.08		3.42
4	60	0.1355	18.		6.68	2.49	11.8
5	75	0.1349	14.2		6.27	3.15	17.6
6	90	0.1343	12.2	2.4	7.98	3.60	18.4
7	105	0.1356	4.0	1.9	7.98	4.70	18.4
8	100	0.1340	4.2	5.9	12.9	8.31	45.
9	150	0.1370		13.4	20.5	14.9	66.
10	180	0.1317		19.6	47.5	21.4	70.
11	210	0.1113	0.1	62.	716	32.1	90.
12	240	0.0829	0.3	335.	6860	33.6	81.
13	270	0.1069	0.6	680.	12860	34.9	87.
14	300	0.1131	2.2	860.	21090	32.9	
15	330	0.1132	5.2	1440.	24360	29.5	
16	360	0.1078	9.6	1040.	26470	24.6	

Table 6.13 Quantitative Results, Experiment 5. The concentration of components which become important after 120 min. The analysis was done by method GC-4. RT is the retention time in seconds.

Sample No.	Time (min)	α-Hydroxy Butyl Sulfide mol/lit × 10^4 RT = 1317	A mol/lit × 10^4 RT = 748	B mol/lit × 10^4 RT = 830
8	120	0.5	0.92	0.33
9	150	1.32	1.12	0.47
10	180	2.06	1.33	0.50
11	210	5.8	2.34	0.94
12	240	6.6	4.80	2.16
13	270	8.7	18.8	7.8

Comments on the Quantitative Analysis

1. Comments 1 and 2, Section 6.1.3 are applicable.
2. Comment 1, Section 6.2.3 is applicable.

6.6 Experiment 6

6.6.1 Experimental Conditions

Hydrocarbon:	Toluene	60.0 grams
Sulfur compound:	Dibutyl sulfide	6.23 grams
Solvent:	Bromobenzene	332.4 grams
Oxidizer:	Oxygen (O_2), P_{O_2} = 636 mm Hg, C_{eO_2} = 5.6×10^{-3} mol/lit	
Catalyst:	Hydrogen bromide (HBr), P_{HBr} = 103 mm Hg, C_{eHBr} = 9.0×10^{-4} mol/lit	
Total Pressure:	739.3 mm Hg	

Temperature: 136.5 ± 0.1 °C

Duration of run: 336 min

6.6.2 Qualitative Results for Experiment 6

Table 6.14 Qualitative Results of Experiment 6

Compound	Method	Support Evidence	Confidence of the Identification and Notes
Butyl Sulfoxide	GC-RT	IR	95
Butyl Sulfone	GC-RT		80
α-Keto Butyl Sulfoxide	GC-RPOL	IR,R-IR	80
α-Keto Butyl Sulfide	GC-RPOL	IR,R-IR	70
α-Hydroxy Butyl Sulfide	GC-RPOL	IR,R-IR	70
α-Hydroxy Butyl Sulfoxide	GC-RPOL	IR,R-IR	80
Benzaldehyde	GC-RT	IR	70

Comments on the Qualitative Results

1. Comments 1, 2 and 3, Section 6.1.2 are applicable.
2. Comments 2 and 3, Section 6.2.2 are applicable.

6.6.3 Quantitative Results for Experiment 6

The products that are formed after 105 min are given in Table 6.16.

Table 6.15 Quantitative Results, Experiment 6

The determination of the toluene and butyl sulfide was done by method GC-9. The sulfur compounds were determined by method GC-6.

Sample No.	Time (min)	Toluene mol/lit	Butyl Sulfide mol/lit	Butyl Sulfoxide mol/lit $\times 10^4$	Butyl Sulfone mol/lit $\times 10^4$	α-Keto Butyl Sulfoxide mol/lit $\times 10^4$
0	0					
1	15	2.30	0.156	0.57		
2	30	2.19	0.144	2.3	1.0	
3	45	2.15	0.145	3.3	1.04	0.49
4	60	2.15	0.150	6.8	3.4	1.01
5	75	2.22	0.139			4.5
6	90	2.18	0.140	7.7	3.85	6.3
7	105	2.01	0.142	8.4	4.75	16.5
8	120	2.13	0.140	10.3	6.35	19.8
9	150	2.12	0.141	10.5	7.7	
10	180	2.11	0.141			18.5
11	210	2.17	0.136	10.3	6.1	10.1
12	240	2.05	0.135	10.0	4.4	15.2
13	270	2.10	0.140	10.2	4.8	28.5
14	300	2.07	0.131	9.2	4.7	29.5
15	330		0.128	10.0	4.1	36.5

Table 6.16 Quantitative Results, Experiment 6. The concentration of the sulfur compounds which become important after 105 min. The determination of the sulfur compounds was by method GC-6. RT is the retention time in seconds.

Sample No.	Time (min)	α-Keto Butyl Sulfide mol/lit × 10^4 RT = 910	α-Hydroxy Butyl Sulfide mol/lit × 10^4 RT = 1105	α-Hydroxy Butyl Sulfoxide mol/lit × 10^4 RT = 1920	A" mol/lit × 10^4 RT = 375	B" mol/lit × 10^4 RT = 845
7	105		0.33			
8	120	0.33	0.61	0.43	1.87	0.42
9	150	0.57			2.5	0.6
10	180		0.95			
11	210	1.01	1.01	0.73	2.7	1.03
12	240	2.00	1.62	1.013	3.5	3.03
13	270	3.3	1.74	2.01	4.4	1.08
14	300	3.3	1.75	1.72	4.6	4.75
15	330	3.65	2.1	2.00	5.4	2.35

Comments on the Quantitative Results

1. Comment 1, Section 6.2.3 is applicable.
2. Comment 2, Section 6.1.3 is applicable.

6.7 Experiment 7

6.7.1 Experimental Conditions

Hydrocarbon:	Tetralin	218 grams
Sulfur compound:	Dibutyl sulfide	6.23 grams
Solvent:	1-Octanol	80.8 grams
Oxidizer:	Oxygen (O_2), P_{O_2}=609 mm Hg, C_{eO_2}=5.5×10^{-3}mol/lit	

Catalyst: Hydrogen bromide (HBr), P_{HBr}=128 mm Hg, $C_{eHBr}=1.15\times10^{-3}$ mol/lit

Total pressure: 736.7 mm Hg

Temperature: 140 ±0.3 °C

Duration of run: 330 min

6.7.2 Qualitative Results for Experiment 7

Table 6.17 Qualitative Results, Experiment 7

Compound	Method	Support Evidence	Confidence of the Identification and Notes
Butyl Sulfoxide	GC-RT	IR,R-IR, S-NMR	100
α-Keto Butyl Sulfoxide	GC-RPOL	IR,R-IR	80

Comments on the Qualitative Results

1. The yellow color that appeared was considerably lighter than that seen in experiments 2 to 6.

2. Fewer sulfur-containing compounds were produced than in experiments 2 to 6. There were only two major ones.

6.7.3 Quantitative Results for Experiment 7

Table 6.18 Quantitative Results, Experiment 7

The determination of the sulfoxides was done by method GC-8. The tetralone was determined by UV; the sulfide by method GC-5.

Sample No.	Time (min)	Tetralone mol/lit $\times 10^3$ UV	Butyl Sulfide mol/lit GC-5	Butyl Sulfoxide mol/lit $\times 10^3$ GC-8	α-Keto Butyl Sulfoxide mol/lit $\times 10^6$ GC-8
0	0		0.1292	0.1	
1	15		0.1167	0.707	
2	30	0.108	0.1143	10.12	4.1

Table 6.18 (continued)

Sample No.	Time (min)	Tetralone mol/lit × 10^3	Butyl Sulfide mol/lit	Butyl Sulfoxide mol/lit × 10^3	α-Keto Butyl Sulfoxide mol/lit × 10^6
3	45	2.95	0.1103	15.4	
4	60	3.0	0.1127	18.4	7.3
5	75	3.1	0.0987	21.4	6.2
6	90	3.9	0.0991	27.3	4.3
7	105	3.95	0.0897	27.8	14.
8	120	5.0	0.0996	29.1	32.
9	150	7.0	0.1073		
10	180	10.5	0.1003	24.4	29.6
11	210	11.3		28.0	32.6
12	240	14.8	0.1011	27.2	20.6
13	270	15.2	0.0961	26.4	20.8
14	300	19.2		25.4	20.7
15	330	22.5			

6.8 Experiment 8

6.8.1 Experimental Conditions

Hydrocarbon:	Tetralin	218 grams
Sulfur compound:	Dibenzothiophene	6.813 grams
Solvent:	Bromobenzene	100 grams
Oxidizer:	Oxygen (O_2), P_{O_2} = 620 mm Hg, C_{eO_2} = 6.4×10^{-3} mol/lit	
Catalyst:	Hydrogen bromide (HBr), P_{HBr} = 117 mm Hg, C_{eHBr} = 1.2×10^{-3} mol/lit	
Total pressure:	737.2 mm Hg	
Temperature:	159.9 ± 0.2 °C	
Duration of run:	335 min	

6.8.2 Qualitative Results for Experiment 8

Table 6.19 Qualitative Results, Experiment 8

Compound	Method	Support Evidence	Confidence of the Identification and Notes
Tetralone	GC-RT	IR,S-IR,LC	100
Tetralol	GC-RT	IR,LC	70

Comments on the Qualitative Results

1. No sulfur-containing compound was found in the product. No IR bands which can be attributed unambiguously to oxidized sulfur compounds were found. Strong carbonyl band (1690 cm^{-1}) is evident and a very weak -OH stretch band (3500 cm^{-1}) can be recognized.

2. Comments 1 and 3, Section 6.1.2 are applicable.

6.8.3 Quantitive Results for Experiment 8

Table 6.20 Quantitative Results, Experiment 8

Sample No.	Time (min)	Tetralone mol/lit $\times 10^3$ GC-2	DBT mol/lit GC-9
0	0		0.1133
1	15	2.265	0.1189
2	30	2.577	0.1090
3	45	2.926	0.1204
4	60	5.837	0.1058
5	75	6.863	0.1084
6	90	9.296	0.1119
7	105	9.036	0.1061
8	120	8.100	0.1098
9	150	8.954	0.1146

Table 6.20 (continued)

Sample No.	Time (min)	Tetralone mol/lit × 10^3	DBT mol/lit
10	180	8.975	0.1056
11	210	8.580	0.1271
12	240	11.93	0.1149
13	270	12.06	0.1167
14	300	15.20	0.1186
15	330	17.75	0.1155
P	335	20.60	0.1147

Comments on the Quantitative Analysis

1. Comment 2, Section 6.1.3 is applicable.

2. Within the error of the analysis the concentration of DBT does not change throughout the run; however, there is a very slight trend toward decrease in the concentration with time.

6.9 Experiment 9

6.9.1 Experimental Conditions

Hydrocarbon:	Tetralin	218 grams
Sulfur compound:	Dibenzothiophene	6.813 grams
Solvent:	1-Octanol	80.8 grams
Oxidizer:	Oxygen (O_2), P_{O_2}=624 mm Hg, $C_{eO_2}=6.4\times10^{-3}$ mol/lit	
Catalyst:	Hydrogen bromide (HBr), P_{HBr}=114 mm Hg, $C_{eHBr}=1.2\times10^{-3}$ mol/lit	
Total pressure:	738.2 mm Hg	
Temperature:	160 ± 0.2 °C	
Duration of run:	339 min	

6.9.2 Qualitative Results for Experiment 9

Table 6.21 Qualitative Results, Experiment 9

Compound	Method	Support Evidence	Confidence of the Identification and Notes
Tetralone	GC-RT	IR,S-IR,LC	100
Tetralol	GC-RT	IR,S-IR,LC	70

Comments on the Qualitative Results

1. Comments 1 and 2, Section 6.8.2 are applicable.

6.9.3 Quantitative Results for Experiment 9

Table 6.22 Quantitative Results, Experiment 9

(The concentrations were determined by method GC-9.)

Sample No.	Time (min)	Tetralone mol/lit $\times 10^3$ GC-2	DBT mol/lit GC-9
0	0	0.784	0.1122
1	15	0.784	
2	30	1.27	0.1102
3	45	3.00	0.1024
4	60	4.41	0.1080
5	75	6.20	0.1051
6	90	6.94	0.0986
7	105	7.43	0.1013
8	120	7.31	0.0985
9	150	8.07	0.1040
10	180	9.21	0.0996
11	210	10.96	0.1007
12	240	13.21	0.1047

Table 6.22 (continued)

Sample No.	Time (min)	Tetralone mol/lit 10^3	DBT mol/lit
13	270	14.14	0.0999
14	300	16.61	0.0995
15	330	17.66	0.0992
P	339	17.17	0.1039

Comments on the Quantitative Results

1. Comments 1 and 2, Section 6.8.3 are applicable.

Chapter 7

ANALYSIS AND DISCUSSION OF THE RESULTS

The two goals of the analysis of the results were: 1) to investigate the reaction mechanism, and 2) to obtain approximate values for the rate constants of the most important reactions which take place in the system.

Several other topics are discussed in this chapter, such as the loss of heating value and the effect of the protic nature of the solvent on the oxidation.

The system is extremely complex and many approximations were made in order to reach some conclusions. Many of the approximations are analyzed; however, some common approximations are not detailed, for the sake of brevity.

7.1 The Structure and the Logic of the Discussion

In the analysis of kinetic data, the most important steps of the mechanism determine the reaction products. Therefore, the qualitative results were used to investigate the reaction mechanism. The quantitative data were used to estimate the rate constants of the reactions and to study the change in enthalpy of various reactions.

The discussion of the results consists of four parts: 1) introduction, in which the tools that were used in the analysis are examined, 2) computer simulation of the system and a comparison of the data with predictions of the model, 3) semi-quantitative discussion of the effects of the catalyst, the solvent, and the hydrocarbon, and 4) semi-quantitative discussion of the loss of heating value vs desulfurization.

Errors in the identification of species and other systematic errors, plus random experimental errors in the quantitative analysis, were not taken into account in the simulation because of the size of the system involved.

In the oxidation of a hydrocarbon many products are formed. Typical products are alcohols, ketones, esters, olefins, and acids. The reactivity of these species toward oxidation is much larger than that of the original hydrocarbon; therefore the course of oxidation changes soon after small amounts of intermediates accumulate. For example, small amounts of acids have enormous effect on the rates of decomposition of peroxides and on their oxidation potential. Within the constraints of the work it was impossible to take the effect of products of advanced oxidation into account. Therefore, the results of the simulation agree with the data for the first 100 min of the oxidation and do a less adequate job after long periods of oxidation when the concentration of secondary and tertiary products become too large.

7.2 System Approach to the Simulation of the Chemical System

The simulation of a complex system is a difficult problem and cannot always be done satisfactorily. Modeling from first principles is usually complex and needs in general more variables than empirical models; however, such models have a better chance of representing a system for an extended range of values of the variables. Empirical and semi-empirical models would, in general, give a better description of a system in a limited range of the variables and would need a smaller

number of parameters; however, extrapolation of such models is more risky and may lead to erroneous results. The area of simulation of complex reaction systems has recently been reviewed by Weekman (W-4).

Modeling of a chemical system, taking into account all the elementary reaction steps, indeed needs many parameters and involves numerous differential equations. However, it has a better chance of representing the system correctly when the interaction with other chemical systems are also considered. The following logic was applied in the modeling of the reactions in systems which contain a hydrocarbon, a sulfur compound, oxygen and a catalyst:

1. Define subsystems and model them from first principles, using elementary reaction steps as much as possible, e.g., subsystem NOCAT contains a hydrocarbon, oxygen and sulfur compound only.

2. Verify the adequacy of the model by comparing the theoretical predictions with the experimental data. Data for the subsystem were used to modify the parameters of the model.

3. Combine the submodels to represent a larger system.

4. Check the predictions of the combined model vs the experimental data and modify it as required.

Although the approach is straightforward, its implementation is difficult. Rate constant data for a few of the elementary steps were available from independent sources. The rest were estimated in this study. Systematic and random errors in the experimental data complicate the task of the evaluation of the adequacy of the mechanism and the values that are obtained for the rate constants.

Moreover, each subsystem is nonlinear and stiff, and additional nonlinearity is introduced when the subsystems are combined. The nonlinearity due to the combining of the subsystems is presented by the new "coupling" reactions, which are not required when the subsystems are considered separately.

Two subsystems are first described and then combined to describe the general reaction system. The nomenclature used is the same as in the computer program, and is given in Table 7.1. Figure 1 shows the reactions in the subsystem hydrocarbon-O_2-HBr (denoted NOSC). The heavy lines describe reaction paths; the broken lines are connection lines of species that take part in several reactions. Data for several of the reactions in NOSC were found in the literature, the values of the rest of the rate constants were estimated theoretically and modified as required to fit the experimental data.

Figure 2 shows the reactions in the subsystem hydrocarbon-O_2-sulfide (denoted NOSC). Since many of the elementary steps of NOSC were known, a detailed mechanism was used in the modeling of NOSC. However, in order to keep the number of equations down, several rate steps in the mechanism of NOCAT were combined. The details of the approximations are given in the next section, the logic of the lumping is given in Section 7.6.

7.3 The Interactions of the Sulfur Compounds in the Subsystem NOCAT

Sulfur compounds (SC) like butyl sulfide (BuS) interact with hydrocarbon-oxygen systems in three ways: 1) lose a hydrogen to a free radical, usually to $RO_2\cdot$, which is the most abundant one; 2) reduce $RO_2\cdot$ to $RO\cdot$ and form sulfoxide; 3) react with the cyclic peroxy

complex and form sulfoxide and alcohol.

The interaction of $RO_2\cdot$ with the hydrogens of the SC is very similar to that of the reaction of a hydrocarbon with $RO_2\cdot$ (see Section 2.2). The result of the initial oxidation is the formation of an alcohol from the sulfide (e.g., α-hydroxy butyl sulfide). A similar mechanism converts the hydroxy sulfide to the corresponding ketone, e.g., α-keto butyl sulfide. α-Hydroxy sulfides and α-keto sulfides are unstable and may oxidize or decompose. The compound α-hydroxy sulfide is a very unstable material, and it decomposes rather rapidly to an aldehyde and a mercaptan. The rate determining step for the oxidation of the side chain is the hydrogen abstraction reaction:

$$C_3H_7\text{—}CH_2\text{—}S\text{—}C_4H_9 + RO_2\cdot \rightarrow C_3H_7\text{—}\dot{C}H\text{—}S\text{—}C_4H_9 \qquad (7.1)$$

Therefore, the rate of (7.1) determines the rate of production of $C_3H_7\text{—}OH\text{—}S\text{—}C_4H_7$ (denoted COHS). Since the α-hydrogen is extremely reactive to abstraction, the α-hydroxy sulfide is rapidly converted to the α-keto sulfide (denoted COS). If the decomposition reaction of COHS to aldehyde and mercaptan is neglected, then the rate of hydrogen abstraction from the sulfide determines the rate of production of COS. As a result, one may write a single equation for the rate of formation of COS from the sulfide:

$$\begin{array}{c} H \\ | \\ -C-S- \\ | \\ H \end{array} + RO_2\cdot \xrightarrow[RH]{O_2,} \begin{array}{c} O \\ \| \\ -C-S- \end{array} + RO_2H \qquad (7.2)$$

Table 7.1 Abbreviations of Species Names Used

Name	Specie	Name	Specie
ALD	Aldehyde, $C_3H_7C\overset{O}{\underset{H}{=}}$	PRAC	HBR-RO2H complex
BR	Bromine radical	R	Tetralyl radical
BR2	Bromine molecule	REN	1,2 Dihydronaphthalene
CIO	Butyl alkoxyl radical	RH	Hydrocarbon
CO	Ketone (tetralone)	RO	Tetralin alkoxyl radical
CO2S	α-peroxy butyl radical	RO2	Tetralin hydroperoxy radical
CO3H	α-hydroxy hydro peroxide	ROH	Tetralol
COHS	α-hydroxy sulfide	RO2H	Tetralyl hydroperoxide
COS	α-keto sulfide	S	Butyl sulfide, or sulfur compound
COSO	α-keto sulfoxide	SO	Sulfoxide
CS	α-butyl sulfide radical	SO2	Sulfone
DICO	Tetralin diketone	SOO	α-peroxy sulfide
FROH	α-tetralol radical	SOOH	α-hydroxy sulfoxide
HBR	Hydrogen bromide	SOS	Butyl hydroxy mercaptyl radical
H2O	Water		
H2O2	Hydrogen peroxide		
O2	Oxygen		

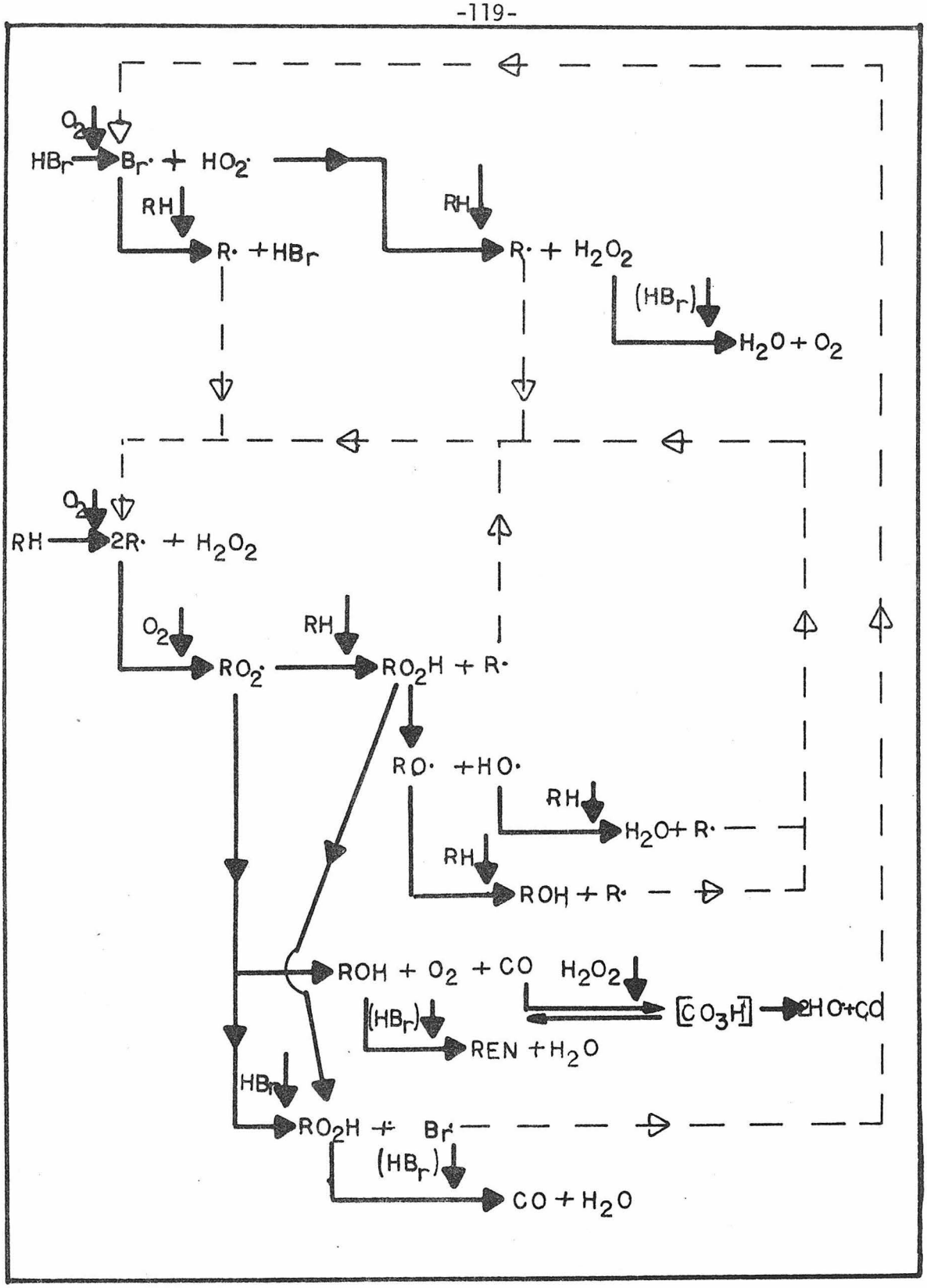


Figure 7.1 The Oxidation of a Hydrocarbon in the Presence of HBr. The nomenclature is explained in Table 7.1.

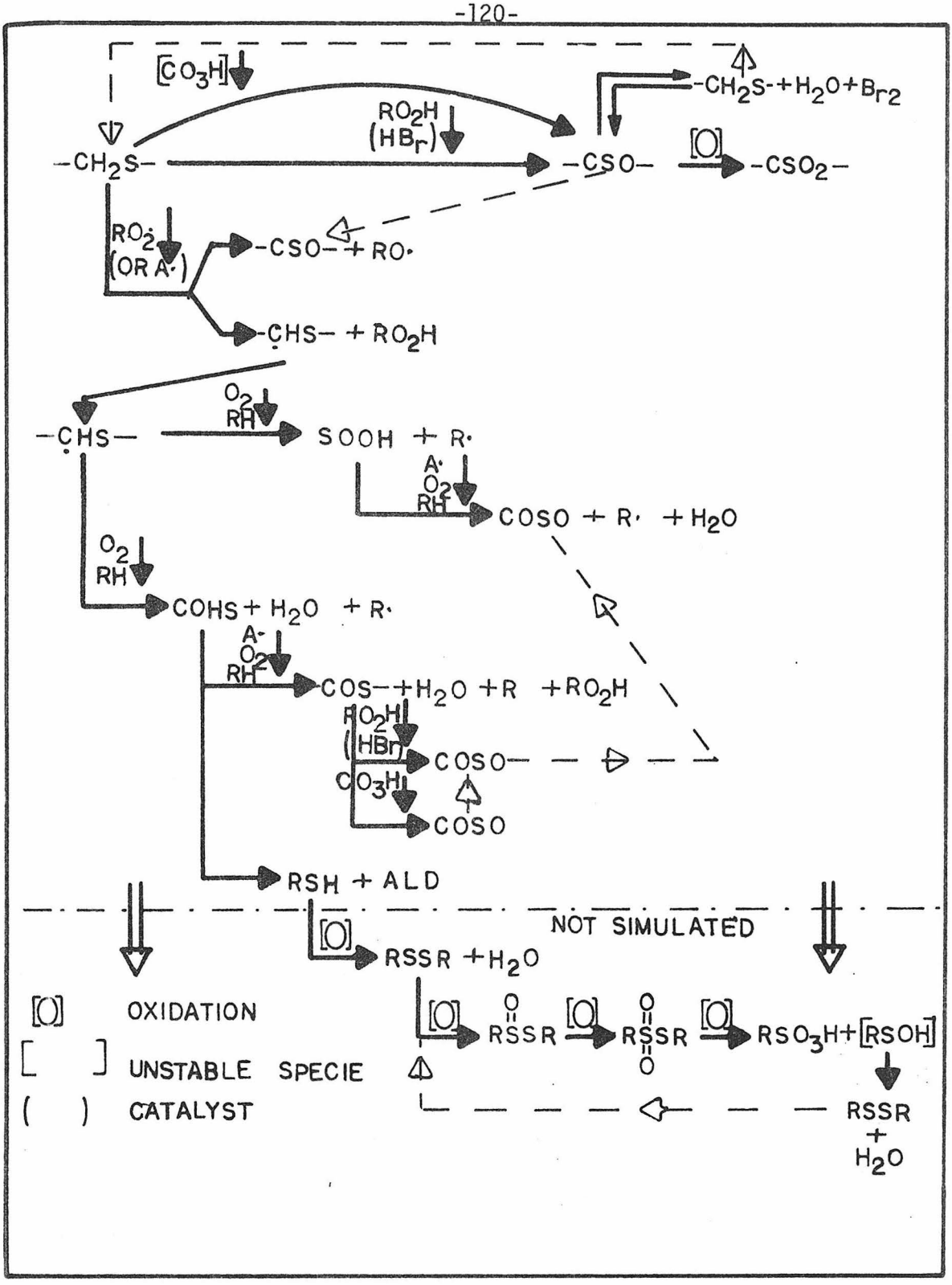
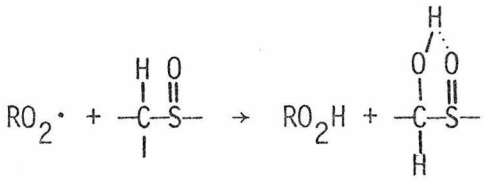


Figure 7.2 The Interaction of an Aliphatic Sulfide with the System Hydrocarbon-O_2-HBr. The nomenclature is explained in Table 7.1. A· is the sum of all the radicals.

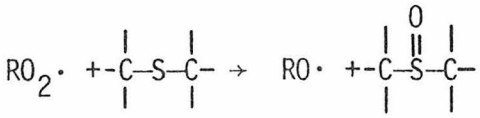
The rate constant for the overall reaction will be approximately the rate of abstraction of hydrogen from S. If the concentration of O_2 and RH do not vary much during the experiment, their value can be incorporated into the rate constant. This modification simplifies the mathematical manipulation of the set of reactions. Similar arguments were applied to derive the rate limiting equations for the formation of the α-hydroxy sulfoxide (SOOH) from the sulfoxide (SO) by reaction (7.3):



(7.3)

Note that the α-hydrogen of SOOH has larger bond energy than that of the α-hydrogen in COHS because the formation of the cyclic intramolecular complex. The rate of reaction of SOOH to the α-keto sulfoxide (COSO) is of comparable order to that of the reaction of SO to SOOH, and therefore they had to be separated. This stabilization effect is observed experimentally, SOOH accumulates in the initial period of the reaction while COHS does not.

At room temperature the rate of reaction (7.4) is very small, and therefore the oxidation of sulfide is not influenced by inhibitors of free radical reactions.



(7.4)

However, at higher temperatures, and when the concentration of $RO_2\cdot$ is relatively large, its effect may be sizable. The product of reaction (7.4), the sulfoxide SO, does not react with $RO_2\cdot$ to the sulfone SO_2.

7.4 On the Coupling Reactions of Subsystems NOSC and NOCAT

The coupling reactions between subsystems NOSC and NOCAT are:

1. Hydrogen abstraction from S by Br:

$$S + Br\cdot \rightarrow \dot{C}S + HBr \tag{7.5}$$

2. Reduction by SO of HBr to water and Br_2·

$$SO + 2HBr \rightarrow S + H_2O + Br_2 \tag{7.6}$$

3. Oxidation of the SC by the peroxide-HBr complex, PRAC, e.g.,

$$S + PRAC \rightarrow SO + ROH + HBr\cdot \tag{7.7}$$

Reactions (7.5) and (7.6) are undesired reactions. Reaction (7.5) initiates a sequence of reactions which ends in the oxidation of the hydrocarbon part of the SC, and therefore in loss of energy. Equation (7.6) shows that HBr can reduce the sulfoxide back to the sulfide. It is therefore the exact opposite of the desired reaction. Moreover, Br_2 is formed which reacts with the hydrocarbon to the organic bromide. The net effect of this reaction is the formation of brominated hydrocarbon and the loss of catalyst. This adverse effect is discussed further in Section 7.8.

7.5 Computer Simulation of the Reaction System

The methodology of the simulation was as follows:

1. Assume a reaction mechanism.
2. Obtain a set of rate constants for the individual steps of the mechanism.

3. Integrate the differential equations with the initial conditions of the relevant experiment.
4. Plot and compare the curve with the experimental data.
5. Correct the mechanism, the values of the rate constants, or modify the initial conditions to obtain a better fit.
6. Repeat steps 3-5 until a good match is obtained.
7. Do steps 1-6 separately for subsystems NOSC and NOCAT.
8. Combine the results of step, add coupling reactions and repeat steps 1-6 for the combined system CATSC.

Because of the size of the program and the limited resources available, the match between the experimental data and the computer prediction was done manually. Introduction of automatic search for the rate constants which fit the data best is recommended for future studies.

7.6 Simplifications Used in the Simulation and Their Justification

Technical limitations do not allow the use of models with too many differential equations or species. Moreover, too large models cannot be easily utilized and therefore their value is limited. In order to obtain smaller systems which will still be useful, it is necessary to reduce the number of differential equations that are used.

One way to reduce the size of the model is by lumping reactions together. A general discussion of lumping was made by Aris and Gavalas (A-9) and by Wei and Kuo (W-5). Only a brief presentation will be given here.

Two kinds of lumping are distinguished: 1) lumping in series; and 2) lumping in parallel. Lumping in series can be used when a series of

reactions are considered in which one step is clearly rate limiting, e.g., in the sequence of reactions A → B → C → D. If the rate of the reaction A → B is limiting the rate of conversion of A to D, the reactions can be lumped to the single reaction A → D, with the rate constant of the reaction A → B. By the use of such a simplification, two components and two reactions were eliminated. Such a simplification may lead to erroneous results if components are added which react with the eliminated species or if the conditions of the reaction change.

When many compounds which belong to the same homolog group react in the same way, with the same reagent, instead of considering the concentration of each specie separately, the sum of their concentrations can be treated as a single specie. For example, a mixture of esters of fatty acids which are hydrolyzed in a basic solution can be treated as a single ester. A special case of parallel lumping involves lumping of functional groups. For example, all the primary hydrogens can be lumped together, or all the olefinic bonds can be lumped into a single "reactant". Such a lumping improved the modeling of the hydrogenation of hydrocarbons tremendously (J-1).

Another special case of parallel lumping is the treatment of many free radicals which react in the same way, as a single specie. This approach is implicit in the classic treatment of oxidation when the SS approximation is used.

The advantage of lumping in parallel is a great reduction in the number of species in the system; however, the mathematical treatment of a system of compounds, some of which belong to several functional groups, may be difficult. The activation energy of reactions

of similar functional groups may be very close. However, the frequency factor of homologs with a wide distribution of molecular weights may be very different.

In this work, the secondary hydrogens of the butyl sulfide were lumped together in order that treatment of many isomers will not be required.

7.6.1 Rate Data for Individual Reaction Steps

The rate data that were used came from three sources: 1) from the literature, 2) from semi-empirical correlations, and 3) from the computations of the "best fit" for the experimental data.

Whenever reliable data were available from the literature, they were used with no change. Data that were estimated were changed within the general range of values for rates of similar reactions. The rates of steps which were not found in the literature were manipulated as necessary to obtain the best fit.

The rate data taken from the literature are given in Table 7.2. The following methods were used to estimate rate constants:

1) Benson's Method for the frequency factor of a reaction in the liquid phase.

Benson (B-15, p. 506) derived an approximate formula to predict the frequency factor for liquid phase reactions if their value in the gas phase is known. This method can be summarized as follows: If the reaction is first order the frequency factor is the same for the gas and for the liquid. If the reaction is of m order, then

Table 7.2 Rate Constants for Elementary Steps in the Oxidation of Tetralin by Molecular Oxygen

The value of the frequency factor k_o is in sec^{-1}, lit/sec/mole, or $(lit/mole)^2/sec$, as required.

Reaction	E kcal/ mole	k_o	$\log_{10} k_o$	Ref.	Notes
$2RH + O_2 \rightarrow 2R\cdot + H_2O_2$	20.7	$3.4 \cdot 10^3$	3.53	D-7	
$2RH + O_2 \rightarrow 2R\cdot + H_2O_2$	23.8	$2.4 \cdot 10^5$	5.38	C-4	Used in the program
$RO_2H \rightarrow RO\cdot + HO\cdot$	24.4	$9.3 \cdot 10^8$	8.97	E-1, p.75	
$HBr + O_2 \rightarrow HO_2\cdot + Br\cdot$	37.7	$2.4 \cdot 10^{13}$	13.38	R-2	Adapted to liquid by Benson's method
$R\cdot + O_2 \rightarrow RO_2\cdot$	0	$6.76 \cdot 10^7$	7.83	B-13	
$RO_2\cdot + RH \rightarrow RO_2H + R\cdot$	4.5	$2.5 \cdot 10^4$	4.4	B-13	
$RO_2\cdot + RH \rightarrow RO_2H + R\cdot$	8.3	$5.62 \cdot 10^6$	6.75	H-6	Used in the program
$2RO_2\cdot \rightarrow CO + ROH + O_2$	0	$6.61 \cdot 10^6$	6.82	H-6	
$2RO_2\cdot \rightarrow$ Non Radicals	4.3	$8.51 \cdot 10^9$	9.93	H-7	
$2RO_2\cdot \rightarrow$ Non Radicals	0	$2 \cdot 10^7$	7.30	B-13	In tetralin
$2RO_2\cdot \rightarrow CO + ROH + O_2$	2.6	$5.5 \cdot 10^8$	8.74	B-13	In CH_3OH
$2RO_2\cdot \rightarrow$ Non Radicals	0.4	$4.2 \cdot 10^7$	7.62	E-1, p.321	Used in the simulation
$2R\cdot \rightarrow R_2$			6.85	B-13	Negligible compared with $2RO_2\cdot \rightarrow$ non-radicals in the presence of excess O_2
$2Br\cdot \rightarrow Br_2$	0	$5.19\ 10^{16}$	16.58	K-2	Adapted to liquid by Benson's method

$$\frac{A_{liq}}{A_{gas}} = \frac{10^{2m-2}}{me^{m-1}}$$

For binary elementary steps $A_{liq}/A_{gas} \simeq 20$. Benson's approximation is valid if the activation energy in the gas is the same as in the liquid, and if the solvent is non-protic.

2. Polayni-Hammet Approximation for the Activation Energy of Reactions of Homologs

The Polayni approximation can be used to estimate the rate and frequency factor for members of a homolog group which reacts with the same reagent. Data for a few members of the group have to be known. The method can be summarized as follows: 1) For a homolog group that reacts in the same way, $\log A = \Delta S^{\dagger}/R \propto E_a$ where A is the frequency factor of the reaction, $\Delta S^{\dagger}$ is the entropy of formation of the activated complex, and E_a is the activation energy of the reaction. 2) The activation energy for members of the same homolog group, which reacts with the same reagent, is linearly related to the heat of their reaction. 3) The heat of the reaction can be predicted from bond energies since it is a thermodynamic property.

7.6.2 Initial Values and the Concentration of O_2 and HBr in the Solution

The initial values for the major components were determined by

the way which the solution was prepared. Minor components, e.g., REN, ROH, CO, etc. were either determined experimentally or given a value below the detection level of the analysis method. The data for the solubility of O_2 in Tetralin were taken from reference (C-4) and fitted into a modified form of Henry's law. The equation obtained is:

$$\log_{10} \frac{[O_2]}{P_{O_2}} = -5.8274 - \frac{503.28}{T} \qquad (7.8)$$

where P_{O_2} is the partial pressure of O_2 in mm Hg, $[O_2]$ is the concentration of O_2 in the liquid in mole/liter, T is the absolute temperature in °K. Equation (7.8) describes the data of Carlsson and Robb (C-4) with accuracy better than 2%. The data were for $130 < P_{O_2} < 700$ mm Hg and 100°C < t < 140°C. However, it is believed the equation can be safely used in the temperature range of 80 to 160°C. The numbers yielded by the equation are of the order of 10^{-3}-10^{-2} mole/liter and are consistent with the data that were reported in Ref. (E-1), p. 94, for various hydrocarbons. The solubility of O_2 in nonpolar hydrocarbons does not vary sharply with the temperature. Therefore, the values that are obtained from equation (7.8) were used to give an estimate for the initial value of $[O_2]$ and [HBr]. The concentration of O_2 and HBr was assumed constant throughout the reaction period and equal to the equilibrium concentration. This assumption is reasonably accurate for O_2 because fast mass transfer from the gas to the liquid is possible (see Section 5.4). The partial pressure of HBr was naturally considerably smaller than that of the oxygen, but can provide adequate mass transfer to

maintain equilibrium concentration for the catalyst. However, after a sufficient amount of oxidation products is formed, reactions in which HBr is rapidly consumed become important. If a large concentration of HBr is used initially, then the concentration of oxidation products will become significant after a short period, and the rate of consumption of HBr may be of comparable magnitude to the rate of HBr mass transfer. In this case, the assumption of constant HBr concentration fails. The conclusion is that the adequacy of the assumption that the concentration of HBr is constant is a function of the concentration of the oxidation products and of the initial concentration of HBr that was used.

7.6.3 On the Computer Programs and the Manipulation of the Data

The complexity of the system warranted mechanical manipulation of the data by the computer. Handling the problem was split into two programs, INTREACT and FILE.

INTREACT is composed of

1. An integration module, capable of integrating stiff differential equations. (Geer's method was used.)
2. An input module which transforms a given reaction mechanism into the form of differential equations, sets the initial conditions, and accepts the control parameters for the integration and the I/O.
3. An output module which stores the values of the concentration, the instantaneous Jacobians and of a few other parameters on disc files for further manipulation. It is also possible to obtain a printout of the rate of the individual reaction steps, the concentrations of the species,

and the rate of change of individual species at any instant of the reaction.

Program INTREACT is a modification of program MODKIN which was developed by Whitney (W-3).* The differences between MODKIN and INTREACT are: 1) INTREACT produces a disc file of the data which allows further manipulation of the results of the integration, e.g., calculations of the eigenvalues of the instantaneous Jacobian, algebraic manipulation of the data, etc. 2) INTREACT accepts the rate data either in the form of activation energy, frequency factor and temperature, or in the form of given constants and the temperature.

Program FILE† was built to manipulate data. FILE performs the following operations: 1) Plots on the Calcomp in a variety of ways data that were produced by INTREACT or experimental data. 2) Performs a variety of algebraic operations on data files (experimental or from INTREACT) and plots the results. 3) Calculates the eigenvalues of matrices that were produced by INTREACT and plots the resultant complex numbers, or their functions, as a function of the reaction time, as a function of the concentration of selected components, or vs other parameters. (This part has not yet been tested.)

---

*The author wishes to thank Mr. S. Sanders for letting me copy his deck and helping me get acquainted with MODKIN.

†The author wishes to thank Mr. Glenn Wood for his help in developing this program.

7.6.4 The Steady State Assumption -- Its Limitations and Application in the Simulation

Modeling the kinetics of a chemical reaction amounts to the integration of a set of differential equations with given initial conditions. For a complex system the mathematical treatment becomes unmanageable because the differential equations are often stiff, coupled and non-linear. The steady state (SS) approximation can reduce the number of differential equations and thus simplify the mathematical operations. Nonetheless, it is an approximation which should be used with caution. The SS can be applied to every intermediate which can be consumed at a much larger rate than it is formed.* If the ratio of the two rates is large, the absolute concentration of the intermediate will be small, and hopefully its rate of change will be virtually zero. A typical application is to reactive intermediates like free radicals. In the following example the validity of the SS in the initial period of the simple autoxidation reaction is discussed. The reaction mechanism can be described by:

$$2RH + O_2 \xrightarrow{k_o} 2R\cdot + H_2O_2$$

$$R\cdot + O_2 \xrightarrow{k_1} RO_2\cdot$$

$$RO_2\cdot + RH \xrightarrow{k_2} RO_2H + R\cdot$$

$$2RO_2\cdot \xrightarrow{k_6} ROH + CO + O_2$$

When large excess of O_2 and RH exist, the concentrations do not

*If the intermediate can be formed by a branching reaction, its concentration may oscillate. The SS approximation fails in this case.

change appreciably; thus the rate of initiation w_o in the beginning of the reaction is approximately constant:

$$w_o = k_o[RH]^2\,[O_2] \tag{7.9}$$

The rate of change of $[RO_2\cdot]$ is

$$\frac{d[RO_2\cdot]}{dt} = k_1[O_2][R\cdot] - k_2[RH][RO_2\cdot] - 2k_6[RO_2\cdot]^2 \tag{7.10}$$

The rate of change of $[R\cdot]$ is

$$\frac{d[R\cdot]}{dt} = w_o - k_1[O_2][R\cdot] + k_2[RH][RO_2\cdot] \tag{7.11}$$

The sum of equations (7.10) and (7.11) is

$$\frac{d([R\cdot] + [RO_2\cdot])}{dt} = 2w_o - 2k_o[RO_2\cdot]^2 \tag{7.12}$$

Since k_1 is very large and the concentration of oxygen is also large, then $[RO_2\cdot] >> [R\cdot]$, and equation (7.12) becomes

$$\frac{d[RO_2\cdot]}{dt} \simeq 2w_o - 2k_6[RO_2\cdot]^2 \tag{7.13}$$

Let $[RO_2\cdot]\big|_{t=0} = 0$ then:

$$t = \frac{1}{2\sqrt{k_6 w_o}} \log\left[\frac{(\sqrt{w_o/k_6} + x)}{(\sqrt{w_o/k_6} - x)}\right] \tag{7.14}$$

The SS value of $[RO_2\cdot]$ is $\sqrt{w_o/k_6}$ and the time required to achieve 99% of its SS value, $t_{0.99}$, is

$$t = \frac{1}{2\sqrt{k_6 w_o}} \log 199 = \frac{2.65}{\sqrt{k_6 w_o}} \qquad (7.15)$$

For Tetralin at 140°C, $[O_2] \sim 10^{-2}$ mole/liter:

$$t_{0.99} = \frac{\log 199}{2\sqrt{6.35 \cdot 10^{-8} \cdot 2.56 \cdot 10^{7}}} = 2.07 \text{ sec}$$

The computer simulation shows that $RO_2\cdot$ reaches its SS value after 50 min (Figure 7.3).

The SS gives valid approximations if the intermediate is rapidly consumed, slowly produced, and autocatalysis does not occur. However, if the autocatalysis is important, the concentration of the free radicals may oscillate. Apparently the branching is not negligible in the case of autoxidation, and therefore the use of the SS approximation is undesirable.

Five models for the kinetics of oxidation of a hydrocarbon with molecular oxygen were developed using the SS. The models are: Autooxidation of a pure hydrocarbon, Model 1 with a homogeneous catalyst, Model 2 with a retardant which reacts via a non-radical mechanism, Model 3 with retardant that reacts via a free radical mechanism and a combination of Models 2 and 3. The SS models are too simple to enable the quantitation of the numerous sulfur containing products, therefore numerical integration was used to account for them. A full discussion of the SS models is given by Attar (A-7).

Algorithms for the numerical integration of stiff differential equations can handle problems with a limited stiffness only. It was found that if the two reactions

$$HBr + O_2 \rightarrow HO_2\cdot + Br\cdot \qquad k(140°C) = 2.68\ \ 10^{-7} \qquad (7.16)$$

and

$$2Br\cdot \rightarrow Br_2 \qquad k(140°C) = 3.79 \cdot 10^{16} \qquad (7.17)$$

are incorporated as part of the set of differential equations, an extremely unstable system results. When the SS is applied to the Br· radical, the system becomes stable and manageable, because its stiffness is drastically reduced. The SS is valid in this case because the ratio of the rates of (7.17) and (7.16) is very large, the Br· is not produced by an autocatalytic step, and the time required for the [Br·] to achieve 99% of its SS value is approximately $5 \cdot 10^{-5}$ sec.

Since the rate of production and the rate of consumption of Br· depend only on the concentration of HBr and of O_2, and these are constant, once the [Br·] achieves its SS value it maintains it throughout the reaction period. Therefore in the computer simulation of the system, the Br· radical was treated as a reagent with a constant concentration

$$[Br\cdot] = \sqrt{\frac{k_m[O_2][HBr]}{k_t}} = \text{constant} \qquad (7.18)$$

where k_m is the rate constant of reaction (7.16) and k_t is the rate constant of reaction (7.17). The SS approximation fails when sufficient oxidation products are formed because in this case the rate of reduction of HBr becomes of comparable magnitude to the rate of mass transfer of HBr.

7.7 The Results of the Computer Simulation

The following programs are presented:

1. EXPERIMENT 1, which simulates subsystem NOSC (denoted EXP 1)
2. EXPERIMENT 3, which simulates subsystem NOCAT (denoted EXP 3)
3. EXPERIMENT 4, which simulates CATSC, a system combined from NOCAT and NOSC (denoted EXP 4).

The computer listing of the reactions that were integrated in EXP 1 is given in Table 7.3. The listing of the reactions used in EXP 3 is given in Table 7.4. The coupling reactions that were added to combine EXP 1 and EXP 3 are given in Table 7.5. The coupled system, CATSC, was very large and technical limitations did not allow inclusion of all the reactions that may occur. As was anticipated, the theoretical predictions do not match the data of EXP 4 very well.

Of particular interest is the reaction between the sulfoxide and the HBr, which reduces the sulfoxide back to the sulfide:

$$SO + 2HBr \rightarrow S + H_2O + Br_2$$

The rate constant of this reaction is large and is extremely sensitive to the concentrations of HBr and H_2O. Thus the concentration of HBr determines not only the rate of oxidation of the hydrocarbon and the sulfur compound, but also the rate of reduction of the sulfoxide back to the sulfide:

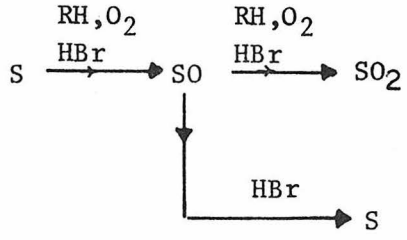


Table 7.3 Reactions and Rate Constants for the Subsystem RH-O_2-HBr (NOSC)

LIST OF REACTIONS

	ENERGY	LOG10(KO)	R. CONST.		REACTANTS				PRODUCTS			
1	0.238E 02	0.540E 01	0.635E-07	O2	RH	RH	= 2.00	R	1.00	H2O2		
2	0.200E 02	0.950E 01	0.823E-01			CCCH	= 2.00	HO	1.00	CO		
3	0.244E 02	0.897E 01	0.114E-03			ROOH	= 1.00	RO	1.00	HO		
4	0.293E 02	0.984E 01	0.216E-05		H2O2	HOO2	= 1.00	HO2	1.00	HO	1.00	H2O
5	0.830E 01	0.575E 01	0.228E 02		RH	ROO	= 1.00	RO2H	1.00	R		
6	0.0	-0.220E 01	0.631E-02		H2O2	CO	= 1.00	CO3H				
7	0.155E 02	0.960E 01	0.250E 02		HBR	ROH	= 1.00	REN	1.00	H2O	1.00	HBR
8	0.205E 02	0.120E 02	0.142E 02		HBR	ROOH	= 1.00	CO	1.00	H2O	1.00	HBR
9	0.116E 02	0.833E 01	0.149E 03		RO2H	ROOH	= 1.00	CO	1.00	ROH	1.00	O2
10	0.550E 01	0.113E 02	0.245E 09		BR	RH	= 1.00	R	1.00	HBR		
11	0.0	0.783E 01	0.676E 08		O2	R	= 1.00	RO2				
12	0.800E 00	0.560E 01	0.150E 06		HBR	ROO	= 1.00	RO2H	1.00	BR		
13	0.450E 01	0.820E 01	0.658E 06		RH	RO	= 1.00	ROH	1.00	R		
14	0.230E 01	0.820E 01	0.961E 07		HO2	RH	= 1.00	H2O2	1.00	R		
15	0.750E 01	0.880E 01	0.677E 05		ROH	ROO	= 1.00	FROH	1.00	RO2H		
16	0.0	0.700E 01	0.100E 08		O2	FROH	= 1.00	CO	1.00	HO2		
17	0.400E 00	0.762E 01	0.256E 08		RO2	ROO	= 1.00	ROH	1.00	CO	1.00	O2
18	0.140E 02	0.850E 01	0.123E 02		HBR	ROOH	= 1.00	PRAC				
19	0.470E 01	0.820E 01	0.516E 06		HBR	HO	= 1.00	H2O	1.00	BR		
20	0.0	0.700E 01	0.100E 08		HBR	HOO	= 1.00	H2O2	1.00	BR		
21	0.0	0.450E 01	0.316E 05	H2O2	H2O2	CO	= 1.00	DICO	2.00	H2O		
22	0.0	0.600E 01	0.100E 07	HBR	H2O2	HOO2	= 1.00	HBR	2.00	H2O	1.00	O2

Table 7.4 Reactions and Rate Constants for the Subsystem Hydrocarbon-O_2-Sulfide (NOCAT)

LIST OF REACTIONS

	ENERGY	LOG10(KO)	R. CONST.		REACTANTS					PRODUCTS			
1	0.238E 02	0.540E 01	0.635E-07	O2	RH	RH	= 2.00	R	1.00	H2O2			
2	0.200E 02	0.950E 01	0.823E-01			CO3H	= 2.00	HO	1.00	CO			
3	0.244E 02	0.897E 01	0.114E-03			RO2H	= 1.00	RO	1.00	HO			
4	0.293E 02	0.984E 01	0.216E-05		H2O2	H2O2	= 1.00	HO2	1.00	HO	1.00	H2O	
5	0.830E 01	0.575E 01	0.228E 02		RH	RO2	= 1.00	RO2H	1.00	R			
6	0.0	-0.220E 01	0.631E-02		H2O2	CO	= 1.00	CO3H					
7	0.116E 02	0.833E 01	0.149E 03		RO2H	RO2H	= 1.00	CO	1.00	ROH	1.00	O2	
8	0.0	0.783E 01	0.676E 08		O2	R	= 1.00	RO2					
9	0.450E 01	0.820E 01	0.658E 06		RH	RO	= 1.00	ROH	1.00	R			
10	0.230E 01	0.820E 01	0.961E 07		HO2	RH	= 1.00	H2O2	1.00	R			
11	0.750E 01	0.880E 01	0.677E 05		ROH	RO2	= 1.00	FROH	1.00	RO2H			
12	0.0	0.700E 01	0.100E 08		O2	FRO2H	= 1.00	CO	1.00	HO2			
13	0.400E 00	0.762E 01	0.256E 08		RO2	RO2	= 1.00	ROH	1.00	CO	1.00	O2	
14	0.0	0.450E 01	0.316E 05	H2O2	H2O2	CO	= 1.00	DICO	2.00	H2O			
15	0.470E 01	0.820E 01	0.516E 06		RH	HO	= 1.00	R	1.00	H2O			
16	0.470E 01	0.820E 01	0.516E 06		RH	HO2	= 1.00	R	1.00	H2O2			
17	0.150E 02	0.940E 01	0.290E 02		CO3H	S	= 1.00	SO	1.00	CO	1.00	H2O	
18	0.186E 02	0.940E 01	0.360E 00		CO3H	SO	= 1.00	SO2	1.00	CO	1.00	H2O	
19	0.220E 02	0.130E 02	0.228E 02		RO2	S	= 1.00	COS	1.00	R	1.00	H2O	
20	0.173E 02	0.960E 01	0.278E 01		CO3H	COS	= 1.00	COSO	1.00	CO	1.00	H2O	
21	0.200E 02	0.140E 02	0.260E 04		RO2	SO	= 1.00	SCOH	1.00	R	1.00	H2O	
22	0.200E 02	0.162E 02	0.413E 06		RO2	SO3H	= 1.00	COSO	1.00	R	1.00	H2O	
23	0.140E 02	0.850E 01	0.123E 02		S	H2O2	= 1.00	SO	1.00	H2O			
24	0.180E 02	0.910E 01	0.375E 00		SO	H2O2	= 1.00	SO2	1.00	H2O			
25	0.650E 01	0.800E 01	0.363E 05	RO2H	RO2H	S	= 1.00	SO	1.00	RO2H	1.00	ROH	
26	0.0	0.455E 01	0.355E 05		S	RO2	= 1.00	SO	1.00	RO			

Table 7.5 Coupling Reactions, Model CATSC

LIST OF REACTICNS

	ENERGY	LOG10(KO)	R. CONST.		REACTANTS							PRODUCTS	
34	0.180E 02	0.800E 01	0.298E-01		PRAC	COS	=	1.00	COSO	1.00	ROH	1.00	HBR
35	0.171E 02	0.116E 02	0.390E 03		PRAC	SO	=	1.00	SO2	1.00	ROH	1.00	HBR
36	0.169E 02	0.103E 02	0.230E 02		PRAC	S	=	1.00	SO	1.00	ROH	1.00	HBR
37	0.800E 01	0.102E 02	0.925E 06		BR	S	=	1.00	CS	1.00	HBR		
38	0.0	0.800E 01	0.100E 09		02	CS	=	1.00	CO2S				
39	0.830E 01	0.575E 01	0.228E 02		RH	CO2S	=	1.00	SOOH	1.00	R		
40	0.200E 02	0.120E 02	0.260E 02			CO2S	=	1.00	C10	1.00	SOS		
41	0.830E 01	0.650E 01	0.128E 03		RH	CO2S	=	1.00	SOOH	1.00	R		
42	0.950E 01	0.800E 01	0.938E 03		BR	SOOH	=	1.00	SOO	1.00	HBR		
43	0.200E 02	0.950E 01	0.823E-01			SOO	=	1.00	SOS	1.00	C10		
44	0.830E 01	0.575E 01	0.228E 02		RH	C10	=	1.00	ALD	1.00	R		
45	0.0	0.790E 01	0.794E 08	HBR	HBR	SO	=	1.00	S	1.00	H2O	1.00	BR2

When water is formed, it separates as a suspension and extracts into it the HBr. Such effects were not included in the model, and therefore we have the poor agreement in CATSC. (See Section 7.8 and Chapt.3 for details.)

The following is a list of general comments on the simulation of a reaction in a complex multi-component system:

1. The reactions in a multi-component system can be simulated using a theoretical model as a base. However, all the phenomena that occur should be accounted for in order to obtain a good match of the data.

2. Several steps of the mechanism can be lumped together and used with the rate constant of the rate-limiting step. This approach simplifies the numerical treatment of the model; however, it may lead to erroneous results when subsystems are coupled.

3. The steady state approximation can be used to reduce the stiffness of the system.

4. The adequacy of the SS approximation is questionable when autocatalytic steps exist. The concentration of free radicals may oscillate for a given system, when the initial values and/or the rate constants are changed. The oscillations can be traced back to free radicals that take part in more than two reactions. Full discussion of this observation is beyond the scope of this thesis, and will not be given here.

In order to avoid the uncertainty of the SS approximation, all the free radicals except for Br· were treated as components of the system.

The implications of the results of the simulation to the system Tetralin-O_2-BuS-HBr are:

1) The mechanism of oxidation that was proposed in Chapters 2 and 3 can be used to adequately simulate the reactions in the subsystems NOCAT and NOSC.

2) The presentation of the data by the model is adequate for the first hundred minutes or so, but it fails for more advanced times. Better presentation could have been obtained if the reactions of secondary products and the effects of the separation of H_2O were included; however, a very large number of reactions and components would have been required in this case.

3) The concentration of HBr and Br· which are assumed affect the results very drastically. Small perturbations in the assumed initial concentration of ROH and CO change drastically the distribution of products in NOSC.

4) The role of HBr is dual at low concentrations ($< \sim 5 \cdot 10^{-4}$ mole/liter) and its effect is mainly as a catalyst to the oxidation of both the hydrocarbon and the sulfide. However, when HBr is present at larger concentrations, the oxidation products that are formed oxidize it to Br_2 and water. The last reaction is very sensitive to the actual concentration of HBr and H_2O. (See the discussion of the role of HBr as a catalyst, Section 7.8).

5) Simulation of CATSC <u>without</u> the reaction

$$SO + 2HBr \rightarrow S + H_2O + Br_2 \qquad (7.19)$$

shows that more than 99.9% of the sulfur compound would have been

converted to the sulfoxide and sulfone. This implies that catalysis of the hydrogen abstraction step is a very efficient way to selectively oxidize the sulfide, but a catalyst other than HBr should be used.

6) The failure of CATSC to represent the data properly is believed to be because it does not include the effects of water. Water extracts the HBr and the surface active sulfoxides, and reaction (7.19) is tremendously enhanced, since it goes via an ionic mechanism. Only representative samples of the results of the simulation are given. The list of figures and the most important results from them are given in Table 7.6:

Table 7.6 A List of Figures from the Simulation with Explanation of Their Significance

Figure* No.	Simulate Experiment No.	Conclusion
7.3	1	The most important free radicals reach SS only after about 50 min. Note also that the assumption $[RO_2\cdot] >> [R\cdot]$ is valid.
7.4	1	The major oxidation products of the hydrocarbon are simulated within the experimental error in the first $\sim$ 100 min.
7.5	1	Water is formed in a relatively large amount. The concentration of the oxidizers RO_2H and H_2O_2 increases and then levels, and remains about constant. The concentration of H_2O_2 is not simulated very well; however, it is believed that a large experimental error in the polarographic method used did introduce some error. Neglecting the redox reaction between H_2O_2 RO_2H and HBr could also have been the source of error.

Table 7.6 (continued)

Figure* No.	Simulate Experiment No.	Conclusions
7.6	3	The conversion to ketone in the oxidation of tetralin in the absence of HBr and in the presence of S is considerably smaller. More alcohol was formed in 3 than in 1, but considerably less ketone, the more advanced oxidation product. The simulation fails again for larger times.
7.7	3	The simulation of the production of SO is good in the first 100 min.
7.8	3	The concentration of oxidizing species is considerably smaller in the absence of HBr. Compare Figure 7.5.
7.9	3	The agreement of the theoretical curve with the data of production of secondary products which contain sulfur is good, although "lumped" rate constants were used in their simulation.

*The scale of some of the components was blown up in order to show the behavior better.

Better fit of the data can be obtained if all of the rate constants are calculated to fit the empirical data. Fewer parameters are required but the applicability of the model is limited to conditions close to those for which the correlations were made. The theoretical prediction of the concentration of sulfide in EXP 5 is presented in Figure 7.10. The equations which were used to obtain Figure 7.10 are given in Table 7.7.

Attempts to model the data of EXP 4 from first principles without taking the separation of water into account, and without the use of more

Table 7.7 Reactions and Rate Constants for the Fit of Experiment 5

	ENERGY	LOG10(KO)	R. CONST.	REACTANTS								
									PRODUCTS			
1	0.238E 02	0.540E 01	0.635E-07	O2	RH	RH	= 2.00	R	1.00	H2O2		
2	0.200E 02	0.950E 01	0.823E-01			CH3H	= 2.00	HC	1.00	CO		
3	0.244E 02	0.897E 01	0.114E-03			RCH	= 1.00	RC	1.00	HO		
4	0.293E 02	0.984E 01	0.216E-05		H2O2	HCH2	= 1.00	HO2	1.00	HO	1.00	H2O
5	0.830E 01	0.575E 01	0.228E 02		RH	RCH	= 1.00	RC2H	1.00	R		
6	0.0	-0.220E 01	0.631E-02		H2O2	CH	= 1.00	CO3H				
7	0.155E 02	0.960E 01	0.250E 02		HBR	RCH	= 1.00	REN	1.00	H2O	1.00	HBR
8	0.205E 02	0.120E 02	0.142E 02		HBR	RCH	= 1.00	CO	1.00	H2O	1.00	HBR
9	0.116E 02	0.833E 01	0.149E 03		RO2H	RCH	= 1.00	CO	1.00	ROH	1.00	O2
10	0.550E 01	0.113E 02	0.245E 09		BR	RH	= 1.00	R	1.00	HBR		
11	0.0	0.783E 01	0.676E 08		O2	R	= 1.00	RO2				
12	0.800E 00	0.560E 01	0.150E 06		HBR	RCH	= 1.00	RO2H	1.00	BR		
13	0.450E 01	0.820E 01	0.658E 06		RH	RH	= 1.00	RCH	1.00	R		
14	0.230E 01	0.820E 01	0.961E 07		HO2	RH	= 1.00	H2O2	1.00	R		
15	0.750E 01	0.880E 01	0.677E 05		ROH	RCH	= 1.00	FROH	1.00	RO2H		
16	0.0	0.700E 01	0.100E 08		O2	FRCH	= 1.00	CO	1.00	HO2		
17	0.400E 00	0.762E 01	0.256E 08		RO2	RCH	= 1.00	ROH	1.00	CO	1.00	O2
18	0.140E 02	0.850E 01	0.123E 02		HBR	RCH	= 1.00	PRAC				
19	0.470E 01	0.820E 01	0.516E 06		HBR	HH	= 1.00	H2O	1.00	BR		
20	0.0	0.700E 01	0.100E 08		HBR	HCH	= 1.00	H2O2	1.00	BR		
21	0.0	0.450E 01	0.316E 05	H2O2	H2O2	CH	= 1.00	CICO	2.00	H2O		
22	0.0	0.600E 01	0.100E 07	HBR	H2O2	HCH2	= 1.00	HBR	2.00	H2O	1.00	O2
23	0.186E 02	0.940E 01	0.360E 00		CO3H	S	= 1.00	SO	1.00	CO	1.00	H2O
24	0.170E 02	0.800E 01	0.101E 00		PRAC	S	= 1.00	SO	1.00	ROH	1.00	HBR
25	0.186E 02	0.940E 01	0.360E 00		CO3H	SH	= 1.00	SO2	1.00	CO	1.00	H2O
26	0.170E 02	0.850E 01	0.319E 00		PRAC	SH	= 1.00	SO2	1.00	ROH	1.00	HBR
27	0.220E 02	0.130E 02	0.228E 02		RO2	S	= 1.00	COS	1.00	R	1.00	H2O
28	0.150E 02	0.830E 01	0.230E 01		PRAC	CH3	= 1.00	COSO	1.00	ROH	1.00	HBR
29	0.183E 02	0.960E 01	0.823E 00		CO3H	CH3	= 1.00	COSO	1.00	CO	1.00	H2O
30	0.200E 02	0.132E 02	0.413E 03		RO2	SH	= 1.00	SOOH	1.00	R	1.00	H2O
31	0.200E 02	0.152E 02	0.413E 05		RO2	SH2H	= 1.00	COSO	1.00	R	1.00	H2O
32	0.160E 01	0.820E 01	0.226E 08		S	HCH2	= 1.00	SO	1.00	H2O		
33	0.165E 02	0.910E 01	0.233E 01		SO	HCH2	= 1.00	SO2	1.00	H2O		

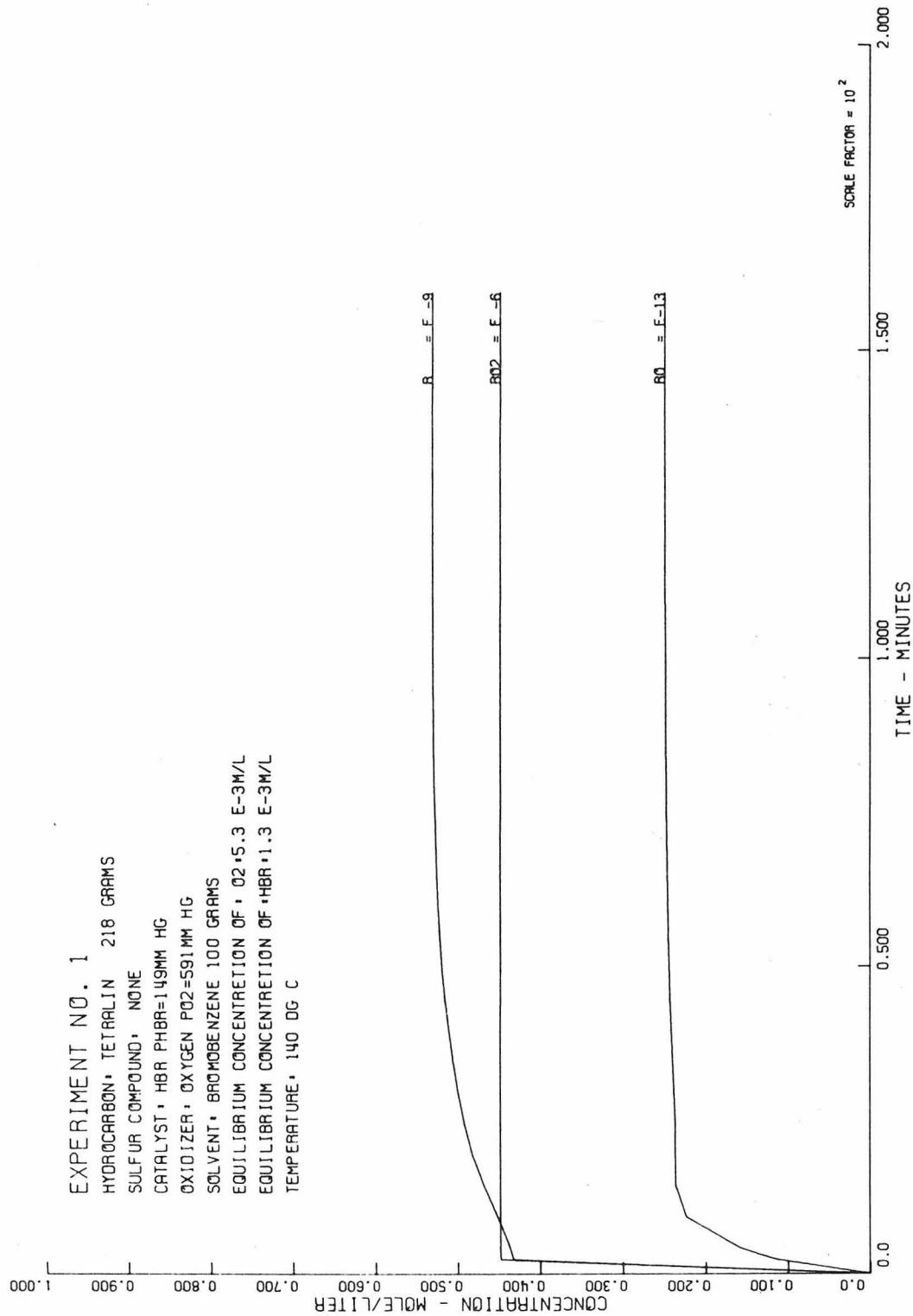


Figure 7.3 Free Radicals vs. Time, Experiment 1

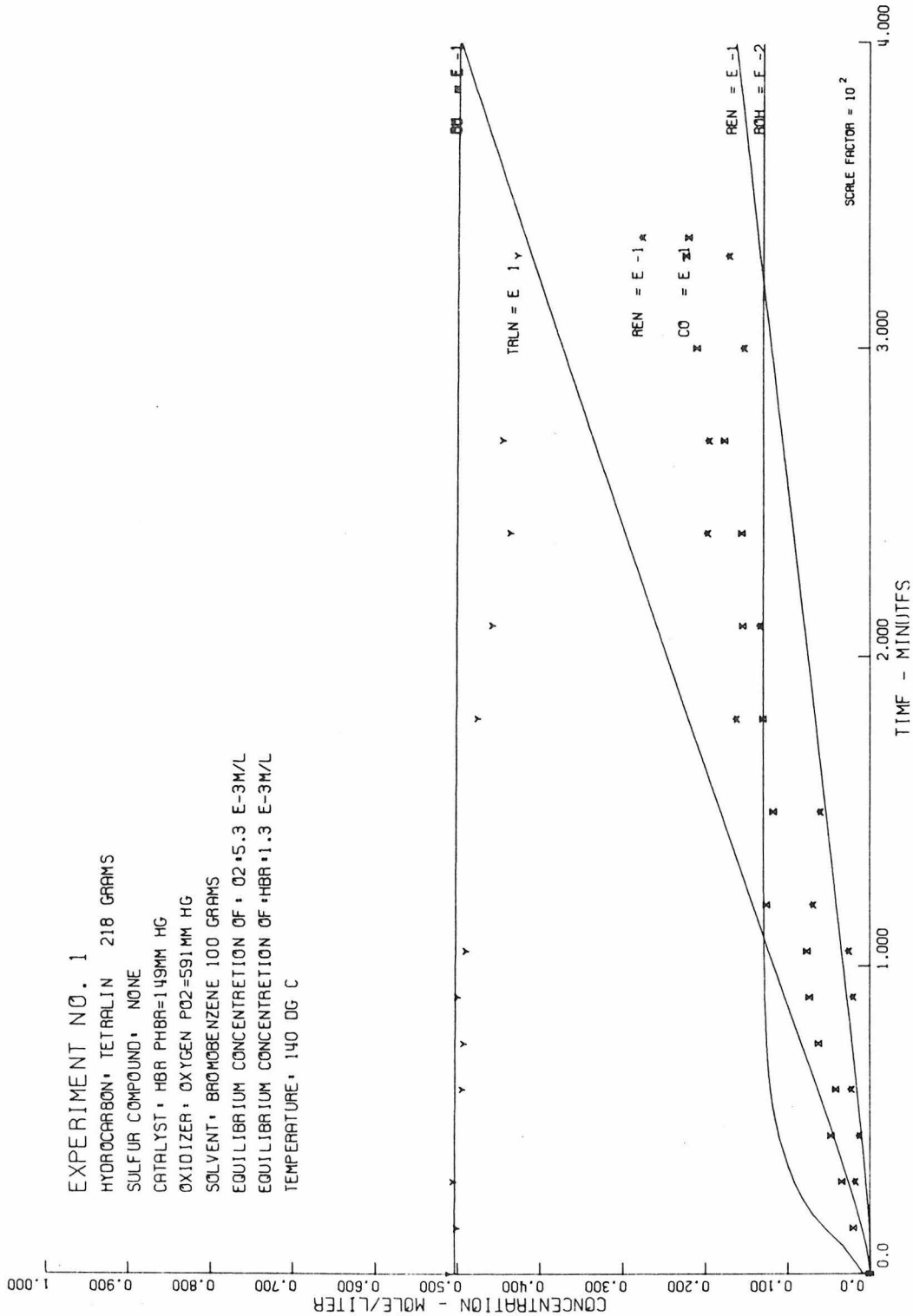


Figure 7.4 Major oxidation products

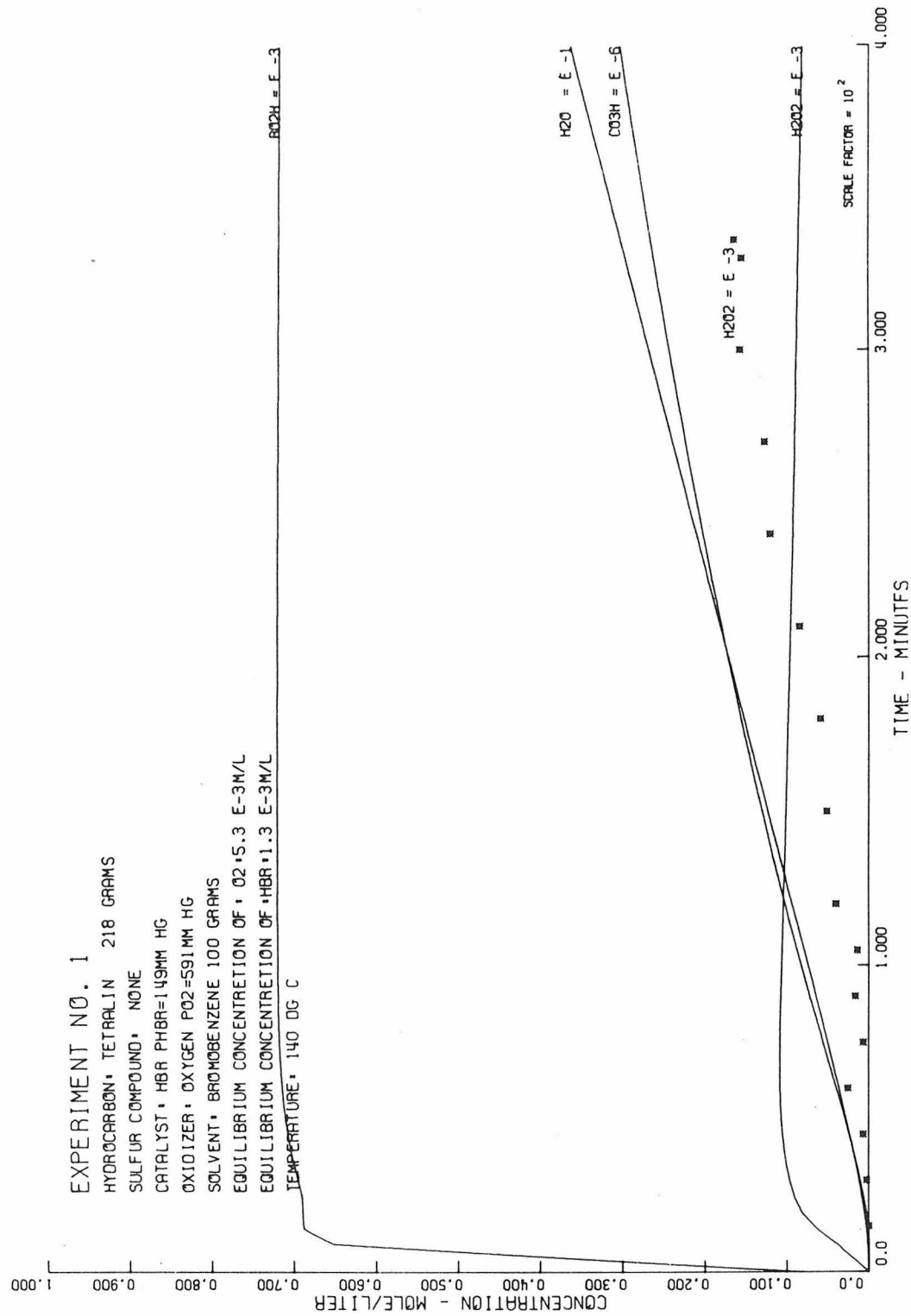


Figure 7.5 Water and oxidizing species.

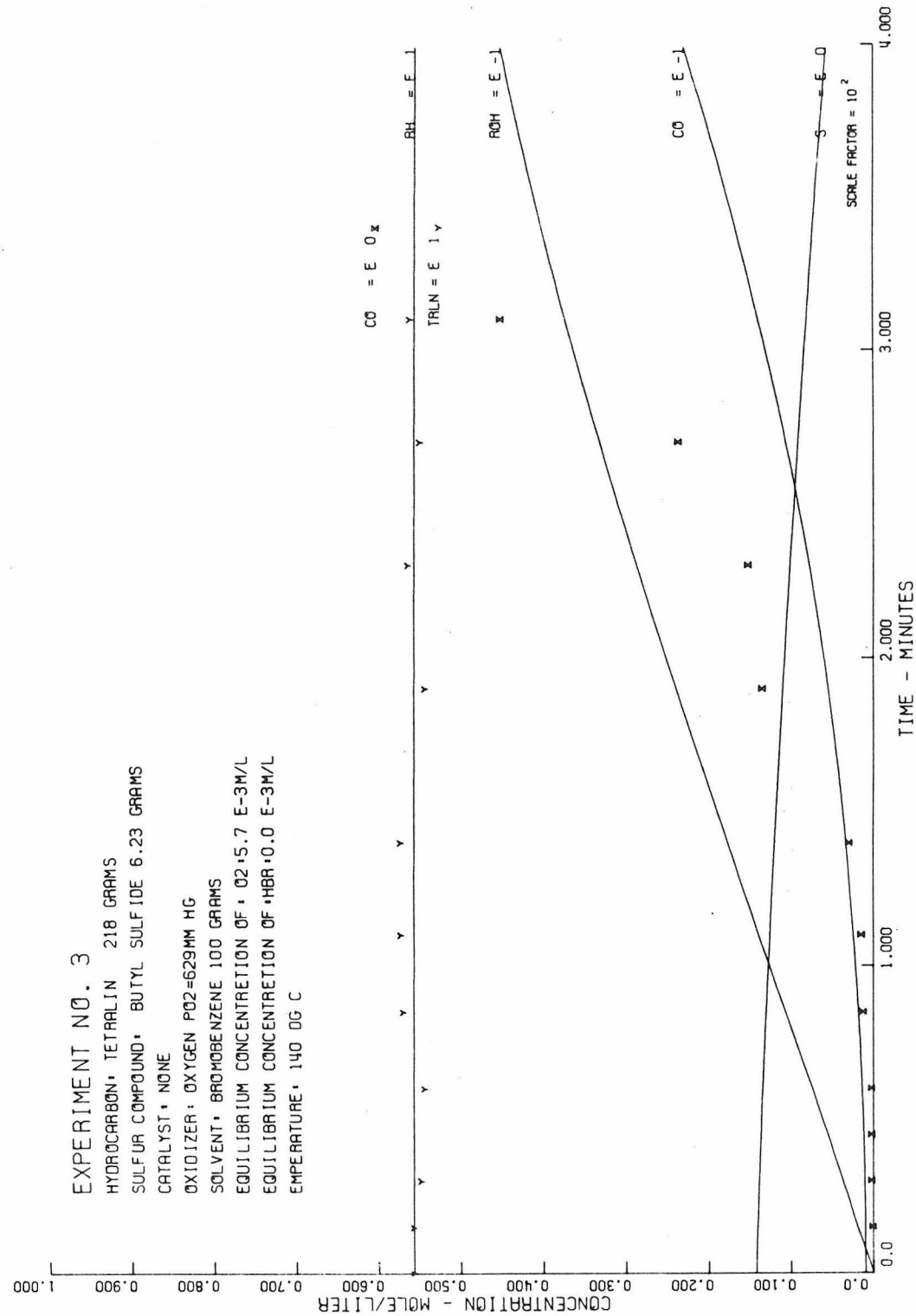


Figure 7.6 Major oxidation products

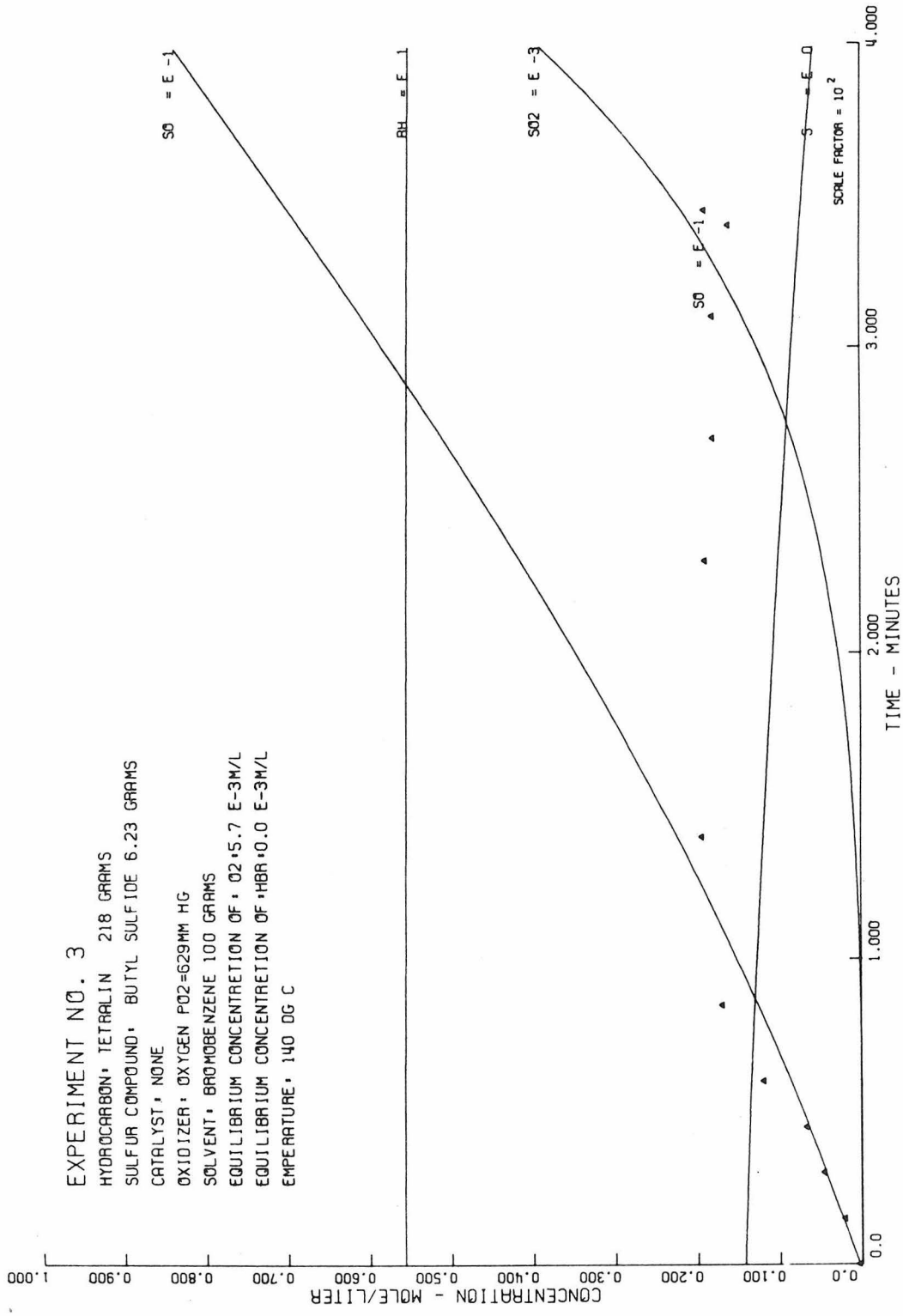


Figure 7.7 Major Sulfur-Containing Oxidation Products

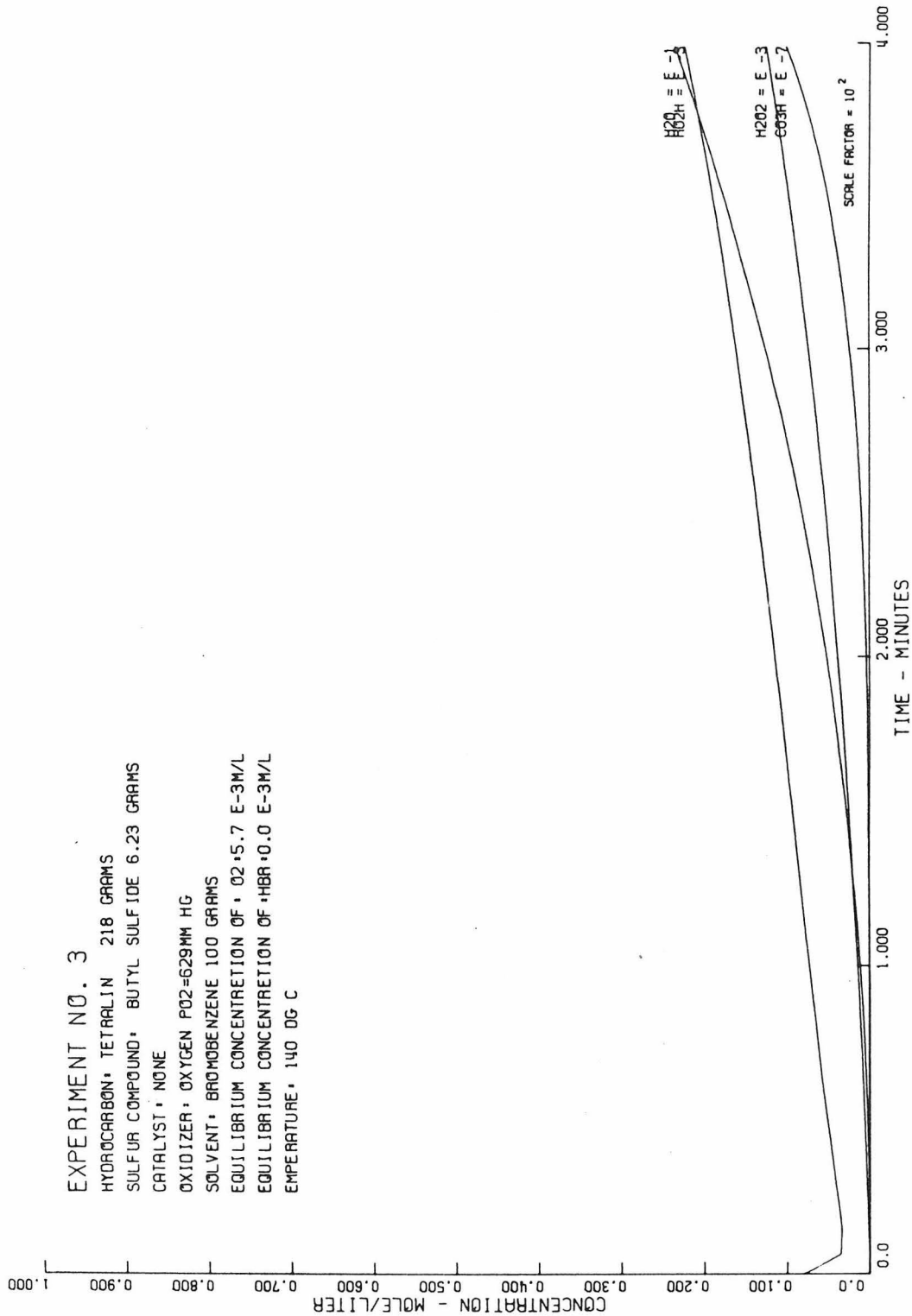


Figure 7.8 Water and Oxidizing Species

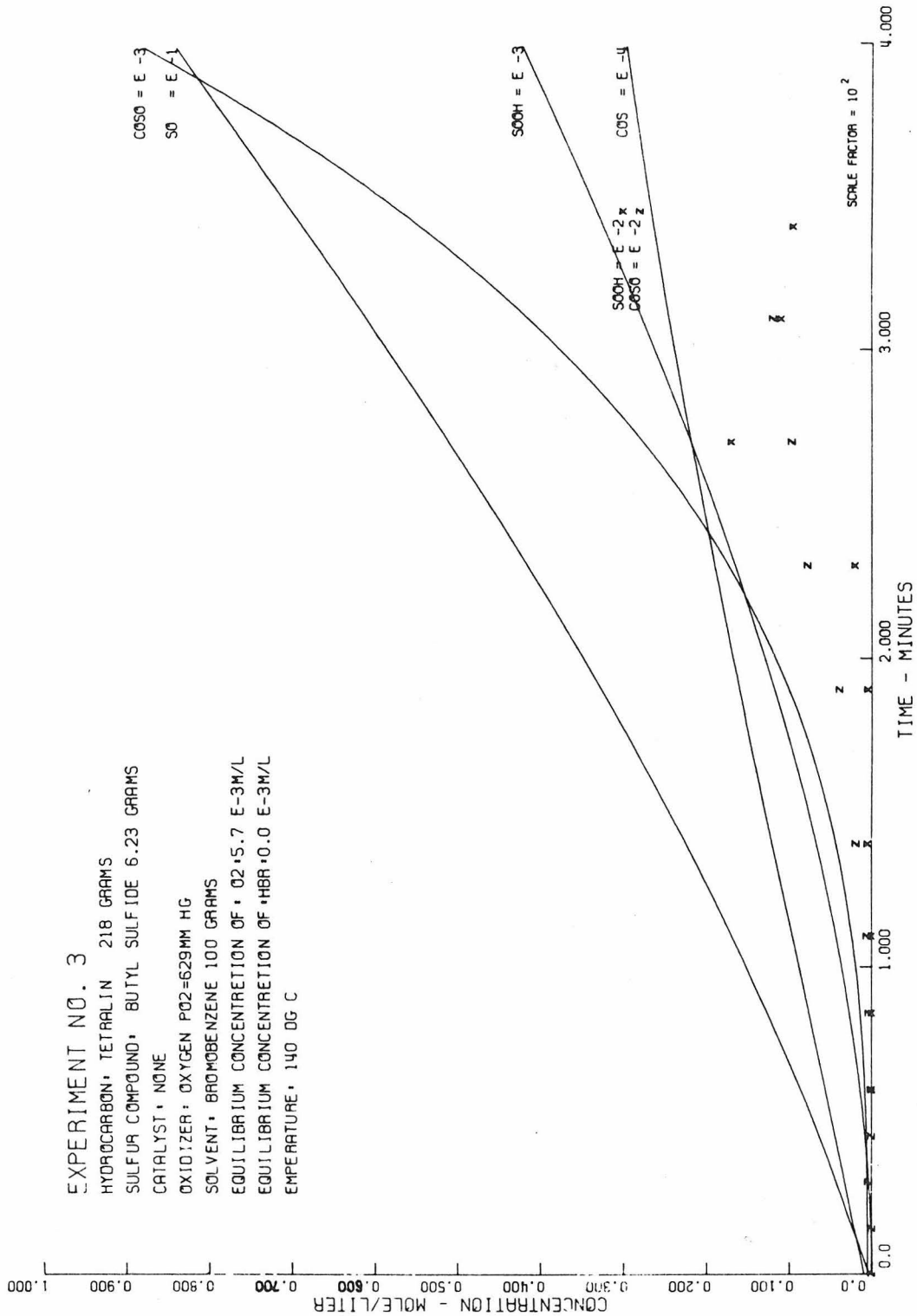


Figure 7.9 Second Generation of Sulfur-Containing Oxidation Products

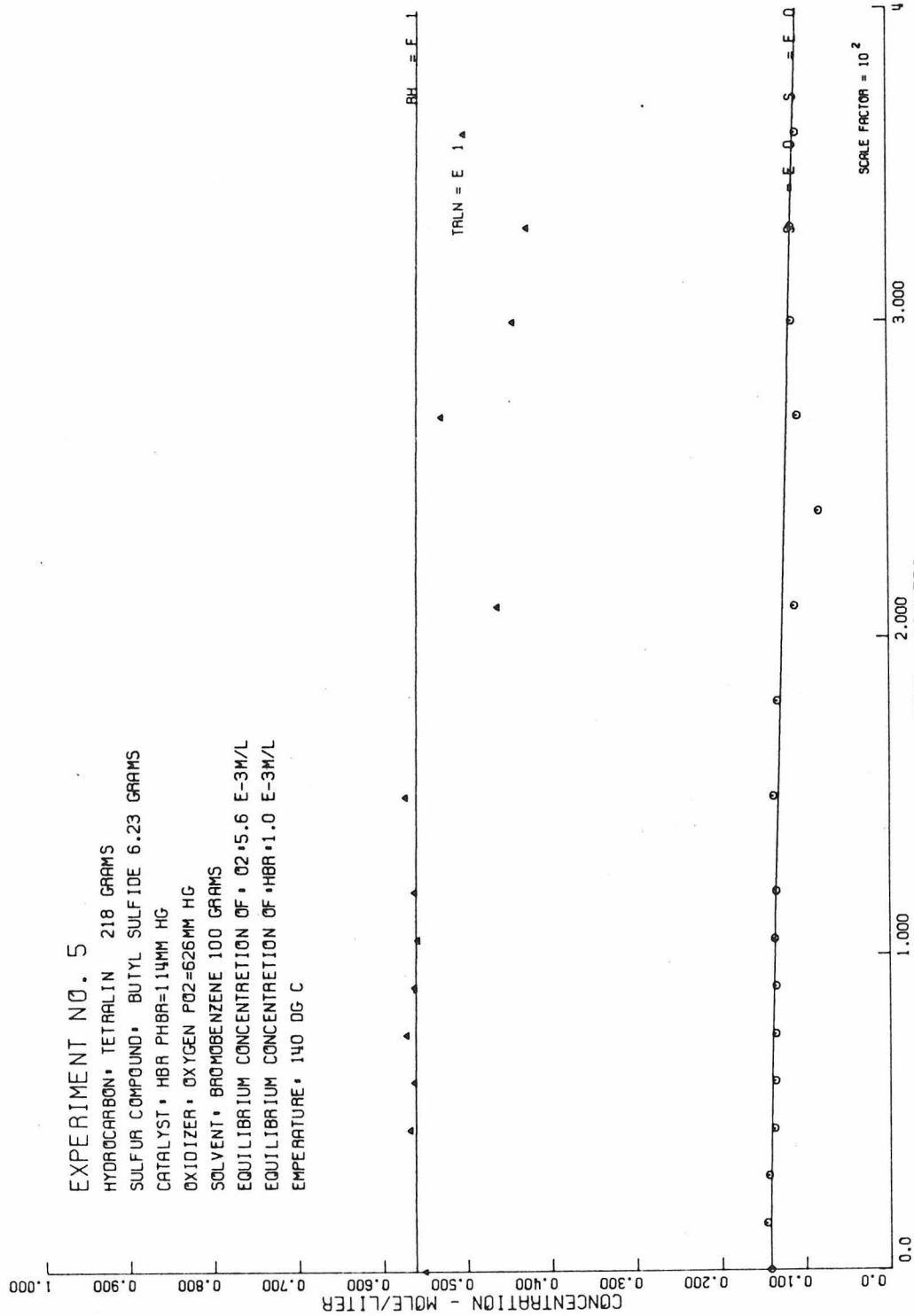


Figure 7.10 Sulfide and Hydrocarbon vs Time. The rate-constants were fitted simultaneously.

than 45 steps, gave results which deviated by up to two orders of magnitude, where secondary sulfur-containing products were concerned. The deviation is because when NOCAT was developed, many steps were lumped together in order to reduce the number of differential equations. Reactions that may occur between lumped species are not recognized when the coupled model CATSC is built; thus the picture is distorted. Attempts to model CATSC with several different lumpings were unsuccessful.

The most important conclusions from the simulation of the oxidation with molecular oxygen of butyl sulfide in Tetralin at 140°C with HBr as a catalyst are:

1) It is possible to obtain models which will describe the subsystems $RH-O_2-S$ (NOCAT) and $RH-O_2-HAr$ (NOSC) within the accuracy of the experimental data.
2) When one model is considered, e.g., NOCAT, it is possible to lump several reactions together, and to use the rate constant of the rate-limiting step as the rate of the lumped reaction; however, when models are combined, lumped reactions should be "delumped", and considered in the structure of the new model. In particular, species that take part in many reactions cannot be lumped.
3) HBr catalyzes the oxidation of hydrocarbon and sulfides retard it.
4) More ketone is formed when HBr is present, while in the presence of aliphatic sulfide, the yield of the alcohol is increased considerably.

A discussion of the use of simulation to predict changes in enthalpy was given in Chapter 4. Examples are given in Section 7.11 .

7.8 Evaluation of HBr as a Catalyst

Catalysts affect the rate of a reaction in two ways: 1) by introducing a new and faster mechanism to effect the conversion of a selected specie; 2) by enhancing the rate-limiting step of the prevailing mechanism. In complex systems, where many species compete for a given amount of reactant, catalysis is bound to change also the distribution of the products.

The role of HBr in the system hydrocarbon-oxygen-sulfide-HBr is much more complex than catalysis of the hydrogen abstraction, which is the rate limiting step of the oxidation. HBr can act as an acid, can share its protons and form covalent complexes, and can reduce oxidizers like peroxides and sulfoxides. The dominant effects are a strong function of the concentration of HBr, the concentration of oxidizers in the solution, and the amount of water in the solution.

In the following sections a semi-empirical discussion of the role of HBr is given. The main object is to define a region of parameters like concentrations, conversions, etc., in which HBr could be used efficiently as a catalyst.

7.8.1 The Effect of HBr on the Overall Rate of Oxidation

The major product of the oxidation of Tetralin is α-tetralone, CO. The extinction coefficient of CO at 310 nm is much larger than that of ROH and REN; therefore, the absorbance of UV light at 310 nm can be used as a gross measure of the overall rate of oxidation of the hydrocarbons. Aliphatic sulfides, sulfoxides and sulfones do not interfere at this wavelength.

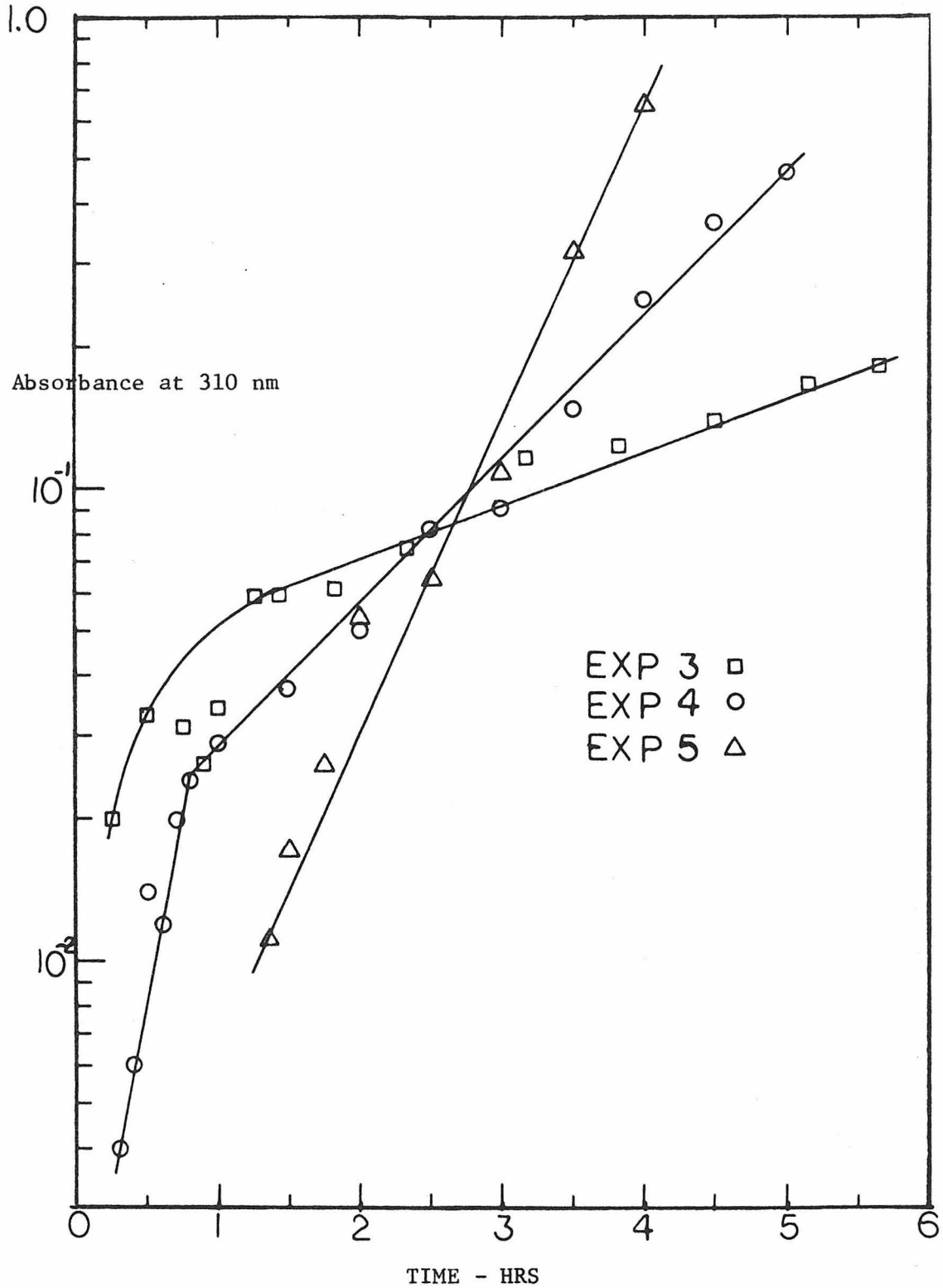


Figure 7.11 The Absorbance at 310 nm vs the Time, Experiments 3, 4, and 5.

Two conclusions are drawn from Figure 7.11, which shows the absorbance at 310 mm vs. the reaction time:

1) HBr increases the overall rate of oxidation;

2) HBr causes the appearance of an induction period.

In Table 7.8 the rate data are summarized:

Table 7.8 The Initial Conditions and the Effect of [HBr] on the Rate of Oxidation of Tetralin. Experiments 3, 4, and 5.

Experiment	[HBr] mode/liter $\times 10^3$	[S] mode/liter	Induction period (minutes)	Rate of Formation of ketone (hr^{-1})
3	0	0.1424	-	0.2908
4	0.64	0.2848	48	0.7223
5	1.34	0.1424	78	1.5463

Since the absorbance is linearly related to the ketone concentration, it can be seen that after the induction period ketone is formed according to a first order rate law. The rate of ketone formation was calculated assuming an overall behavior as a first order reaction. The ratio of the first order rate constants for Experiments 5 and 4 is 2.14, very close to the ratio of concentration of 2.094. When these observations are coupled with the actual values of concentration of tetralone, the following rate equation describes the formation of tetralone:

$$\frac{d[CO]}{dt} = k_c [HBr][RH] \qquad (7.20)$$

where t is in hr, $k_c = 0.608$(lit/mole)/hr at 140°C.

A very crude estimate of the Arrhenius parameters A and E_a of the rate constant can be obtained if the effect of the DBT on the rate of

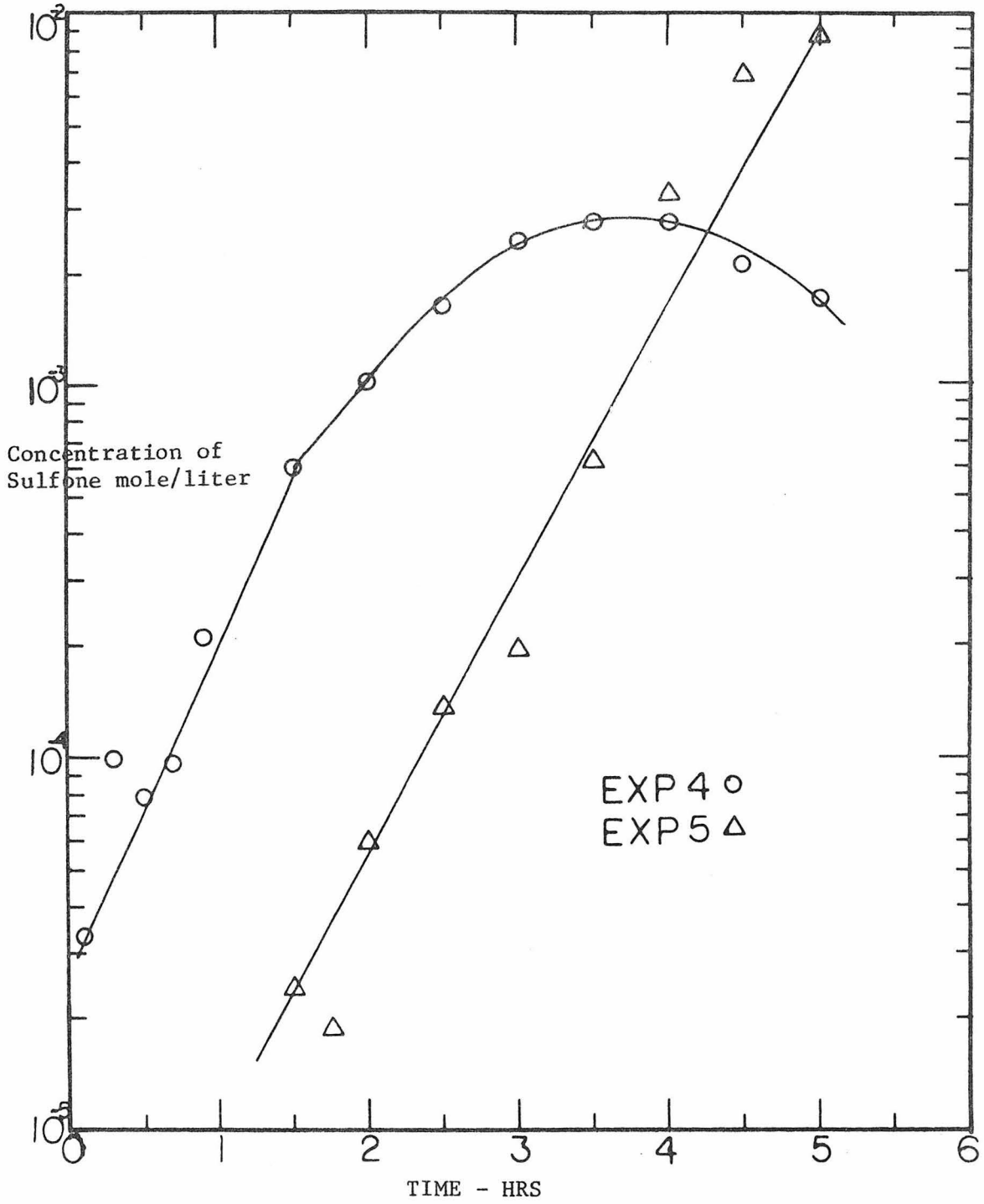


Figure 7.12 Variation of the Concentration of Butyl-Sulfone vs Time Experiments 4 and 5. No sulfone was found in Experiment 3.

ketone formation in Experiment 8 is neglected. (Since the concentration of DBT did not change, this assumption is valid.) In this case, the initial rate of ketone formation is about $1.265 \pm 0.3\ hr^{-1}$ and the Arrhenius coefficients are $A = 4.74 \cdot 10^6$ (lit/mole)/hr and $E_a = 13.02$ kcal/mole. The error in A and E can be up to 20%, but the values of A and E have the right magnitude. Note that the rate constant was not presented as the sum of the rates of CO production with catalyst and without it. The presentation as a sum of rates is required when isolated steps of the mechanism are considered. However, relation (7.20) is an empirical rate law in which many steps were lumped. The induction period that was observed when HBr is present is because the HBr catalyzes the decomposition of RO_2H and of H_2O_2. Initiation by the reaction of HBr and O_2 is very slow, and it is believed that most of the initiation is by decomposition of RO_2H:

$$RO_2H \rightarrow RO\cdot + \cdot OH \qquad (7.21)$$

The RO_2H produced when O_2 is introduced to the system reacts as follows:

$$RO_2H + HBr \rightleftarrows PRAC \rightleftarrows CO + H_2O + HBr \qquad (7.22)$$

(PRAC $\xrightarrow{HBr}$ $H_2O + Br_2 + ROH$)

When sufficient PRAC is produced, equilibrium is achieved and an approximately constant $[RO_2H]$ is obtained. The RO_2H decomposes and initiates the reaction. This mechanism contradicts the assumption that [Br] is at SS from the very beginning; however, the computer simulation

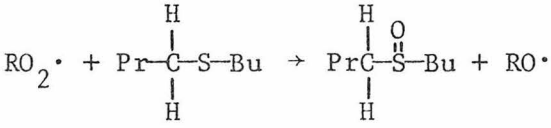
indicates that this is a valid working assumption. Moreover, the concentration of RO_2H does not vary much after the initial period.

7.8.2 The Effect of HBr on the Rate and Selectivity of the Oxidation of Aliphatic Sulfides in Tetralin

HBr influences the rate and the selectivity of oxidation of butyl sulfide in the following ways:

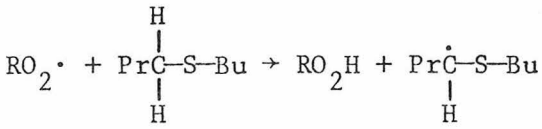
1. It increases the overall rate of oxidation, as discussed in Section 7.8.1. The increased rate of oxidation results in an increased level of oxidants like RO_2H and H_2O_2, and in turn in an increased rate of oxidation of S by the homolytic mechanism (Chapter 3).

2. It increases the activity of the radicals in the system. The free radicals react with S in two ways: to oxidize the sulfur,



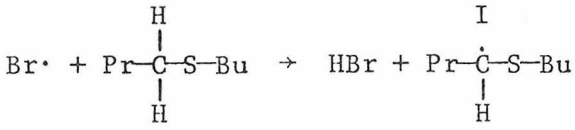
(7.23)

and to abstract hydrogen from the sulfide,



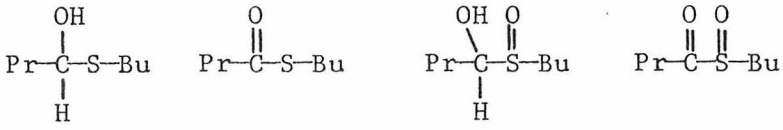
(7.24)

and



(7.25)

The α-butyl sulfide radical I (denoted CS) reacts very rapidly with oxygen and ends finally as the corresponding ketone (COS), alcohol (COHS), α-keto sulfoxide (COSO) or α-hydroxy sulfoxide.



COHS COS SOOH COSO

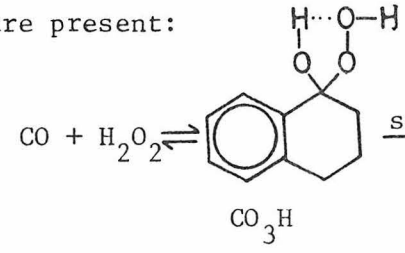
The oxidation of the hydrogen on the carbon is an undesired process which results only in loss of energy. Such processes are parasitic and cause a decrease in the selectivity toward the desired products, the sulfoxides and sulfones.

3. It increases the degree of oxidation of the sulfur compound. When no HBr is present, the sulfur is not oxidized beyond the sulfoxide; however, sulfone (SO_2) and other sulfur-containing, highly oxidized compounds are obtained when HBr is present. The advanced oxidation of the sulfur can be due to one of the following: a) the formation with HBr of an oxidizing complex which has a large oxidation potential; b) the formation at a large rate of secondary and tertiary oxidation products, e.g., peroxy acids, which have much larger oxidation potential than the primary peroxides.

The data do not provide a clear answer as to which mechanism dominates. Figure 7.11 shows the concentration of sulfone as a function of time for experiments 4 and 5. The SO_2 appears approximately at the same time the induction period ends; this may support the theory that SO_2 is formed by the reaction:

$$SO + PRAC \rightarrow SO_2 + HBr + ROH \qquad (7.26)$$

(See Section 7.8.1 where the induction period is discussed.) However, other advanced oxidation products may have been the oxidizers, e.g., the hydroxy-hydroperoxide (denoted CO_3H) which is formed only when sufficient CO and H_2O_2 are present:



(7.27)

CO_3H is believed to have an oxidation potential similar to that of peracids.

7.8.3 Ionic Reactions and Their Relation to the HBr

One of the products of the oxidation is water which, when present in large concentrations, can change the course of the reaction. If water is produced at a slow rate, it evaporates out of the liquid; however, when a large concentration of catalyst is present, the rate of production of water may be so large that it separates from the organic phase. The presence of water in this case shows as a turbidity in the system. Turbidity appeared in experiment 5 after about two hours.

When water separates, the following changes in the course of the reaction occur: 1) the HBr is extracted from the organic phase to the aqueous phase; 2) the solubility of HBr in H_2O is so large that the maximum mass transfer rate possible is still too small to replenish it; 3) the oxidized sulfur compounds e.g., sulfoxides, which have a strong surface activity, concentrate on the interphase between the organic and the aqueous phase; 4) ionic reactions can occur in the aqueous phase and on its surface. The most important ones are believed to be:

a) Formation of acid-base complex (I) with the sulfoxide

$$SO + HBr \rightleftarrows \underset{I}{[S\!-\!\overset{+}{O}\!-\!\overset{-}{H}\!-\!Br]} \qquad (7.28)$$

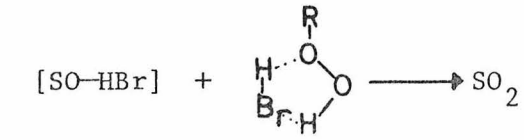
b) Reduction of the complex by an ionic reaction with an HBr molecule

$$[S\!-\!O\!-\!HBr] + HBr \rightarrow S + H_2O + Br_2 \qquad (7.29)$$

The Br_2 which is formed reacts with the Tetralin or with REN. In both

cases the hydrocarbon is partially brominated.

c) Oxidation of I by a peroxide-HBr complex



(7.30)

Reactions (7.29) and (7.30) are parallel; however, (7.29) reduces the sulfoxide into unoxidized sulfide, while (7.30) is the most beneficial reaction, since it converts the sulfoxide to sulfone.

When the concentration of HBr is large, water will be formed at a larger rate and will separate after shorter time. However, if only a small amount of water is formed, it may evaporate with the gas stream and never reach the concentration required to separate.

Figure 7.13 shows the concentration of SO in the solution in experiments 3, 4, and 5. The concentration is the largest in EXP 3, where HBr was not used. It is smaller in EXP 4, where the concentration of HBr was small ($\sim 6.4 \cdot 10^{-4}$ mole/liter). It is even smaller in EXP 5, where the HBr concentration was large ($\sim 1.34 \cdot 10^{-3}$ mole/liter). The SO concentration becomes undetectable shortly after the water separates in the form of turbidity. A myriad of other reactions can occur in the aqueous phase; however, the data available are not sufficient to evaluate their effects.

7.8.4 The Potential of HBr as a Catalyst for the Selective Oxidation of Aliphatic Sulfides to Sulfones and Sulfoxides

The most desired product of the oxidation is the sulfone, since sulfones decompose to hydrocarbons and SO_2. Less desired products are the

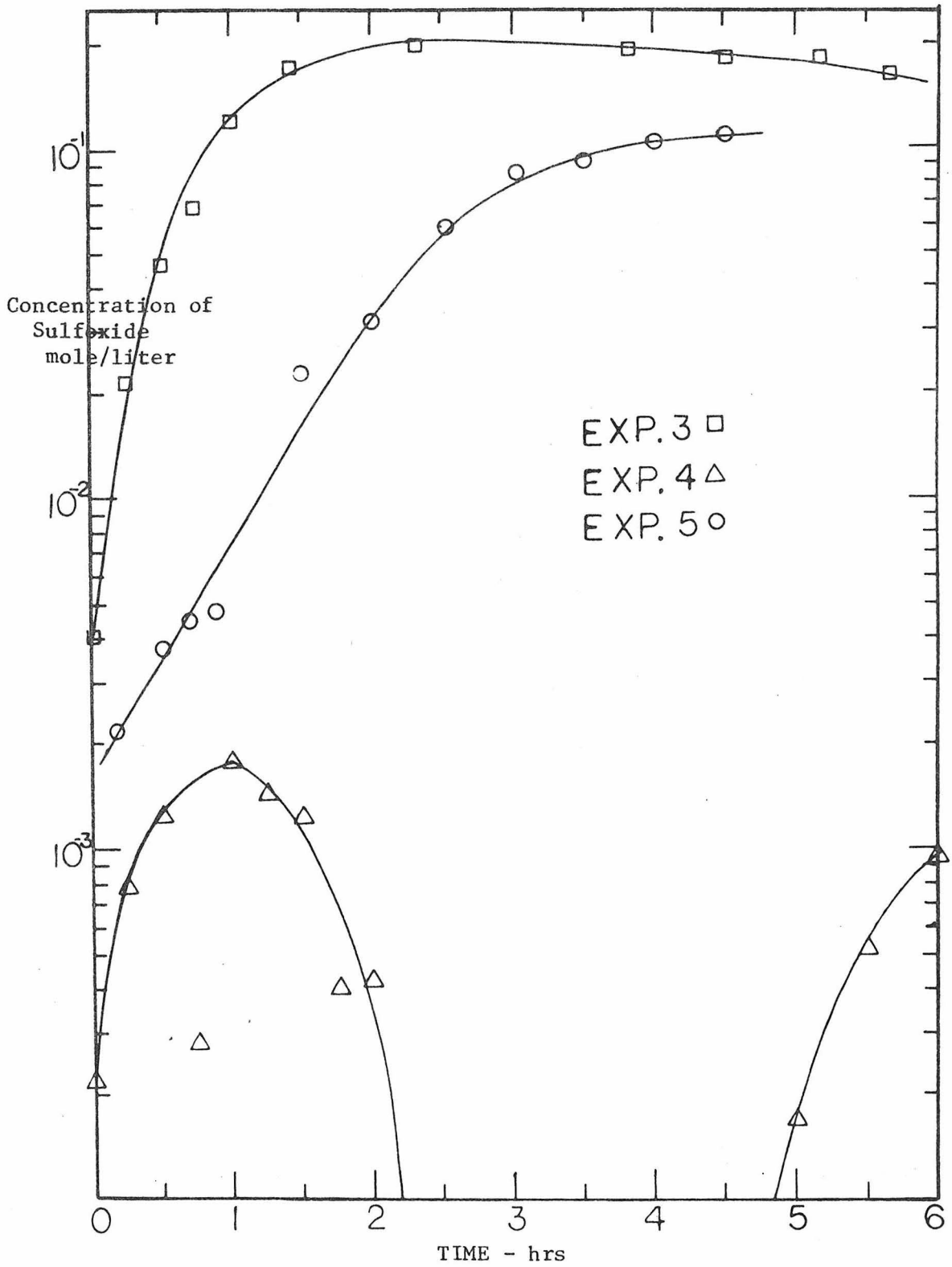


Figure 7.13 Variation of the Concentration of Sulfoxide as a Function of Time, Experiments 3, 4, and 5

sulfoxides, which form a sulfide and sulfone molecule when pyrolyzed under mild conditions:

$$2C_2H_5{-}CH_2{-}CH_2{-}\overset{\overset{O}{\|}}{S}{-}C_4H_9 \xrightarrow{\Delta} C_4H_9SC_4H_9 + C_4H_9SO_2C_4H_9 \tag{7.31}$$

$$C_4H_9SO_2C_4H_9 \equiv C_2H_5{}^{+}CH_2{-}CH_2{-}SO_2{-}C_4H_9 \xrightarrow{\Delta} C_2H_5{-}CH\ CH_2 + SO_2\,1_{gas} + C_4H_{10} \tag{7.32}$$

Here SO_2 denotes gaseous sulfur dioxide.

The evaluation of HBr is made based on the following functions:

1. The "desulfurization selectivity", ψ_{DS}, which is a measure of the fraction of sulfur compounds that can be desulfurized by a mild pyrolysis:

$$\psi_{DS} = \frac{[SO_2] + 0.5[SO] + 0.5\ [COSO] + 0.5[SOOH]}{[SO_2] + [SO] + [COSO] + [SOOH] + [COHS] + [COS] + [S]} \tag{7.33}$$

Define the numerator as DSO and the denominator as TS, then

$$\psi_{DS} = \frac{DSO}{TS} = \frac{DSO}{[S]_o} \tag{7.34}$$

2. The "relative desulfurization selectivity", ψ_{rDS}, which is a measure of the selectivity of the oxidation to products which can be desulfurized.

$$\psi_{DS} = \frac{DSO}{TS - [S]} \equiv \frac{DSO}{[S]_o - [S]} \tag{7.35}$$

3. The "relative desulfurization selectivity for sulfone and sulfoxide", ψ_{rDSO}, which is a measure of the conversion of sulfide to desulfurizable species without loss of energy to reactions on the side

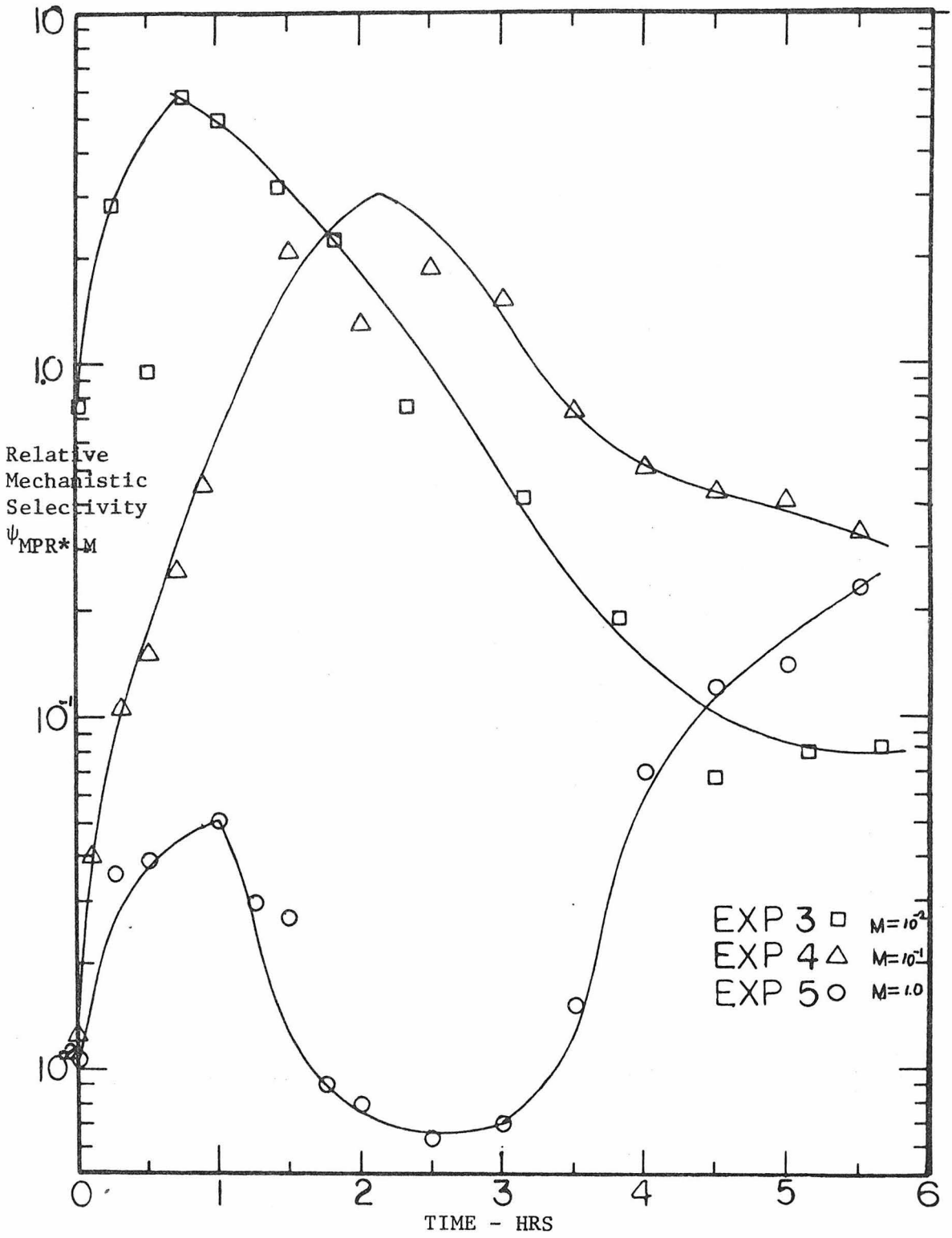


Figure 7.14 The Variation of the Relative Mechanistic Selectivity as a Function of the Time, Experiments 3, 4, and 5

chain

$$\psi_{rDSO} = \frac{[SO_2] + 0.5[SO]}{TS - [S]} = \frac{[SO_2] + 0.5[SO]}{[S]_o - [S]} \qquad (7.36)$$

4. The "selectivity of incorporation of oxygen into desulfurizable species", ψ_{DOS}, which is a measure of the selectivity of the oxidation to the sulfur atom:

$$\psi_{ODS} = \frac{DSO}{S[O]_{system}} \simeq \frac{[SO_2] + 0.5[SO]}{[CO] + [H_2O] +](H_2O_2] + [ROH]} \qquad (7.37)$$

ψ_{ODS} is closely related to the energy penalty of the desulfurization. Since the latter is discussed in Section 7.11, it will not be discussed here.

5. The "mechanistic selectivity", ψ_{MPR}, which relates the concentration of sulfoxides and sulfones to the other oxidation products of the sulfur

$$\psi_{MPR} = \frac{[SO_2] + [SO]}{TS - [S] - [SO] - [SO_2]} \qquad (7.38)$$

If it is assumed that SO and SO_2 are produced predominantly by reactions with peroxides, while all the other compounds are products of free radical reactions, then ψ_{MPR} is a measure of the relative importance of the two mechanisms. The author is aware that species like COSO and COOH could have formed also by a combined free radical and homolytic mechanism. However, it is believed that basically ψ_{MPR} represents correctly the relative importance of the two mechanisms.

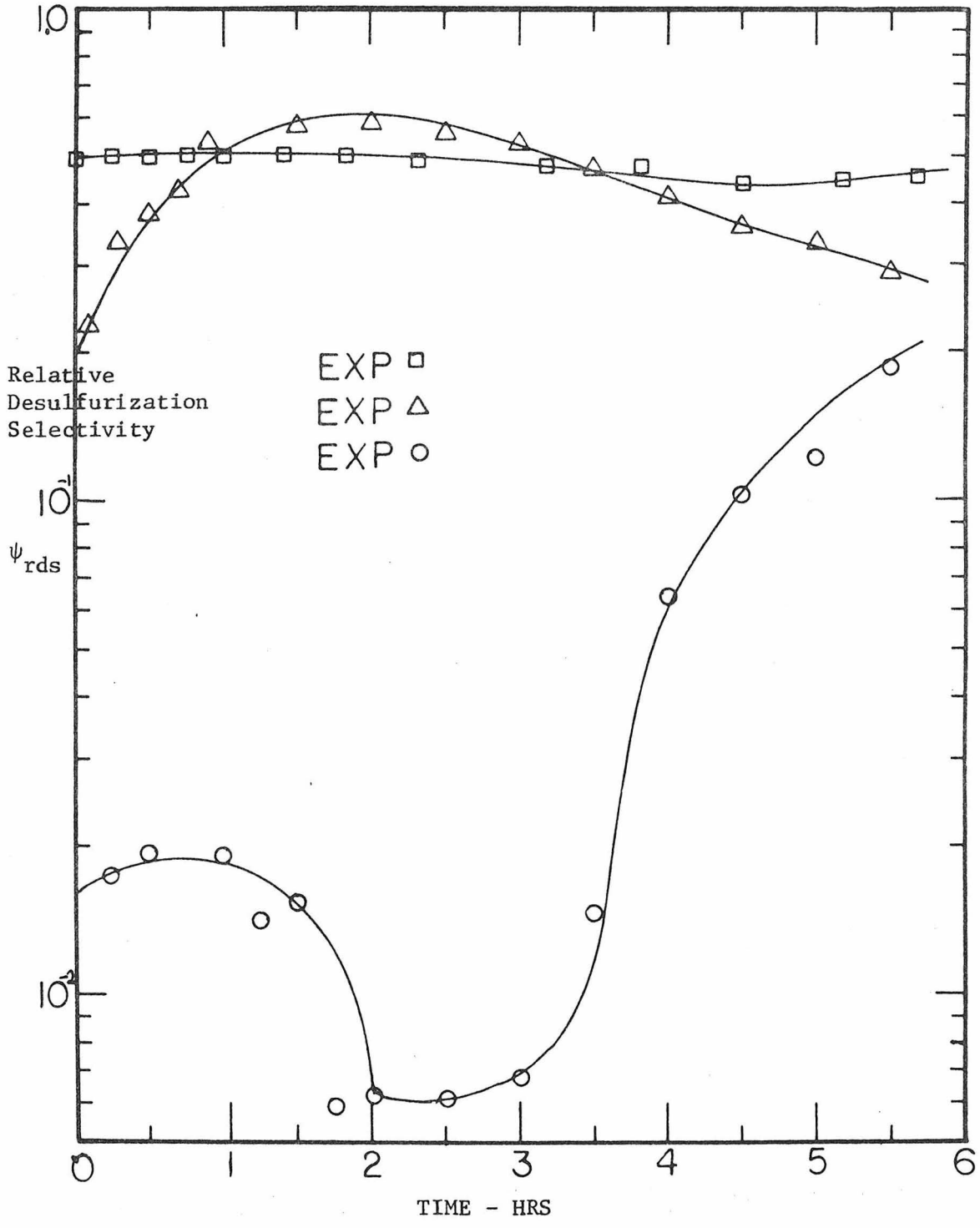


Figure 7.15 The Variation of the Relative Desulfurization Selectivity as a Function of the Time, Experiments 3, 4, and 5

In order to eliminate redundancy, and because our main interest is the mechanism of the reaction, only ψ_{rds} and ψ_{MPR} will be discussed. Figure 7.14 shows ψ_{MPR} vs. the time of the reaction for experiments 3, 4, and 5. The most important conclusions that can be made are:

1. Oxidation of the sulfide proceeds via a non-radical mechanism when no catalyst is used, however, when HBr is added, a large fraction of the sulfide is consumed by a free radical mechanism. Oxidation by a free radical mechanism proceeds not only on the sulfur but on the carbons as well. This observation was anticipated, since the function of adding HBr was to increase the activity of the free radicals.

2. The activity of the free radicals is a very strong function of the concentration of HBr. Increasing the HBr concentration from $\sim 6.4 \cdot 10^{-4}$ mole/liter to $1.3 \cdot 10^{-3}$ mole/liter results in a decrease of more than an order of magnitude in the mechanistic selectivity.

3. In experiments 3, 4 and 5 the selectivity increases first and then decreases. The increased selectivity in experiment 5, which is observed after three hours, is attributed to the separation of colloidal water and a change in the reaction mechanism. This increased selectivity is due to the formation of SO_2 which was not detected at earlier times.

4. An optimal residence time can be found for which maximum selectivity is obtained. This time is a function of the HBr concentration.

The relative desulfurization selectivity, ψ_{rDS}, is of interest when the main goal is to estimate the optimal residence time for desulfurization. Figure 7.15 shows the variation of ψ_{rDS} vs. the time, for

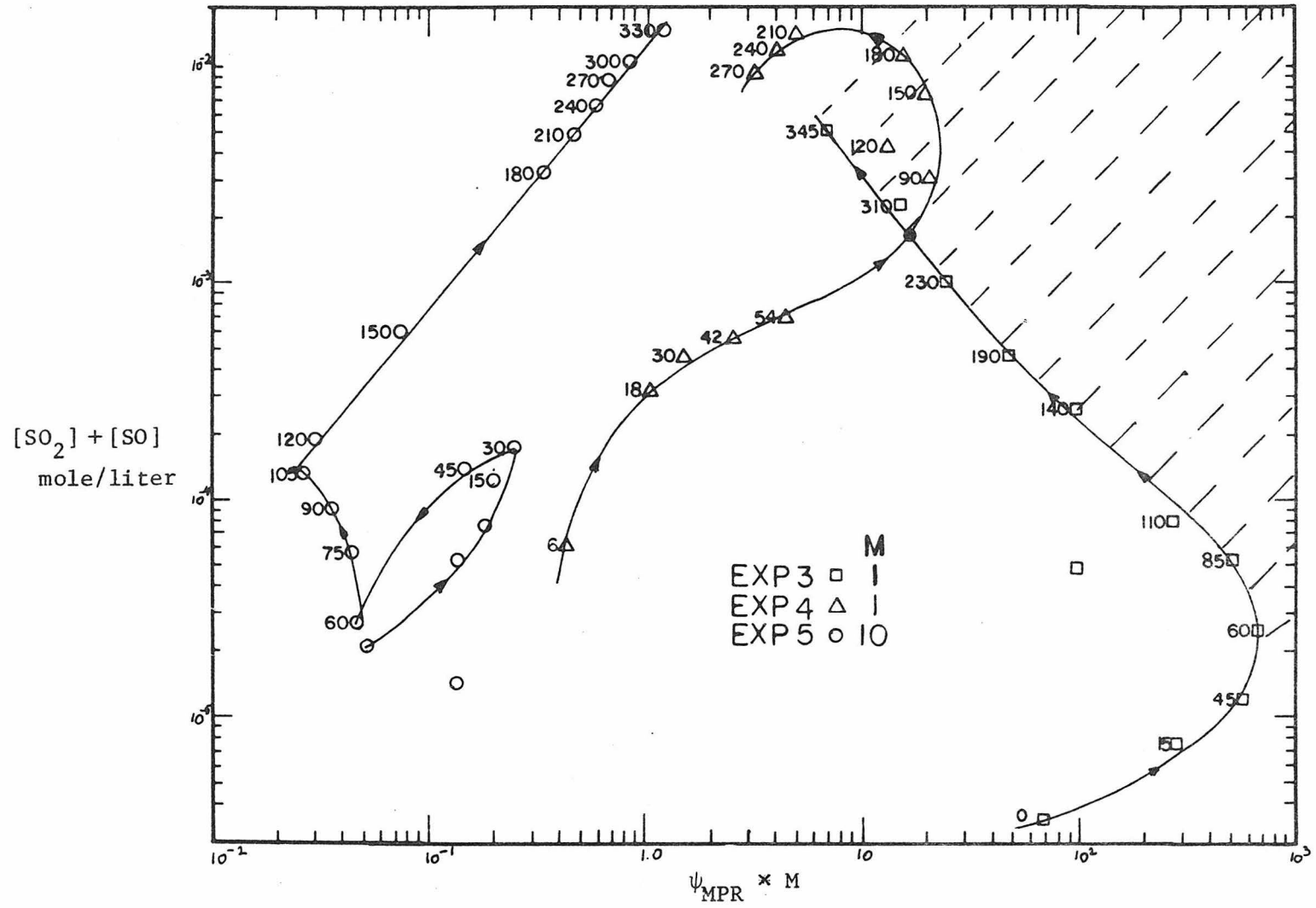


Figure 7.16 The Sum of Concentrations of Sulfoxides and Sulfones vs the Relative Mechanistic Selectivity

experiments 3, 4 and 5. The most important conclusions from the plot are:

1. An optimal concentration of HBr exists for which the desulfurization selectivity is maximized. This value is larger than 0.0 and smaller than $6.4 \cdot 10^{-4}$ mole/liter.

2. The selectivity is a very strong function of [HBr]. An increase in [HBr] above $6.4 \cdot 10^{-4}$ mole/liter increases the overall rate of reaction of free radicals and therefore of ψ_{rDS}. However, if SO_2 is the only desired product [HBr] concentrations larger than 10^{-3} should be used.

The optimal conditions are a function not only of the selectivity but also of the reactivity. Figure 7.16 shows the phase plane diagram of [SO] + [SO_2] vs. ψ_{MPR}. The time was used as a parameter; the arrows indicate the course of progress of the reaction. The most important conclusions from Figure 7.16 are: 1) At small conversions, considerably larger selectivity is obtained when no catalyst is used. 2) When catalyst is used, the general trend of the selectivity is to increase with the increase in the conversion, but when no catalyst is used, the selectivity decreases with the conversion.

A region in the phase plane exists in which larger conversions and selectivities can be obtained in the presence of a catalyst. This area was shaded. Mapping of this area into the subspace of [HBr]-time can be used to obtain the optimum operation conditions. When [HBr] $\simeq$ $6.4 \cdot 10^{-4}$ mole/liter at times larger than about 65 min but smaller than about 315 min, better selectivities and conversions will be obtained

due to the presence of HBr. Note that $\psi = 15$ and $[SO] + [SO_2] = 1.8 \cdot 10^{-3}$ is obtained after about 65 min when $[HBr] = 6.4 \cdot 10^{-3}$ mole/liter, and after about 300 min in the absence of HBr.

7.8.5 Summary of the Evaluation of HBr as a Catalyst to the Selective Oxidation of Aliphatic Sulfides

The following effects were observed due to the presence of HBr in the system:

1. The oxidation proceeds after a short induction period.

2. The rate of formation of ketone after the induction period can be correlated with the equation:

$$\frac{d[CO]}{dt} = k_o e^{-\frac{E}{R_T}} [HBr][RH]$$

The approximate values of k_o and E around 140-160°C are $A = 4.74 \cdot 10^6$ (lit/mole)/hr and $E = 13.02$ kcal/mole.

3. HBr enhances the rate of formation of water and when the [HBr] is large, turbidity appears. When colloidal water is present, SO is rapidly reduced back to the sulfide.

4. SO_2 is formed only when HBr is present.

5. HBr increases the total activity of free radical attack on the hydrocarbon part of the aliphatic sulfide.

6. A range of parameters exist for which better selectivities and larger conversion of the sulfide to the sulfoxides and sulfones will be obtained due to the presence of HBr., e.g., when $[HBr] = 6.4 \cdot 10^{-4}$ mole/liter the same selectivity and conversions are obtained as when HBr is not present after about 310 minutes.

It is believed that if a very small concentration of HBr is used, the reduction of sulfoxide back to sulfide will be minimized, since its dependence on [HBr] is at least second order.

The HBr indeed enhances the rate of oxidation, however, since it also reduces the sulfoxides to the sulfides when the goal is the oxidation of sulfur compounds. A more suitable catalyst for the hydrogen abstraction should be used. The use of other catalysts may help to eliminate the experimental error due to the extraction of HBr into colloidal water and due to the tendency of HBr to take part in ionic reactions.

7.9 The Hydrocarbon Medium and Its Effect on the Oxidation of Butyl Sulfide

Three experiments are compared: EXP 2 with no hydrocarbon, EXP 4 with Tetralin, and experiment 6 with toluene. The initial conditions given in Table 7.9, the temperature of the reaction was 140°C except in experiment 6, where it was 136.5°C.

Table 7.9 The Initial Conditions of Experiments 2, 4, and 6

Experiment No.	Hydrocarbon	Hydrocarbon Concentration $\equiv C_{RH}$ mole/liter	Sulfide Conc. = C_S mole/liter	$\frac{C_{RH}}{C_S}$	HBr Conc. mol/lit $\times 10^3$	O_2 conc. mol/lit $\times 10^3$
2	Butyl Sulfide	0.1423	0.1423	1	1.1	5.6
4	Tetralin	5.395	0.2784	19.4	0.64	6.0
6	Toluene	2.177	0.1424	15.3	0.9	5.6

The main goal of the comparison is to try to determine how the system would behave if other hydrocarbons are used instead of tetralin and

toluene. The reader is reminded at this point that the rates of hydrogen abstraction (HA) from virtually all the aryl hydrocarbons is between the rate of HA from Tetralin and toluene, and that the rate of HA is the rate limiting step of the oxidation. The kinetic results of the three experiments for the behavior of two of the products is compared for SO which is formed mainly by a homolytic oxidation, and for COSO in the formation of which free radicals play a key role.

7.9.1 The Kinetics of SO and SO_2 Formation in Different Hydrocarbons

Figure 7.17 shows the concentration of SO vs. the time. The most important conclusions from the data are:

1. The concentration of SO in the first 2-3 hours can be correlated according to first order kinetics, after which it levels.

2. The curves for the first 2 hours can be almost superimposed when the ratio of hydrocarbon to sulfide is similar (EXP 4 and 6). The ratio of the concentrations of [SO] in the presence of a hydrocarbon to that when neat sulfide is reacted varies in the range of 10-30, but for the most part it is 10-20.

3. The concentration of SO when it reaches a steady value is about $9.8 \cdot 10^{-3}$ mole/liter when Tetralin is used, and about 10^{-3} mole/liter when toluene is used. The ratio of the two is 9.8, which is considerably larger than can be accounted for by the concentration of the original hydrocarbons.

The following arguments can provide a simple explanation of the phenomenon. From Chapter 3 it is known that a larger oxidation potential is required to oxidize sulfoxide to sulfone than to oxidize sulfide to sulfoxide. Secondly, if it is assumed that both toluene and tetralyl

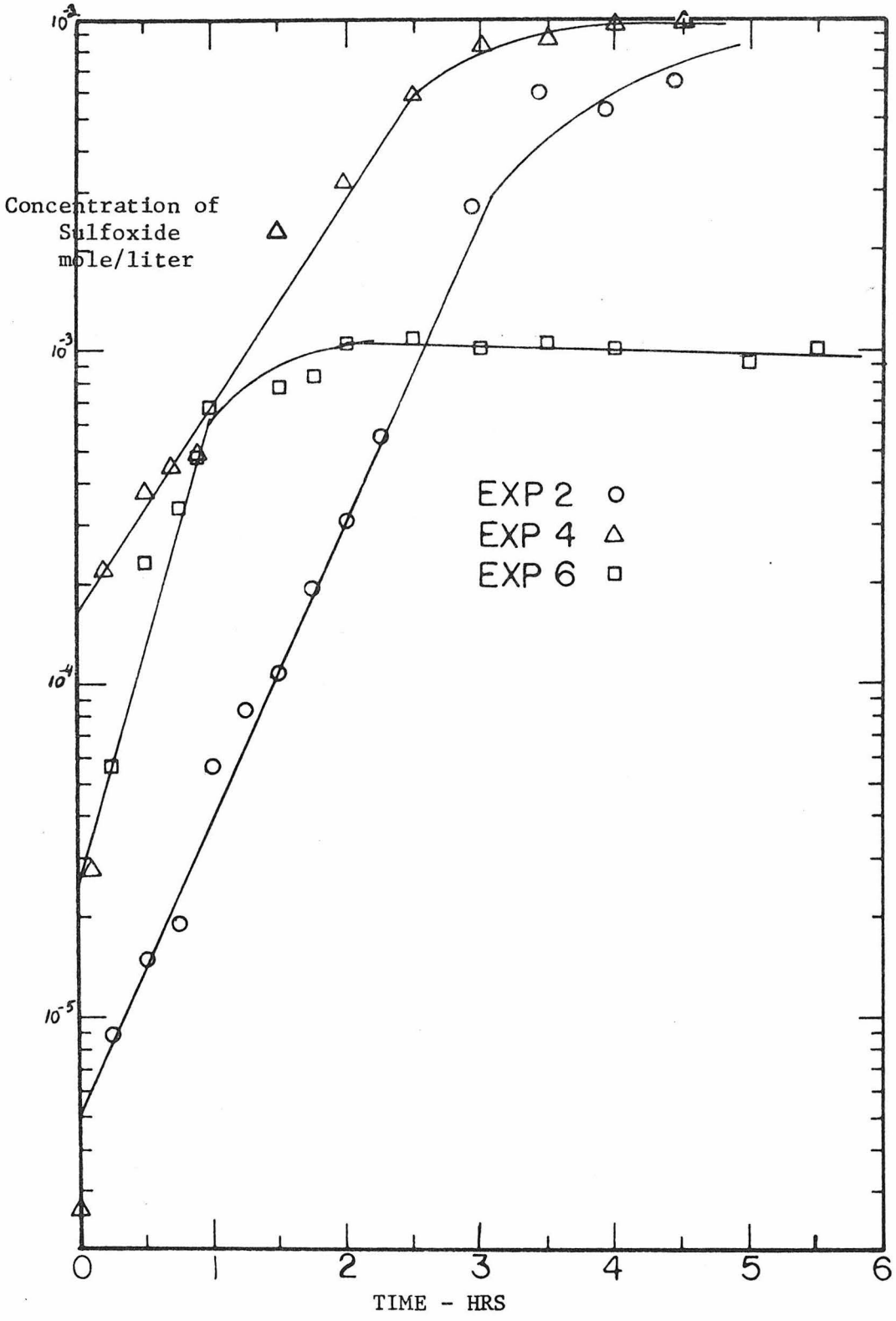


Figure 7.17. The Effect of the Hydrocarbon Medium on the Formation of Sulfoxide.

hydroperoxides can oxidize the sulfide to the sulfoxide, then the similarity of the initial rate of formation of SO is clear. However, since larger oxidation potential is required to convert the SO to the sulfone, a difference in the rate of removal of SO may be observed when oxidizers with different oxidation potential are used. Tetralyl hydroperoxide is more stable than tolyl hydroperoxide, and therefore is a weaker oxidizer. The arguments that were presented can be used to derive the following rate equations:

Let the rate of change of [SO] be controlled by equation (7.39):

$$\frac{d[SO]}{dt} = k_f P[S] - k_c P[SO] \tag{7.39}$$

where P is an unspecified oxidizing specie, k_f and k_c are respectively the lumped rates of formation and consumption of SO. Let us also assume that [S] and P are approximately constants*, so

$$\frac{[SO]}{[S]} = \frac{k_f}{k_c}\left(1 - e^{-k_c pt}\right) \tag{7.40}$$

and after long enough time,

$$\frac{[SO]}{[S]} \simeq \frac{k_f}{k_c} \qquad t \to \infty \tag{7.41}$$

If two different hydroperoxy species oxidize the sulfur compounds, then

$$\left(\frac{[SO]}{[S]}\right)_1 \Big/ \left(\frac{[SO]}{[S]}\right)_2 \equiv \frac{k_{f_1}}{k_{c_1}} \frac{k_{c_2}}{k_{f_2}} \tag{7.42}$$

---

*From the computer simulation $[RO_2H]$, $[RO_2\cdot]$, and $[H_2O_2]$ reach approximately constant level shortly after the beginning of the reaction. The effect of the different [HBr] was neglected.

Several approximations lead to an interesting corollary:

1. Assume that the rate of formation of [SO] is a weak function of the hydrocarbon, namely, $k_{f_1} \simeq k_{f_2}$. Then

$$\frac{[SO]_1}{[SO]_2}\frac{[S]_2}{[S]_1} = \frac{A_2}{A_1} e^{(E_{a2}-E_{a1})/RT} \tag{7.43}$$

The similarity of the initial part of the [SO] accumulation curves in the presence of toluene and Tetralin support this assumption.

2. The elementary step in the oxidation of S or of SO which requires the largest energy is the breaking of the oxygen-oxygen bond of the peroxide ($\sim$ 32 kcal/mole). The other steps involve hydrogen bonds or tautomerization (3-8 kcal/mole). The strength of the O-O bond is determined by the structure of R·; more stable R· will form more stable peroxides (B-16). However, when R· is more stable, the energy of the bond R–H will be smaller. If the previous arguments are used with the Polanyi relation for hydrogen abstraction with $\alpha = 0.86$ then

$$\frac{[SO]_1}{[SO]_2} \cdot \frac{[S]_2}{[S]_1} \quad e^{-\alpha(\Delta H_1-\Delta H_2)/RT} \tag{7.44}$$

A_1 and A_2 were taken to be approximately the same. Substitution of numbers leads to

$$\Delta H_2 - \Delta H_1 = \Delta H_{toluene} - \Delta H_{tetralin} = 1.54 \text{ kcal/mole}$$

Considering all the approximations that were made, the value is surprisingly close to what one would anticipate for the difference between the two benzylic hydrogens:

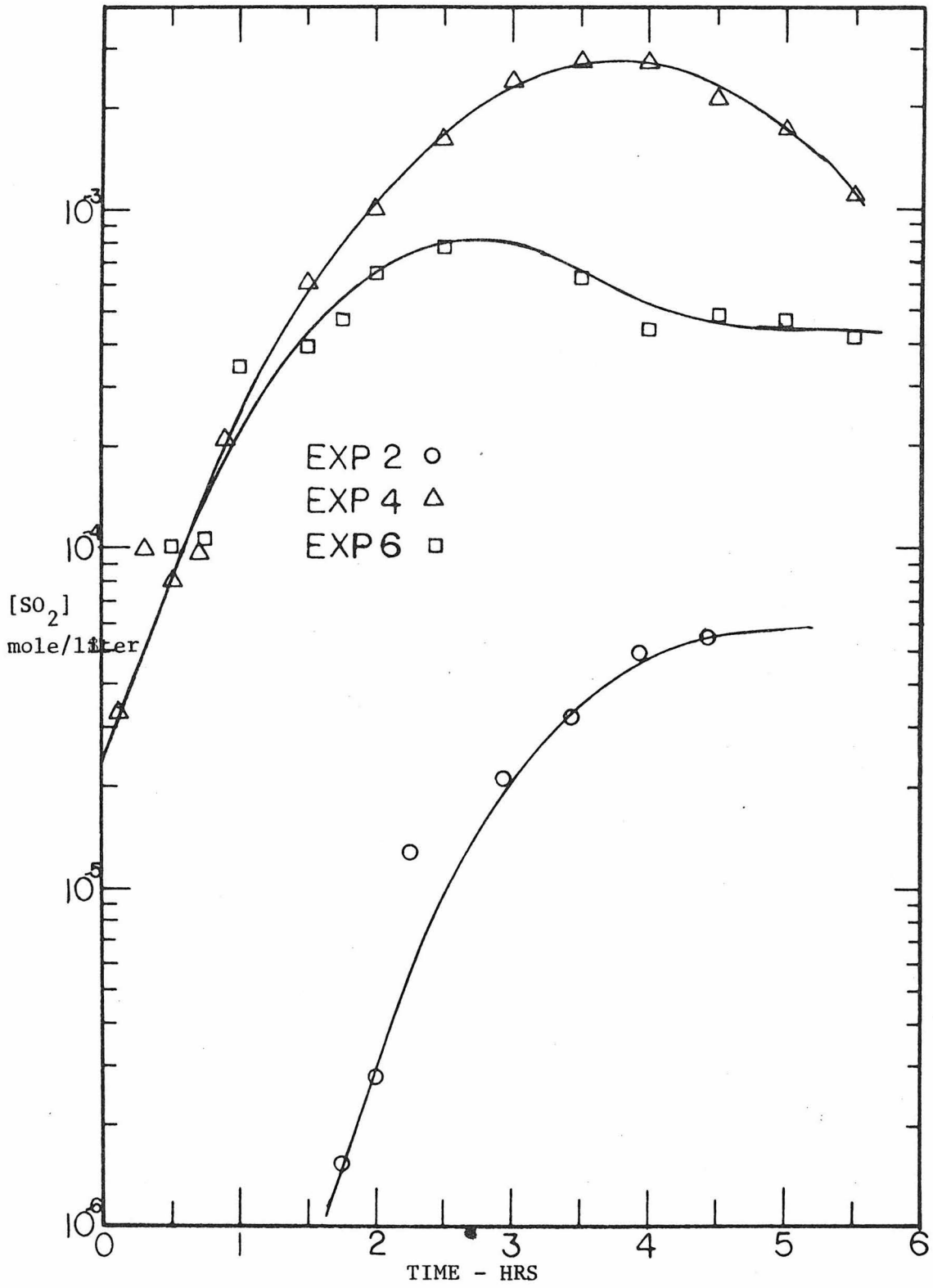
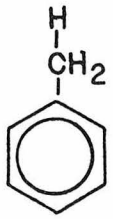
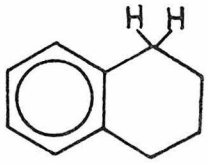


Figure 7.18 The Concentration of Sulfones vs Time, Experiments 2, 4 and 6



toluene



tetralin

No value was found in the literature for the bond energy of the tetralyl hydrogen. For the benzylic hydrogen of toluene, $\Delta H_2 \sim 85$ kcal/mole. The value of ΔH_1 is therefore approximately 83.5 kcal/mole.

The accumulation of SO_2 is shown in Figure 7.18. The most important observation is that the concentration of sulfone does not continue to increase, but after sufficiently long time it decreases. The decrease in the concentration of SO_2 is attributed to the accumulation of secondary oxidation products with a much larger oxidation potential. The secondary products can oxidize the sulfones to the sulfonic acids, etc. Large enough concentration of oxidation products is never realized in experiment 2 where the only hydrocarbon source is the sulfide itself. Note that the SO_2 is oxidized faster in toluene than in Tetralin, and that the value of $[SO_2]$ reaches its maximum after about 210 min in toluene and after about 375 min in tetralin. These observations are consistent with the previous assumption that stronger oxidizers are formed in toluene.

7.9.2 The Kinetics of COSO Formation in Different Hydrocarbons

The principle that more reactive species will be less selective is clearly demonstrated when the accumulation of COSO in different media is considered.

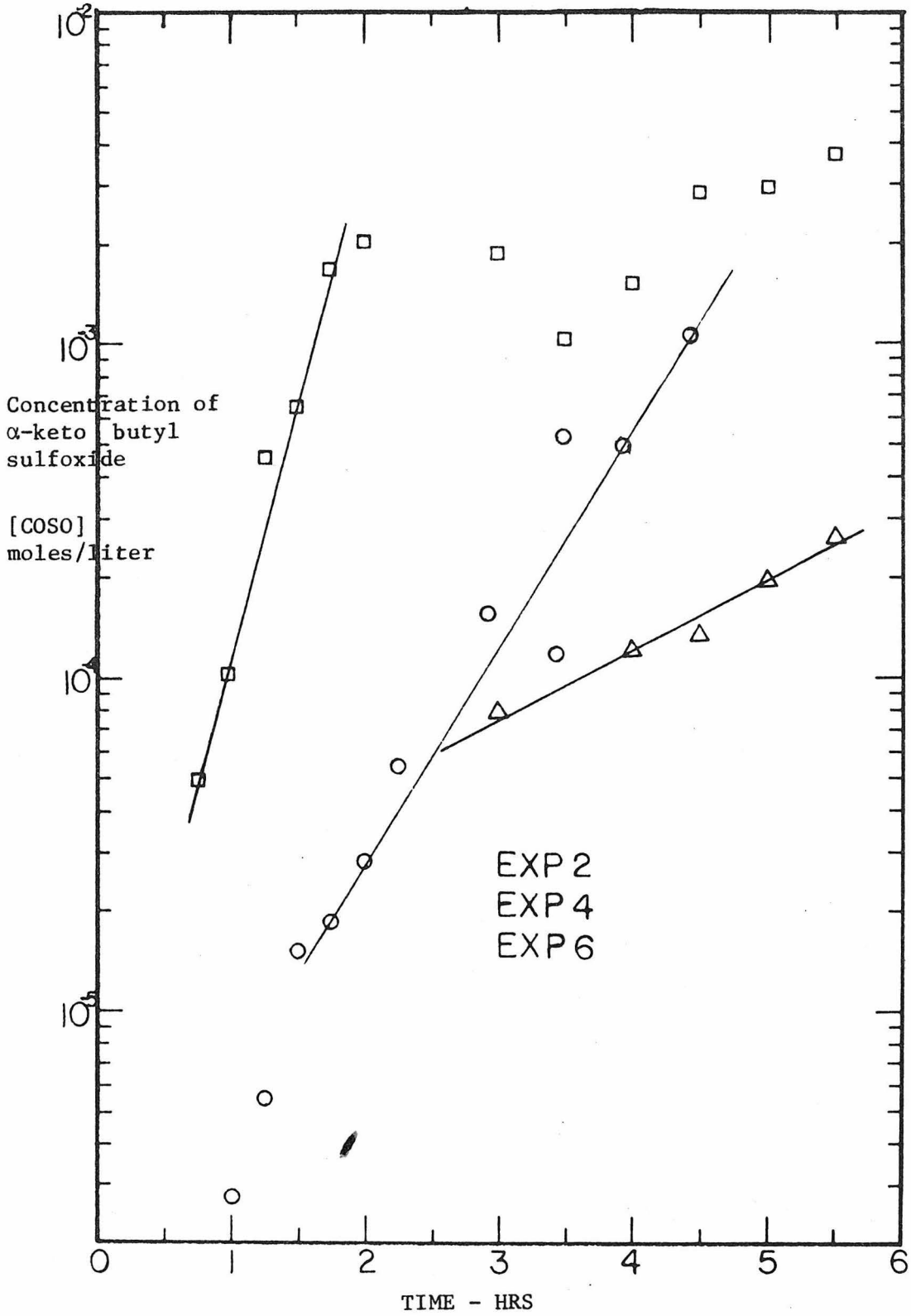


Figure 7.19 The Concentration of α-Keto Butyl Sulfoxide vs Time, Experiments 2, 4 and 6

Figure 7.19 shows the concentration of COSO vs. time in experiments 2, 4, and 6. Since COSO is a product of free radical reactions, its concentration provides information on the reactivity of free radicals. The most important conclusions that were derived from Figure 7.19 are:

1. COSO accumulates at the earlier stages of the reaction according to a first order rate law. The rate constants at 140°C are

$$k_2 = 1.50\ hr^{-1} \quad k_4 = 0.494\ hr^{-1} \quad k_6 = 3.58\ hr^{-1}$$

2. The slope of the curve is 7.25 times larger when the hydrocarbon is toluene than when it is Tetralin. The reason is again the large activity of the benzyl radical, which results from the larger C—H bond energy in toluene. The more reactive benzyl radicals (or benzyl peroxy radicals) will not differentiate between the hydrogens and abstract all of them, while the more stable tetralyl radicals will preferentially abstract the weaker hydrogen on the Tetralin.

7.9.3 Summary of the Discussion of the Effect of the Hydrocarbon

The hydrocarbon media influence both the oxidation potential available in the solution and the relative importance of the free-radical and the non-radical oxidation. The most important conclusions from the discussion are:

1. The oxidation of butyl sulfide to the sulfoxide is initially independent of the hydrocarbon, but the level of the equilibrium concentration it reaches is determined by the stability of the radical R·. When R· is more stable it will be possible to obtain larger concentrations of sulfoxides and sulfones.

2. The bond energy of the tetralyl hydrogen is smaller than that of the toluyl radical by about 1.54 kcal/mole.

3. When the free radical R· is less stable, the medium is more reactive and more sulfur products of free-radical reactions are obtained. The rate of abstraction of a hydrogen from sulfide by a benzyl radical is estimated to be about $7.25 \cdot \frac{0.2784}{0.1423} = 14.2$ times that by a tetralyl radical.

The results show that as far as oxidation to the sulfoxide was concerned, no major difference could have been detected in the initial rate of oxidation when toluene or Tetralin were the hydrocarbons. The equilibrium concentration of sulfoxide was, however, about 10 times as large when Tetralin was used, and the sulfone concentration was 2-5 times. Since the reactivity of all the aryl hydrocarbons is intermediate between that of toluene and tetralin, no major difference can be anticipated when these results are applied to a mixture of many aryl hydrocarbons, e.g., fuel.

The parasitic side-chain oxidation of the sulfide by a free-radical mechanism change significantly from one hydrocarbon to the other, and may influence the final optimization of a process.

7.10 The Influence of the Protic Nature of the Solvent on the Rate of the Reaction

Two experiments are compared, No. 4 and No. 7. The main difference between the initial conditions of the two is the solvent used. In experiment 4 the non-protic solvent bromobenzene was used to modify the properties of the Tetralin. In experiment 7 1-octanol (OCTOL) was used to introduce protons to the system. The volume of OCTOL was taken

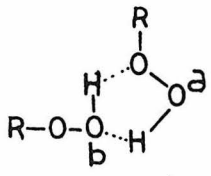
to provide the same volumetric concentration of tetralin as in experiment 4.

7.10.1 The Effect of the Protic Nature of the Solvent on the Selectivity of the Oxidation

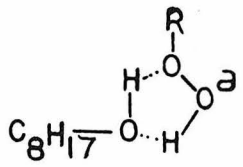
Only four major SC products were detected in experiment 7, compared with some 25 compounds in the product of experiment 4. The major two components found in experiment 4 were SO and COSO.

The selectivity of a reaction depends on the reactivity of the reagents; less reactive reagents are more selective. If this principle is applied to the oxidation of butyl sulfide, it can be inferred that the oxidant in experiment 7 was less reactive than the oxidant in experiment 4.

A plausible explanation is that the oxidant in experiment 4 was a hydroperoxide dimer (I), while in 7 a complex of an octanol molecule and a hydroperoxide molecule (II)



I



II

Since two peroxy components are present in I, and only one hydroperoxide molecule in II, the oxidation potential of I can be expected to be larger than that of II. The oxidation potential of the peroxy-oxygens that are marked a may be different than that of the peroxy-oxygens marked b ; the fact that sulfone was not detected in experiment 7 supports the conclusion that larger oxidation potential was

available in experiment 4 than in experiment 6, since larger oxidation potential is required to oxidize SO to SO_2 than S to SO (see Chapter 3.)

An interesting stipulation can be made on the mechanism of the oxidation in the two solvents. Figure 7.21 shows that the concentration of COSO in experiment 7 is considerably smaller than that of the COSO in experiment 4, although the concentration of SO in EXP 7 is about three times that in EXP 4. In EXP 4 the whole gamut of products of free-radical attack on the sulfide was found, while in EXP 7 only small concentrations of COSO, a product of free-radical reactions, were detected. A plausible explanation is that the octanol solvates the free-radical $RO_2\cdot$ and thus reduces its reactivity.

7.10.2 On the Interaction between Sulfoxides and Protic Solvents

Sulfoxides are bases and can interact with protons. In fact, the basicity of the sulfoxide bond was used to separate butyl sulfoxide from sulfone by ion exchanging (H-9). A crude estimate of the energy of the hydrogen bond of butyl sulfoxide and octanol can be obtained as follows:

1. The bond energy of the sulfoxide-octanol complex is the heat of reaction (7.45):

$$SO + C_8H_{17}OH \rightleftarrows [SOHO\text{-}C_8H_{17}] \qquad \Delta H_H \qquad (7.45)$$

2. Reaction (7.43) is the difference of the following two reactions:

$$SO + 2HBr \rightarrow S + H_2O + Br_2 \text{ in bromobenzene} \quad \Delta H_B \qquad (7.46)$$

$$[SOHO\text{-}C_8H_{17}] + 2HBr \rightarrow S + H_2O + C_8H_{17}OH + Br_2 \text{ in octanol} \quad \Delta H_o \qquad (7.47)$$

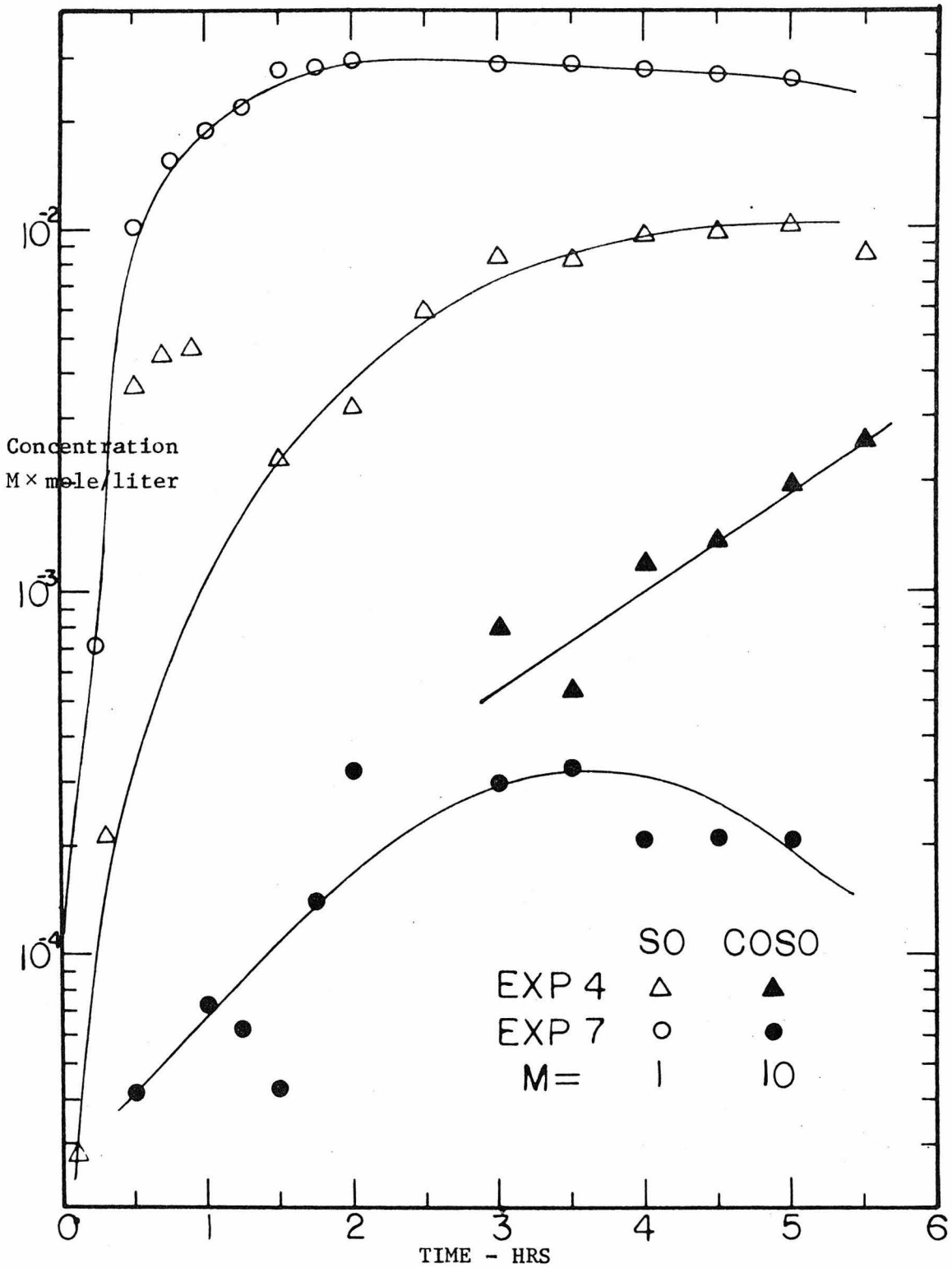


Figure 7.20 The Concentration of Butyl Sulfoxide and α-Keto-Butyl-Sulfoxide vs Time, Experiments 4 and 7.

If the arguments that were used to develop equation (7.44) are used again, and the difference in the "activation energies" of reactions (7.44) and (7.45) are equated to the difference in the heat of the reactions, then

$$\left(\frac{[SO]}{[S]}\right)_{protic} \Big/ \left(\frac{[SO]}{[S]}\right)_{non\text{-}protic} \Bigg|_{steady\ value} = e^{-(\Delta H_B - \Delta H_O)\alpha/RT} \qquad (7.48)$$

Let $\alpha = 1$ then:

$$\frac{3 \cdot 10^{-2}}{0.1292} \cdot \frac{0.2848}{10^{-2}} \simeq e^{-\frac{\Delta H_B - \Delta H_O}{1.987 \cdot 413}} \simeq e^{-\frac{\Delta H_H}{1.987 \cdot 413}} \qquad (7.49)$$

$\Delta H_H \simeq -1.55$ kcal/mole. The value is in the general range of energies of hydrogen bonds, 0-8 kcal/mole. The enthalpy of mixing of dimethyl sulfoxide and water at 0.1 mole fraction was found to be -0.352 kcal/mole (L-4). The value of the "enthalpy of interaction" of dimethyl sulfoxide and phenol is -6.5 ± 0.2 kcal/mole, and that of tetramethylene sulfone and phenol -4.9 ± 0.3 kcal/mole. Phenol is, however, much more acidic than octanol and therefore considerably stronger interaction can be anticipated.

7.10.3 Summary of the Effect of the Solvent on the Oxidation of Butyl Sulfide

Protic solvents affect the oxidation of aliphatic sulfides in the presence of Tetralin, HBr and O_2 in the following ways: 1) increase the selectivity of the oxidation to the sulfoxide; 2) stabilize the sulfoxide by hydrogen bonding and thus allow more of it to remain in the solution; 3) reduce the reactivity of free radicals, in particular of

$RO_2^{\cdot}$ by solvating it.

A crude estimate of the enthalpy of interaction between butyl sulfoxide and octanol is -1.55 kcal/mole.

Considerably improved yield and larger rates of oxidation of sulfide to the sulfoxide can be obtained when the reaction is conducted in a protic medium, e.g., octanol. However, the increased selectivity comes with a smaller reactivity toward the production of sulfones.

7.11 Loss of Heating Value Due to the Oxidation

Attempts to evaluate experimentally the loss of heating value by direct calorimetry has shown that the heat loss is within the experimental error. For example, the heat of combustion of the initial mixture of experiment 4 was 8688 cal/gram and that of the product of the reaction was 8594 cal/gram, about 1.08% difference. The heat of combustion of the initial mixture of experiment 1 was 8504 cal/gram and that of the product was 8483 cal/gram, about 0.25% difference. The value of these results is questionable as a tool to evaluate the overall loss of heating value due to a very mild oxidation. However, for the purpose of this study it indicated that a very small fraction of the heating value was indeed lost.

The method described in Chapter 4 was used to estimate the loss of heating value from the computer model. Figure 7.21 shows a typical result. The heat loss is very small, 2 cal/gr (2 kcal/liter) and is essentially negligible. The loss of heat increases when HBr or sulfide is added; however, the total value of lost heat remains negligible.

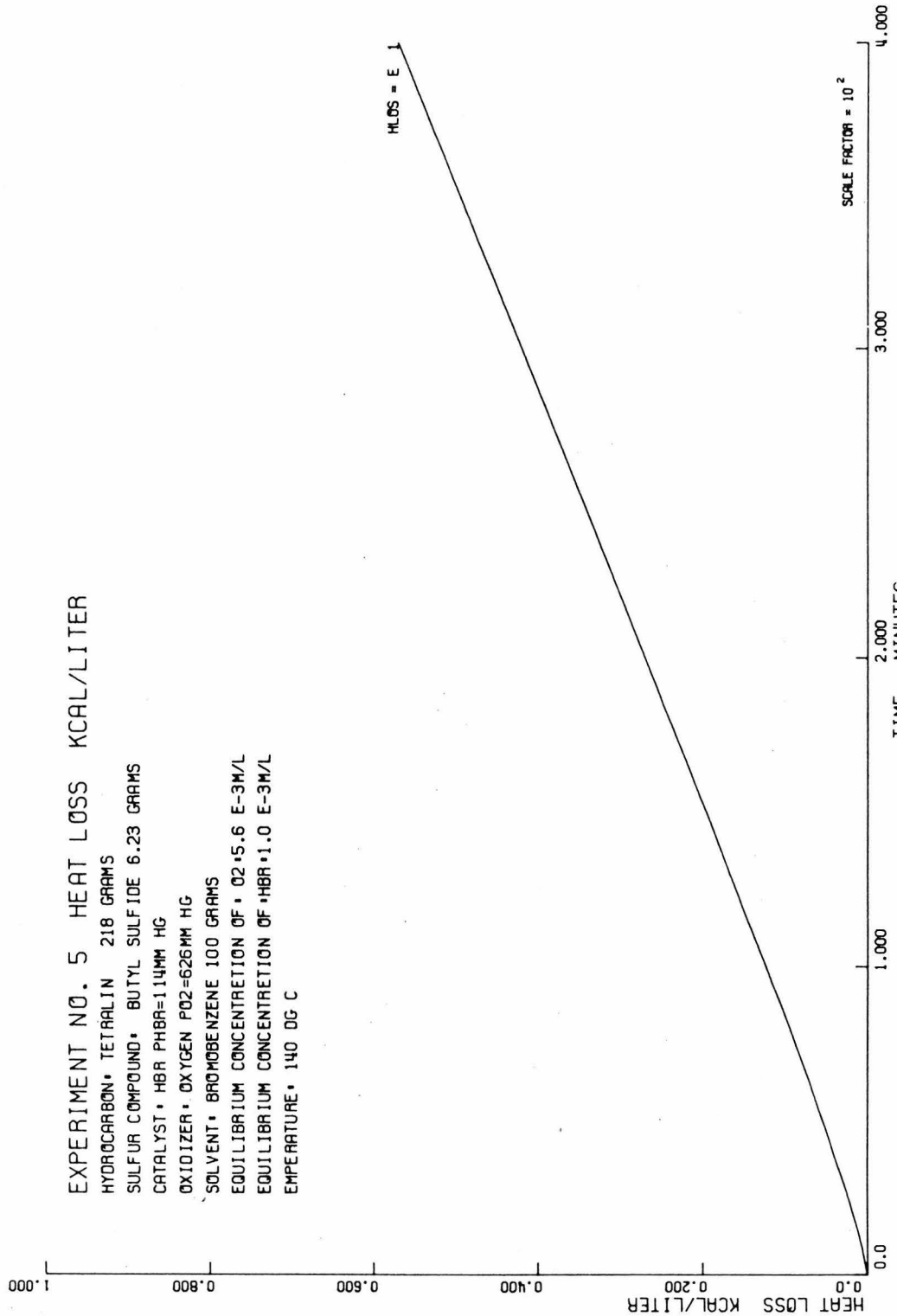


Figure 7.21 The Loss of Heat of Combustion Due to the Oxidation, Experiment 5

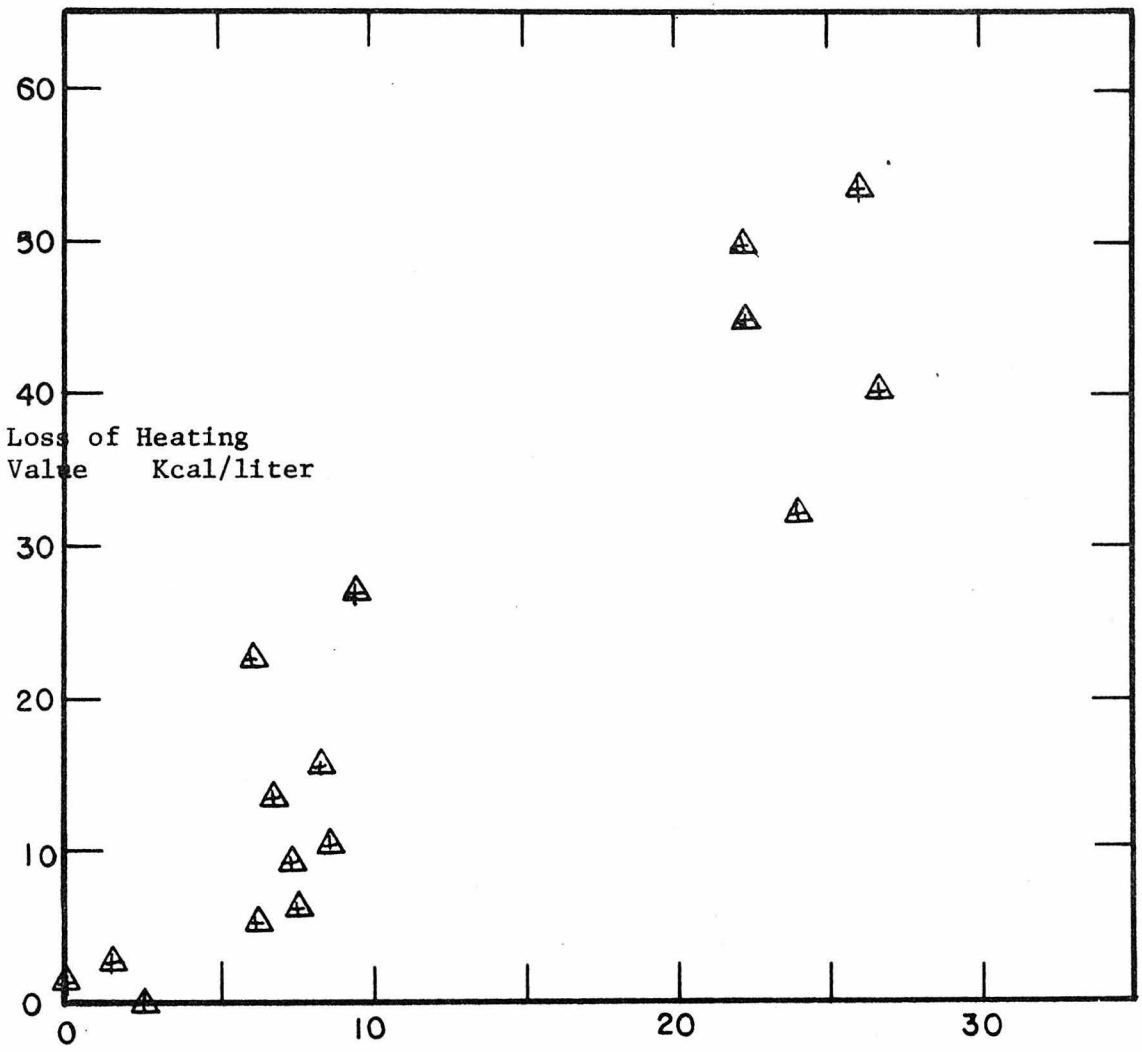


Figure 7.22 The Loss of Heating Value vs the Percent of Sulfide that Was Oxidized

Moreover, the data indicate that the loss of heat varies linearly with the sulfide that reacted.

Although 15-30% of the sulfide were converted, the heat lost was very small. This indicates that the oxidation is relatively very selective to the sulfide, and that loss of heating value due to the oxidation will not play a major economic role if low conversion is maintained.

7.12 Oxidation of Dibenzothiophene

A few exploratory experiments were made in order to see the applicability of the oxidation method to other classes of sulfur compounds e.g., to condensed thiophenes. No oxidized sulfur compounds were detected in the product, and the concentration of the thiophene did not change as a result of the oxidation. The type of solvent or hydrocarbon used did not influence the sulfur compound.

The area of selective oxidation of thiophenic compounds is of extreme importance, and is recommended for future study.

Chapter 8

SUMMARY AND RECOMMENDATIONS

8.1 Summary

The most important result of the study is the demonstration that selective oxidation of an aliphatic sulfide in a hydrocarbon medium can be achieved by conducting the oxidation with molecular oxygen, at a low temperature (e.g., 140°C), and in the presence of a catalyst for the hydrogen abstraction step (e.g., HBr).

When HBr is used to catalyze the rate of hydrogen abstraction, the oxidation rate is larger, the oxidation potential of the solution is larger, and the rate of oxidation of the side chain of the sulfide is also increased. Sulfone was found only when HBr was introduced into the system.

The energy of the bond of the hydrogen that can be most easily abstracted, D(R–H), determines the effect of the hydrocarbon on the oxidation of the sulfur compound. The larger D(R–H) is, the more sulfur-containing products are formed, and the deeper and faster the oxidation of the side chain occurs. This observation is consistent with the rule that more reactive species are less selective, since if the D(R–H) is larger, R· and RO_2H will be less stable and stronger oxidizers.

The rate of formation of sulfoxides and their equilibrium concentration is larger when a protic solvent (e.g., 1-octanol) is present, compared with when the solvent is aprotic (e.g., bromobenzene). Less than 1% loss of heating value is observed as a result of the oxidation. Since about 25% of the sulfides were oxidized, the selectivity of the process is satisfactory.

8.2 Recommendations

Knowledge in three areas is required in order to be able to evaluate a desulfurization process by selective oxidation:

1. Kinetic data on the oxidation of the sulfur compound.
2. Kinetic data on the pyrolysis of the oxidized sulfur compounds which were formed.
3. The magnitude of the loss of heating value due to the oxidation.

In this study, a novel method to selectively oxidize aliphatic sulfides was demonstrated. However, attempts to oxidize dibenzothiophene by this method were unsuccessful. Because thiophenic compounds constitute a major fraction of the sulfur compounds in heavy oils and coal, it is imperative to devise a method to oxidize them. The oxidation potential that is required to oxidize aliphatic sulfoxide to the sulfone is approximately the same as that required to oxidize a thiophene to the corresponding sulfoxide and sulfone. Since butyl sulfone was found as a product of the oxidation of butyl sulfide, it is believed that a modification of the proposed method can be used to oxidize thiophenes to the sulfoxides and sulfones.

The author recommends that the work be continued according to the following sequence:

1. Establish conditions in which it is possible to oxidize thiophenes to the corresponding sulfoxides and sulfones.
2. Derive kinetic data on the oxidation.
3. Derive kinetic data on the rate of decomposition of the oxidized sulfur compounds that were formed.

It is recommended not to use HBr as a catalyst because it complicates the

system by many side reactions. Other catalysts for the hydrogen abstraction step should be found.

References

A-1 Attar, A., "Desulfurization of Heavy Fuel Oil by Oxidation", MS Thesis, Chemical Engineering Dept., Technion, Israel Institute of Technology, Haifa, Israel (1972).

A-2 Attar, A., "Introduction to Fuel Desulfurization", Internal Report, Chemical Eng. Dept., California Institute of Technology, Pasadena, Ca. 91125, Feb. 1973. Available from Professor W. H. Corcoran.

A-3 Attar, A., "Sulfur Compounds in Coal", submitted for publication.

A-4 Attar, A. and Corcoran, W. H., "Quantitative Evaluation of Chromatographic Data from Nonlinear Detectors and the Sulfur Flame-Photometric Detector", Part I, submitted for publication.

A-5 Attar, A., Forgey, R., Horn, J., and Corcoran, W. H., ibid, Part II, submitted for publication.

A-6 Attar, A., "Selective Oxidation of Organosulfur Compounds", Progress Report, Chemical Eng. Dept., California Institute of Technology, Pasadena, Ca., March 1973.

A-7 Attar, A., "Selective Oxidation of Organosulfur Compounds", Interim Report, Caltech, Feb. 1976.

A-8 Ashworth, M.R.F., The Determination of Sulfur-Containing Groups , Academic Press, London (1972).

A-9 Aris, R., Gavalas, G. R., Philos. Trans. R. Soc. London 260, 357 (1966).

B-1 Barnard, D., Fabian, J. M., and Koch, H. P., J. Chem. Soc., 2442 (1949).

B-2 Bahrman, E. J. and Edwards, J. O. in Progress in Physical Organic Chemistry, Vol. 4, p. 93, Streitwieser, A. and Taft, R.W. (eds.), Wiley-Interscience, New York (1967).

B-3 Barnard, D., Bateman, L., and Cunneen, J. I., in Organic Sulfur Compounds, Vol. I, p. 229, Kharasch, N. (ed.), Pergamon Press, London (1961).

B-4 Bateman, L. and Hargrave, K. B., Proc. Roy. Soc. A224, 389 (1954).

B-5 IDEM, IBID, A-224, 399 (1954).

B-6 Barnard, D., J. Chem. Soc., 489 (1956).

B-7 Bateman, L. and Shipley, F. W., J. Chem. Soc., 1996 (1955).

B-8 Bateman, L., Cunneen, J. I., and Ford, J., J. Chem. Soc., 3056 (1956).

B-9 IDEM, IBID, 1539 (1957).

B-10 Barnard, D., Bateman, L., Cain, M. E., Colclough, T., and Cunneen, J. I., J. Chem. Soc., 5333 (1961).

B-11 Bateman, L., Cain, M., Colclough, T. and Cunneen, J. I., J. Chem. Soc., 3570 (1962).

B-12 Barnett, B., Bell, E. R., Dickey, F. W., Rust, F. F., and Vaughan, W. F., Ind. Eng. Chem. 41, 2613 (1949).

B-13 Bamford, C. H. and Dewar, M.J.S., Proc. Roy. Soc. A198, 252 (1949).

B-14 Benson, S. W., Thermochemical Kinetics, Wiley, New York (1968).

B-15 IDEM, The Foundation of Chemical Kinetics, McGraw-Hill, New York, (1961).

B-16 Benson, S. W. and Shaw, R., "Thermochemistry of Organic Peroxides, Hydroperoxides, Polyoxides and Their Radicals", Vol. I, p. 105 in Organic Peroxides, D. Swern (ed.), Wiley, New York (1970).

C-1 Curci, R. and Edwards, J. O., in Organic Peroxides, Vol. I, p. 230, Swern, D. (ed.), Wiley-Interscience, New York (1970).

C-2 Capozzi, G. and Modena, G. in The Chemistry of the Thiol Group, Vol. 2, p. 785, Patosi, S. (ed.), John Wiley and Sons, London (1974).

C-3 Cain, M. E. and Cunneen, J. I., J. Chem. Soc., 2959 (1962).

C-4 Carlsson, D. J. and Robb, J. C., Trans. Farad. Soc. 62, 3404 (1966).

C-5 Calderband, P. H. and Moo-Young, M. B., Chem. Eng. Sci. 16, 35 (1961).

D-1 Drushel, H. V., Miller, J. F., Hubis, W. and Clark, R. O., Anal. Chim. Acta 15, 394 (1956).

D-2 Dankleff, M.A.P., Curci, R., Edwards, J. O., and Pyum Hae-Yung, J. Am. Chem. Soc. 90, 3209 (1968).

D-3 Drago, R. S., Wayland, B., and Carlson, R. L., J. Am. Chem. Soc. 85, 3125 (1963).

D-4 Denison, G. H. Jr. and Condit, P. C., Ind. Eng. Chem. 37(11), 1102 (1945).

D-5 Davies, A. G., Organic Peroxides, Butterworths, London (1961).

D-6 Drushel, H. V. in The Analytical Chemistry of Sulfur and Its Compounds, Part II, p. 49, Karchmer, J. H. (ed.), Wiley, New York (1972).

D-7 Denisov, E. T., Kinetka i Kataliz 4, 53 (1963).

E-1 Emannual, N. M., Denisov, E. T., Maizus, Z. K., Liquid-Phase Oxidation of Hydrocarbons, Plenum, New York (1967).

E-2 Eckstein, B. H., Scheraga, H. A., and Artsdalen, E.R.V., J. Chem. Phys. 22(1), 28 (1954).

E-3 Ettre, L. S. and Zlalkis, A., The Practice of Gas Chromatography, Interscience, New York (1967).

F-1 Ford, J. F. and Young, V. O., Prep. Div. Pet. Chem., ACS 10(2), C-111 (1965).

G-1 Greco, A., Modena, G., and Todesco, P. E., Gaz. Chim. Ital. 90, 671 (1960).

G-2 Gerdil, R. and Lucken, E.A.C., J. Am. Chem. Soc. 88(4), 733 (1966).

G-3 Germin, J. E., Intra-Science Chem. Report 6(3), 101 (1972).

G-4 Gallegas, E. J., Anal. Chem. 47(7), 1150 (1975).

H-1 Heimlich, B. N. and Wallace, T. J., Tetrahedron 22, 3571 (1966).

H-2 Hargrave, K. R., Proc. Roy. Soc. A235, 55 (1956).

H-3 Hiatt, R., "Hydroperoxides", Chapt. I, p. 1 in Organic Peroxides, Vol. 2, Swern, D. (ed.), Wiley-Interscience, New York (1971).

H-4 Hartough, H. D., Thiophene and Its Compounds, Interscience, New York (1957).

H-5 Hartough, H. D. and Meisel, S. L., Compounds with Condensed Thiophene Rings, Interscience, New York (1954).

H-6 Howard, J. A. and Ingold, K. V., Can. J. Chem. 44, 1119 (1966).

H-7 Howard, J. A. and Ingold, K. V., Adv. in Chem., Ser. 75, 258 (1968).

H-8 Higuchi, T. and Bensch, K. H., J. Am. Chem. Soc. 68, 5486 (1966).

H-9 Horak, V. and Pecka, J., J. Chrom. 14, 97 (1964).

H-10 Horne, W. A. and McAfee, J., "Hydrogenation of Petroleum and Its Fractions", Chapt. 5 in Advances in Petrol. Chem. and Refinery, Vol. 3, Kobe, K. A. and McKetta, J. J. (eds.), Interscience, New York (1960).

I-1 Ingold, K. V., Chem. Rev. 61, 563 (1961).

I-2 Ingold, K. V., 7th World Petrol. Cong., Mexico City (1967), Vol. 7, p. 15.

J-1 Jaffe, S. B., Ind. Eng. Chem., Proc. Res. and Develop. 13, 34 (1974).

K-1 Kucharczyk, N. and Horrak, V., Collect Czech. Chem. Commun. 34 2417 (1969) (Eng. Trans.).

K-2 Kondratiev, V. N., "Rate Constants for Gas-Phase Reactions", U.S. Dept. of Commerce (1972).

K-3 Kirkland, J. J. (ed.), Modern Practice of Liquid Chromatography, Wiley-Interscience, New York (1971).

K-4 Kerr, J. A. and Trotman-Dickenson, A. F., Prog. React. Kinet. 1, 107 (1961).

K-5 Kirk, A. D. and Knox, J. H., Trans. Farad.Soc. 56, 1296 (1960).

L-1 Landis, P. S. and Sedlak, M. in The Analytical Chemistry of Sulfur and Its Compounds, Part II, p. 793, Karchmer, J. H. (ed.), Wiley-Interscience, New York (1972).

L-2 Lin, A. and Kehat, E., Ind. Eng. Chem., Prod. Res. and Develop. 8(4), 436 (1969).

L-3 Lloyd, A.C., Int. J. Chem. Kin. VI, 169 (1974).

L-4 Lawrence, H. C. and Pigott, S. P., J. Chem. Thermod. 3, 221 (1971).

M-1 Modena, G. and Miola, L., Gazz. Chim. Ital. 87, 1306 (1957).

M-2 Medvedev, S. S. and Pad'yapol'skaya, A., Zh. Fiz. Khem. 13, 719 (1939) (Ref. E-1, p. 109).

M-3 McNair, H. M. and Bonelli, E. J., "Basic Gas Chromatography", Varian Aerograph, Palo-Alto, California (1969).

M-4 Miotti, U., Modena, G, and Sedea, L., J. Chem. Soc. B, 802 (1970).

M-5 McKinley, J. B., "The Hydrodesulfurization of Liquid Petroleum Fractions", Chapt. 6, p. 405 in Catalysis, Vol. V, Emmett, P. H. (ed.), Reinhold, New York (1957).

O-1 Overberger, C. G. and Cummins, R. W., J. Am. Chem. Soc. 75, 4250 (1953).

O-2 IDEM, IBID, 75, 4783 (1953).

P-1 Perry, R. H. (ed.), Chemical Engineer's Handbook, 4th Ed., McGraw-Hill, New York (1974), p. 3-197.

R-1 Rust, F. F. and Vaughan, W. E., Ind. Eng. Chem. 41(11), 2595-2616 (1949).

R-2 Rosser, W. A. and Wire, H., J. Phys. Chem. 63, 1753 (1959).

R-3 Robertson, A. and Waters, W. A., J. Chem. Soc., 1574 (1948).

R-4 Reid, E. E., Organic Chemistry of Bivalent Sulfur, Vol. III, Chemical Pub. Co., New York (1960).

S-1 Swern, D., "Organic Peroxy Acids", Chapt. VI in Organic Peroxides, Vol. I, Swern, D. (ed.), Wiley-Interscience, New York (1956).

S-2 Suter, C. M., The Organic Chemistry of Sulfur, John Wiley, New York (1944).

S-3 Sheldon, R. A. and Kochi, J. K., Oxid. and Combust. Rev. 5, 135 (1973).

S-4 Swern, D. (ed.) Organic Peroxides, Vol. I, II and III, Wiley-Interscience, New York (1971).

S-5 Schuman, S. C. and Shalit, H., Catalysis Rev. 4(2), 245 (1970).

S-6 Silverstein, R. M., Bassler, G. C., and Morril, T. C., Spectrometric Identification of Organic Compounds, John Wiley and Sons, New York (1967).

S-7 Schuit, G.C.A. and Gates, B. C., A.I.Ch.E.J. 19(3), 417 (1973).

S-8 Sugiyama, T., Suzuki, Y., and Takeuchi, T., J. Chrom. Sci. 11(12), 639 (1973).

T-1 Thomas, J. R., J. Am. Chem. Soc. 77, 246 (1955).

T-2 Twigg, G. H., Disc. Farad. Soc. 14, 240 (1953).

U-2 Urbanski, T., Talanta 9, 799 (1962).

W-1 Willits, C. D., Ricciuti, C., Knight, H. B., and Swern, D., Anal. Chem. 24(5), 785 (1952).

W-2 Wilke, C. R. and Chang, P., A.I.Ch.E.J. 1, 264 (1955).

W-3 Whitney, D. C., "Modkin: A Computer Program for the Automatic Construction of Chemical Kinetics Mechanisms and Solutions of Their Governing Equations", Report R73-51, prepared for EPA Research Center, Triangle Park, N. Carolina, 27711, Feb. (1974).

W-4 Weekman, V. W. Jr., "Chemical Reaction Engineering Reviews", Hurlburt, H. M. (ed.), ACS, Adv. in Chemistry Series 148, p. 98 (1974).

W-5 Wei, J. and Kuo, J.C.W., Ind. Eng. Chem. Fundam. 8, 114 (1969).

W-6 White, W. B., Johnson, S. M. and Dantzig, G. B., J. Chem. Phys. 751 (1958).

Z-1 Zuman, P. Substitution Effects in Organic Polarography, Plenum, New York (1967).

Appendix A

Analytical Procedures

A.1 Separation of Acidic Oxidation Products for MS

Extract 10 ml reaction product with 10 ml 2N NaOH. Separate the phases and acidify the aqueous phase with concentrated HCl. The yellow color fades when the pH becomes acidic. Extract the acidic liquid with two 5 ml fractions of di-ethyl ether. Separate the phases, wash the ether phase with 2×2 ml distilled water. Separate the ether phase and let it dry in an open beaker. Yellow-brown liquid separates and often crystals show.

Appendix B

Purification Procedure

B.1 Purification of Tetralin

Extract 300 ml tetralin with 5 × 10 ml concentrated H_2SO_4 and separate the red-yellow sulfuric acid fraction. If the fifth extraction is still yellow, keep extracting with H_2SO_4 until the yellow color becomes barely visible. All the next stages of the experiment should be done under inert atmosphere. Wash the tetralin twice with 50 ml distilled water and twice with 20 ml 0.1N NaOH. Separate the organic phase and dry it over $MgSO_4$. Vacuum distill the tetralin (5 mm 76°C, 1 mm 64°C) and pass it through a column with freshly activated alumina. Vacuum distill it again and keep it under argon atmosphere. Keep the purified tetralin in a dark place. If the purification was done more than a week before use, distillation may be required. To check the purity use 1 μℓ samples and a Carbowax 20 column at 145°C. At range $1 \cdot 10^3$ better than 99.3% purity should be obtained.

B.2 Deactivation of the Reactor Wall

Mix hexamethyl disilazone, I, trichlorosilane, II, and dry pyridine, III, in the proportion 3:1:5. Apply on the dry surface of the reactor immediately after preparation. Exercise caution and keep away from moisture. Do not apply on rubber parts.