I. THE THERMOLYSIS OF ACETYL PEROXIDE

and

II. THE PHOTOSENSITIZED DECOMPOSITION OF ACETYL PEROXIDE IN SOLUTION

Thesis by

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DEDICATED

TO MY PARENTS

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ABSTRACT

Part I.

The mechanism of the thermal decomposition of acetyl peroxide has been reinvestigated. The intermediacy of acetoxyl radicals has been demonstrated by a scavenging technique and evidence is presented which strongly suggests that the rate constant for acetoxyl radical decarboxylation is of the order of $2X10^9$sec.$^{-1}$ A primary process involving mainly simple O-O bond scission followed by acetoxyl radical decarboxylation at a rate competitive with diffusive separation of the radicals satisfies the results quite consistently.

Part II.

The photosensitized decomposition of acetyl peroxide by certain aromatic hydrocarbons and ketone has been studied. The evidence suggests that the extent of "primary" decarboxylation is a function of the triplet state energy of sensitizer. A second major mode of destruction of peroxide appears to be operative in the decompositions sensitized by ketones. Mechanisms are suggested to explain these processes.

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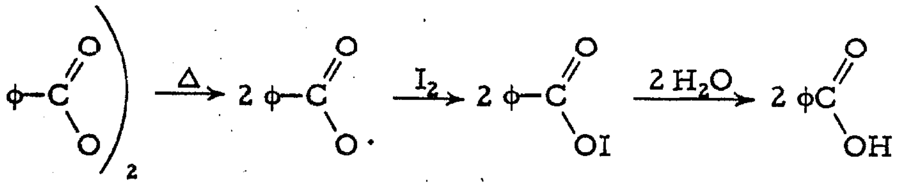
I. THE THERMOLYSIS OF ACETYL PEROXIDE

INTRODUCTION

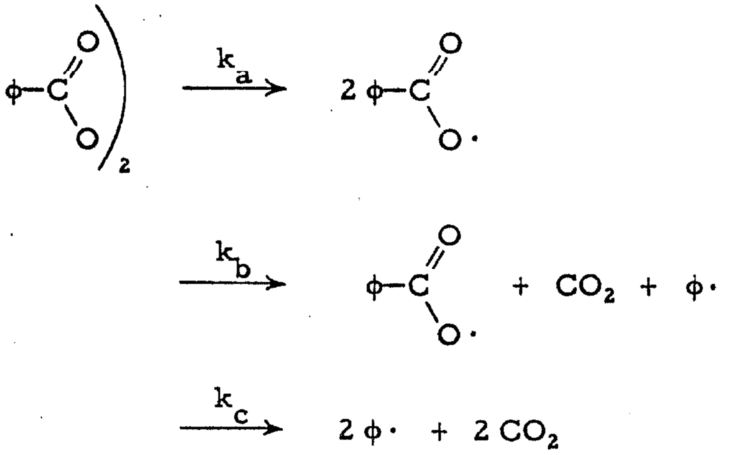
The mechanisms of the thermal decomposition of acetyl peroxide and related acyl peroxides have been studied extensively during the past twenty-five years (1). From these researches has come a vast amount of data and a considerable understanding of the processes involved. The importance of this class of compounds as initiators for polymerization and other radical reactions accounts for this sustained interest. In spite of the wealth of information available, very little concrete knowledge exists about the nature of the primary process except in the case of benzoyl peroxide (2).

In 1950, Hammond and Soffer (2) demonstrated that the primary process in the thermolysis of benzoyl peroxide is simple 0-0 bond scission. They succeeded in trapping the intermediate benzoyloxy radicals almost quantitatively as benzoic acid by using iodine in moist carbon tetrachloride as the trapping agent. It was shown that these conditions did not affect the nature of the primary process.



(1)

In the absence of scavenger the situation is confused somewhat due to induced decomposition by radicals derived from solvent; however, this alternate path for destruction of peroxide has been studied in some detail by Bartlett and Nozaki (3) and is now somewhat better understood. On the basis of the products from the decomposition of benzoyl peroxide in benzene, earlier workers in the field (1a) suggested the possibility of concerted fragmentation of benzoyl peroxide.



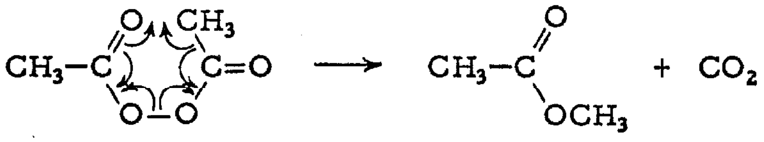
(2)

(3)

(4)

After the primary process in the thermolysis of benzoyl peroxide was shown to be simple 0–0 bond scission, Szwarc published a series of papers concerning the thermolysis of acetyl peroxide (4). Because of the similarity in the decomposition rates of acetyl and benzoyl peroxide, it was concluded that the rate-determining step in the fragmentation of acetyl peroxide is also 0–0 bond cleavage. The solution decomposition of acetyl peroxide produces ethane and methyl acetate. In the presence of sufficient free radical scavenger to trap all the kinetically free radicals produced, the ethane and methyl acetate yields are hardly affected. However, under similar conditions benzoyl peroxide produces no analogous products (i. e. biphenyl and phenyl benzoate). Szwarc (4, 5) suggested that ethane and methyl acetate are the products of geminate radical recombination (20). If the primary process produces two acetoxyl radicals then the formation of these products via geminate recombination requires that the rate of acetoxyl radical decarboxylation be sufficiently rapid to permit extensive decarboxylation in the "cage."

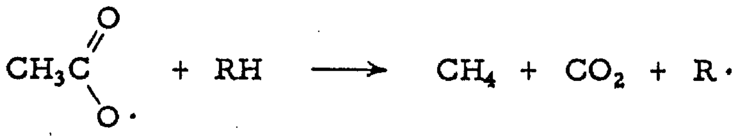
Two alternative explanations for the production of these products were also considered by Szwarc. Either these products are formed in a cyclic decomposition of peroxide yielding ethane or methyl acetate with concomitant extrusion of carbon dioxide or the primary

e.g.  (5)

process is mixed one, two and three bond cleavage.

The extrusion mechanism was eliminated to Szwarc's satisfaction by the observation that ethane and methyl acetate are not produced in the gas phase decomposition of acetyl peroxide in the presence of iodine, where geminate and radical-radical reactions are presumably eliminated. Thus Szwarc interprets the formation of methyl acetate as arising from geminate recombination of an acetoxyl with a methyl radical or by the reaction of two acetoxyl radicals.

When the decomposition of acetyl peroxide was carried out in isoöctane, products which could arise from kinetically free acetoxyl radicals were absent. From this fact an estimate was made of the lifetime of acetoxyl radicals. It was shown by relative reactivities (6) that the methane formed under these conditions was not produced by the decarboxylative hydrogen abstraction by acetoxyl radicals (Equation 6) from solvent suggested earlier by Mayo (7); but by hydrogen abstraction by methyl radicals (Equation 7). Thus, it was concluded that acetoxyl radicals decarboxylated faster than methyl radicals abstracted hydrogen from solvent. Since reaction of the radicals with solvent was estimated to occur in about 10^{-7} to 10^{-8} sec., "the average lifetime of acetate radicals must be substantially shorter than 10^{-8} sec., i.e., of the order 10^{-9} to 10^{-10} sec." As added evidence that acetoxyl radicals are extremely short-lived relative to



$$\mathrm{CH_3C(=O)O\cdot} + \mathrm{RH} \longrightarrow \mathrm{CH_4} + \mathrm{CO_2} + \mathrm{R\cdot} \qquad (6)$$

$$\mathrm{CH_3\cdot} + \mathrm{RH} \longrightarrow \mathrm{CH_4} + \mathrm{R\cdot} \qquad (7)$$

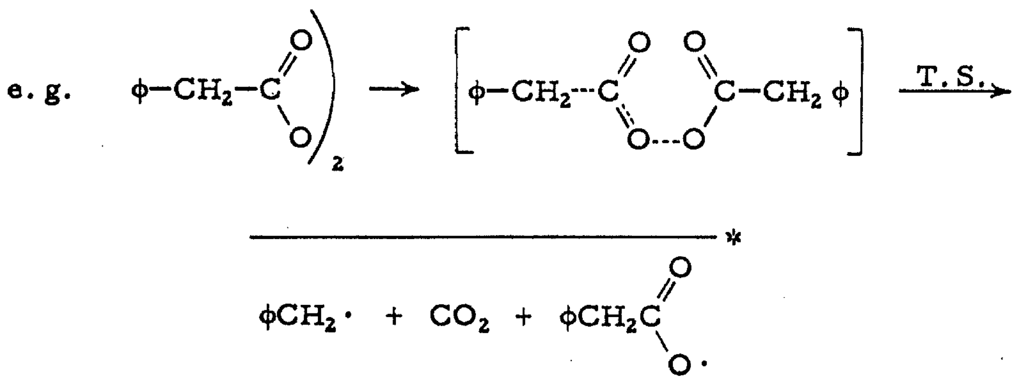
$$\mathrm{CH_3{-}C(=O)O\cdot} + \mathrm{RH} \not\longrightarrow \mathrm{CH_3C(=O)OH} + \mathrm{R\cdot} \qquad (8)$$

benzoyloxy radicals, Szwarc cites the reported failure (without experimental details) of Walling and Hodgdon (8) to trap acetoxyl radicals in the thermolysis of acetyl peroxide under conditions known to trap benzoyloxy radicals. Shine, however, reported (9a) extensive reduction of the carbon dioxide yield from acetyl peroxide decomposition under similar conditions, but was forced to qualify his reported trapping of acetoxyl radicals later, when it was found (9b) that extensive hydrolysis of peroxide occurred under his conditions.

The intermediacy of acetoxyl radicals in the thermolysis of acetyl peroxide is an important point in Szwarc's arguments concerning the nature of the primary process. The formation of methyl acetate in solution but not in the gas phase suggests, but does not require, that this product arises from geminate recombination of methyl and acetoxyl radicals. For example, an ionic rearrangement to ester via an acyl alkyl carbonate (18), might well occur in solution but probably would not be a favored reaction path in the gas phase. Thus, the intermediacy of acetoxyl radicals, which is required for a primary process involving simple 0–0 bond cleavage, is supported by suggestive but not conclusive evidence.

Szwarc's further evidence in support of simple 0–0 bond cleavage as the primary process rests on a kinetic criterion, i. e., that the primary processes in the decomposition of acetyl and benzoyl peroxide must be the same in order for the rates of decomposition to be so similar. Bartlett (10, 11) has explored another aspect of this question in connection with studies of acyl peroxides with decomposition rates considerably greater than those of acetyl and benzoyl peroxide.

The rate of thermal decomposition of phenylacetyl peroxide at 0° is slightly greater than that for acetyl and benzoyl peroxide at 70°. This rate acceleration by phenyl substitution in the α-position of acetyl peroxide was ascribed to concurrent C—C and O—O bond breaking in the rate-determining step, allowing the resonance energies of the benzyl radical and carbon dioxide to assist the fragmentation process. A careful study (11) was then made of a series of t-butyl peresters (A) in which a wide range of incipient radicals could be conveniently treated kinetically. It was found that the decomposition rate correlated strongly with the stability of the



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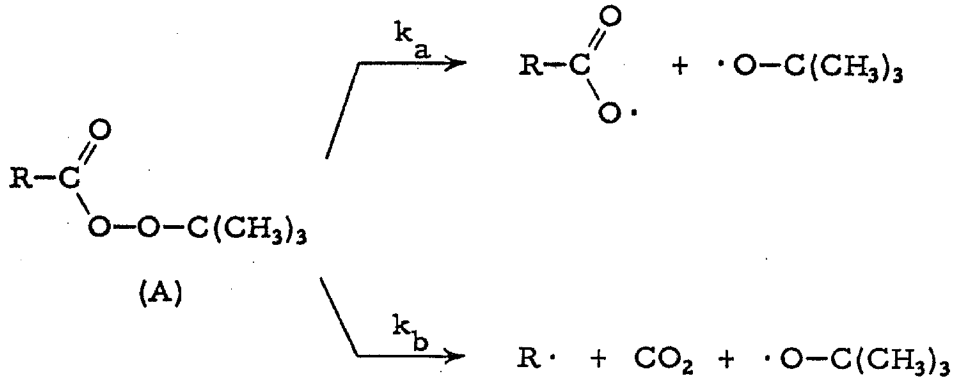

(A)

(10)

(11)

incipient radical ($R\cdot$). The series in which R was methyl, phenyl, benzyl, trichloromethyl, t-butyl, 3-phenylallyl, diphenylmethyl, cumyl, 1, 1-diphenylethyl and 1-phenylallyl showed a range of 10^5 in decomposition rates, with nearly quantitative yields of carbon dioxide from the peresters with the faster decomposition rates. In addition, the series of peresters showed a relation between enthalpy and entropy of activation. A marked tendency was observed for a lowering of the activation energy for perester decomposition to be accompanied by a

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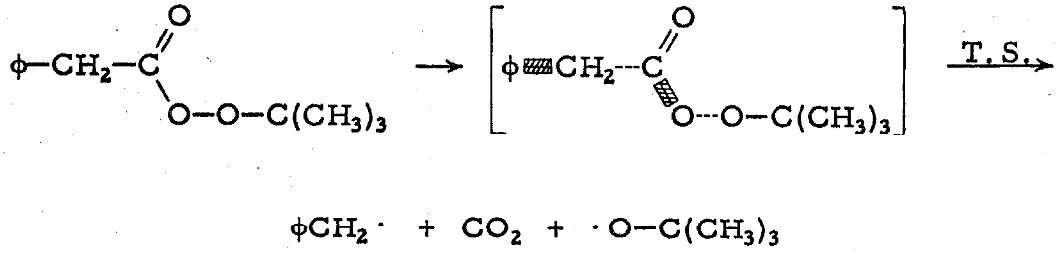
*A line over radical pair indicates that the original pair has not been separated by diffusion, i. e., a "cage" pair.

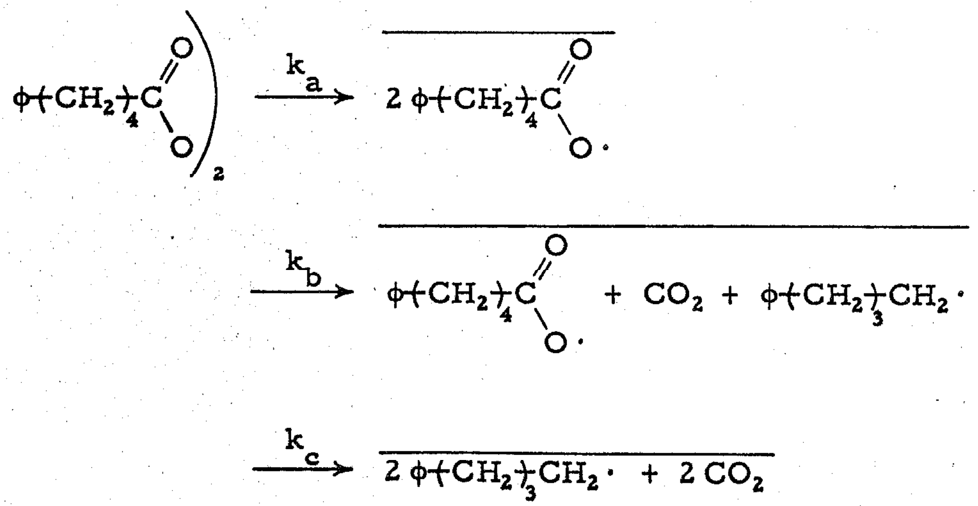
lowering in the activation entropy, with the direction of the overall effect being indicated by the enthalpies of activation. This parallelism was taken to mean that assistance by partially developed resonance in lowering the energy barrier (enthalpy of activation) in the transition state for dissociation was obtained at the expense of conformational freedom (entropy of activation). For example, in the case of t-butyl phenylperacetate the rotation about two bonds is constrained in the transition state for two bond cleavage, the C—O bond because the



$$\phi\text{—}CH_2\text{—}C(=O)\text{—}O\text{—}O\text{—}C(CH_3)_3 \longrightarrow \left[\phi\cdots CH_2\text{---}C(=O)\cdots O\text{---}O\text{—}C(CH_3)_3\right] \xrightarrow{T.S.} \phi CH_2\cdot + CO_2 + \cdot O\text{—}C(CH_3)_3 \qquad (12)$$

realization of the resonance energy of carbon dioxide requires the incipient orbitals to be nearly parallel and the C—C bond between the phenyl group and the α-carbon because any contribution from benzyl radical resonance must be at the expense of free rotation. Even though the actual transition state should reflect a balancing of these opposing effects, a rather consistent grouping of the peresters into zero (t-butyl peracetate being taken as a standard), one, two and three frozen rotations was observed.

The use of kinetic parameters to qualitatively demonstrate concertedness in the decomposition of certain peresters in the series, appears to be quite justified in view of the observed enthalpy and entropy of activation relation. However, DeTar (12) has questioned such a kinetic test as evidence for the absence of mixed simple and multibond cleavage in the primary process (i.e. Szwarc's use of it). DeTar and Lamb (12) studied the carbon dioxide yield from decomposition of δ-phenylvaleryl peroxide (whose rate of decomposition is comparable to that of acetyl peroxide) in toluene in the presence and absence of iodine and water. They found that the yield of carbon dioxide was reduced from 1.7 moles per mole of peroxide to 1.4 by the presence of approximately 0.2 M. iodine and water. This result was taken to mean that iodine was trapping kinetically free acyloxy radicals. DeTar reasoned that if acyloxy radicals lived long enough to become kinetically free, the decarboxylation rate could not be great enough to produce the extent of "cage" decarboxylation necessary to give the amounts of "cage" products (1,8-diphenyloctane, 4-phenylbutyl 4-phenylpentanoate, etc.) observed (13). Thus, DeTar concluded that the primary process involves mixed one, two and three bond scission because the acyloxy radicals do not decarboxylate in the cage. These conclusions are questionable in the absence of proper control



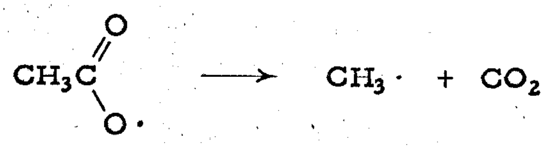
(13)

(14)

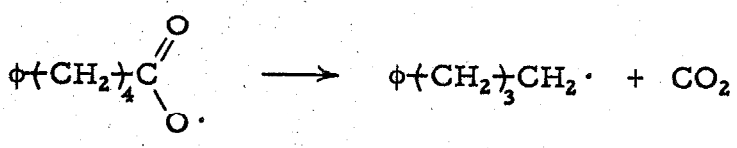
(15)

experiments. The estimate of the rate of reaction of acyloxy radicals with iodine as being much slower than diffusion, the disregarding of scavenging of geminate pairs before they are separated and the assumption of the absence of hydrolysis appear unsupported; however, the results could not be altogether dismissed. Thus, the nature of the primary process in the decomposition of acetyl peroxide could not be considered established.

As noted earlier, Walling and Hodgdon (7) reported that acetoxyl radicals were not intercepted during the thermolysis of acetyl peroxide under conditions which were reported to scavenge benzoyloxy (2) and δ-phenylvaleryloxyl (12) radicals. If both DeTar's and Walling's results are correct, then an apparently anomolous situation exists. Since there is little a priori reason to expect any great difference in the stability of the acyloxy radicals (B and C) and since the methyl radical is the less stable of these two primary alkyl radicals, acetoxyl (B) radicals should decarboxylate less rapidly than the δ-


(16)

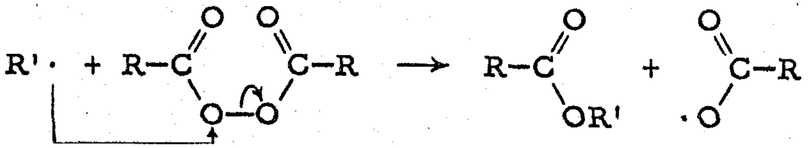
(B)


(17)

(C)

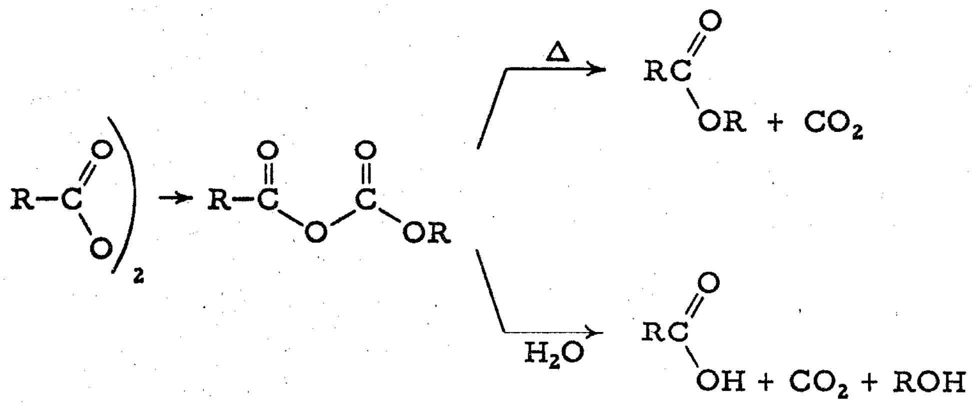
phenylvaleryloxyl radicals (C). Hammond (14) suggested that the faster decarboxylation of acetoxyl than δ-phenylvaleryloxyl radicals was due to a very rapid decarboxylation of vibrationally excited ("hot") acetoxyl radicals. Due to their small size and simplicity relative to δ-phenylvaleryloxyl radicals, acetoxyl radicals could have considerably more difficulty in dissipating excess vibrational energy to the surroundings, perhaps allowing a fast decarboxylation process to compete with vibrational relaxation. The amount of excess energy in the "hot" acetoxyl radical is unknown, but 0^{18} labeling (5) of the carbonyl oxygen of peroxide and examination for scrambling of label after half decomposition of peroxide indicates that acetoxyl radicals do not recombine to peroxide. Thus, the recombination probably is an activated process, and the acetoxyl radicals first formed in the fragmentation process have some excess energy to dissipate to reach thermal equilibrium. However, it was impossible to draw any satisfying conclusions about the timing of the decarboxylation step(s) in the thermolysis of acetyl peroxide on the basis of the data available at the outset of this work.

Numerous complications confront attempts to determine the mechanism of the decomposition of a diacyl peroxide. First, at normal concentrations of peroxide (0.05 to 0.3 M.), induced decomposition may be a major mode of peroxide destruction (15). Before meaningful rate or product data can be obtained, the extent of such processes


(18)

must be estimated by careful kinetic analyses (3) or eliminated either by working at extremely low peroxide concentrations or by using radical scavengers such as iodine (16).

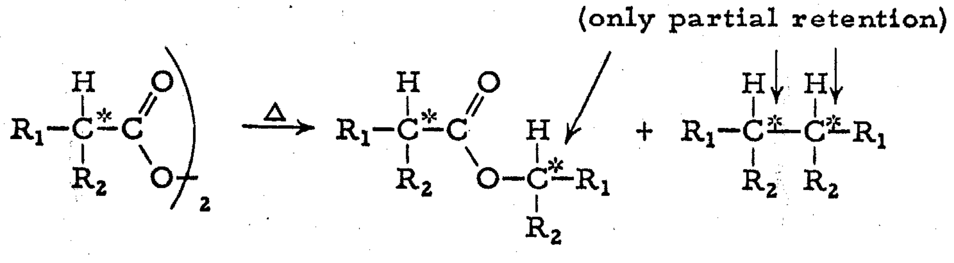
The possibility of ionic rearrangement (17) of peroxide to acyl alkyl carbonates must also be given due consideration. Greene (18) has recently demonstrated that this type of rearrangement can occur simultaneously with radical fragmentation even in non-polar solvents, and that the acyl alkyl carbonate may also eliminate carbon dioxide, producing ester, usually a major product of peroxide decomposition.



(19)

(20)

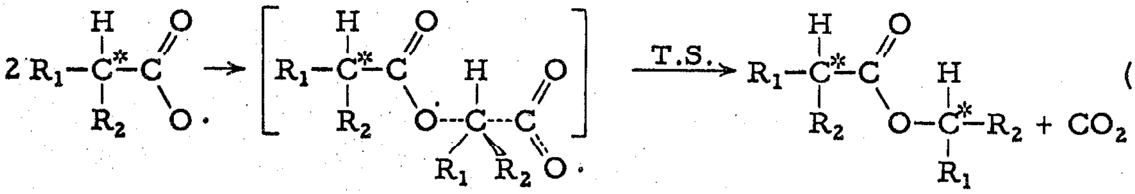
In view of the tendency of secondary aliphatic diacyl peroxides such as cyclohexylformyl and methylethylacetyl peroxides (18), to produce ester *via* acyl alkyl carbonate, Greene has suggested this process as an attractive route to the stereospecific fraction of the alcohol portion of the ester (D) formed in the decomposition of optically active diacyl peroxides (19). However, this explanation does not account for the net retention of configuration in the alkyl-alkyl coupling product (E) which Greene reported earlier (19b). Rearrangement of peroxide



(D) (E)

(21)

to ester may account for part of the activity in the alcohol portion of the ester, but is probably not the only stereospecific pathway to ester. The observed partial retention of configuration in the alcohol portion of the ester (D) was thought by Greene (19b) and DeTar (19c) to indicate that the ester was produced <u>via</u> geminate recombination of radicals, at least part of the time before the alkyl radical could become randomly oriented relative to the second radical in the pair. This partially stereospecific process was offered as suggestive evidence against cyclic concerted processes, which should lead to completely stereospecific ester formation and against reaction of two acyloxy radicals to produce ester (Equation 22) since that should lead to inversion rather than the retention observed.



(22)

<u>Objectives</u>: This investigation was initiated in an effort to obtain insight into the nature of the primary process in the thermal decomposition of acetyl peroxide. The original project was

determination of the deuterium isotope effect on the rate of the decomposition and on the product yields. The largely ambiguous results (21) obtained in these experiments and the confused state of diacyl peroxide chemistry led to a more comprehensive investigation of the thermolysis of acetyl peroxide.

We hoped to be able to document the salient features of the decomposition of acetyl peroxide. A scavenging technique was to be used to demonstrate the intermediacy of acetoxyl radicals and to estimate their lifetime. The importance of geminate radical scavenging in this system was to be investigated and the production of ethane and methyl acetate via geminate recombination demonstrated. Even if the mechanism of the decomposition was not demonstrated unambiguously a meaningful approach for future researches was to be outlined.

RESULTS AND DISCUSSION

GENERAL

Products of the Thermolysis of Acetyl Peroxide

We have reinvestigated the products of the thermal decomposition of acetyl peroxide in carbon tetrachloride and chlorobenzene and find reasonable agreement with most of the previously reported results (1b). Representative product distributions in these solvents, with and without scavengers, are given in Table I. Concentrated peroxide solutions (~0.3 M.) were employed because the reaction mixtures were analyzed by n.m.r. spectrometry. Use of these concentrated peroxide solutions introduces the possibility that a substantial fraction of the peroxide will be destroyed by chain decomposition induced by solvent derived radicals (3, 15). Thus, identification of those products which arise from simple fragmentation was somewhat confused by this extraneous mode of peroxide destruction. However, this process could be eliminated by use of an excess of an efficient radical scavenger.

In the presence of an excess of iodine, induced decomposition and the normal reactions of kinetically free methyl radicals are eliminated. Since ethane and methyl acetate are formed under conditions such that all free radicals are scavenged they must arise <u>via</u> a pathway not involving kinetically free radicals. The process(es) responsible for this inefficient production of kinetically free radicals from acetyl peroxide whether due to competing cyclic processes and/or to

TABLE I

Products of the Decomposition of Acetyl Peroxide (0.28 M.) in Chlorobenzene at 91° by N.m.r.: Scavenged and Unscavenged[a]

A. Run No. 121-C		B. Run No. 120-A (0.32 M. Iodine)	
Products	% Yield[b]	Products	% Yield[b]
Ethane[c]	4.7	Ethane[c]	1.5
Methyl acetate	13.9	Methyl acetate	16.8
Acetic acid	29.7	Acetic acid and Methyl iodide[d]	158.9
Methane[c]	9.3		
o-Chlorotoluene	26.6	Methane[c]	0
m & p-Chlorotoluene	10.6	Other[e]	2.3
Other[e]	43.3		

Products of the Decomposition of Acetyl Peroxide (0.28 M.) in Carbon Tetrachloride at 91° by N.m.r.[a]

Run No. 121-D	
Products	% Yield[e]
Ethane[c]	4.9
Methyl acetate	21.1
Other acetyl cpds	6.3
Methyl chloride	132.6
Methane[c]	trace
Other[e]	4.5

[a] Internal standard *t*-butyl benzene, degassed, sealed samples, abstracted from Table IX.

[b] (Moles of product/mole of peroxide) × 100.

[c] Only dissolved gas was determined

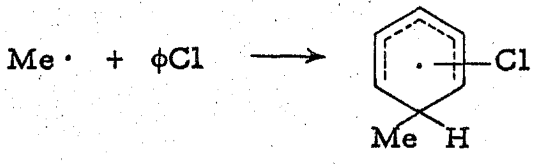
[d] Chemical shifts in chlorobenzene too similar to allow separate determination.

[e] Includes material in gas phase and material in solution without well-defined peaks (assumed 2 methyl groups per mole).

geminate recombination, shall be referred to as the "cage effect" or "cage reactions."

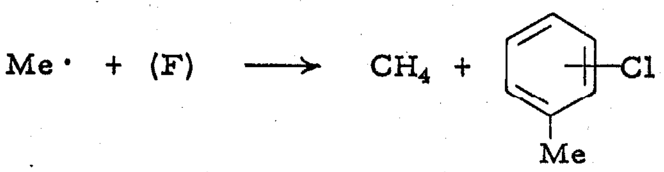
In view of the increase in the methyl acetate yield from 14% in chlorobenzene alone to 17% in 0.32 M. iodine in chlorobenzene, it is most probable that only insignificant amounts of methyl acetate are formed by any process other than "cage reactions." The lower yield of methyl acetate in the unscavenged decomposition is consistent with destruction of a considerable fraction of the peroxide through decomposition induced by solvent-derived radicals.

Most of the products other than ethane and methyl acetate observed in the unscavenged decompositions can be satisfactorily attributed to the reactions of "free" (kinetically free) methyl radicals. In chlorobenzene the major mode of reaction of the "free" methyl radicals appears to be addition to solvent to give substituted cyclohexadienyl radicals. The yield of chlorotoluenes, however, reflects the fate of only a part of the cyclohexadienyl radicals formed; the large percentage of peroxide-derived methyl groups which do not show up as well-defined peaks in the n.m.r. are probably "lost" in the complex side reactions of free radical aromatic substitution (22). These processes may be represented as follows:



(23)

(F)



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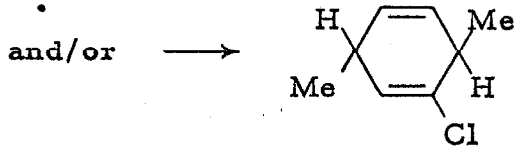

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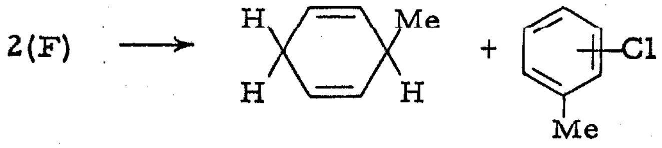
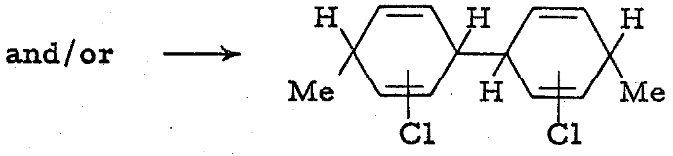


(26)

(G)



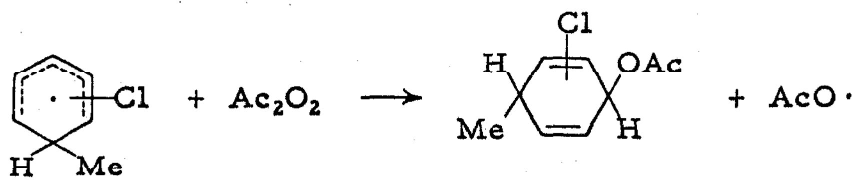
(27)

(H)

The methane observed could arise via disproportionation (Equation 24) or by abstraction from dihydro- and tetrahydro-compounds such as (G) and (H). Such abstraction reactions would lead to complex products whose methyl groups are not well defined in the n. m. r. spectra. High temperature v. p. c. analysis of the final reaction mixtures show a great variety of products with retention times longer than those of the chlorotoluenes.

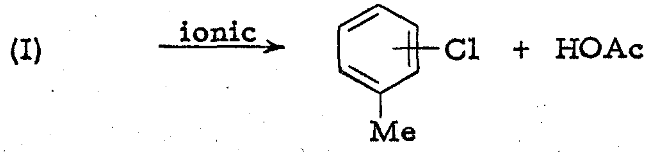
Acetic acid formed in the unscavenged decompositions in chlorobenzene, seems to arise from induced decomposition of peroxide by cyclohexadienyl radicals. Two mechanisms to account for the formation of acetic acid in the induced decomposition process are considered:

Mechanism I:



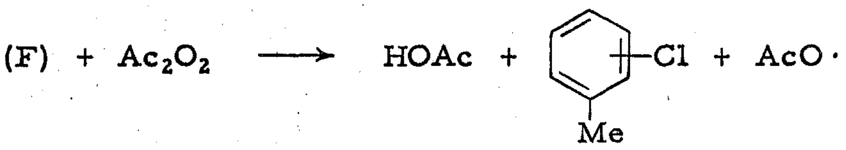
(F) (I)

(28)



(29)

Mechanism II:



(30)

In mechanism I, the normal induced decomposition process produces the dihydro-compound, I, which should undergo a facile ionic elimination of acetic acid. The rate-determining step of the induced process envisioned in mechanism II is transfer of a hydrogen atom to peroxide, forming acetic acid directly. It is conceivable that reactions of "free" acetoxyl radicals also give rise to some of the acetic acid observed. However, since induced decomposition is kinetically demonstrable, and acetic acid and methyl acetate are the only products which contain the acetate moiety, the accepted mechanism (23) for induced decomposition (attack at peroxidic oxygen giving a product containing the acetate moiety) prohibit an explanation in which formation of acetic acid is attributed solely to reactions of kinetically free acetoxyl radicals. In addition, variations in the yield of acetic acid (*vide infra*) are paralleled by variations in the yield of chlorotoluenes and the yield of the chlorotoluenes consistently exceeds that of acetic acid.

The cage effect: The overall results of several decompositions of acetyl peroxide in chlorobenzene at 91° are erratic (see Table II). However, the ratio of the yield of ethane to that of methyl acetate is nearly constant under a given set of conditions. Since the analyses are done by n. m. r. spectrometry only that fraction of the ethane (and methane) which is in solution is observable. The apparent ratio of the yield of ethane to that of methyl acetate is, therefore, a function of the volume of stock peroxide solution used because the n. m. r. tubes were uniformly sealed to contain approximately two milliliters. Thus, the half milliliter samples which gave a ratio of ethane to methyl acetate of 0.24 ± .02 (av. 9 detm.) had approximately 50 percent *more* volume over the liquid phase and 50 percent *less* ethane was produced than the one milliliter sample which gave a ratio of 0.37 ± .02 (av. 4 detm.). The uniformity of the ratio of the two products from cage reactions, when the other products occur in such varying amounts, is further evidence that only insignificant quantities of ethane and methyl acetate arise from the reaction of "free" radicals in the decompositions in the absence of scavenger. Their *exclusive*

TABLE II

Product Ratios in the Thermolysis of Acetyl Peroxide (0.314 M.) in Chlorobenzene at ~91° by N.m.r.: 1.0 ml. Samples[a]

Run No.	121-C[d]	82-B	82-A	76-A
Products				
Ethane[b]	0.34	0.35	0.38	0.39
Methyl acetate	1.0	1.0	1.0	1.0
Acetic acid[c]	2.14	0.81	0.80	0.39
Chlorotoluenes	2.68	1.78	1.79	1.65
Methane[b]	0.67	0.68	0.57	1.07

[a] Entries are moles of product relative to moles of methyl acetate. The same stock solution of peroxide was used unless otherwise noted. All sample tubes were sealed and approximately of the same total volume (2 ml.). [b] Only the dissolved gases were determined. [c] Possibly includes a small amount of other acetyl compounds. [d] Another stock solution (0.28 M.) was used in this run.

Product Ratios in the Thermolysis of Acetyl Peroxide (0.314 M.) in Chlorobenzene at ~91° by N.m.r.: 0.5 ml. Samples[a]

Run No.	82-C[d]	88-A[e]	88-B[f]	88-C[g]	88-E[d]
Products					
Ethane[b]	0.22	0.24	0.22	0.29	0.22
Methyl acetate	1.0	1.0	1.0	1.0	1.0
Acetic acid[c]	0.68	0.72	0.32	0.94	0.66
Chlorotoluenes	1.66	1.70	1.46	1.86	1.71
Methane[b]	0.29	0.35	0.34	0.39	0.34

[a, b, c] Same as above. [d] To be washed with acid, neutralized and rinsed with water prior to run. [e] Washed with soap and rinsed with water. [f] Washed with acid and rinsed with water. [g] Washed with alcoholic KOH and rinsed with water.

Table II (continued)

Product Ratios in the Thermolysis of Acetyl Peroxide (0.314 M.) in Chlorobenzene at ~91° by N.m.r.: 0.5 ml. Samples[a]

Run No.	78-B_1[d]	78-B_2[e]	78-B_3[f]	78-B_4
Products				
Ethane[b]	0.24	0.22	0.22	0.26
Methyl acetate	1.0	1.0	1.0	1.0
Acetic acid[c]	2.08	2.39	0.57	2.53
Chlorotoluenes	2.61	2.78	1.73	3.03
Methane[b]	0.41	0.37	0.40	0.44

[a, b, c] Same as preceding. [d] Containing also 0.0135 g. of benzophenone. [e] Containing also 0.017 g. of benzil. [f] Containing also 0.0098 g. of 2-acetonapthone.

formation by cage reactions would account for the insensitivity of the ratio of these products to minor variations in the reaction conditions.

MECHANISTIC POSSIBILITIES

The following mechanisms for the thermal decomposition of acetyl peroxide are representative of those that have been given serious consideration in our work.

Simple Homolytic Scission of the 0-0 Bond

This family of mechanisms is predicated on the assumption that the primary process produces a geminal pair of acetoxyl radicals. The extent of formation of ethane and methyl acetate is then controlled by the lifetime of the acetoxyl radicals and by the characteristics of geminate recombination phenomena. Unfortunately, these geminate processes are not understood well enough to allow accurate prediction of the decarboxylation rate required to yield the observed product ratios. Some specific limiting cases are described below.

Decarboxylation much faster than diffusion: In this case the cage products, ethane and methyl acetate, would arise in a straightforward manner if the coupling of methyl radicals with acetoxyl radicals is competitive with the rate of decarboxylation and the probability of recombination of two methyl radicals is small. This situation may be represented as follows (5):

Mechanism III:

$$\mathrm{Ac_2O_2} \longrightarrow \overline{2\,\mathrm{AcO}\cdot} \qquad (31)$$

$$\overline{2\,\mathrm{AcO}\cdot} \longrightarrow \overline{\mathrm{Me}\cdot + \mathrm{CO_2} + \mathrm{AcO}\cdot} \longrightarrow \mathrm{MeOAc} \qquad (32)$$

$$\overline{\mathrm{Me}\cdot + \mathrm{CO_2} + \mathrm{AcO}\cdot} \longrightarrow \overline{\mathrm{Me}\cdot\ 2\,\mathrm{CO_2} + \mathrm{Me}\cdot} \longrightarrow \mathrm{C_2H_6} \qquad (33)$$

$$\overline{\mathrm{Me}\cdot + 2\,\mathrm{CO_2} + \mathrm{Me}\cdot} \longrightarrow \text{"Me}\cdot\text{"}^{*} \qquad (34)$$

Because of the rapid decarboxylation only methyl radicals would be produced kinetically free.

Decarboxylation competitive with diffusion: If loss of carbon dioxide from the acyloxy radicals is competitive with diffusive separation of the geminate radical pair, then both acetoxyl radicals and methyl radicals will be produced kinetically free. However, the "free" acetoxyl radicals will be so short lived that only extremely rapid reactions will intercept them prior to decarboxylation.

Mechanism IV:

$$\mathrm{Ac_2O_2} \longrightarrow \overline{2\,\mathrm{AcO}\cdot} \qquad (35)$$

$$\overline{2\,\mathrm{AcO}\cdot} \longrightarrow \text{"AcO}\cdot\text{"} \qquad (36)$$

$$\text{"} \longrightarrow \overline{\mathrm{Me}\cdot + \mathrm{CO_2} + \mathrm{AcO}\cdot} \longrightarrow \mathrm{McOAc} \qquad (37)$$

---

[*] Quotation marks are used throughout to denote kinetically free species.

$$\overline{\text{Me}\cdot\ + \text{CO}_2 + \text{AcO}\cdot} \longrightarrow \text{''AcO}\cdot\text{''} + \text{''Me}\cdot\text{''} \tag{38}$$

$$\text{''} \longrightarrow \overline{\text{Me}\cdot\ + 2\,\text{CO}_2 + \text{Me}\cdot} \rightarrow \text{C}_2\text{H}_6 \tag{39}$$

$$\overline{\text{Me}\cdot\ + 2\,\text{CO}_2 + \text{Me}\cdot} \longrightarrow \text{''Me}\cdot\text{''} \tag{40}$$

Since considerable cage decarboxylation (30-50 percent) is required to yield the quantities of geminate products observed, the rate of decarboxylation must be nearly equivalent to the rate of diffusive separation if this mechanism obtains.

"Hot" acetoxyl radicals: Since 0^{18} labeling experiments (5) indicate that recombination of acetoxyl radicals to regenerate peroxide does not compete with decarboxylation, the former process appears to be activated. Consequently, it is conceivable that the acetoxyl radicals initially possess some excess vibrational energy and that such "hot" species decarboxylate at a rate competitive with vibrational relaxation. Formation of the cage products might then be due exclusively to decarboxylation of "hot" acetoxyl radicals and thermally equilibrated radicals may have considerably longer lifetimes.

Mechanism V:

$$\text{Ac}_2\text{O}_2 \longrightarrow \overline{2\,\text{AcO}\cdot^{*}} \tag{41}$$

$$\overline{2\,\text{AcO}\cdot^{*}} \rightarrow \overline{2\,\text{AcO}\cdot} \rightarrow \text{''AcO}\cdot\text{''} \tag{42}$$

$$\begin{aligned} \text{''} \longrightarrow \overline{\text{Me}\cdot\ + \text{CO}_2 + \text{AcO}\cdot} &\rightarrow \text{MeOAc} \\ &+ \text{''AcO}\cdot\text{''} + \text{''Me}\cdot\text{''} \end{aligned} \tag{43}$$

$$\overline{2\,\mathrm{AcO}\cdot^{*}} \longrightarrow \mathrm{Me}\cdot + 2\,\mathrm{CO_2} + \mathrm{Me}\cdot \longrightarrow \mathrm{C_2H_6} + \text{"}\mathrm{Me}\cdot\text{"} \tag{44}$$

Alternatively decarboxylation of thermally equilibrated acetoxyl radicals, however, need not be slow relative to diffusion. In such a case the yields of ethane and methyl acetate would also be affected by the "normal" decarboxylation rate as well as by the activation energy of the primary process.

Simultaneous Two and Three Bond Scission

There is considerable kinetic evidence that for diacyl peroxides in which the incipient alkyl radicals are quite stable, multibond cleavage is the primary mode of decomposition (10, 11). The basic features of the thermolysis of acetyl peroxide might be accommodated by three essentially isoenergetic fragmentation paths. If the rate of decarboxylation of acetoxyl radicals were slow, then the yield of ethane and methyl acetate would be determined by the extent of two and three bond scission in the primary process (12):

Mechanism VI:

$$\mathrm{Ac_2O_2} \xrightarrow{k_1} \overline{2\,\mathrm{AcO}\cdot} \longrightarrow \text{"}\mathrm{AcO}\cdot\text{"} \tag{45}$$

$$\xrightarrow{k_2} \overline{\mathrm{Me}\cdot + \mathrm{CO_2} + \mathrm{AcO}\cdot} \longrightarrow \mathrm{MeOAc} + \text{"}\mathrm{AcO}\cdot\text{"} + \text{"}\mathrm{Me}\cdot\text{"} \tag{46}$$

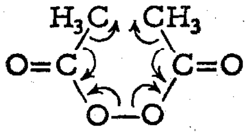
$$\xrightarrow{k_3} \overline{\mathrm{Me}\cdot + 2\,\mathrm{CO_2} + \mathrm{Me}\cdot} \longrightarrow \mathrm{C_2H_6} + \text{"}\mathrm{Me}\cdot\text{"} \tag{47}$$

This mechanism is similar to the "hot" acetoxyl radical mechanism (Mechanism V), in that the rate of decarboxylation of acetoxyl radicals need not be competitive with the rate of diffusion. However, both mechanisms (V and VI) can accommodate extensive normal decarboxylation in the cage.

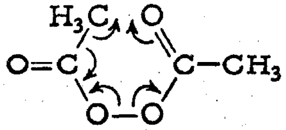
Cyclic and Non-radical Pathways to the "Cage" Products

Cyclic radical and non-radical pathways can be envisioned for the formation of ethane and methyl acetate:

Mechanism VII:



$$\longrightarrow C_2H_6 + 2\,CO_2 \qquad (48)$$



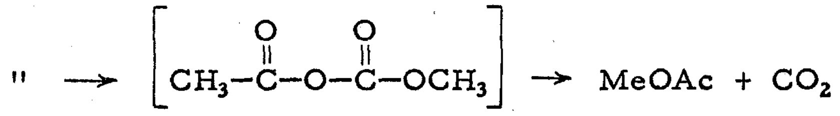
$$\longrightarrow \text{MeOAc} + CO_2 \qquad (49)$$

$$Ac_2O_2 \longrightarrow \text{"radicals"} \qquad (50)$$

From the vast amount of data available we know that a radical-producing process must accompany any ionic or concerted decomposition paths (1b). Thus, ethane could arise as a side product (i.e. geminate recombination) of the process producing kinetically free radicals, while methyl acetate might be produced <u>via</u> an ionic rearrangement. Ionic rearrangements of some diacyl peroxides to acyl alkyl carbonates are known to compete with heterolysis (10, 18). Since these carbonates often produce esters thermally (18), it was necessary to consider the following mechanistic possibility:

Mechanism VIII:

$$Ac_2O_2 \longrightarrow \overline{2\,Me\cdot} \longrightarrow C_2H_6 + \text{"}Me\cdot\text{"} \qquad (51)$$



$$\text{"} \longrightarrow \left[CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-OCH_3\right] \longrightarrow MeOAc + CO_2 \qquad (52)$$

SCAVENGING EVIDENCE FOR THE INTERMEDIACY OF ACETOXYL RADICALS IN THE THERMOLYSIS

The available data suggest that acyloxy radicals are intermediates in the thermolysis of aliphatic diacyl peroxides, but the evidence is *not* compelling. Since little more than intuition supported the intermediacy of acetoxyl radicals in the decomposition of acetyl peroxide, investigation of this possibility by a scavenging technique was a primary objective of this work.

Evaluation of scavengers: The reaction of interest was the thermal fragmentation of acetyl peroxide, thus the elimination of side reactions such as induced decomposition was essential. The first order rate constant for the disappearance of peroxide was chosen as a convenient, sensitive indicator of the incursion of side reactions. It was assumed that the rate constant for the simple fragmentation of peroxide was adequately approximated by that measured in the presence of excess iodine. This assumption was based on the observations that the decomposition rates are at a minimum (24) in the presence of iodine and that the rates are independent of iodine concentration. These facts strongly suggest the absence of any induced modes of peroxide decomposition in the presence of iodine.

The kinetic criterion for elimination of other than unimolecular decomposition can be used in conjunction with the measured yields of carbon dioxide to give evidence of scavenging of acetoxyl radicals. The theoretical maximum yield of carbon dioxide is not two moles per mole of peroxide, because correction must be made for carbonyl groups retained in methyl acetate, the product of a geminate reaction. The magnitude of this correction for non-decarboxylative reaction of acyloxy radicals is determined by the yield of methyl acetate since there is no evidence that this product can arise from any reaction involving kinetically free radicals.

Several radical trapping agents have been tested as scavengers for acetoxyl radicals. The rate constant for the decomposition of peroxide and the yield of gaseous products have been measured concurrently in the presence of various candidates. The results of these experiments are shown in Table III.

Unfortunately, it was not experimentally feasible to measure the rates of disappearance of peroxide and the carbon dioxide yield directly in the same experiment. However, it is possible to retain the semiquantitative significance of the measurement of the carbon dioxide yields in conjunction with a kinetic control measurement in the same run by determining the yields and rates of production of all the gaseous products under different conditions. Since the gaseous

TABLE III

Gas Evolution Results for the Decomposition of Acetyl Peroxide in Chlorobenzene

Run No.	Bath[a] Temp. °C	Substances Added[b]	Init. P Conc. (M/c)	obs: $t_{1/2}$ (min.)	obs:[c] $\frac{\Delta CO_2 + C_2H_6}{\Delta P}$	calc: $\frac{\Delta CO_2}{2\,\Delta P}$	calc:[d] relative $\frac{\Delta CO_2}{\Delta P}$
26–IV	92.7	0.2 M. iodine	—[e]	31	1.83_4[e]	—[e]	1.00[f]
98–II	92.0	"	0.0621	38	1.68_4	80.7	0.99[g]
36–III	92.5	"	"	32	1.73_2	83.1	1.01[g]
52–IV	92.8	0.25 M. iodine	0.0738	33	1.55_2	74.1	—
28–III	92.5	0.2 M. iodine – ϕOCH_3 (3 ml.)	0.0621	30	1.47_1	70.1	0.86[g]
46–IV	92.8	0.26 M. iodine – ϕOCH_3 (2 ml.)	0.0492	34	1.41_0	67.0	—
70–III	92.6	styrene (2 ml.)	—[e]	32	1.70_5[e]	—[e]	0.93[f]
72–III	92.6	"	—[e]	35	1.70_1[e]	—[e]	0.93[f]
36–IV	92.7	0.2 M. iodine[h] – H_2O (0.5 ml.)	—[e]	?	1.73_2[e]	—[e]	0.94[f]
104–II	92.0	0.2 M. iodine[h] – H_2O (0.5 ml.)	0.0621	36	1.60_1	76.6	0.94[g]

Table III (continued)

Run No.	Bath[a] Temp. °C	Substances Added[b]	Init. P Conc. (M/c)	obs: $t_{1/2}$ (min.)	obs:[c] $\frac{\Delta CO_2 + C_2H_6}{\Delta P}$	calc: $\frac{\Delta CO_2}{2\,\Delta P}$	calc:[d] relative $\frac{\Delta CO_2}{\Delta P}$
106-II	92.0	0.2 M. iodine[h] - H_2O (0.5 ml.)	0.0621	36	1.64_8	78.9	0.96[g]
100-II	92.0	none	0.0621	36	2.08_5	100.8	1.23[g]
102-II	92.0	"	"	35	1.99_2	96.1	1.17[g]
34-III	92.5	anisole (3 ml.)	"	18	1.66_6	79.8	0.97[g]
30-III	92.5	2.35 M. di-*t*-butyl *p*-cresol	"	28	1.57_6	75.3	0.92[g]
30-IV	92.7	0.2 M. DPPH	—[e]	9.2	1.09_5[e]	—[e]	0.62[f, i]

[a] Actual temperature of decomposition mixture probably 90-92°.

[b] Total volume of organics 5.0 ml.

[c] During warmup period of 2-4 min. gas was not collected.

[d] Values relative to 0.2 M. iodine in ϕCl runs with same stock solution (64-B: one run, 96-A: Av. two runs) with C_2H_6 substracted.

[e] Peroxide liter of the stock solution used here (64-B) not acceptable.

[f] Stock solution 64-B used in this run.

[g] Stock solution 96-A used in this run.

[h] Concentration of compound in organic phase.

[i] No correction made for ethane.

products consist predominately of carbon dioxide plus small amounts of ethane and the experiments in which methane is formed are predictable, semi-quantitative results can be obtained for some reaction conditions.

The presence of either diphenylpicrylhydrazyl (DPPH, 0.2 M.) or di-t-butyl-p-cresol (2.4 M.) markedly increases the rate of gas production relative to that observed for simple fragmentation. Thus, some or all of the observed reduction in the gas yield by these common radical scavengers relative to simple fragmentation (see Table III), must be attributed to the induced decomposition process responsible for the rate acceleration. The process responsible for the rate enhancement and the reduction in gas yield is probably attacked by scavenger or scavenger derived radicals on peroxide. Clearly, then, the recent interpretation of a reduction of the carbon dioxide yield from the thermal decomposition of acetyl peroxide in the presence of DPPH relative to decomposition in its absence to indicate acetoxyl radical scavengers is suspect (9b).

An attempt to approximate the conditions used by Hammond and Soffer (2), to trap benzoyloxy radicals with iodine and small amounts of water resulted in an increased rate of gas evolution. The nature of this rate acceleration has not been investigated in these laboratories; however, Shine has recently shown that under similar conditions hydrolysis of acetyl peroxide competes with thermolysis (9b).

In the presence of styrene or iodine the rates are at a minimum, implying that induced deomposition has been eliminated. However, the observed gas yields are less than the maximum expected in the absence of acetoxyl radical scavenging. This evidence strongly suggests that these scavenger systems are trapping acetoxyl radicals. It was decided that more rigorous documentation of acetoxyl radical scavenging was required in view of the ambiguous and contradictory (8, 9, 12) results obtained by other workers.

Iodine in chlorobenzene was chosen as the scavenger system for further investigation. Although the results in styrene suggest that nearly neat olefin can trap acetoxyl radicals, an increased viscosity due to polymerization may have drastically increased the extent of geminate recombination and therefore be responsible for the observed low yield of gas in this system.

Mechanism and demonstration of scavenging: Experimental determination of the yields of carbon dioxide and ethane characteristic of the simple fragmentation process in the absence of acetoxyl radical scavenging could not be made conveniently in our experiments. This direct check of the expected maximum carbon dioxide and ethane yield in the absence of scavenger was not possible, because the finite amount of induced decomposition (see Table III) which yields approximately 50 percent carbon dioxide, will, therefore, be reflected in the carbon dioxide yield and because an indeterminate amount of methane (varying with concentration of peroxide and nature of solvent) is also produced under these conditions. Therefore, the gas yield observed in the absence of scavenger includes methane and carbon dioxide and ethane in amounts dependent upon the extent of induced decomposition.

A part of the reduction of the total gas yield (moles gas/2 moles peroxide) from 0.98 in the absence of scavenger (0.064 M. peroxide) to 0.82 in the presence of 0.2 M. iodine (both in chlorobenzene) must result from elimination of methane formation (see Table III), since essentially none is formed in presence of iodine but considerable is formed in chlorobenzene alone. However, when the iodine concentration is increased to 0.25 M. or the solvent changed to anisole the gas yield falls off even more to 0.74 and 0.70 respectively, indicating that a reduction of the carbon dioxide plus ethane yield must also occur in some of these experiments. Since n.m.r. product studies for runs with various concentrations of iodine in chlorobenzene indicate (see Table IV) that only a small fraction of the reductions could result from a decrease in the ethane yield, most of these decreases must result from a decrease in the carbon dioxide yield.

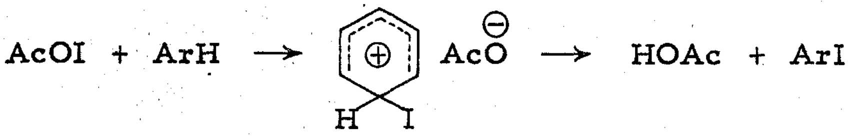
If the observed dependence of the carbon dioxide yield on the concentration of iodine indicates scavenging of acetoxyl radicals, then some <u>stable</u> acetyl compound(s) other than methyl acetate must be produced in the decomposition. It was found that acetic acid was an important product of the decomposition of acetyl peroxide for runs containing 0.2 M. and higher concentrations of iodine in chlorobenzene. The infrared absorption characteristics of acetic acid in chlorobenzene (e.g. C=O stretching frequency of 1713 cm^{-1}) were observed as were those of methyl acetate (e.g. C=O stretching frequency of 1745 cm^{-1}).

In agreement with the gas yield measurements, the yield of acetic acid also increased when a higher iodine concentration was used. Unfortunately, anisole is nearly opaque (0.1 mm path length) in the region where infrared absorption characteristic of carbonyl compounds occurs, and, the production of acetic acid in that solvent could not be established in an analogous manner. However, it appears unlikely that anything markedly different occurs in anisole.

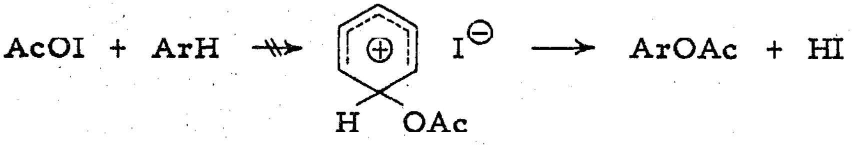
The mechanism of the reaction forming acetic acid <u>via</u> the interception of acetoxyl radicals is probably analogous to that proposed by Hammond for the formation of benzoic acid from thermolysis of benzoyl peroxide in solutions of iodine in benzene and chlorobenzene (16):

$$\mathrm{AcO\cdot} + \mathrm{I_2} \longrightarrow \mathrm{AcOI} + \mathrm{I\cdot} \qquad (53)$$

$$\mathrm{AcOI} \longrightarrow \mathrm{CH_3I} + \mathrm{CO_2} \qquad (54)$$



(55)



(56)

The greater scavenging ability of iodine in anisole relative to that in chlorobenzene can now be adequately explained. Anisole is much more reactive than chlorobenzene in the electrophilic aromatic substitution step (Equation 55) and, as observed for benzoyl hypoiodite, substitution is probably inefficient relative to decarboxylation of the intermediate acetyl hypoiodite. Interestingly, production of aromatic acetates (Equation 56) analogous to the aromatic benzoates from benzoyl hypoiodite, is not observed for chlorobenzene. The pertinent data are not available for anisole.

It is concluded that acetoxyl radicals are intermediates in the thermolysis of acetyl peroxide and that iodine is an efficient scavenger for these radicals.

EVIDENCE FOR THE TRAPPING OF KINETICALLY FREE ACETOXYL RADICALS

In view of the mechanistic significance of the timing of the decarboxylation of the intermediate acetoxyl radicals (vide infra), an attempt has been made to establish whether the lifetime of these intermediates is sufficiently long to allow them to escape geminate reactions and become kinetically free radicals. An approximate rate constant for their decarboxylation was also sought.

Criteria for scavenging of "free" acetoxyl radicals: The success of an attempt to determine whether kinetically free acetoxyl radicals occur in the thermolysis of acetyl peroxide is dependent on the character of the control experiments. These must rule out any pathways which might lead to results indistinguishable from those expected from scavenging of "free" acetoxyl radicals. Therefore, it must be established that the unimolecular decomposition and subsequent geminate processes are not altered under the conditions of the experiments. The following conditions must be satisfied: 1) The rate of the fragmentation must not be affected by the presence of scavenger or by the occurrence of other reactions. [Since radical chain induced decomposition appears important even at the lowest peroxide concentration used (0.06 M.), the rate of disappearance of peroxide should be reduced in the presence of scavenger and the reduced rate must be independent of peroxide and scavenger concentration.] 2) At the scavenger concentrations used in the crucial experiments, the yield of the purely geminate recombination products should not be affected (i.e. cage scavenging must not be involved). 3) To substantiate a negative result, the trapping reagents must have a demonstrated ability to intercept acetoxyl radicals.

Since it has been concluded that the primary process for thermolysis of acetyl peroxide in iodine-chlorobenzene is only simple fragmentation, criterion 1 has been fulfilled. Criterion 3 has also been satisfied since the production of acetic acid in the presence of iodine in anhydrous chlorobenzene has been shown to arise from the trapping of acetoxyl radicals. Thus, observation that acetic acid is formed at an iodine concentration where cage scavenging is not involved, should demonstrate the presence of kinetically free acetoxyl radicals.

SCAVENGING OF GEMINATE RADICAL PAIRS

Iodine concentration effects on methyl acetate yield: In view of the absence of direct peroxide–iodine reactions and the elimination by iodine of induced decomposition by solvent derived radicals, demonstration of cage scavenging requires only that increasing the scavenger concentration decrease the yield of one of the cage products. Thus, the reduction in the methyl acetate yield from 19% in 0.21 M. iodine to 17% in 0.32 M. iodine for the thermolysis of 0.28 M. acetyl peroxide in chlorobenzene is attributed to cage scavenging (see Table IV). Since these results indicate only that more geminate radical scavenging occurs in the more concentrated iodine sample, an attempt has been made to establish the minimum iodine concentration necessary to effect significant cage scavenging.

The work of Hammond and Waits (20f) on the scavenging of geminate cyanocyclohexyl radicals with iodine in chlorobenzene indicates that cage scavenging becomes significant in the range of 0.05 to 0.10 M. iodine for a solution 10^{-5} M. in azo-1-cyanocyclohexane. The rate of disappearance of peroxide was estimated for a chlorobenzene solution initially 0.10 M. in acetyl peroxide and 0.102 M. in iodine, by a procedure which assumed that the consumption of iodine ($\Delta I_2/\Delta P$) was constant throughout the run. Where cage scavenging is not important, the consumption of iodine should reflect the constant fraction of radicals which characteristically would escape geminate recombination in the absence of scavenger, at infinite dilution. Samples taken at various times during the run were treated with

TABLE IV

Product Yields in the Thermolysis of Acetyl Peroxide in Chlorobenzene at ~91° in the Presence of Iodine by N.m.r.: 1.0 ml. Samples[a]

Run No.	120-A[e]		126-A[b, c]		70-B	
Peroxide Conc.	0.28 M.		0.28 M.		0.314 M.	
Iodine Conc.	0.32 M.		0.2 M.		<0.3 M.	
Products	% Yield[c]	Ratio[d]	% Yield[c]	Ratio[d]	% Yield[c]	Ratio[d]
Ethane[f]	1.5	0.09	2.4	0.13	—	0.13
Methyl acetate	16.8	1.0	18.9	1.0	—	1.0
Acetic acid and Methyl iodide	158.9	9.46	147.2	7.79	—	8.22
Methane[f]	0.0	—	0.0	—	0.0	—
Other[g]	2.3	—	4.1	—	—	—

[a] All sample tubes were sealed and of approximately the same total volume (~2.0 ml.).
[b] Part of this sample was colorless at the end of the run and a trace of chlorotoluenes may have been included in the "other" products as well as undissolved gases.
[c] Entries are moles of product per mole of peroxide.
[d] Entries are moles of product relative to moles of methyl acetate.
[e] *t*-Butylbenzene was included as an internal standard.
[f] Only the dissolved gases were determined.
[g] Peroxide not accounted for by observed products probably undissolved ethane.

potassium iodide and acid and both the iodine liberated by peroxide and the remaining initial iodine were titrated together; thus a constancy of the stoichiometry of iodine consumption is required if the analytical data are to be given a simple interpretation. The observed instantaneous rate constants obtained by this procedure should increase if the iodine consumption decreases and then level off after the iodine uptake reaches its minimum value. A plot of the data from this experiment is shown in Figure I, and values for the calculated* rate constants at various times through the run are given in Table V. The linearity of this plot and the uniformity of the observed rate constants with time are within the experimental error of the kinetic procedure. Therefore, we conclude that little or no scavenging of the geminate radicals produced by decomposition of the acetyl peroxide in chlorobenzene occurs below iodine concentrations of 0.1 molar.

The ratio of the moles of iodine consumed to the moles of peroxide decomposed in this experiment was 0.71, indicating that 29 percent of the peroxide decomposed by way of a cage reaction. If it is assumed that ethane and methyl acetate are produced exclusively by cage reaction, even in the reactions with initial peroxide concentration of 0.28 M., then the ratio of ethane to methyl acetate (for which a minimum value of 0.37 ± .02 was obtained by n.m.r., see Table II) can be used to calculate the yields of ethane and methyl acetate in this experiment. This value for the ratio gives a maximum

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*See Appendix.

TABLE V

Comparison of Calculated Rate Constants for Various Extents of Decomposition during a Run:[a] [Peroxide]$_o$ = 0.1 M. and [Iodine]$_o$ = 0.1 M.

Time (min.)	$k \times 10^3$ (min.$^{-1}$)[b]	$t_{1/2}$ (min.)
17.90	17.1	40.5
35.75	17.5	39.7
54.71	17.2	40.2
72.15	17.6	39.3
Average	17.4 (± 1.2%)	39.9

[a] The iodine and peroxide content with time was measured and the rate constant for peroxide decomposition calculated assuming $\Delta I_2/\Delta P$ to be constant throughout the run. See Appendix for calculation procedure. During the time interval of the above measurements the iodine concentration varies by a factor of 2.

[b] Rate constants for decomposition from t_o to t_i.

yield of methyl acetate of 21 percent and a minimum yield of ethane of 8 percent at 91° in chlorobenzene.

Iodine concentration effects on the observed ethane to methyl acetate ratio: Reduction of the ethane to methyl acetate ratio by the inclusion of iodine, as observed by n. m. r., is quite substantial (see Table IV). Although the decrease in the ratio in the scavenging experiment relative to the unscavenged experiment is outside of the reproducibility of the analytical technique, this does not necessarily reflect a real decrease in the yield of ethane relative to methyl acetate under geminate scavenging conditions. If the solubility of ethane in the final reaction mixture is markedly reduced by the presence of iodine or methyl iodide, the observed ratio would be reduced.

If it is assumed that the dependence of the relative yields of ethane and methyl acetate on iodine concentration is not an artifact of the analytical procedure, several explanations of this effect must be considered. First, the coupling of kinetically free methyl radicals might be responsible for a part of the ethane yield in the unscavenged decomposition. The addition of the minimum amount of iodine (e. g. 0. 71 mole of I_2 per mole of P for 0. 1 M peroxide solution) to trap all of the kinetically free radicals, would eliminate this ethane producing pathway, thus reducing the ratio of ethane to methyl acetate to a constant value. However, the observed ratio is depressed even further when a higher iodine concentration is used (see Table IV). Furthermore, the constancy of the ratio in chlorobenzene in the absence of scavenger would be very surprising if this interpretation were valid, since it contrasts so dramatically with the large effects that subtle medium changes have on the "other" reactions of kinetically free methyl radicals (see Table II). This explanation is also intuitively unlikely in view of the reactivity of methyl radicals toward aromatic substrates (25).

The second explanation is based on processes defined by Noyes as "secondary recombination" (20a-20e). These processes occur when the radicals make excursions of the order of several molecular diameters away from their original partners and still recombine with high probability. As the separation of the geminate pair is increased, the probability increases that on recombination ethane will be produced rather than methyl acetate. Therefore, the yield of ethane should be reduced by scavenger to a greater extent than the yield of methyl acetate. In order that this process occur it is clear that scavenging of geminate radicals by non-nearest neighbor scavenger molecules must be involved. This view as well as the view that solvent separated geminate radicals extensively recombine have been challenged recently by Hammond and Waits (20f).

It is conceivable that due to the greater reactivity of the radicals involved in this study, decarboxylation and coupling may compete with nearest neighbor scavenging.

Having explored the possibility that the observed dependence of the ethane to methyl acetate ratio on iodine concentration was real, the results will now be examined for compatibility with the contrary assumption. As was pointed out previously, the best experimental value for the ratio of ethane to methyl acetate is ~0.37. If it is assumed that this value is correct and independent of iodine concentration, it is possible to calculate from the methyl acetate yield the sum of the methyl iodide and acetic acids yields.* Observed and calculated values for the sum of the yields of these non-cage products are shown in Table VI. The agreement is good and suggests that the drop in the observed ethane yield is an artifact of the analytical procedure, as was previously suggested (26).

IODINE CONCENTRATION EFFECTS ON ACETIC ACID YIELDS

Production of acetic acid in the absence of cage scavenging: From evidence presented above, it was concluded that little or no cage scavenging occurs for iodine concentrations below 0.1 M. In the same experiment in which this was demonstrated, approximately 4 percent of the theoretical two equivalents of acetic acid was observed. Since trapping of geminate radicals has been eliminated in this experiment, this acid must arise from the interception of kinetically free acetoxyl radicals.

Relative rate constants for decarboxylation and scavenging of kinetically free acetoxyl radicals: The yields of acetic acid observed from the decomposition of acetyl peroxide in chlorobenzene in the

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*Assuming ethane, methyl acetate, methyl iodine and acetic acid are the only products of the decomposition.

TABLE VI

Decomposition of Acetyl Peroxide in Chlorobenzene
at ~91° in Various Concentrations of Iodine

Iodine Conc. (M. /l.)	Yields		$\frac{RR}{RCO_2R}$	Yield of Non-cage Products	
	MeOAc	Ethane		obs.	calc.
0.10	0.21[a]	0.08[a]	0.37	0.71	—
.21	.19	.072[b]	.37	.74	0.74
.32	.17	.065[b]	.37	.79	.77

[a] Calculated from ratio of RR/RCO_2R and total cage effect.

[b] Calculated from ratio of RR/RCO_2R and experimental ester yield.

presence of various concentrations of iodine are given in Table VII. Assuming the following mechanism for the formation of acetic acid, the effect of iodine concentration upon its yield, in the absence of cage scavenging, can be predicted:

Mechanism IX:

$$Ac_2O_2 \xrightarrow{k_o} \text{(cage)} \qquad (57)$$

$$\text{(cage)} \longrightarrow MeOAc + C_2H_6 + \text{"}AcO\cdot\text{"} + \text{"}Me\cdot\text{"} \qquad (58)$$

$$\text{"}AcO\cdot\text{"} \xrightarrow{k^{-CO_2}} Me\cdot + CO_2 \qquad (59)$$

$$\text{"}AcO\cdot\text{"} + I_2 \xrightarrow{k_s} AcOI \qquad (60)$$

$$AcOI \longrightarrow MeI + CO_2 \qquad (61)$$

$$AcOI + ArH \longrightarrow HOAc + ArI \qquad (62)$$

From steady-state approximations for AcO· and AcOI we can derive the following relationship:

$$-\frac{d[Ac_2O_2]}{d[HOAc]} = \frac{1}{af}\left(\frac{k^{-CO_2} + k_s[I_2]}{k_s[I_2]}\right) = \frac{1}{af}\left(\frac{k^{-CO_2}}{k_s[I_2]}\right) + \frac{1}{af} \qquad (63)$$

Where: a = the fraction of acetoxyl radicals which become kinetically free.

f = the fraction of acetyl hypoiodite molecules which yield acetic acid.

This expression may be approximated by equation 64, if the iodine concentration is fairly constant:

TABLE VII

Yield of Acetic Acid from the Decomposition of Acetyl Peroxide at ~91° in Various Concentrations of Iodine in Chlorobenzene

Run No.	$[\text{Peroxide}]_o$	$[\text{Iodine}]_o$	$[\text{Iodine}]_{\text{Av.}}$ [a]	$\frac{\text{Moles of acetic acid}}{\text{Mole of peroxide}}$
112-IV	0.107_2	0.101_5	0.064	0.08[b]
36-III 98-II	0.0621	0.20	0.176	0.19_2[e]
106-IV	0.277	0.307	0.199	0.23_5[b]
52-IV	0.0738	0.257	0.228	0.34_8[c]

[a] Calculated assuming consumption of iodine per mole of peroxide constant throughout the reaction. See Appendix for Procedure.

[b] Determined by infrared.

[c] Calculated from gas evolution carbon dioxide yields.

$$\frac{\Delta P}{\Delta HOAc} = \frac{1}{af}\left(\frac{k^{-CO_2}}{k_s}\right) \times \frac{1}{[I_2]_{Average}} + \frac{1}{af} \qquad (64)$$

A plot of $\Delta P/\Delta HOAc$ versus $1/[I_2]_{Av.}$ for the data in Table VII is shown in Figure II. Part of this data is for the region of iodine concentration in which it has been shown that extensive scavenging of geminate radicals occurs in this system. The curvature in this plot is due to a marked increase in the yield of acetic acid where cage scavenging is important. The linear relationship described by equation 64, should be approximated by a tangent to the curve in the region where only kinetically free radicals are being intercepted by iodine. From the slope ($1/af \times k^{-CO_2}/k_s$) and intercept ($1/af$) of this tangent, the ratio of the rate constant for decarboxylation (k^{-CO_2}) to the rate constant for scavenging (k_s) of "free" acetoxyl radicals can be estimated. The value obtained by this procedure for the ratio, k^{-CO_2}/k_s, is 0.24. The uncertainty in this value is quite large, but it appears reasonable from the curve that it should lie between 0.1 and 1.0 (see dotted lines on Figure II).

This crude estimate of the rate constant for decarboxylation relative to the rate constant for scavenging, defines the system sufficiently well to allow a rough estimation of the rate constant for decarboxylation. If both scavenging and decarboxylation are slow relative to diffusion, then the yield of acetic acid should deviate from the linear relationship predicted by equation 64, only as a result of scavenging of geminate methyl radicals. This deviation must result from an increase in the fraction of acetoxyl radicals which escape

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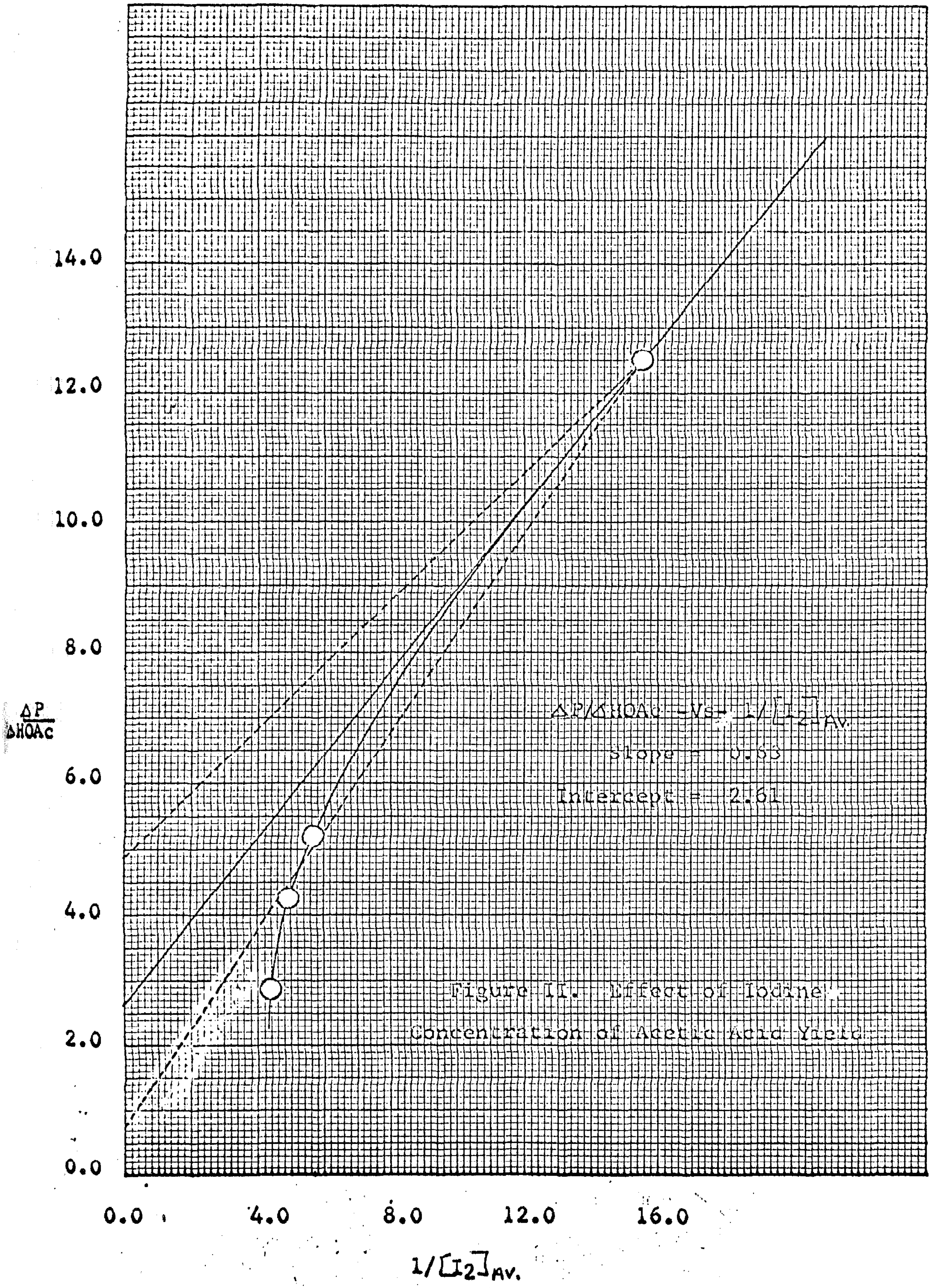


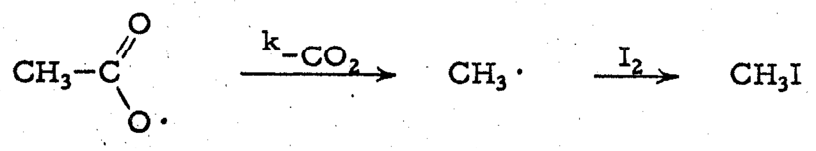
Figure II. Effect of Iodine Concentration of Acetic Acid Yield geminate recombination, and should be equal to half of the decrease in the methyl acetate yield. The observed acetic acid yields exceed those predicted by slow decarboxylation and scavenging. Thus, scavenging of geminate acetoxyl radicals by iodine is indicated. Since this is most conveniently accomplished by a process which is diffusion controlled (representing the maximum value for k_s), the assumption that scavenging of acetoxyl radicals is diffusion controlled, or just slightly slower, gives an estimate for k^{-CO_2} of 2.4×10^9 sec.$^{-1}$ (± 100 percent) where $k_s = 10^{10}$ sec.$^{-1}$ l/M. (20).

DECOMPOSITION OF ACETYL PEROXIDE-d_6

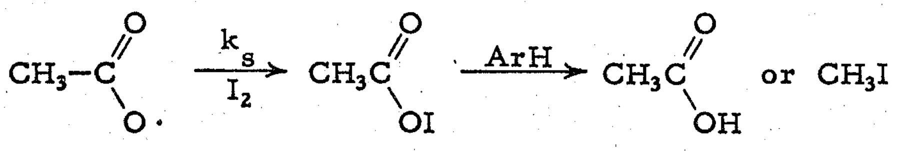
Acetyl peroxide-d_6 was prepared and its rate of decomposition determined, in an effort to obtain evidence bearing on the importance of C—C bond stretching in the rate-determining step of the fragmentation. It was anticipated that if methyl radicals were being formed in the primary process, deuteration would slow the rate of decomposition (27). The effect of six deuteriums on the rate does not appear to be great at 90°, but the results of the rate experiments were too inconsistent to permit accurate estimation of the isotope effect, k_{h_6}/k_{d_6}.

The effect of deuteration of acetyl peroxide on the product yields was also investigated. Thermolysis of a mixture of acetyl peroxide and acetyl peroxide-d_6 in chlorobenzene containing styrene at 91°, isolation of the combined ester fraction by v. p. c. and mass spectrometric analysis of the mixture gave a ratio of the yield of methyl acetate to the yield of methyl acetate-d_6 of 1.01. Decomposition of a mixture of peroxides in the presence of excess iodine and determination of the relative yields of methyl iodide and methyl iodide-d_3 at two iodine concentrations, 0.4 and 0.77 M., showed an apparent iodine concentration dependence of the isotope effect, methyl iodide/ methyl iodide-d_3 = 1.20 and 1.04 respectively.

These results can be quite adequately explained because these concentrations of iodine lead to considerable geminate radical scavenging. The greater efficiency of geminate acetoxyl radical scavenging at the higher iodine concentration reduces the fraction of the acetoxyl radicals which escape from the "cage." Thus, the isotope effect on the competition of decarboxylation with scavenging of "free" acetoxyl radicals is dependent upon the iodine concentration, since acetyl hypoiodite also produces methyl iodide.



$$CH_3-C(=O)O\cdot \xrightarrow{k_{-CO_2}} CH_3\cdot \xrightarrow{I_2} CH_3I \qquad (65)$$



$$CH_3-C(=O)O\cdot \xrightarrow[I_2]{k_s} CH_3C(=O)OI \xrightarrow{ArH} CH_3C(=O)OH \text{ or } CH_3I \qquad (66)$$

Where: $k^h_{-CO_2}/k^d_{-CO_2} > 1$

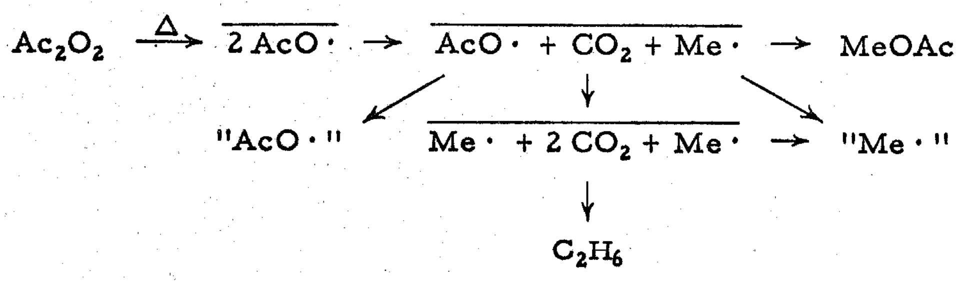
In view of the reasonably large isotope effect on the rate of decarboxylation of acetoxyl radicals, the lack of an effect on the methyl acetate yield requires some comment. The dependence of the yield of methyl acetate on the extent of decarboxylation prior to diffusive separation of the geminate radical pairs appears to be small in this region. Braun (28) measured the ethane and methyl acetate yields in isoöctane as a function of temperature, and found that even though the ethane yield decreased as the temperature was lowered, the methyl acetate yield was, within experimental error, unaffected. If only the activation energy for diffusion determined the direction of the temperature effect on the ethane yield, then the ethane yield should *increase* as the temperature is lowered. The *decrease* observed for lower temperatures indicates that there is an activation energy for the decarboxylation of acetoxyl radicals which is probably greater that for diffusion. Thus, although the rate of decarboxylation of acetoxyl-d_3 radicals is slower than that for acetoxyl radicals it is not necessary that the effect on the ester yield be appreciable.

One of the mechanisms which were given serious consideration (Mechanism V) involved the possibility of an abnormally large isotope effect. If the first step in the decomposition produces vibrationally excited ("hot") acetoxyl radicals and an extremely fast decarboxylation of the hot species competes with vibrational relaxation, deuteration of the acetoxyl radicals might greatly facilitate deactivation relative to decarboxylation. The magnitude of this effect, due to an increase in the number of vibrational energy levels and a decrease in their separation, could not be estimated; therefore, only a large effect would be definitive. Since the isotope effect on ester yield is probably not an effective indicator of the extent of "primary" decarboxylation, the results are ambiguous. Even so, there is nothing in these results that does not agree with our previously discussed experiments (*vide supra*). The indication that "cage" *acetoxyl* radicals are scavenged by iodine and that acetoxyl radicals escape from the "cage" to be scavenged by iodine at a rate competitive with decarboxylation strengthens the case (29) for the elimination of DeTar's (12) multibond cleavage mechanism (Mechanism VI).

CONCLUSIONS

Our results, coupled with previously available data allow us to draw a consistent, convincing picture of the processes involved in thermolysis of acetyl peroxide. That the mechanistic problem has been difficult to define, and still involves residual uncertainties, is not surprising. There is clear evidence (11, 18) that there is a multiplicity of mechanisms for decomposition of diacyl peroxides. In such cases one must always expect that some members of a series will show elements of transitional behavior in the mechanisms of their reactions.

The simplest mechanism consistent with the data is shown in equation 67. Without scavengers, the reaction is complicated for



(67)

peroxide concentrations greater than 0.01 M. by radical induced decomposition; however, the primary process of the unimolecular decomposition appears to involve purely 0-0 bond scission.

The evidence against the involvement of cyclic (Mechanism VII) or ionic (Mechanism VIII) pathways for the formation of the "cage" products is now convincing. First, it has been shown that the reactions leading to "cage" products can be reduced by scavenging the radicals from the decomposition of acetyl peroxide (30) with iodine concentrations in excess of 0.1 M. It follows then that at least part of the "cage" products is formed <u>via</u> geminate radical recombination. Furthermore, any significant contribution to the formation of the "cage" products by non-geminate recombination processes is ruled out by the apparent constancy of the relative yields of ethane and methyl acetate under conditions of varying efficiency of geminate scavenging (see Table VII). If non-geminate recombination reactions were producing ethane or methyl acetate to any significant extent under scavenging conditions, the overall ratio of their yields should not be constant for varying efficiencies of geminate radical scavenging. This does not hold in the event that the ratio of the yields of ethane and methyl acetate from geminate radical recombination and non-radical process(es) are the same. This unlikely situation would require a non-geminate radical path to each of the "cage" products, thus, the ionic path to ester <u>via</u> acyl alkyl carbonate (Mechanism VIII) can be eliminated. Since neither ethane nor methyl acetate is formed in the gas phase decomposition of acetyl peroxide (5) in the presence of iodine, which strongly suggests that cyclic concerted processes are not important, formation of these products by processes other than geminate radical recombination is probably unimportant.

Our knowledge of the nature of geminate recombination processes (20) is limited. However, assuming that the rate of reaction of iodine with acetoxyl radicals is diffusion controlled (31), our estimate of the rate constant for decarboxylation of acetoxyl radicals relative to the rate constant for diffusion ($k_{-CO_2}/k_{diff.} \cong 0.24 \pm 100$ percent) represents a rate of decarboxylation large enough to account for the decarboxylated geminate recombination products by "cage" decarboxylation of acetoxyl radicals and yet small enough to permit an extremely reactive scavenger such as iodine to intercept the acetoxyl radicals as kinetically free entities as well. There is sufficient uncertainty in the time scale of geminate processes to also allow either a small fraction of the decomposition to proceed <u>via</u> multibond cleavage or for "hot" acetoxyl radicals to be responsible for some of the "cage" decarboxylation.

The main reason for considering such processes was the report by DeTar (12) that δ-phenylvaleryl peroxide decomposed <u>via</u> mixed simple and multibond cleavage, producing long-lived acyloxy radicals ($k_{-CO_2} < 10^8$ sec.$^{-1}$). Since the possibility of long-lived acetoxyl radicals (i.e. $k_{-CO_2} < 10^8$ sec.$^{-1}$) has been eliminated and since there is no reason to expect δ-phenylvaleryloxy radicals to decarboxylate <u>slower</u> than acetoxyl radicals, a crucial link in DeTar's (12) chain of reasoning is broken. The evidence makes DeTar's mechanism untenable in the case of acetyl peroxide and by analogy in his case as well, therefore, the evidence suggesting the involvement of multibond cleavage in the thermolysis of acetyl peroxide has been eliminated.*

Thus, a relatively simple mechanistic picture (Mechanism IV) involving competitive decarboxylation and diffusion of acetoxyl radicals satisfactorily accommodates the results of the decomposition of acetyl peroxide. It also suggests a convenient explanation for the higher yields of alkyl radical coupling and disproportation products from other primary aliphatic peroxides (33) than from acetyl peroxide. Thus the 30-35 percent yield of ethyl radical "cage" coupling and disproportation products from propionyl peroxide (5) in comparison to the corresponding 5-7 percent yield of ethane from acetyl peroxide in isoöctane (5) can be explained simply by the relative acyloxy radical decarboxylation rates rather than by invoking particle size effects on rates of escape from the "cage" (5). As would be expected from

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*The measurement of the C^{13} and O^{18} isotope effects on the rate of decomposition of acetyl peroxide at 44.8° in isoöctane have been recently reported by Goldstein (32). He suggests that the primary process is probably completely three bond cleavage, on the basis of a comparison of the magnitudes of calculated and observed isotope effects. Unless a complete change of mechanism results from changing the solvent from chlorobenzene to isoöctane, complete decomposition *via* three bond cleavage is impossible in view of the production of methyl acetate by geminate recombination in chlorobenzene. In addition, Szwarc's measurement of the carbon dioxide yield in isoöctane suggests that methyl acetate is also produced in that solvent. Goldstein's results are interesting but the magnitude of the isotope effects ($k_{C}12/k_{C}13 = 1.023$ and $k_{O}16/k_{O}18 = 1.023$) are small, making the calculations less reliable.

radical stabilities (34), i.e., ethyl greater than methyl, the decarboxylation of propionyloxyl radicals is faster than that of acetoxyl radicals. Therefore, more geminate ethyl radicals are produced than methyl radicals and the probability of alkyl-alkyl radical interaction increased due to the greater rate of decarboxylation compared to the rate of escape from the "cage."

EXPERIMENTAL

MATERIALS

Chlorobenzene. — (Matheson, Coleman and Bell Reagent Grade) was shaken with concentrated sulfuric acid until the acid was no longer colored. The organic layer was then washed with base and water, dried over anhydrous calcium sulfate and distilled through a 30 cm. packed column (3 × 3 mm. stainless wire gauze). The material boiling 131-131.5° and free of impurities by v.p.c. (on Apieson and β,β-oxydipropionitrile) was used throughout.

Iodine. — (Baker and Adamson Reagent Grade) was used without purification.

Pyridine. — (Baker and Adamson Reagent Grade) was dried over barium oxide and distilled through a 30 cm. packed column. The fraction boiling 114-114.5° was collected.

Ether. — (Mallinckrodt Analytical Reagent) was used from freshly opened 1 lb. cans without purification.

Anisole. — (Matheson, Coleman and Bell Reagent Grade) was used without purification.

Styrene. — (Reagent Grade) was used without purification.

2,6-Di-*t*-butyl *p*-cresol. — (Eastman Reagent Grade) was used without purification.

1,1-Diphenyl-2-picrylhydrazyl. — The material used was obtained from Dr. H. P. Waits (m.p. = 134-136°).

Isopropanol. — (Baker and Adamson Reagent Grade) was used in the iodometric titrations. It did not liberate iodine on addition of iodide and acid and was therefore used without purification.

Carbon tetrachloride. — (Eastman Spectro Grade) was used without purification.

t-Butyl benzene. — (Matheson, Coleman and Bell Reagent Grade) was used without purification.

ACETYL PEROXIDE

Procedure 1. — Into an erlenmeyer flask (500 ml.) was placed acetic anhydride (20 g.) in reagent ether (100 ml.), and sodium peroxide (10 g.). This mixture was cooled in an ice-salt bath to 0° and ice (35 g.) added with stirring, at such a rate that the temperature remained below 5°. The cooling was discontinued after the addition was complete (1 hr.) and the mixture stirred until it reached room temperature. The ether solution was decanted carefully and the aqueous layer washed with ether (50 ml.). The combined ether fractions were washed with portions (50 ml.) of 5 percent sulfuric acid, 5 percent sodium carbonate and distilled water. The resulting ether solution of acetyl peroxide was dried over magnesium sulfate and stored in a refrigerator until used.

Procedure 2. — A suspension of sodium peroxide (14.3 g.) in ether (100 ml.) was placed in an erlenmeyer flask (500 ml.) equipped with a magnetic stirring bar. An ether solution of acetyl chloride (26.3 g.) was added slowly and the mixture stirred at room temperature until the yellow color of sodium peroxide disappeared (24 hrs.). The resulting ether solution of acetyl peroxide was treated as in procedure 1 and stored.

Procedure 3. — To a solution of acetyl chloride (8 g.) in ether (100 ml.) cooled to 0° in an ice-salt bath was carefully added 98 percent hydrogen peroxide (2 g.) in ether (50 ml.) which had been previously mixed with a solution of pyridine (9 g.) in ether (50 ml.). A rate of addition which maintained the temperature below 5° took approximately two hours to complete the addition. The ether solution of acetyl peroxide was treated as in procedure 1 and stored.

Isolation and preparation of stock solutions. — Shine's procedure (35) was used for isolating large quantities of peroxide from its ether solutions. Small, pure samples of peroxide could be conveniently obtained from a slightly modified isolation procedure: Into a filter beaker (10 ml.) equipped with a coarse fritted disk was placed the concentrated ether solution of peroxide (2-8 ml.). The system was closed to exclude atmospheric moisture. Peroxide was precipitated at -78° and maintained at that temperature for an extended period to ensure good crystallization. The filter beaker was rotated into position for vacuum filtration and the ether phase filtered off. The receiver was removed and replaced by a clean, dry flask. The beaker was returned to its original position and the remaining solvent removed under vacuum (along with a part of the peroxide). The white crystals of peroxide were dissolved in the desired solvent, the solution filtered, and stored in a refrigerator.

Concentration and purity of stock solutions. — Three iodometric analytical procedures for determination of peroxide content of the non-aqueous stock solutions were used. The procedures in which peroxide is reduced with potassium iodide and acid in glacial acetic acid (36) or refluxing isopropanol (37) gave erratic and/or low peroxide titers. However, a modification of the procedure of Wagner, Smith and Peters, gave reproducible results and the precise method used is described below.

To a known volume of stock solution in isopropanol (50 ml.) in an erlenmeyer flask (20/40 $\mathbb{T}$, 250 ml.) was added a saturated solution of sodium iodide in isopropanol (10 ml.) followed by glacial acetic acid (2 ml.). The flask was attached to a reflux condenser and heated just below reflux temperature for exactly 5 min. To the hot solution was added water (5 ml.). Dimethylsulfoxide (5 ml.) was also added occasionally to sharpen the iodine end points. The liberated iodine was titrated with aqueous potassium thiosulfate which had been standardized against potassium iodate, under a stream of nitrogen to the disappearance of the iodine color. If the saturated sodium iodide solution was colorless, essentially no iodine was liberated in the blank.

As a result of the preparation and isolation procedures the main impurities in the acetyl peroxide stock solutions were small amounts of water, acetic acid, peracetic acid and ether. Acetic acid and peracetic acid were removed by washing the stock solutions with 2 percent aqueous sodium carbonate and distilled water followed by drying over anhydrous calcium sulfate. The samples used in the kinetic runs and for product analyses were dry and free of impurities by n.m.r. and infrared analyses.

DEUTEROACETYL PEROXIDE

Trideuteroacetyl chloride. — Acetic acid-d_4 (Isotope Specialties Co., 10.5 g.) was placed in a side-arm distilling flask (50 ml.) equipped with stirring bar and dropping funnel into which fresh phosphorous trichloride (8.0 g.) was added dropwise with stirring and occasional cooling. Following complete addition, the mixture was stirred for 30 min. and then heated for another 30 min. at 45-50°. The low boiling material was separated from the phosphorous acid layer by flash distillation (b.p. = 45-50°). A few drops of acetic acid-d_4 were added to the crude distillate to react with any volatile phosphorous compounds. Redistillation through a 10 cm. vigreaux column yielded 4.76 g. (36 percent) of material b.p. = 50°. When the distillation receiver was cooled in ice-water a 68 percent yield was obtained.

Hexadeuteroacetyl peroxide. — The material used was prepared by procedure 3 (38) used for the synthesis of acetyl peroxide.

2, 2'-Dideuteroacetyl peroxide. — This peroxide was prepared by procedure 1 (39) used for the synthesis of acetyl peroxide, from 2, 2'-dideuteroacetic anhydride obtained from Professor J. D. Roberts.

Trideuteromethyl iodide. — Into a side-arm distilling flask equipped with an addition funnel was placed 55 percent aqueous hydriodic acid (25 ml.). To the acid was added methanol-d_4 (1.8 g.) with stirring. The mixture was heated to such a temperature that the iodide distilled slowly. The iodide was collected in a trap at -78°. The yield of crude methyl iodide-d_3 was 5.2 g. (70 percent). This material was passed through a 2 cm. dry packed alumina colum neat and distilled at atmospheric pressure. The fraction b.p. = 42-43° was collected and used as a mass spectrometric reference.

Methyl iodide. — The material used as a mass spectrometric reference was prepared by the procedure given for the deuterated methyl iodide.

Hexadeuteramethyl acetate. — Acetyl chloride-d_3 (4.0 g.) was placed in a round bottom flask and cooled to -12°. To this was added methanol-d_4 (1.8 g.) at such a rate that the temperature remained below 30°. The cooling bath was removed; the flask was allowed to warm to room temperature and stirred for an additional hour. The ester was distilled out of the pot at reduced pressure (20 mm. of Hg) and collected in a trap at -78°. The yield of crude product was 3.8 g. (95 percent). This material was passed through a 2 cm. dry packed alumina column neat and allowed to stand over barium oxide. This material was transferred to a bulb-to-bulb distillation apparatus, degassed using five freeze-thaw cycles and distlled (10^{-4} mm. of Hg). The final yield was approximately 40 percent.

Methyl acetate. — The material used as a mass spectrometric reference was prepared by the method given for the deuterated methyl acetate.

GAS EVOLUTION EXPERIMENTS

Procedure for kinetic runs. — The apparatus used in these experiments has been adequately described elsewhere (40).

Into a reaction cell previously charged with scavenger or other reagents, was pipetted a known volume of peroxide stock solution. After dilution with solvent to a convenient volume (usually 5 ml.) the cell was closed and attached to the gas collection system. The solution was then degassed by repeatedly exchanging the air over the sample for purified nitrogen and equilibrating the dissolved gases (by rapid stirring). Water at a constant temperature was then circulated rapidly through a jacket surrounding the decomposition chamber and after a 2-3 min. delay for the reaction mixture to come to temperature, the volume of gas evolved was monitored as a function of time. Readings were taken during two or three half-lives; a final reading was obtained after complete decomposition. The results are shown in Table VIII.

Rate constants. — First order rate constants were determined graphically from the slope of the line obtained by a plot of ln $(V_\infty - V/V_\infty)$ versus time: V_∞ = final volume of gas produced; V = gas produced by time, t. It was assumed that the moles of gas produced per mole of peroxide decomposed were constant throughout a run; this demands the following relationship: $P/P_0 = V_\infty - V/V_\infty$, where P_0 = initial peroxide concentration; P = peroxide concentration at time, t.

TABLE VIII

Results of the Gas Evolution Measurements for the Decomposition of Acetyl Peroxide in Chlorobenzene

Run No.	98-II	100-II	102-II	104-II
Peroxide stock solution				
No.	96-A	96-A	96-A	96-A
Volume (ml.)	2.00	2.00	2.00	2.00
Conc. (M./l.)	0.1553	0.1553	0.1553	0.1553
Total sample Volume (ml.)	5.00	5.00	5.00	5.50
Initial peroxide Conc. (M./l.)	0.0621	0.0621	0.0621	0.0565[b]
Scavenger				
Cpd.	Iodine	—	—	Iodine
Wt. or vol.	0.250	—	—	0.250
Conc. (init.)	0.1969	—	—	0.1790[b]
Other substances added				
Cpd.	—	—	—	H_2O
Wt. or vol.	—	—	—	0.50 ml.
Bath temperature[a] °C (uncorr.)	92.0	92.0	92.0	92.0
Gas collection temp. °C (uncorr.)	29.5	29.5	29.5	29.5
Calc. theo. CO_2 Yield (ml.)	15.74	15.74	15.74	15.74
Observed gas yield (ml.)	13.25	16.41	15.68	12.60
Moles of gas evolved Per mole of peroxide	1.68_4	2.08_5	1.99_2	1.60_1
Calc. correction for ~7% ethane yield (ml.)	0.55	0.55	0.55	0.55
Percent theo. CO_2 Yield	80.7	100.8	96.1	76.6
Observed half-time (min.)	37.5	35.6	35.3	36.3

Table VIII (continued)

Run No.	106-II	28-III	30-III	34-III
Peroxide stock solution				
No.	96-A	96-A	96-A	96-A
Volume (ml.)	2.00	2.00	2.00	2.00
Conc. (M./l.)	0.1553	0.1553	0.1553	0.1553
Total sample Volume (ml.)	5.50	5.00	5.00	5.00
Initial peroxide Conc. (M./l.)	0.0565[b]	0.0621	0.0621	0.0621
Scavenger				
Cpd.	Iodine	Iodine	DBC[c]	none
Wt. or vol.	0.250	0.250	2.30	—
Conc. (init.)	0.1790[b]	0.1969	2.3469	—
Other substances added				
Cpd.	H_2O	anisole	—	anisole
Wt. or vol.	0.50 ml.	3.00 ml.	—	3.00
Bath temperature[a] °C (uncorr.)	92.0	92.5	92.5	92.5
Gas collection temp. °C (uncorr.)	29.5	29.5	29.5	29.5
Calc. theo. CO_2 Yield (ml.)	15.74	15.74	15.74	15.74
Observed gas yield (ml.)	12.47	11.58	12.40	13.11
Moles of gas evolved Per mole of peroxide	1.64_8	1.47_1	1.57_6	1.66_6
Calc. correction for ~7% ethane yield (ml.)	0.55	0.55	0.55	0.55
Percent theo. CO_2 Yield	78.9	70.1	75.3	79.8
Observed half-time (min.)	35.6	30.0	27.5	17.5

Table VIII (continued)

Run No.	36-III	60-III	70-III	72-III
Peroxide stock solution				
No.	96-A	56-B	64-B[d]	64-B[d]
Volume (ml.)	2.00	1.00	1.00	1.00
Conc. (M./l.)	0.1553	0.1072	0.2680	0.2680
Total sample				
Volume (ml.)	5.00	6.00	6.00	6.00
Initial peroxide				
Conc. (M./l.)	0.0621	0.0179	0.0447	0.0447
Scavenger				
Cpd.	Iodine	Styrene	Styrene	Styrene
Wt. or vol.	0.250	3 ml.	2 ml.	2 ml.
Conc. (init.)	0.1969	—	—	—
Other substances added				
Cpd.	—	—	—	—
Wt. or vol.	—	—	—	—
Bath temperature[a] °C (uncorr.)	92.5	92.5-.6	92.55-.68	92.55-.70
Gas collection temp. °C (uncorr.)	29.5	29.5	29.5	29.5
Calc. theo. CO_2 Yield (ml.)	15.74	5.43	13.56	13.56
Observed gas yield (ml.)	13.63	5.28	11.56	11.53
Moles of gas evolved Per mole of peroxide	1.73_2	1.94_5	1.70_5	1.70_1
Calc. correction for ~7% ethane yield (ml.)	0.55	0.19	0.47	0.47
Percent theo. CO_2 Yield	83.1	93.7	81.8	81.6
Observed half-time (min.)	31.5	31.8	32.1	35.0

Table VIII (continued)

Run No.	12-IV-d_6	22-IV-d_6	26-IV	30-IV
Peroxide stock solution				
No.	46-A	85-A	64-B[d]	64-B[d]
Volume (ml.)	3.00	0.500	2.00	2.00
Conc. (M./l.)	0.1368	0.7617	0.2588	0.2588
Total sample Volume (ml.)	5.00	5.50	5.00	5.00
Initial peroxide Conc. (M./l.)	0.0822	0.0693	0.1035	0.1035
Scavenger				
Cpd.	Iodine	Iodine	Iodine	DPPH[e]
Wt. or vol.	0.250	0.2565	0.2553	0.3986
Conc. (init.)	0.1969	0.1836	0.2010	0.2023
Other substances added				
Cpd.	—	—	—	—
Wt. or vol.	—	—	—	—
Bath temperature[a] °C (uncorr.)	92.4-.6	92.6-.8	92.6-.75	92.6-.8
Gas collection temp. °C (uncorr.)	29.5	29.5	29.5	29.5
Calc. theo. CO_2 Yield (ml.)	20.79	19.29	26.22	26.22
Observed gas yield (ml.)	18.74	18.01	24.05	14.35
Moles of gas evolved Per mole of peroxide	1.80_3	1.86_7	1.83_4	1.09_5
Calc. correction for ~7% ethane yield (ml.)	0.73[f]	0.68[f]	0.92	none
Percent theo. CO_2 Yield	86.6	89.8	88.2	54.7
Observed half-time (min.)	37.7	39.8	31.3	9.2

Table VIII (continued)

Run No.	36-IV	42-IV	44-IV	46-IV
Peroxide stock solution				
No.	64-B[d]	40-A	40-A	50-B
Volume (ml.)	2.00	5.00	4.00	4.00
Conc. (M./l.)	0.2588	0.03806	0.03806	0.07378
Total sample				
Volume (ml.)	5.50	5.00	5.00	6.00
Initial peroxide				
Conc. (M./l.)	0.0941[b]	0.0381	0.0304	0.0492
Scavenger				
Cpd.	Iodine	Iodine	Iodine	Iodine
Wt. or vol.	0.2366	0.1978	0.2237	0.3905
Conc. (init.)	0.1694[b]	0.1556	0.1762	0.2562
Other substances added				
Cpd.	H_2O	—	Glac. HOAc	anisole
Wt. or vol.	0.50 ml.	—	1.00 ml.	2.00 ml.
Bath temperature[a] °C (uncorr.)	92.6-.75	92.65-.78	92.67-.82	92.7-.8
Gas collection temp. °C (uncorr.)	29.5	29.5	29.5	29.5
Calc. theo. CO_2 Yield (ml.)	26.22	9.64	7.71	14.96
Observed gas yield (ml.)	22.71	9.71	5.53	10.55
Moles of gas evolved Per mole of peroxide	1.73_2	2.01_5	1.43_5	1.41_0
Calc. correction for ~7% ethane yield (ml.)	0.92	0.34	0.27	0.52
Percent theo. CO_2 Yield	83.1	97.2	68.2	67.0
Observed half-time (min.)	—	37.5	32.4	34.1

Table VIII (continued)

Run No.	52-IV	58-IV	84-IV	86-IV
Peroxide stock solution				
No.	50-B	50-B	56-A	56-B
Volume (ml.)	4.00	4.00	4.00	4.00
Conc. (M./l.)	0.07378	0.07378	0.314	0.1067
Total sample				
Volume (ml.)	4.00	8.00	4.00	4.00
Initial peroxide				
Conc. (M./l.)	0.0738	0.0369	0.314	0.1067
Scavenger				
Cpd.	Iodine	Styrene	none	none
Wt. or vol.	0.2567	2 ml.	—	—
Conc. (init.)	0.2527	—	—	—
Other substances added				
Cpd.	—	anisole	—	—
Wt. or vol.	—	2.00 ml.	—	—
Bath temperature[a] °C (uncorr.)	92.75-.90	92.8-93.0	92.69-.85	92.75-.86
Gas collection temp. °C (uncorr.)	29.5	29.5	29.5	29.5
Calc. theo. CO_2 Yield (ml.)	14.96	14.96	63.61	21.62
Observed gas yield (ml.)	11.61	11.50	60.35	21.75
Moles of gas evolved Per mole of peroxide	1.55_2	1.53_7	1.89_8	2.01_2
Calc. correction for ~7% ethane yield (ml.)	0.52	0.52	1.78	0.76
Percent theo. CO_2 Yield	74.1	73.4	92.1	97.1
Observed half-time (min.)	32.8	—	21.6	26.7

[a] See page 64 for significance of bath temperature. [b] Calculated assuming solution in homogeneous, thus, initial concentration is low since material is mainly in organic phase. [c] DBC = di-*t*-butyl *p*-cresol. [d] Calibration of stock solution not reliable. [e] DPPH = N,N'-diphenylpicrylhydrazyl. [f] Calculated assuming ethane-d_6 yield approximately 7 percent under these conditions.

Yield of gaseous products. — The yield of the gaseous products was estimated (since an indeterminate amount of decomposition occurs in the warm up) from the observed infinity volume of gas obtained in the kinetic experiments and the amount of peroxide decomposed.

INFRARED KINETIC EXPERIMENTS

Kinetic procedure. — Several culture tubes were constricted about an inch from the top and dried overnight in an oven at 120-140°. When scavenger was to be included, it was weighed or pipetted into a volumetric flask, dissolved in the desired volume of standardized stock solution of peroxide in chlorobenzene and diluted to volume with chlorobenzene. This solution was then introduced into the prepared culture tubes using an all glass hypodermic syringe equipped with a glass needle and the tubes attached to a vacuum line. The samples were degassed using three freeze-thaw cycles and the tubes sealed at the contriction. If the samples were not decomposed immediately they were stored in a refrigerator at 5°.

The whole batch of tubes was placed in a preheated wire basket and quickly immersed in a constant temperature bath (±0.05°). After two of three minutes the first tube, corresponding to the initial point, was removed from the bath and cooled in Dry Ice-acetone. Points were taken during the first two to three half-lives and after complete decomposition of the peroxide (~10 half-lives). After reaction the tubes were stored in a refrigerator to permit simultaneous determination of unreacted peroxide. The analyses were run on a Beckman IR-7 spectrophotometer using the procedure of Bartlett and Hiatt (11).

N. M. R. PRODUCT ANALYSES

New n. m. r. tubes (Varian A-60), were cleaned by one of the following procedures and then rinsed five to ten times with distilled water: 1) by washing with a solution of Orvus (soluble detergent) in distilled water; 2) by standing in aqua regia overnight; 3) by standing in aqua regia overnight followed by washing with concentrated ammonia solution; 4) by standing for a few hours in saturated ethanolic potassium hydroxide. The water-rinsed, air dried tubes were then heated at 120-140° for a minimum of 24 hrs. Since procedures 2 and 4 gave spurious results (see Table IX parts K, L, M and N), procedures 1 and 3 were used unless otherwise noted.

Scavenger or other reagents were weighed into the n. m. r. tubes prior to addition of the peroxide solution. The peroxide solutions were measured and introduced into the tubes with a hypodermic syringe through a glass needle. The filled sample tubes were carefully attached to a vacuum line, degassed using at least three freeze-thaw cycles and sealed under vacuum (10^{-4} mm. of Hg).

The peroxide was then decomposed by heating in a constant temperature bath. The relative yields of products having well defined absorptions in the proton n. m. r. spectrum were determined by repeated upfield and downfield integrations using a Varian n. m. r.

TABLE IX

Products of the Thermolysis of Acetyl Peroxide in Chlorobenzene at ~91° by N. m. r.

A. Run No. 70-B; 1.0 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene; 0.0741 g. of iodine.

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	2.4	0.127
Methyl acetate	19.1	1.00
Acetic acid and Methyl iodide	57.0	8.22
Methane[d]	—	—

B. Run No. 76-A; 1.0 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene.

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	13.2	0.386
Methyl acetate	34.2	1.00
Acetic acid[e]	13.2	0.39
Methane[d]	36.6	1.07
o-Chlorotoluene	40.2	1.63
m,p-Chlorotoluene	15.6	

Table IX (continued)

C. Run No. 78-B-1; 0.5 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene; 0.01349 g. of benzophenone.

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	6.3	0.239
Methyl acetate	26.4	1.00
Acetic acid[e]	55.0	2.08
Methane[d]	10.7	0.41
o-Chlorotoluene	47.8	2.61
m,p-Chlorotoluene	21.2	

D. Run No. 78-B-2; 0.5 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene; 0.01074 g. of benzil.

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	5.4	0.215
Methyl acetate	25.1	1.00
Acetic acid[e]	60.0	2.39
Methane[d]	9.3	0.37
o-Chlorotoluene	48.6	2.78
m,p-Chlorotoluene	21.1	

Table IX (continued)

E. Run No. 78-B-3; 0.5 ml. of sample;[a] 0.314 peroxide in chlorobenzene; 0.00978 g. of 2-acetonaphthone.

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	8.5	0.218
Methyl acetate	39.0	1.00
Acetic acid[e]	22.0	0.57
Methane[d]	15.5	0.40
o-Chlorotoluene	48.5	1.73
m,p-Chlorotoluene	18.8	

F. Run No. 78-B-4; 0.5 ml. of sample;[a] 0.314 peroxide in chlorobenzene.

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	6.2	0.263
Methyl acetate	23.6	1.00
Acetic acid[e]	59.7	2.53
Methane[d]	10.5	0.44
o-Chlorotoluene	50.8	3.03
m,p-Chlorotoluene	20.6	

Table IX (continued)

G. Run No. 82-A; 1.0 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene; used tubes were treated with cleaning solution, NH_4OH and rinsed with water.

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	12.8	0.379
Methyl acetate	33.8	1.00
Acetic acid[e]	26.9	0.80
Methane[d]	19.1	0.57
o-Chlorotoluene	42.9	1.78
m,p-Chlorotoluene	17.5	

H. Run No. 82-B; 1.0 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene; used tubes were treated with cleaning solution, NH_4OH and rinsed with water.

Products	Percent of observed products[b]	Ratio Relative to methyl acetate[c]
Ethane[d]	11.7	0.350
Methyl acetate	33.4	1.00
Acetic acid[e]	27.1	0.81
Methane[d]	22.8	0.68
o-Chlorotoluene	42.2	1.79
m,p-Chlorotoluene	17.4	

Table IX (continued)

I. Run No. 82-C; 0.5 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene; used tubes were treated with cleaning solution, NH_4OH and rinsed with water.

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	8.8	0.223
Methyl acetate	39.4	1.00
Acetic acid[e]	26.6	0.68
Methane	11.3	0.29
o-Chlorotoluene	45.7	1.66
m,p-Chlorotoluene	19.9	

J. Run No. 82-E; 0.5 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene; used tubes were treated with cleaning solution, NH_4OH and rinsed with water; 0.04 g. of iodine (insufficient).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	2.1	0.148
Methyl acetate	14.2	1.00
Acetic acid and Methyl iodide	154.1	10.85
o-Chlorotoluene	3.3	0.34
m,p-Chlorotoluene	1.5	
Methane[d]	—	

Table IX (continued)

K. Run No. 88-A; 0.5 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene; tube washed with detergent and water (Procedure 1, page 72).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	9.1	0.239
Methyl acetate	38.1	1.00
Acetic acid[e]	27.6	0.72
Methane[d]	13.5	0.35
o-Chlorotoluene	44.5	1.70
m,p-Chlorotoluene	20.1	

L. Run No. 88-B; 0.5 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene; tube washed with *aqua regia* and water (Procedure 2, page 72).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	9.5	0.216
Methyl acetate	43.9	1.00
Acetic acid[e]	14.1	0.32
Methane[d]	15.1	0.34
o-Chlorotoluene	44.3	1.46
m,p-Chlorotoluene	19.8	

Table IX (continued)

M. Run No. 88-C; 0.5 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene; tube washed with alcoholic potassium hydroxide and water (Procedure 3, page 72).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	10.0	0.288
Methyl acetate	34.7	1.00
Acetic acid[e]	32.6	0.94
Methane[d]	13.5	0.39
o-Chlorotoluene	44.5	1.86
m,p-Chlorotoluene	19.9	

N. Run No. 88-E; 0.5 ml. of sample;[a] 0.314 M. peroxide in chlorobenzene; tube washed with <u>aqua regia</u>, NH_4OH and water (Procedure 4, page 72).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	8.5	0.219
Methyl acetate	38.8	1.00
Acetic acid[e]	25.7	0.66
Methane[d]	13.1	0.34
o-Chlorotoluene	47.0	1.71
m,p-Chlorotoluene	19.5	

Table IX (continued)

O. Run No. 92-A; 1.0 ml. of sample;[a] ~0.3 M. peroxide in chlorobenzene (40 percent by voluem) and carbon tetrachloride (60 percent).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	5.8	0.270
Methyl acetate	21.5	1.00
Acetic acid and other acetyl cpds.	27.5	1.28
Methane[d]	5.3	0.25
o-Chlorotoluene	16.4	1.06
m,p-Chlorotoluene	6.4	
Methyl chloride	90.0	4.19

P. Run No. 92-B; 1.0 ml. of sample;[a] ~0.3 M. peroxide in chlorobenzene (25 percent by volume) and carbon tetrachloride (75 percent by volume).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	5.7	0.256
Methyl acetate	22.3	1.00
Acetic acid and other acetyl cpds.	16.6	0.74
Methane[d]	3.3	0.15
o-Chlorotoluene	6.9	0.44
m,p-chlorotoluene	2.9	
Methyl chloride	114.3	5.13

Table IX (continued)

Q. Run No. 95-A; 1.0 ml. of sample;[a] ~0.2 M. chloroacetyl peroxide in carbon tetrachloride.

Products	Percent of observed products[b]	Ratio relative to chloromethyl chloroacetate[c]
1,2-Dichloroethane	31.0	2.23
Chloromethyl chloroacetate	13.9	1.00
Chloroacetic acid (?)	6.2	0.45
Trichloromethyl chloroacetate	24.0	1.73
Methylene chloride	74.5	5.36
Unknown	5.5	0.40

R. Run No. 99-A; 1.0 ml. of sample;[a] ~0.3 M. peroxide in carbon tetrachloride.

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	4.8	0.225
Methyl acetate	21.3	1.00
Acetic acid and/or other acetyl cpds.	9.0	0.42
Methane[d]	3.4	0.16
Methyl chloride	135.0	6.34

Table IX (continued)

S. Run No. 120-A; 1.0 ml. of sample;[a] 0.277 M. peroxide in chlorobenzene; 0.321 M. in iodine; *t*-butylbenzene as internal standard.

Products	Percent yield[f]	Ratio relative to methyl acetate[c]
Ethane[d]	1.5	0.089
Methyl acetate	16.8	1.00
Acetic acid and Methyl iodide	158.9	9.46
Methane[d]	0.0	0.0
Total observed	97.8	

T. Run No. 120-B; 1.0 ml. of sample;[a] ~0.3 M. peroxide in carbon tetrachloride; 0.0821 g. of iodine; *t*-butylbenzene as internal standard.

Products	Percent yield[f]	Ratio relative to methyl acetate[c]
Ethane[d]	2.0	0.118
Methyl acetate	16.9	1.00
Acetic acid and/or other acetyl cpds.	8.1	0.48
Methyl chloride[d]	9.3	0.55
Methyl iodide	128.1	7.58
Methane[d]	0.0	0.0
Total observed	91.6	

Table IX (continued)

U. Run No. 121-C; 1.0 ml. of sample;[a] 0.277 M. peroxide in chlorobenzene; *t*-butylbenzene as internal standard.

Products	Percent yield[f]	Ratio relative to methyl acetate[c]
Ethane[d]	4.7	0.338
Methyl acetate	13.9	1.00
Acetic acid[e]	29.7	2.14
o-Chlorotoluene	26.6	2.68
m,p-Chlorotoluene	10.6	
Methane[d]	9.3	0.67
Total observed	56.7	

V. Run No. 121-D; 1.0 ml. of sample;[a] 0.28 M. peroxide in carbon tetrachloride; *t*-butylbenzene as internal standard.

Products	Percent yield[f]	Ratio relative to methyl acetate[c]
Ethane[d]	4.9	0.232
Methyl acetate	21.1	1.00
Acetic acid or other acetyl cpds.	6.3	0.30
Methyl chloride[d]	132.6	6.28
Methane[d]	trace	trace
Total observed	95.5	

Table IX (continued)

W. Run No. 126-A; 1.0 ml. of sample;[a] 0.277 M. peroxide in chlorobenzene; 0.206 M. in iodine; at end of reaction part of solution not colored by iodine.

Products	Percent yield[f]	Ratio relative to methyl acetate[c]
Ethane[d]	2.4	0.127
Methyl acetate	18.9	1.00
Acetic acid and Methyl iodide	147.2	7.79
Methane[d]	0.0	—
Total observed	95.9	

[a] See page 19 for explanation of significance of sample volume.

[b] (Moles of product/mole of peroxide decomposed) × 100, assuming moles of peroxide decomposed is represented by the total of the observed products.

[c] Moles of product/mole of methyl acetate produced.

[d] Only the dissolved gases were determined.

[e] Possibly includes a small amount of other acetyl compounds.

[f] Absolute yields as obtained using t-butylbenzene as an internal standard.

spectrometer model A-60. Absolute yields were determined in some experiments using t-butylbenzene as an internal standard.

IODINE CONSUMPTION EXPERIMENTS

Iodine uptake at low iodine concentrations. — A solution of a known ratio of concentrations of iodine and acetyl peroxide in chlorobenzene was prepared by dissolving a weighed amount of iodine (1.295 g.) in chlorobenzene (50.0 ml.) 0.1079 M. in peroxide. An all glass hypodermic syringe (5.0 ml.) fitted with a device to allow delivery of reproducible sample volumes (1.992 ± .001 ml.) was set and calibrated by titration of peroxide stock solution. Two samples delivered at this syringe setting were reduced with sodium iodide and acetic acid in hot isopropanol (41) and the free iodine present titrated with standardized sodium thiosulfate solution (the same batch of thiosulfate solution was used throughout this experiment), yielding the sum of the iodine and peroxide concentrations. From the ratio and sum of their concentrations the solution was determined to be 0.1015 M. in iodine and 0.1072 M. in peroxide.

Into each of several constricted culture tubes (100 × 13 mm.) was placed the same volume (1.992 ml.) of the above iodine and peroxide solution. These samples were carefully degassed using three freeze-thaw cycles, and the tubes sealed (10^{-4} mm. of Hg) at the constriction. The peroxide was decomposed at 90.8-90.9° in a manner analogous to that used in the infrared kinetic runs (42) and the points analyzed concurrently. Each tube was washed repeatedly with Reagent Grade isopropanol, the tubes opened and sample plus tube placed in an erlenmeyer flask (250 ml.) containing isopropanol (50 ml.), the peroxide reduced with excess iodide (41) and the total free iodine present titrated with standardized thiosulfate. This yielded the decrease in the iodine plus peroxide content as a function of time.

Rate constants and iodine uptake. — Since the initial concentrations of both iodine and peroxide are known and since only iodine remains at the infinity point (12 half-lives), the average number of moles of iodine consumed per mole of peroxide decomposed ($\Delta I_2/\Delta P$) can be calculated directly. The consumption of iodine ($\Delta I_2/\Delta P$) obtained from the decomposition of 0.1072 M. acetyl peroxide in chlorobenzene 0.1015 M. in iodine was 0.71.

If it is assumed that the rate of iodine consumption is constant throughout the entire run, it is possible to calculate from the following relationship (see Appendix A) the ratio of the concentration of peroxide at time, t, to the initial peroxide concentration.

$$P_i/P_o = [V_i - V_\infty]/[V_o - V_\infty]$$

Where: P_o = peroxide concentration at time, t_o

P_i = peroxide concentration at time, t_i

V_o = volume of thiosulfate used to titrate sample pulled at time, t_o

V_i = volume of thiosulfate used to titrate sample pulled at time, t_i

V_∞ = volume of thiosulfate used to titrate sample pulled at time, t_∞

Thus, the apparent rate constants for the disappearance of peroxide can be calculated individually or an average value can be obtained graphically (see Figure I) from the first order rate expression: $\ln(V_i - V_\infty/V_o - V_\infty) = -kt.$

EFFECT OF DEUTERATION ON PRODUCT RATIOS

Ratio of methyl acetate to methyl iodide from acetyl peroxide and acetyl peroxide-d_6. — The decomposition of acetyl peroxide and acetyl peroxide-d_6 in chlorobenzene containing iodine was run in parallel experiments by the following procedure: Iodine (0. 1 g.) was weighed into a constricted culture tube (13 × 100 mm.) and dissolved in 1 ml. of a solution of peroxide in chlorobenzene (0. 1 M. in benzene). The tubes were attached to a vacuum line (10^{-3} mm. of Hg), degassed using three freeze-thaw cycles and sealed. The sealed sample tubes were then heated for six or more hours (10 half-lives) in a constant temperature bath at 93-94°.

The ratio of methyl acetate to methyl iodide and methyl acetate-d_6 to methyl iodide-d_3 were determined by v. p. c. analysis on a $\frac{1}{4}$" × 12' β, β'oxydipropionitrile column. The response of the thermal conductivity detector to ester and iodide was determined using known mixtures of benzene and either methyl acetate or methyl iodide. It was assumed that deuteration did not markedly affect the thermal conductivities.

Relative yields of methyl acetate and methyl acetate-d_6 and of methyl iodide and methyl iodide-d_3. — A solution containing a known ratio of acetyl peroxide and acetyl peroxide-d_6 in chlorobenzene was prepared by pipetting 0.585 M. acetyl peroxide (4 ml.) and 0.788 M. acetyl peroxide-d_6 (4 ml.) into a volumetric flask (10 ml.) and diluting the mixture to volume with chlorobenzene (d_6/h_6 = 1.35). This mixture of peroxides was used in each of the three following experiments:

1) Iodine (0.979 g.) was weighed into a flask (5 ml.) having a 10/30 Ŧ joint. To this was added chlorobenzene (2 ml.) and the mixture of acetyl peroxide and acetyl peroxide-d_6 (3 ml.). The flask was then attached to a vacuum line, the solution degassed using three freeze-thaw cycles and the flask sealed under vacuum (10^{-3} mm. of Hg). The sample was heated in a constant temperature bath at 92.5° for 10 half-lives to insure complete decomposition of the peroxides.

2) A duplicate was run using a different weight of iodine (0.982 g.).

3) Styrene (2 ml.) and the chlorobenzene solution of acetyl peroxide and acetyl peroxide-d_6 (3 ml.) was pipetted into a flask (5 ml.). The sample was degassed, sealed and decomposed as in experiment 1.

Small samples of the final reaction mixture from the above experiment were separated by v.p.c. on a $\frac{1}{4}$'' × 12' β,β-oxydipropionitrile column. In the iodine scavenged experiments both the methyl iodide (d_3 and h_3) and the methyl acetate (d_6 and h_6) fractions from the v.p.c. were collected in U-tubes cooled in Dry Ice-acetone. In the styrene scavenged experiment, the methyl acetates were collected.

These v. p. c. fractions were transferred to breakseal ampoules used for mass spectrometric analysis, degassed using three freeze-thaw cycles and the ampoules sealed (10^{-4} mm. of Hg).

The mass spectrometer used in the analyses was a Consolidated Electrodynamics Mass Spectrometer. The relative ratios of deuterated to undeuterated material were determined from the mass spectra with the aid of calibration spectra of known mixtures of either esters or iodides.

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In the iodine uptake experiment (43, 44) the sum of the iodine and acetyl peroxide concentration was followed as a function of time. The data thus obtained were evaluated in terms of an apparent rate constant for the decomposition of peroxide by use of the following relationship:

$$\ln\left(\frac{V_i^{I_2} - V_\infty^{I_2}}{V_0^{I_2} - V_\infty^{I_2}}\right) = -k_{\text{app.}}\ t_i \qquad (68)$$

where V^{I_2} = Sum of the concentration of iodine and peroxide remaining in the samples at time t_0, t_i . . . t_∞.

Equation 68 represents the relationship (Equation 69)

$$\ln\left(\frac{[Ac_2O_2]_i}{[Ac_2O_2]_0}\right) = -kt_i \qquad (69)$$

for the treatment of the first order decomposition process, if the iodine consumption ($\Delta I_2/\Delta P$) is constant throughout the decomposition. The fraction of peroxide remaining at time t_i and the quantity assumed to represent it in equation 68 are related by the following:

$$\frac{[Ac_2O_2]_i}{[Ac_2O_2]_0} \times \frac{(1 + f_i)}{(1 + f_0)} = \frac{V_i^{I_2} - V_\infty^{I_2}}{V_0 - V_\infty^{I_2}} \qquad (70)$$

$$\text{where } f_i = \left(\frac{\Delta I_2}{\Delta P}\right)_{\text{from } t_i \text{ to } t_\infty} = \frac{[I_2]_i - [I_2]_\infty}{[Ac_2O_2]_i}$$

$$f_0 = \left(\frac{\Delta I_2}{\Delta P}\right)_{\text{from } t_0 \text{ to } t_\infty} = \frac{[I_2]_0 - [I_2]_\infty}{[Ac_2O_2]_0}$$

Thus, if $\Delta I_2/\Delta P$ is a constant throughout the decomposition, equations 68 and 69 are identical. Equation 70 follows directly from the nature of the quantities measured:

$$f_i = \frac{[I_2]_i - [I_2]_\infty}{[Ac_2O_2]_i} \quad (71)$$

So: $$[Ac_2O_2] fi = [I_2]_i - [I_2]_\infty \quad (72)$$

and since: $$[Ac_2O_2]_\infty = 0 \quad (73)$$

and $$V_i^{I_2} = [Ac_2O_2]_i + [I_2]_i \quad (74)$$

$$V_\infty^{I_2} = [I_2]_\infty \quad (75)$$

Therefore: $$V_i^{I_2} - V_\infty^{I_2} = [I_2]_i - [I_2]_\infty + [Ac_2O_2]_i \quad (76)$$

Substitution of equation into equation gives:

$$V_i^{I_2} - V_\infty^{I_2} = f_i[Ac_2O_2]_i + [Ac_2O_2]_i = (1 + f_i)[Ac_2O_2]_i \quad (77)$$

Thus: $$\frac{V_i^{I_2} - V_\infty^{I_2}}{V_0^{I_2} - V_\infty^{I_2}} = \frac{(1 + f_i)}{(1 + f_0)} \times \frac{[Ac_2O_2]_i}{[Ac_2O_2]_0} \quad (78)$$

II. THE PHOTOSENSITIZED DECOMPOSITION OF ACETYL PEROXIDE IN SOLUTION

INTRODUCTION

The decomposition of acetyl peroxide by direct ultraviolet irradiation in the solid phase, in the liquid phase and in solution (cyclohexane and ethanol) was reported in 1937 by Walker and Wild (1). The gaseous products they observed were the same for photochemical and thermal decompositions (ethane, methane, O_2, CO and CO_2); however, the yield of ethane was generally higher in the photochemical decompositions.

The photosensitized decomposition of dilute solutions of acetyl peroxide has been reported by Szwarc and Luner (2). They found that benzene, anthracene and naphthacene sensitized the fragmentation. Preliminary quantitative experiments, in isoöctane solutions, with anthracene as sensitizer and irradiation only with 3660 Å light, showed that the rate of carbon dioxide evolution was independent of anthracene concentration above 1.5×10^{-4} M. anthracene, corresponding to 99 percent or more absorption of incident light. A threefold increase in the ethane yield was found for the sensitized decomposition at 25° relative to thermolysis at 80° in isoöctane. It was concluded that the anthracene sensitized and thermal decompositions were mechanistically similar. The increase in the ethane yield was ascribed to the effect of temperature on the geminate recombination processes; and since the production of methyl acetate in the "cage" reaction was unknown to Szwarc at that time, the yield of ester was not determined.

The question of the multiplicity of the donor and the mechanism of energy transfer was not considered.

RESULTS AND CONCLUSIONS

A number of aromatic hydrocarbons and ketones were found to photosensitize the decomposition of acetyl peroxide in chlorobenzene at 30°. The results are given in Table I. Szwarc's mechanistic rationalization (2) of the marked increase in the yield of ethane in the anthracene sensitized decomposition relative to thermolysis at 80° (both in isoöctane), is incompatible with the results in Table I. If the temperature dependence of geminate recombination processes (3) were the major factor determining the yield of "cage" products, then all the sensitizers should yield the same ratio of ethane to methyl acetate. Crude photosensitized (dibromoanthracene) and thermal decompositions were conducted at approximately 60°, and the ratio of the "cage" products were still markedly different. Braun (4) has recently reported a study of the effect of temperature on the yields of ethane and methyl acetate from acetyl peroxide finding that while the yield of methyl acetate is little effected the ethane yield decreases as the decompositions are carried out at lower temperatures. Thus, both the yield of ethane and the ratio of ethane to methyl acetate should be lower at 25° than at 80°. The observed effect of temperature on the yield of the "cage" products probably results from the activated character of the decarboxylation of acetoxyl radicals. Braun (4) estimates that the energy of activation for decarboxylation of an acetoxyl radical is about 6 kcal/mole. This further information renders Szwarc's explanation insufficient.

TABLE I

Products of the Sensitized Decomposition of Acetyl Peroxide in Chlorobenzene at ~30° Relative to Methyl Acetate by N. m. r.

Sensitizer	Exp. No.	Obs. Ethane[a]	Methyl Acetate	Acetic Acid[b]	Chloro-toluenes	Obs. Methane[a]	Remarks	
							Filter	Vol.[c]
Chlorobenzene	70-A	2.00	1.00	3.00	2.99	1.13	290 mμ	1.0
Benzophenone	78-A-1	1.89	1.00	59.1	33.7	6.63	338	0.5
2-Acetonaphthone	78-A-3	1.40	1.00	11.8	10.4	2.08	"	0.5
Benzil	76-B	1.44	1.00	20.5	8.54	3.15	290	0.5
Pyrene	127-B	1.51	1.00	—	—	—	330	1.0
Anthracene	78-A-5	1.37	1.00	2.55	1.66	0.36	338	0.5
9, 10-Dibromo-anthracene[d]	119	1.32	1.00	—	—	—	330	1.0
Thermal	121-C	0.338	1.00	2.14	2.68	0.67	—	1.0

[a] Only material dissolved in solvent was observed.

[b] May include a small amount of acetyl compounds other than methyl acetate or acetic acid.

[c] See page for explanation of importance of sample volume.

[d] Decomposition run at 60°.

Correlation of "primary" decarboxylation with sensitizer energy: As is shown in Figure I, the ratio of the observed ethane to methyl acetate yields appears to be dependent on the triplet state energy of the sensitizer. Methyl acetate and ethane are the products of geminate recombinations (5), which require one or two decarboxylations respectively. The ratio of their yields, thus, reflects the extent of "primary" decarboxylation (decarboxylation occurring simultaneously with 0-0 bond scission and/or in the "cage"). The poor fit of the ketone sensitizers (see Figure I), benzil and 2-acetonaphthone, probably result from the low "yield" (see Table III) of ethane in these experiments and from the use of half milliliter sample volumes (6), both of which tend to reduce the fraction of the ethane produced which is observed by the n.m.r. analytical procedure. It, therefore, appears that the extent of "primary" decarboxylation in the sensitized decomposition of acetyl peroxide is determined at least in part by the excitation energy of the donor.

The extremely high ratio of non-"cage" to "cage" products for the ketone sensitized decompositions (see Table I) suggests that another process ("photoinduced" decomposition), which does not produce the normal cage products, is also involved to a significant extent in these decompositions.

Mechanism of energy transfer and the subsequent decomposition: The lowest excited singlet state for acetyl peroxide is probably of considerably higher energy than the lowest excited singlet states of the sensitizers (1, 2). Singlet energy transfer from the

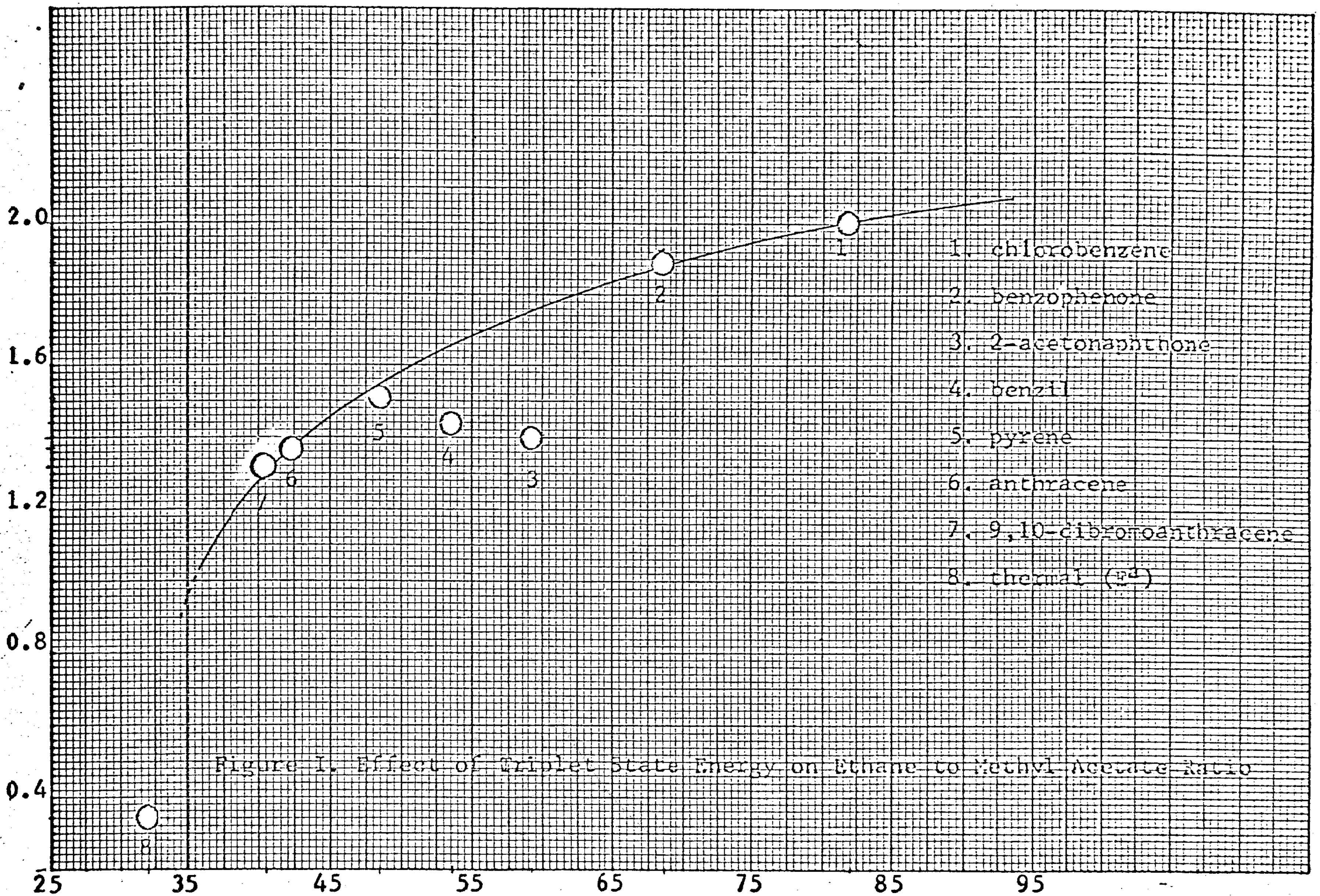


Figure I. Effect of Triplet State Energy on Ethane to Methyl Acetate Ratio sensitizer to the peroxide appears unlikely from an energetic standpoint. The transfer of triplet energy would also be inefficient unless there is a low energy triplet state of the peroxide. Unfortunately, no studies have been conducted to establish the energy of the lowest triplet state of acetyl peroxide. However, relatively unlikely processes are at least conceivably of import, because of the relatively long lifetimes of triplet states in solution.

One such relatively inefficient process (7) that has been recently documented, is the excitation of ground state cis-stilbene to a triplet state of non-cisoid configuration by sensitizers which do not possess sufficient energy to excite cis-stilbene to its spectroscopic triplet state. The rate of this excitation is less than diffusion controlled, presumably because movement of atoms occurs during the energy transfer process. Because this type of process is not in accord with the Franck-Condon principle, it has been termed "non-vertical energy transfer."

The view that the donor in the peroxide decomposition is the triplet state of the sensitizer, is supported by the observed dependence of the extent of "primary" decarboxylation on the triplet state energy of the sensitizer. Such a correlation indicates that if a low energy triplet state of the peroxide is produced, it is dissociative, at least in the energy range we have studied. If the triplet state of peroxide did not fragment immediately, the excess vibrational energy should be lost too efficiently to permit observation of any differences between the various sensitizers (e.g., the solution irradiation of azomethane with various wavelength light produces no "hot" methyl radical) reactions (8).

In the energy range we have studied (82-40 kcal/mole), the overall reaction of excited sensitizer with peroxide to produce ground state acetoxyl radicals and sensitizer is exothermic. Therefore, the extent of "primary" decarboxylation must be determined by some process before vibrational relaxation can deactivate the system. This can be accomplished if some decarboxylation occurs either by fragmentation of the initially formed species (e.g. "hot" acetoxyl radicals) at a rate competitive with vibration deactivation or simultaneously with energy transfer (multibond cleavage).

The production of vibrationally excited acetoxyl radicals can be responsible for the energy control phenomenon if the relative rates of deactivation and decarboxylation vary with the excess vibrational energy in such a manner that increasing the excess energy favors decarboxylation. Such a process may be represented as follows:

$$\begin{array}{rcl} T_{S^*} + Ac_2O_2 & \longrightarrow & S + (\overline{2\,AcO\cdot^*})^{T?} \\ AcO\cdot^* & \longrightarrow & AcO\cdot \\ " & \longrightarrow & CH_3\cdot + CO_2 \end{array}$$

and effectively:

$$\begin{array}{rcl} (\overline{2\,AcO\cdot^*}) & \longrightarrow & \overline{2\,AcO\cdot} \\ " & \xrightarrow{\text{and/or}} & \overline{AcO\cdot + CO_2 + CH_3\cdot} \\ " & \xrightarrow{\text{and/or}} & \overline{CH_3\cdot + 2\,CO_2 + CH_3\cdot} \end{array}$$

Due to the rapidity of deactivation and decarboxylation of "hot" acetoxyl radicals, little or no diffusive separation of the "hot" radicals should have occurred prior to production of these geminate radical pairs.

A simple mechanistic picture of an energy transfer process that produces acetoxyl radicals whose degree of vibrational excitation reflects primarily the energy of the sensitizer is shown in Figure II. The peroxide is treated in Figure II as having a dissociative triplet state. Assuming that the σ-electrons of the 0-0 bond are unpaired in the transfer, one possible representation of this state is as a continuation of the portion of the Morse curve describing van der Waal's repulsion between the oxygens as their separation is decreased. Since recombination of acetoxyl radicals does not appear to occur in the thermolysis (8), a finite activation energy for this process is indicated in Figure II.

To obtain a correlation which is independent of every feature (e.g. separation of the vibrational levels of the ground state) of the donor except triplet energy, essentially all of the triplet state energy must be transferred.

The above treatment accommodates this requirement if the Franck-Condon principle is extended to include non-vertical energy transfer. Thus the efficiency of energy transfer should decrease as the process becomes more non-vertical since more movement of nuclei will be involved. Each sensitizer with a triplet state energy below that required for vertical energy transfer will choose

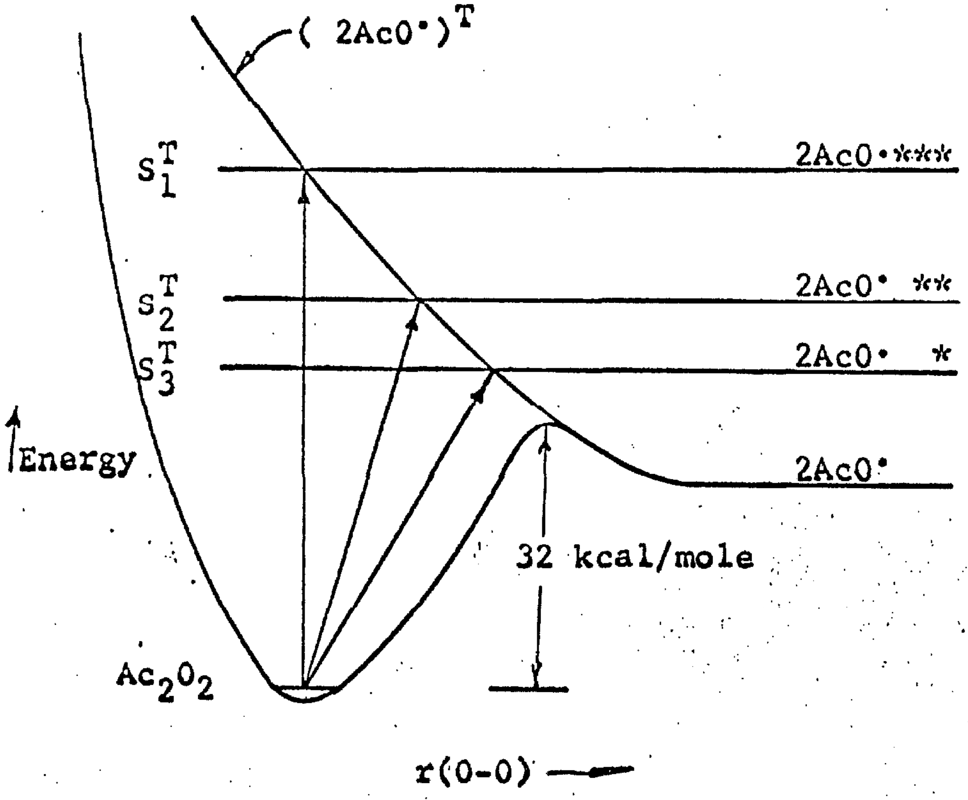


Figure II. O-O Bond Distance versus Energy predominately the process in which the least movement of nuclei is required. The energetically most efficient process possible, in each case, will require *all* of the donor's energy. This predicts that the rate constants for energy transfer from the excited sensitizer to peroxide *may* depend on the triplet state energy of the sensitizer, and that sensitizers with energies above that required for a vertical transfer process (i. e. unpairing of δ-electrons in 0-0 bond without movement of nuclei) may give ethane to methyl acetate ratios which vary considerably depending on other characteristics of the donor.

According to this mechanism, in the non-vertical energy transfer range the acetoxyl radicals will initially possess an amount of excess vibrational energy which is related to the triplet state energy of the donor.

An alternative explanation of the correlation of the triplet state energy with the ethane to methyl acetate ratio, is concurrent energy transfer and multibond cleavage. Where multibond cleavage is demonstrable kinetically, as in the thermolysis of phenylacetyl peroxide (9), there is a dramatic increase in the extent of "primary" decarboxylation (1, 2-diphenylethane to benzyl phenylacetate is approximately 4. 0) relative to the thermolysis (10) of acetyl peroxide (ethane to methyl acetate is approximately 0. 4). Therefore, if the energy of the sensitizer determines the relative importance of one, two and three bond breaking in the energy transfer step, a correlation with energy would be mandatory. The caged pairs produced by the following paths should be free to produce their characteristic quantities of the cage product(s), essentially independent of sensitizer after energy transfer:

$$\begin{array}{llll} T_{S*} & + \ Ac_2O_2 & \xrightarrow{k_1} & \overline{2\,AcO\cdot \ + \ S} \\ '' & \quad '' & \xrightarrow{k_2} & \overline{AcO\cdot \ + \ S} \\ & & \xrightarrow{k_2} & \overline{Me\cdot \ + \ CO_2 + Me\cdot \ + S} \end{array}$$

It has been concluded that C—C bond cleavage does not compete with simple 0-0 bond cleavage in the thermolysis of acetyl peroxide in chlorobenzene at ~90° (11). Thus two and three bond scission processes probably have higher activation energies than the 0-0 bond cleavage process; this is consistent with the estimates of 5-6 kcal/mole activation (4, 8) for the decarboxylation of acetoxyl radicals. In the range of sensitizer triplet state energies we have studied (40.2-81.9 kcal/mole) the overall reaction of excited sensitizer with peroxide to produce ground vibrational state radical fragments and sensitizer is exothermic. The triplet state energy control of the extent of "primary" decarboxylation can, therefore, be viewed as resulting from the reduced discrimination as the exothermicity of processes is increased.

There exists a spectrum of possibilities between the extremes of multibond cleavage where vibrational relaxation is much faster than subsequent reactions, and simple 0-0 bond scission where fragmentation of initially "hot" acetoxyl radicals competes with deactivation.

Mechanism of the "photoinduced" decomposition: A major mode of destruction of peroxide which does not produce normal caged pairs seems necessary for the ketone sensitized decompositions. The ratio of ethane to methyl acetate in the ketone sensitized decompositions fits fairly well into the triplet state energy correlation. However, the relative yields of acetyl compounds other than methyl acetate (predominately acetic acid) are significantly higher for the ketone-sensitized photolyses.

The most consistent explanation of the production of acetic acid in thermolysis of acetyl peroxide in aromatic solvents is that it is a product of radical chain induced decomposition (12). Some solvent derived induced decomposition in both the ketone and aromatic hydrocarbon sensitized photolyses is expected. However, there is no reason to suppose that the extent should vary greatly with sensitizer. Under the conditions of our experiments, the ketone sensitizers generally destroy peroxide at a rate considerably slower than any of the hydrocarbons except chlorobenzene. Since the chlorobenzene experiment yields results analogous to the other hydrocarbons, such rate effects cannot be important in determining the extent of induced decomposition. The mere presence of the ketones themselves in the reaction mixtures is also unimportant, because concentrations of the ketones such as are used in the sensitized photolysis do not significantly affect the course of the thermolysis (see Table II). Two mechanisms for the "photoinduced" decomposition are considered on the following page.

TABLE II

Product Ratios in the Thermolysis of Acetyl Peroxide (0.314 M.) in Chlorobenzene at ~91° by N.m.r.: 0.5 ml. Samples[a]

Run No.	78-B_1[d]	78-B_2[e]	78-B_3[f]	78-B_4
Products				
Ethane[b]	0.24	0.22	0.22	0.26
Methyl acetate	1.0	1.0	1.0	1.0
Acetic acid[c]	2.08	2.39	0.57	2.53
Chlorotoluenes	2.61	2.78	1.73	3.03
Methane[b]	0.41	0.37	0.40	0.44

[a] Entries are moles of product relative to mole of methyl acetate. The same stock solution of peroxide was used unless otherwise noted all sample tubes were sealed and approximately of the same total volume (2 ml.).

[b] Only the dissolved gases were determined.

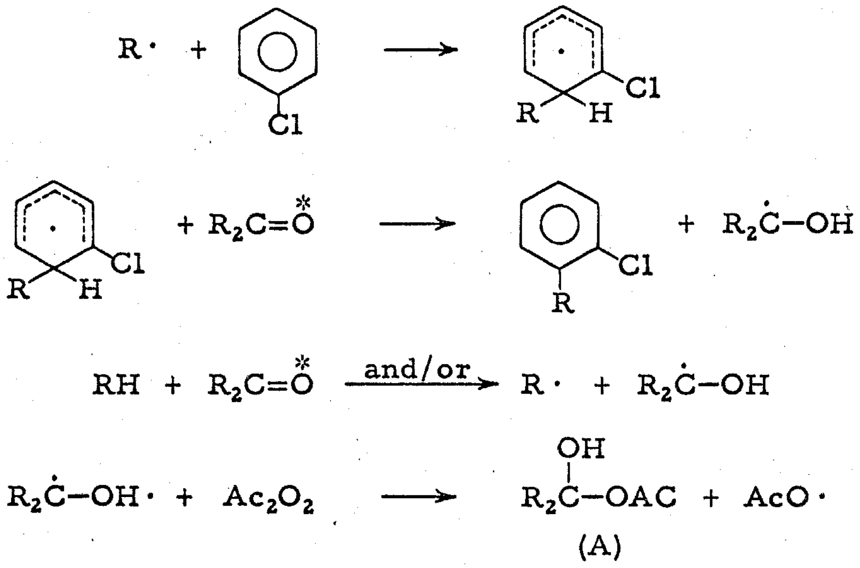
[c] Possibly includes a small amount of other acetyl compounds.

[d] Containing also 0.0135 g. of benzophenone.

[e] Containing also 0.0107 g. of benzil.

[f] Containing also 0.0098 g. of 2-acetonaphthone.

Mechanism I:



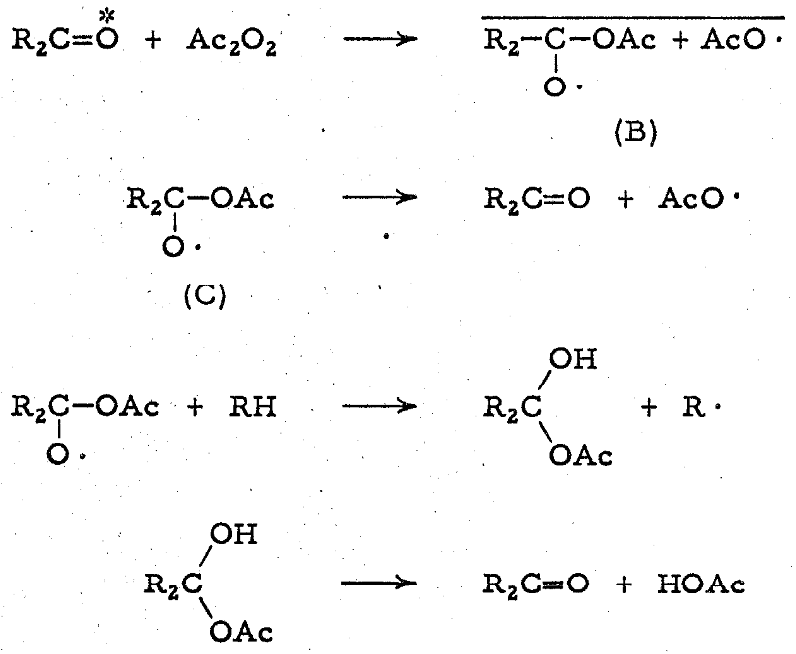
$$RH + R_2C{=}\overset{*}{O} \xrightarrow{\text{and/or}} R\cdot + R_2\dot{C}{-}OH$$

$$R_2\dot{C}{-}OH\cdot + Ac_2O_2 \longrightarrow R_2\overset{OH}{\overset{|}{C}}{-}OAC + AcO\cdot$$

(A)

$$R_2\overset{OH}{\overset{|}{C}}{-}OAc \longrightarrow R_2C{=}O + HOAc$$

Mechanism II:



$$R_2C{=}\overset{*}{O} + Ac_2O_2 \longrightarrow \overline{R_2{-}\underset{O\cdot}{\underset{|}{C}}{-}OAc + AcO\cdot}$$

(B)

$$R_2\underset{O\cdot}{\underset{|}{C}}{-}OAc \longrightarrow R_2C{=}O + AcO\cdot$$

(C)

$$R_2\underset{O\cdot}{\underset{|}{C}}{-}OAc + RH \longrightarrow R_2C\genfrac{}{}{0pt}{}{OH}{OAc} + R\cdot$$

$$R_2C\genfrac{}{}{0pt}{}{OH}{OAc} \longrightarrow R_2C{=}O + HOAc$$

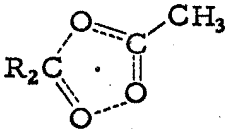
Mechanism I involves abstraction by the triplet state of the sensitizer of a hydrogen atom from one of the numerous products of free radical aromatic methylation (e. g. dihydrochlorotoluene) or from a cyclohexadienyl radical species (13). The light induced reduction of ketones involving the abstraction of an activated hydrogen, is normally an extremely efficient process (14), which should allow such processes to compete with energy transfer to peroxide. Hydrogen abstraction from cyclohexadienyl radicals by excited ketone, in a process analogous to radical-radical disproportionation, should be extremely facile; however, there is considerable doubt about the efficiency of their encounters. The next step, attack by the radical derived from the ketone on peroxide, is essentially the same as the chain carrying step discussed by Walling (15) for the induced decomposition of acetyl peroxide in primary and secondary alcohols. The hydroxyacetate (A) can regenerate sensitizer and produce the required acetic acid.

In mechanism II the excited sensitizer attacks the peroxide directly instead of transferring its triplet state energy. This process can be viewed as a displacement at the peroxidic oxygen atom by a triplet diradical. The resulting radical pair (B) would presumably separate by diffusion with little geminate recombination. The ketone-acetoxyl radical complex (C) could then fragment or abstract a hydrogen from the medium. The high yields of acetic acid from the ketone experiments are most easily accommodated if abstraction is the major mode of reaction for C. There is no compelling reason to expect acetoxyl radicals produced by the fragmentation of C to yield significantly more acetic acid than those produced by the thermolysis of acetyl peroxide.

Two alternative structures might also be suggested for the

$$R_2\dot{C}-O-OAc$$

(C')



(C'')

ketone-acetoxyl radical complex (C' and C'').

Considering the amount of data available at present no satisfying conclusions can be drawn concerning the mechanism of the "photoinduced" decomposition. However, mechanism I appears more likely.

EXPERIMENTAL

MATERIALS

Anthracene. — (Matheson, Coleman and Bell Reagent Grade) was used without purification.

9, 10-Dibromoanthracene. — Material prepared by Dr. K. R. Kopecky was chromatographed over rosite and recrystallized three times from carbon tetrachloride, m.p. = 219.2-219.8°.

Benzophenone. — (Matheson, Coleman and Bell Reagent Grade) was recrystallized twice from ether.

Pyrene. — This material was obtained pure from Dr. J. Saltiel, m.p. = 149.0-149.2°.

2-Acetonaphthone. — This material was obtained pure from Dr. J. Saltiel, m.p. = 54.1-54.6°.

Benzil. — This material was obtained pure from Dr. J. Saltiel, m.p. = 96.2-96.6°.

Chlorobenzene. — The purification of this material is described in Part I (16).

ACETYL PEROXIDE

The procedure used for the preparation and purification of the acetyl peroxide solutions in chlorobenzene which were used in these experiments is given in detail in Part I (17).

N. M. R. PRODUCT ANALYSES

New n. m. r. tubes (Varian A-60), were washed in a hot solution of Orvus (soluble detergent) in distilled water, rinsed five to ten times with distilled water, drained, air dried, and heated at 120-140° for a minimum of 24 hrs.

The sensitizers (except chlorobenzene) were weighed into the n. m. r. tubes prior to addition of peroxide solution. Into each tube was measured a sample of <u>the</u> peroxide solution (0.28 M. in acetyl peroxide), with a hypodermic syringe through a glass needle. The filled sample tubes were carefully attached to a vacuum line, degassed using at least three freeze-thaw cycles and sealed under vacuum (10^{-4} mm. of Hg).

The peroxide and sensitizer were then irradiated using a 450-watt Hanovia medium pressure mercury lamp. Various filter systems were used, each cutting off the reported absorption of acetyl peroxide. The sealed sample tubes were removed periodically to check the extent of decomposition. The product ratios were generally determined (see Table III) after complete decomposition of peroxide, by repeated upfield and downfield integration on a Varian n. m. r. spectrometer model A-60.

TABLE III

Products of the Photosensitized Decomposition of Acetyl Peroxide in Chlorobenzene at ~30° by N. m. r.

A. Run No. 70-A; 1.0 ml. of sample;[a] 0.277 M. peroxide in chlorobenzene; Pyrex glass filter (290 mμ).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	29.6	2.00
Methyl acetate	14.8	1.00
Acetic acid[e]	44.4	3.00
Methane[d]	16.7	1.33
o-Chlorotoluene	33.0	2.99
m,p-Chlorotoluene	11.2	

2.99

B. Run No. 78-A-1; 0.5 ml. of sample;[a] 0.277 M. peroxide in chlorobenzene; 0.01083 g. of benzophenone; Corning 052 filter (338 mμ).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	3.6	1.89
Methyl acetate	<1.9	1.00
Acetic acid[e]	112.3	59.1
Methane[d]	12.6	6.63
o-Chlorotoluene	42.6	33.7
m,p-Chlorotoluene	21.5	

33.7

Table III (continued)

C. Run No. 78-A-3; 0.5 ml. of sample;[a] 0.277 M. peroxide in chlorobenzene; 0.01153 g. of 2-acetonaphthone; Corning 052 filter (338 mμ).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	10.9 (8.6)*	1.40
Methyl acetate	7.8 (6.1)	1.00
Acetic acid[e]	91.9 (72.1)	11.8
Methane[d]	16.2 (12.8)	2.08
o-Chlorotoluene	55.0 (43.5)	10.4
m,p-Chlorotoluene	26.4 (20.9)	

10.4

*Absolute yields as determined using 2-acetonaphthone as an internal standard.

D. Run No. 76-B; 0.5 ml. of sample;[a] 0.277 M. peroxide in chlorobenzene; 0.02244 g. of benzil; pyrex filter (290 mμ).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	7.8	1.44
Methyl acetate	5.4	1.00
Acetic acid[e]	110.5	20.5
Methane[d]	17.0	3.15
o-Chlorotoluene	32.5	8.54
m,p-Chlorotoluene	13.6	

8.54

Table III (continued)

E. Run No. 127-B; 1.0 ml. of sample;[a] 0.277 M. peroxide in chlorobenzene; 0.00480 g. of pyrene; U-glass filter (330 mμ).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	—	1.51
Methyl acetate	—	1.00
Acetic acid[e]	—	—
Methane[d]	—	—
o-Chlorotoluene	—	—
m,p-Chlorotoluene	—	—

F. Run No. 78-A-5; 0.5 ml. of sample;[a] 0.277 M. peroxide in chlorobenzene; 0.00471 g. of anthracene; Corning 052 filter (338 mμ).

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	29.4	1.37
Methyl acetate	21.5	1.00
Acetic acid[e]	54.9	2.55
Methane[d]	7.8	0.36
o-Chlorotoluene	23.3	1.67
m,p-Chlorotoluene	12.5	

1.67

Table III (continued)

G. Run No. 119; 1.0 ml. of sample;[a] 0.277 M. peroxide in chlorobenzene; 0.00540 g. of 9,10-dibromoanthracene; U-glass filter (330 mμ); ~60°.

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	—	1.32
Methyl acetate	—	1.00
Acetic acid[e]	—	—
Methane[d]	—	—
o-Chlorotoluene	—	—
m,p-Chlorotoluene	—	—

H. Run No. 121-C; 1.0 ml. of sample;[a] 0.277 M. peroxide in chlorobenzene; thermolysis at ~91°.

Products	Percent of observed products[b]	Ratio relative to methyl acetate[c]
Ethane[d]	4.7*	0.34
Methyl acetate	13.9	1.00
Acetic acid[e]	29.7	2.14
Methane[d]	9.3	0.07
o-Chlorotoluene	26.6	2.68
m,p-Chlorotoluene	10.6	

2.68

*Absolute yields determined using t-butyl benzene as an internal standard.

[a] For significance of sample volume see page 19, Part I.

[b] Total observed methyl groups in products assumed to represent initial amount of peroxide; products containing one methyl group based on 200 percent and products containing two methyl groups based on 100 percent.

[c] Moles of product to mole of methyl acetate observed.

[d] Only the material dissolved in the solvent are observed.

[e] May include some acetyl compound other than acetic acid or methyl acetate.

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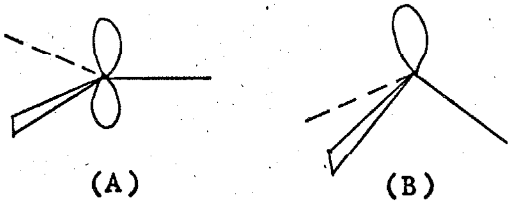
(17) This Dissertation, p. 59.

PROPOSITION 1

THE CONFIGURATION OF ALIPHATIC FREE RADICALS

Abstract: Investigation of the stereochemistry of geminate scavenging reactions is proposed. It is hoped that the results will be interpretable in terms of the configuration of aliphatic free radicals studied.

Considerable attention has been given to the question of the configuration at the trivalent carbon of an aliphatic free radical (1). There are two basic configurations to consider: planar (A)-sp^2 (bonding electrons) and p (odd electron); or "pyramidal" (B)-sp^3 (all electrons). However, any non-planar form would be pyramidal and potentially asymmetric, while the planar form would be symmetric.

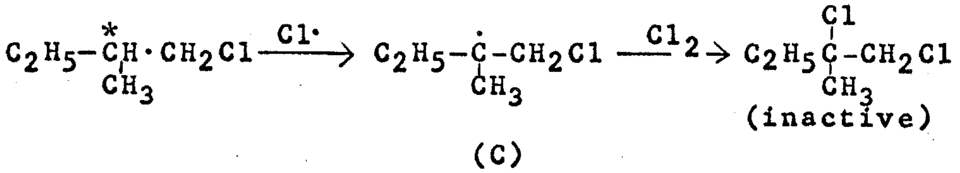

(A) (B)

It has been suggested from theoretical considerations that the methyl radical should be non-planar, with H-C-H bond angles somewhere between 120° and the H-N-H bond angles of ammonia. The energy difference between the planar and pyramidal (non-planar) forms of radicals should be less than in the case of either carbonium ions or carbanions and the barrier to inversion considerably <u>less</u> for the methyl radical than for ammonia (2).

Vacuum ultraviolet spectroscopic studies (3) of the methyl radical indicate "that in the ground state the molecule [CH_3] is not planar but does not deviate much from a planar structure". Tentatively, Herzberg sets the deviation from planarity at less than 10°. The proton and carbon-13 hyperfine splitting of the electron paramagnetic resonance absorption of the methyl radical have been determined (4) and compared with the calculated angular dependence of the hyperfine interactions. The proton hyperfine splitting excludes deviation from planarity greater than 10 to 15°. Unfortunately, the relationship between ground state configuration and carbon-13 hyperfine splittings, which McConnell used so elegantly to demonstrate the planarity of the methyl radical, has been seriously questioned (5).

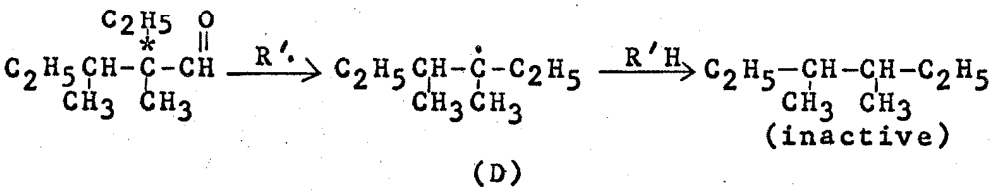
Chemical evidence concerning the configuration of free radicals has generally come from studies of the ability of the trivalent carbon to support optical activity. For example, attempts to prepare optically active phenyl-*p*-biphenyl-α-naphylthioglycolic acid with triphenylmethyl radicals (6), or by resolution of this stable radical by chromatography on various optically active column packings (7), yielded only <u>inactive</u> material.

Furthermore, reactions proceeding <u>via</u> "kinetically free" radicals at an optically active center in a molecule appear to result in <u>loss</u> of activity at the reaction site. Chlorination of (+)1-chloro-2-methylbutane <u>via</u> the 1-chloro-2-methyl-2-butyl radical (C) gave inactive



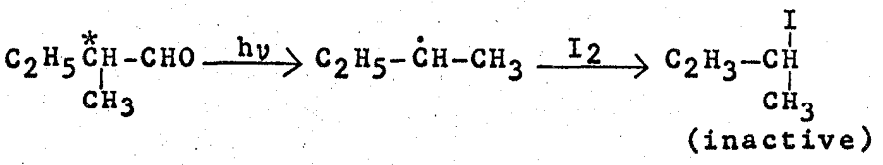
$$C_2H_5-\underset{CH_3}{\overset{*}{C}H}\cdot CH_2Cl \xrightarrow{Cl\cdot} \underset{(C)}{C_2H_5-\underset{CH_3}{\dot{C}}-CH_2Cl} \xrightarrow{Cl_2} \underset{\text{(inactive)}}{C_2H_5\overset{Cl}{\underset{CH_3}{C}}-CH_2Cl} \qquad (1)$$

1, 2-dichloro-2-methylbutane (8). Decarbonylation of (-) methylethylisobutylacetaldehyde with di-<u>t</u>-butyl peroxide <u>via</u> the methylethylisobutylmethyl radical (D) yields



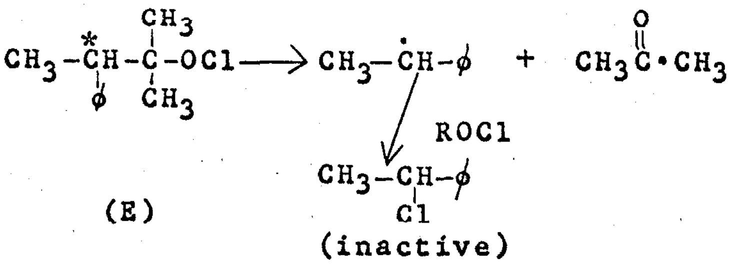
$$C_2H_5\underset{CH_3}{CH}-\overset{C_2H_5}{\underset{CH_3}{\overset{*}{C}}}-\overset{O}{\overset{\|}{C}}H \xrightarrow{R'\cdot} \underset{(D)}{C_2H_5\underset{CH_3}{CH}-\underset{CH_3}{\dot{C}}-C_2H_5} \xrightarrow{R'H} \underset{\text{(inactive)}}{C_2H_5-\underset{CH_3}{CH}-\underset{CH_3}{CH}-C_2H_5} \qquad (2)$$

inactive 2,4-dimethylhexane (9). In addition, the photolysis of optically active 2-methylbutanal in the presence of iodine (10) and the chain decomposition of E yields



$$C_2H_5\underset{CH_3}{\overset{*}{C}H}-CHO \xrightarrow{h\nu} C_2H_5-\dot{C}H-CH_3 \xrightarrow{I_2} \underset{\text{(inactive)}}{C_2H_3-\overset{I}{\underset{CH_3}{CH}}} \qquad (3)$$

inactive alkyl halides (11).



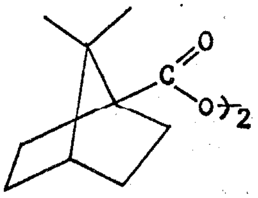
$$CH_3\text{-}\overset{*}{C}H(\phi)\text{-}C(CH_3)_2\text{-}OCl \longrightarrow CH_3\text{-}\dot{C}H\text{-}\phi + CH_3\overset{O}{\overset{\|}{C}}\cdot CH_3 \qquad (4)$$

$$CH_3\text{-}\dot{C}H\text{-}\phi \xrightarrow{ROCl} CH_3\text{-}CH(Cl)\text{-}\phi$$

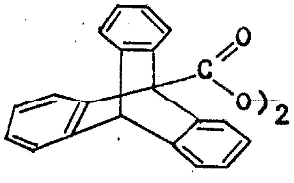
(E) (inactive)

As predicted by Walsh (12) from theoretical consideration many examples of loss of optical activity are observed for reactions proceeding _via_ free radicals.

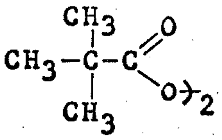
In contrast to carbonium ions, bridgehead free radicals can be formed quite readily (13). Some dramatic differences are observed when apocamphoyl (F) or tripyoyl (G) peroxide is compared with open chain aliphatic diacyl peroxides such as pivaloyl peroxide (H). The considerably greater thermolysis rate of pivaloyl peroxide (H) relative to acetyl peroxide is associated with formation of the _t_-butyl radical in the _rate-determining_ step. No such acceleration present in the thermolysis of (F) and (G); their decomposition rates are hardly greater than acetyl peroxide's. This absence of multibond cleavage to form the bridgehead radicals directly suggests that these



(F)



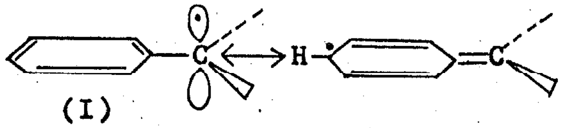
(G)



(H)

radicals are not very stable. However, the intermediate acyloxy radicals do decarboxylate and products derived from them are observed. For example; F yields nearly 40% of 1-chloroapocamphane for decomposition in carbon tetrachloride. The differences in the ease of formation and reactivity of _t_-butyl and these bridgehead radicals has been ascribed in large part to the preference of aliphatic radicals to be planar (14).*

In view of the probably small energy difference between planar and pyramidal radical forms, it would not be surprising if both types of radicals were important. Certainly, radicals with extensive resonance stabilization (I) should be planar, and the work on the methyl radical is not inconsistant with it being planar. However, in

e.g.  (5)

(I)

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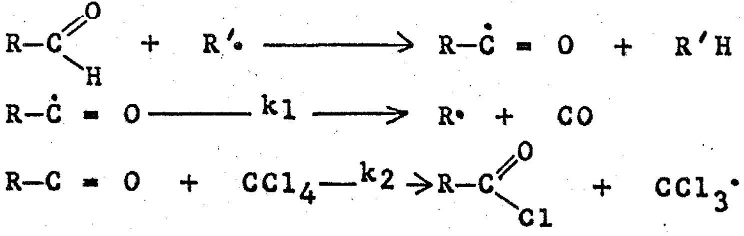
*This conclusion is somewhat less convincing in view of some recent work of Applequist's, on the relative rate of decarbonylation and chlorine abstraction from carbon tetrachloride of several aliphatic acyl radicals. He compared a series of open chain aldehydes and found that the relative rates (assuming all R-C = O react with carbon

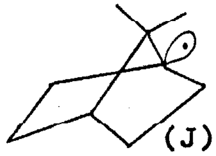


$$R-\overset{O}{\underset{H}{C}} + R'\cdot \longrightarrow R-\dot{C}=O + R'H$$

$$R-\dot{C}=O \xrightarrow{k1} R\cdot + CO$$

$$R-C=O + CCl_4 \xrightarrow{k2} R-\overset{O}{\underset{Cl}{C}} + CCl_3\cdot$$

other systems such as cyclic and bicyclic the situation may favor non-planar species. In the case of the bridgehead radical, 1-apocamphyl (J) the trivalent carbon can hardly be other than pyramidal.



(J)

In the case of non-cyclic systems, such as t-butyl, it would not be unreasonable to expect a preference for a planar configuration; and the experiments with potentially optically active free radicals as "kinetically free" entities seems perfectly consistent with that view. The partial retention of optical activity (via a center which presumably is the trivalent carbon of a radical) in the "cage" products of the decomposition of optically active diacyl peroxides (15) requires further comment (Eq. 6).

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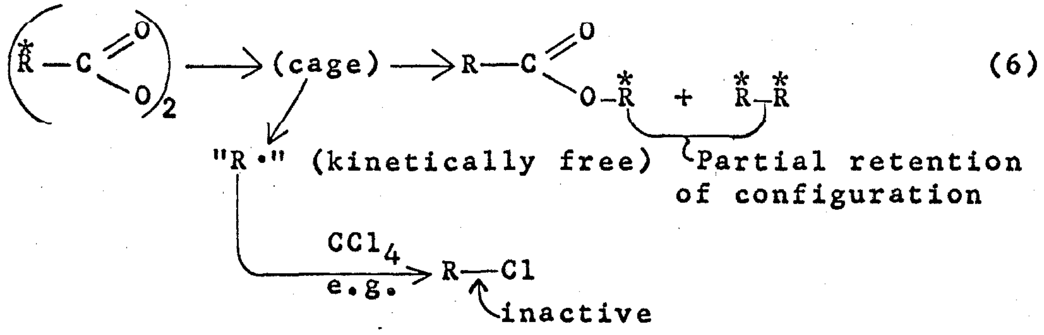
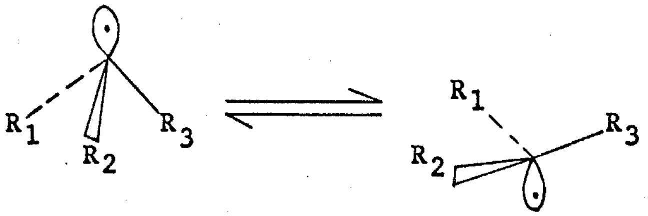
tetrachloride at the same rate) of decarbonylation correlated with stability of the alkyl radical. Several bridgehead aldehydes, 1-adamantanecarboxaldehyde, 1-norbornanecarboxaldehyde and bicyclo [2.2.2] octane-1-carboxaldehyde, were compared as well. The results indicate that the 1-adamantyl radical and the 1-bicyclo [2.2.2] octyl radical are more stable than the t-butyl radical, while the 1-bicyclo [2.2.2] heptyl radical is somewhat less stable than the n-propyl radical. These results seem to suggest that slightly non-planar radicals (an asymmetric species) are not necessarily very unstable relative to the corresponding planar radical.


(6)

Obviously, simple planar radicals interacting and reacting randomly, in the solvent "cage" would be expected to yield products completely racemic at the radical site. Rationalization of the observed results can be acceptably accomplished with several mechanisms.

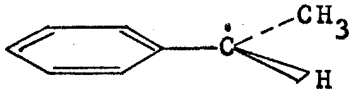
One mechanism accounts for the retention of configuration in the ester by invoking a competing <u>ionic</u> rearrangement to ester <u>via</u> an acylalkylcarbonate which is stereospecific and a non-stereospecific radical recombination pathway. Since such ionic processes have been demonstrated (16) to compete with radical decomposition in some cases this explanation is not wholly unreasonable. One drawback to this mechanism is that optical activity is also retained in the alkyl-alkyl coupling product (17), for which <u>no</u> non-radical pathway appears likely. Another more satisfying proposal still involving planar radicals, requires that geminate recombination is not a random process but that coupling can compete with the rotation of the alkyl radical in the cage. Thus, cage recombination occurs with a preference for retention of configuration due to the original formation of the radicals face to face (18).

This observed preference for retention of configuration could *also* be explained by assuming that the alkyl radical is *non*-planar and that its rate of inversion is competitive



(7)

with geminate recombination. Such a mechanism could yield the partial retention of configuration observed and since this would require an extremely rapid inversion rate the reaction of the "kinetically free" radicals would be *expected* to yield racemic material, as observed. A major difficulty with the non-planar radical mechanism is that the phenylmethylmethyl radical (K), which would be expected to be planar, due to resonance interaction with the phenyl



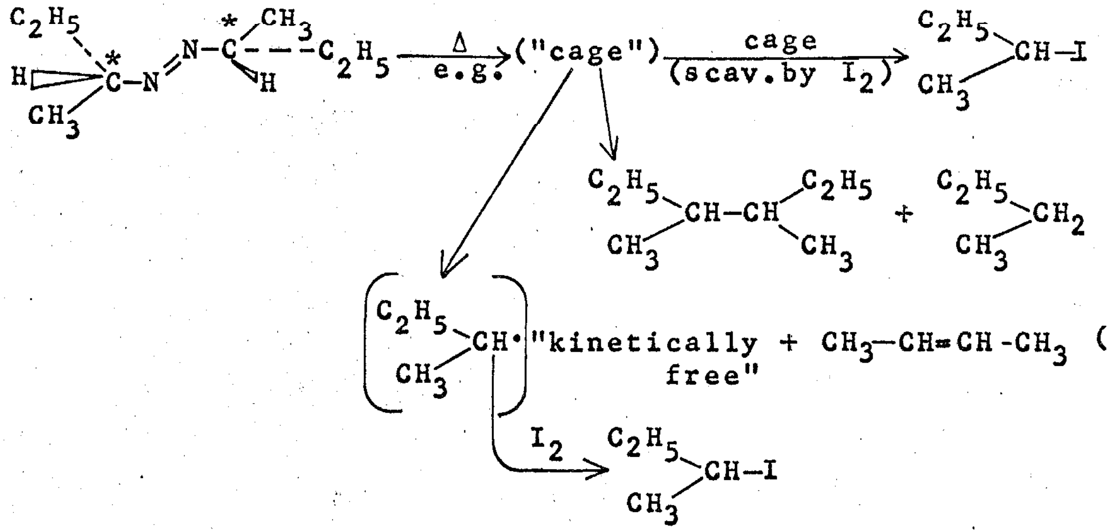
(K)

group, presumably produces only partially racemized "cage" products from the decomposition of hydrotropyl peroxide (17).

The stereochemistry of radical additions to olefins may also be related to the configuration of free radicals (19) but the treatment of that field is outside of the scope of this proposal.

It is proposed that the stereochemistry of geminate radical reactions be reinvestigated where the trivalent carbon of the alkyl radicals were asymmetric prior to homolysis. In particular the stereochemical course of geminate radical scavenging reactions could yield informative results.

The actual choice of a system to study may not be straightforward, however, the simple system azoisobutane-iodine (Eq. 8) should serve as a model on which to numerate the salient features of the proposal. Naturally, only if



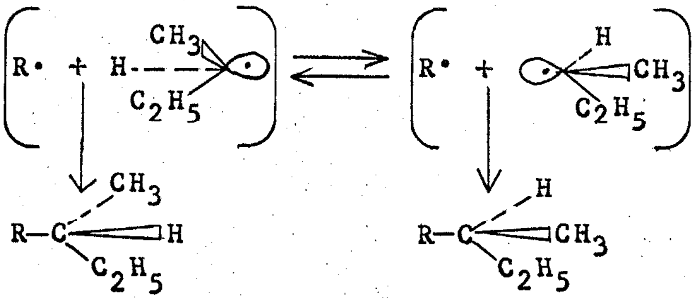
(8)

the geminate combination of the isobutyl radicals, from an optically active azoisobutane, was significantly stereospecific would there be any point to investigating azoisobutane further. Having demonstrated stereospecificity in the geminate formation of 2, 3-dimethylhexane and presumably the absence of stereospecificity in the formation of 2-iodobutane from "kinetically free" isobutyl radicals, the significant results would be how the stereospecificity of the 2, 3-dimethylhexane formation *via* geminate coupling and the stereospecificity of 2-iodobutane formation are affected by scavenging the geminate pairs to various extents with iodine.

Measurement of effect of the iodine concentration on the stereospecificity of 2, 3-dimethylhexane formation should be a very sensitive test of whether nearest-neighbor scavenging (20) is the sole mechanism for geminate radical trapping by scavenger. If as seems to be indicated by the work of Hammond and Waits (21), a radical pair is only and essentially 100% efficiently trapped when it is produced with a scavenger molecule for a nearest-neighbor, then the degree of stereospecificity in the geminate coupling process should be independent of the iodine concentration.

The 2-iodobutane would be examined for even *minor* optical activity at iodine concentration requiring extensive geminate scavenging. If the *secondary* butyl radical is planar or inverting much much faster than the coupling process and the partial retention of configuration in the 2-butyl-2-methylbutyrate from optically active 2-methylbutyl peroxide results from competitive coupling and rotation (within the "cage") of the radicals, then the 2-iodobutane might be expected to show a net inversion of configuration relative to the starting azo-compound. If the radicals are planar then some degree of shielding of the frontside of the radicals by the other radical of the pair might be expected to yield a net inversion of configuration in the 2-iodobutane by favoring backside attack.

However if the 2-butyl radical is non-planar and the stereospecificity of its "cage" reaction is due to recombination competing with inversion of the radicals (Eq. 9), then the 2-iodobutane should also show a net retention of

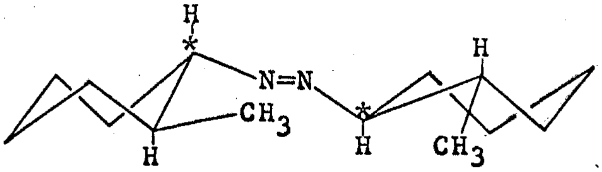


(9)

configuration since geminate scavenging of the "cage" radical(s) by a neighboring iodine molecule should be even better at competing with inversion than recombination.

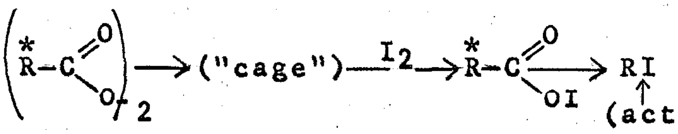
Having studied a radical like 2-butyl which is very likely to be planar (or inverting very much faster than geminate recombination), this method would then be extended to include other systems. For example cyclic systems, where the radical might be a non-planar species (L), should

e.g.



(L)

certainly be looked at. The acyl peroxides might also be used as sources for the geminate pairs if acyl hypoiodites yield racemic alkyl iodides.



(activity unknown)

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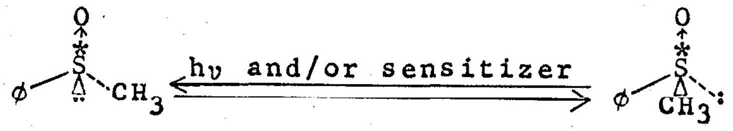
PROPOSITION 2

PHOTOCHEMICAL OPTICAL ISOMERISM OF SULFOXIDES AND RELATED COMPOUNDS

Abstract: It is proposed that optically active sulfoxides be prepared and their optical stability to ultraviolet irradiation and to suitable excited triplet state sensitizers be studied.

Racemization of an optically active sulfoxide induced photochemically, *via* either direct irradiation or triplet state sensitization (Eq. 1), would represent an example of a novel process, epimerization of an asymmetric center photochemically. The observed photoracemization of biphenyls (1) and *cis-trans* isomerization of Platinum(II) complexes (2) may be related processes.

e.g.

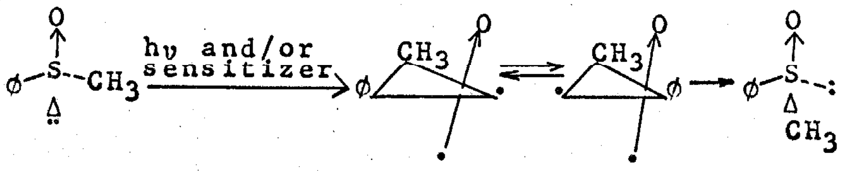


(1)

Several modes of optical-isomer interconversion can be envisioned. The most mundane mechanism would involve breaking and reforming a sulfur-carbon bond, to yield racemic sulfoxide. The more interesting possible mechanisms involve formation of a symmetric excited state, formation of interconvertable asymmetric electronic excited state or isomerization of a vibrationally excited ground state (3).

If reasonably long-lived asymmetric excited states, e.g., triplet states, are involved it may be possible to quench these excited states under suitable conditions. Reducing the isomerization rate _via_ quenching of excited states would suggest strongly the involvement of asymmetric electronic excited states which are either easily interconvertable or isomerized in a vibrationally excited ground state. Such electronic states _might_ be represented by the following:*

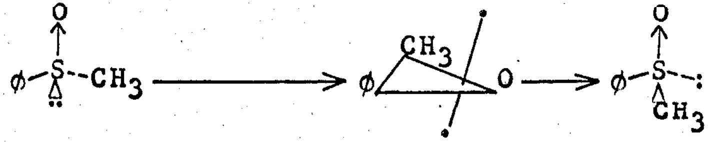
e.g.



(2)

or

asymmetric



(3)

symmetric

This representation of the asymmetric excited states assumes that the locus of electronic excitation is the asymmetric center and that it is an n-π state which is _not_ necessarily the case.

If asymmetric excited states are involved they may be potential doners of energy with a preference for one of the optical isomers in a racemic pair. Study of suitable quencher reactions might, therefore, show asymmetric induction with energy transfer.**

**Since the original submission of this proposition several papers concerning these processes or similar processes have been published (4, 5, 6).

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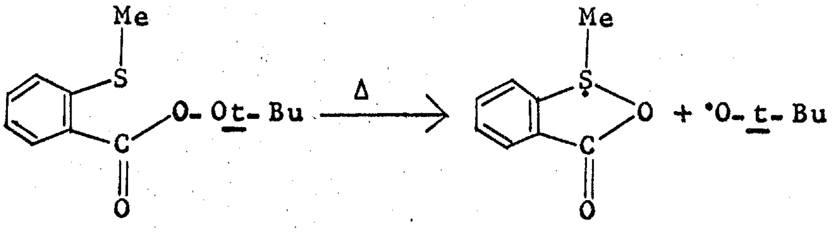
PROPOSITION 3

NEIGHBORING GROUP PARTICIPATION IN FREE RADICAL REACTIONS. NEIGHBORING SULFUR

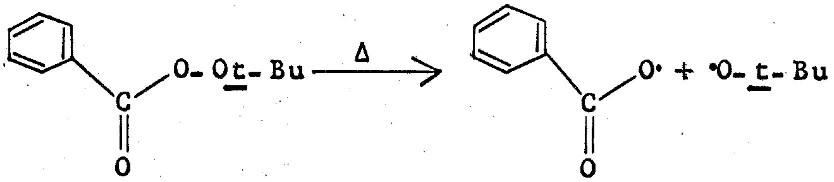
Abstract: A system and experiments are proposed to investigate the importance of neighboring group effects by sulfur in free radical reactions.

It has been suggested by Martin (1), that the neighboring divalent sulfur atom in t-butyl o-thiomethoxyperbenzoate (A) participates in the homolytic cleavage of the oxygen-oxygen bond in its thermolysis. Participation is invoked to explain a greatly enhanced rate of decomposition and a reduced carbon dioxide yield of A relative to unsubstituted t-butyl perbenzoate (C). A rate enhancing



(1)

(A) (B)



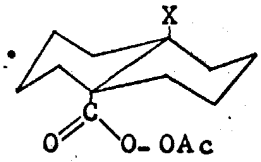
(2)

(C) (D)

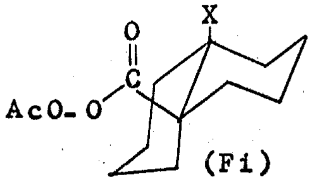
interaction by sulfur at oxygen which leads to formation of a bridged species (B), might account for the lower carbon dioxide from A than C. Comparison of the results of the thermolyses of A with C is not very satisfying or informative. However, the magnitude of the observed effects suggests that Martin's proposal may have merit and warrant further investigation.

It is proposed that neighboring group participation by sulfur be documented and some measure of the scope of the phenomenon obtained. To implement this it is suggested that the thermal decompositions of compounds such as Ei and Fi be studied.

e.g.



(Ei)



(Fi)

where:

E_1,X = RS-

E_2,X = $R\text{-}\overset{O}{\overset{\uparrow}{S}}\text{-}$

E_3,X = $R\text{-}\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\text{-}$

E_4,X = $R\text{-}CH_2\text{-}$

E_5,X = H-

F_1,X = RS-

F_2,X = $R\overset{O}{\overset{\uparrow}{S}}\text{-}$

F_3,X = $R\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\text{-}$

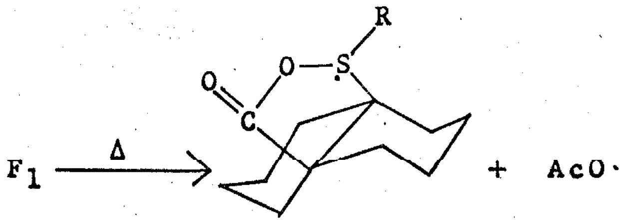
F_4,X = $R\text{-}CH_2\text{-}$

F_5,X = H-

This particular system, 9, 10-disubstituted decalin is not unique but it is representative of the type of system which could be employed. It is desired that the system be rigid to eliminate conformation transitions, allowing investigation of species of constrained geometry. Thus, in the *trans*-isomer, e.g., E_1, interaction between the 9-thioalkoxy group with the carboxylate oxygens would be impossible, while in the corresponding *cis*-isomer (F_1) participation or contact interaction by sulfur at either oxygen would be geometrically quite favorable. The two isomers differ vastly in geometry but factors such as inductive effects should be quite similar.

Another reason for chosing the decalin system was because Bartlett and Pincock (2) have shown that the *t*-butyl peresters of *cis*- and *trans*- 9-carboxydecalin, decarboxylate simultaneously with the oxygen-oxygen bond breaking process in their thermolyses. Thus, if F_1 produces a bridged intermediate (G) and as a result yields a smaller amount of carbon dioxide than E_1, then the participation by divalent sulfur at oxygen must occur in the transition state for decompositon and represent a quite favorable process.

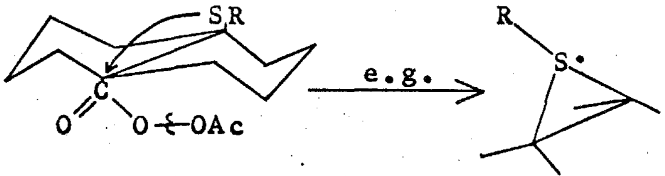
e.g.



(G)

(3)

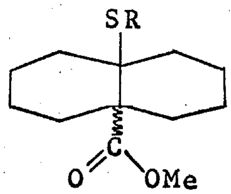
The standard tools (3) for kinetic examination of such a system for evidence of neighboring group participation, e.g., rate acceleration and activiation parameters require comparable systems where in one the investigated phenomenon is absent but otherwise the two quite similar. Thus, comparison of the products and kinetics of E_1 and F_1 should yield interesting results. In the case of the trans-isomer, however, the possibility of another mode of sulfur participation becomes possible due to geometry and the concerted character of thermolysis: sulfur participation in the formation of the carbon radical at the 9-position (Eq. 4).



(E_1) (H) $+ CO_2 + AcO\cdot$ (4)

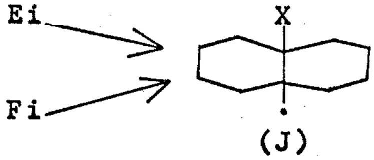
As a result of this possibility it is necessary to have other similar systems for comparison purposes; therefore the compounds E_1 through E_5 and F_1 through F_5 may also be of interest. For example, if F_1 (sulfide) and F_3 (sulfone) show markedly different rates, activation parameters (in particular $\Delta S^{\ddagger}$) and carbon dioxide yields, while E_1 and E_3 show similar results then the type of participation shown in Equation 4 probably is unimportant and oxidation of the sulfide to sulfone eliminates (or at least greatly reduces) sulfur's ability to participate effectively in the radical process. A comparison of the results from Ei and Fi should allow determination or estimation of most of effects operative in this system i.e., inductive effects, ring juncture efforts, steric effects, etc.

The choice of a unsymmetrical diacyl peroxide rather than a perester was in part necessitated by the eventuality that even if the cis-isomer (E_1) yield a bridged species (G) that it (G) would be a short-lived species due to the possibility that the decarboxylation step is energeticly very favorable. Therefore, unless a very efficient radical trap were nearby the proposed decrease in decarboxylation rate might go unobserved. Production of a geminate radical simultaneously with the one to be studied and one which had been investigated extensively seemed a reasonable approach. A comparison of yields of I from E_1 and F_1 should offer a more sensitive measure of the rate and extent of acyloxy radical decarboxylation than the carbon dioxide yield does.



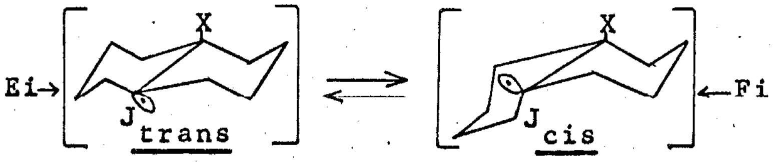
(I)

The isomeric diacyl peroxides, Ei (trans ring juncture) and Fi (cis ring juncture) are potential sources of the 9-(10-substituted) decalyl radical (J), which may be formed



(5)

in the primary process or later via decarboxylation of the acyloxy radicals derived from Ei or Fi. Whatever the nature of J or how it is formed, Ei is potentially a source of a trans-isomer (^{J} trans) of J and Fi a cis-isomer (^{J} cis). Whether, either ^{J}trans or ^{J}cis are stable isomers of the 9-(10-substituted) decalyl radical and what effect

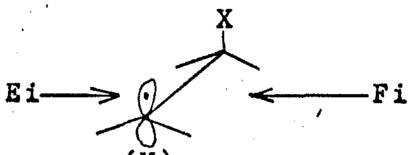


(6)

the 10-substituent has on their stability are important questions.

A tool by which the nature of J may be investigated is inherent in the design of Ei and Fi. This tool is provided by a multiple time scale phenomenon in the radical decomposition of these unsymmetrical diacyl peroxides, Ei and Fi, in solution.

Since the anticipate energy difference between a planar and a pyramidal arrangement at the trivalent carbon of a radical is small (5), there is some question as to whether the trivalent carbon (9-position) in J is planar or pyramidal. If the radical is planar K then both Ei and Fi should yield one and the same radical (K) in the absence of interference by the substituent in the 10-position. If



(K) (7)

a pyramidal form of the radical is more stable in the decalin ring system then $J_{\underline{\text{trans}}}$ and $J_{\underline{\text{cis}}}$ may be discrete species; however they should be interconvertible (Eq. 8).

$$\mathrm{Ei} \longrightarrow \underset{(L)}{\left[J_{\underline{\text{trans}}} \rightleftarrows J_{\underline{\text{cis}}} \right]} \longleftarrow \mathrm{Fi} \qquad (8)$$

The difference between a planar species (K) and two pyramidal species ($J_{\underline{\text{trans}}}$ and $J_{\underline{\text{cis}}}$) displays itself most dramatically before the pyramidal species are fully equilibrated. Thus in this case (Eq. 8) the stereoselectivity of reactions of L is a <u>time dependent</u> function, prior to establishment of equilibriums. The stereoselectivity of reactions of K should not be a time dependent phenomenon.

The unsymmetrical diacyl peroxides, Ei and Fi, were chosen in part because in solution it is possible to assign an order to the reaction products corresponding on the average to the time between formation of the radical and reaction. The average time interval between fragmentation and reaction in the case of geminate reactions is very short, however, the two major expected "cage" products from Ei and Fi each represents a separate interval of time (Eq. 9). Since decarboxylation of an acetoxyl radical is

e.g.

$$\begin{tikzcd} \mathrm{Ei} \arrow[r, "\Delta"] & \overline{J + CO_2 + AcO\cdot}^{\,*} \arrow[r] \arrow[d] & \underbrace{J_{\underline{cis}}\text{-OAc and/or } J_{\underline{trans}}\text{-OAc}}_{(M)} \\ & \overline{J + 2CO_2 + Me\cdot} \arrow[r] & \underbrace{J_{\underline{cis}}\text{-Me and/or } J_{\underline{trans}}\text{-Me}}_{(N)} \end{tikzcd} \qquad (9)$$

required for formation of a "cage" methyl radical (6) the formation of M will on the average represent interception of J sooner after fragmentation (primary) than N. Admittedly the difference in these time intervals is small. However, such a subtle technique may be needed for very

---

*A line over intermediates denotes "cage" species.

rapid reactions. Variation of the scavenger concentration in "inert" solvents offers a wide variation for the time interval between geminate separation and reaction for "kinetically free" radicals (Eq. 10). Thus under non-geminate scavenging conditions, O represents reaction of J after a longer time interval than the cage products.

e.g.

$$\text{Ei} \longrightarrow \text{"J"} \xrightarrow[\text{RX (scavenger)}]{} \underbrace{J_{\underline{cis}}\text{-X} + J_{\underline{trans}}\text{-X}}_{\text{(O)}} \qquad (10)$$

If J is planar and/or a single species is involved then to a first approximation** neither the source of J (i.e. from Ei or Fi) nor the interval between formation and reaction should effect the stereoselectivity of its reactions. Thus, similar isomer ratios (<u>cis</u> and <u>trans</u>) should be expected in the products M, N and O from both Ei or Fi. On the other hand if J is actually two or more radicals, e.g., pyramidal radicals, then the intermediate radical(s) might be trapped prior to establishment of equilibrium (Eq. 11), then differences in stereoselectivity will be

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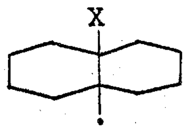
**Excluding consideration of non-random geminate processes, for example.

observed depending on whether the radical source is Ei or

$$J_{\underline{trans}} \rightleftharpoons J_{\underline{cis}} \qquad (11)$$

Fi and depending on the time interval between fragmentation and product formation. With the wide range of time intervals available in this system, it should be possible to differentiate between the situations where one radical best represents J and where more than one radical intermediate is involved. Unless full equilibration of $J_{\underline{trans}}$ and $J_{\underline{cis}}$ is obtained almost instantaneously (i.e. faster than geminate processes) our system, unsymmetrical diacyl peroxide, should allow interception of the non-equilibrated radicals if they are involved. In the situation where two pyramidal radicals are involved, a fairly good estimate of the rate of interconversion should be possible.

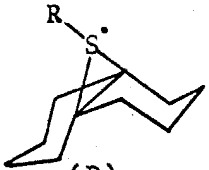
In evaluating the influence of the 10-substituent on the trivalent carbon in the 9-position, a comparison of results from the above treatment for various J's should be



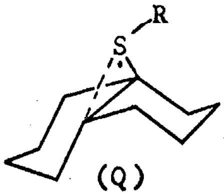
(J)

where: J^1, X = RS- J^4, X = R-CH_2-
J^2, X = $R\overset{O}{\overset{\uparrow}{S}}$- J^5, X = H-
J^3, X = R-$\underset{O}{\overset{O}{\overset{\uparrow}{S}}}$-

exceedingly informative. In the special case of neighboring sulfur, J^1, the intermediacy of bridged species, P or Q, would be expected if sulfur participates either in the



(P)



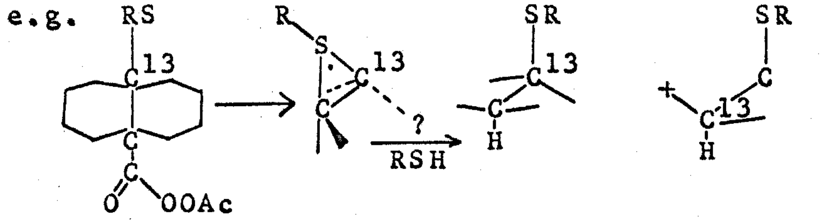
(Q)

transition state for primary fragmentation of E_1 (<u>trans</u>-isomer) or at carbon at all. Evaluation of data from E_1 and F_1 alone should decide whether one or more than one radical best represented the alkyl radical intermediate. From the results obtained in thiol additions to cyclic olefins (7), e.g., variation in the addition stereochemistry with thiol (scavenger) concentration, two or more radical intermediates are expected.

Deciding whether P or Q are involved and therefore participation by sulfur, can probably be done by comparing the systems producing J^1 through J^5. For example, both J^3 and J^4, where participation is unlikely, should be similar sterically to J^1, therefore, any major difference in the isomer ratios in M, N or O for J^1 relative to J^3 and J^4 would be indicative of involvement of bridged species. Given such a difference it might then be worthwhile to label the 9- or 10-position of the original peroxides with C^{14}

or C^{13} to see if a relatively symmetrical species such as P,

e.g.



(12)

which would very likely lead to RS-group migration, is involved.

It would be extremely interesting to run a thiol addition to an olefin, which produced the same intermediate radical as an unsymmetrical diacyl peroxide and compare the stereochemical results.

There are a number of other neighboring groups which might yield a great deal of interesting if not important results, if subjected to this sort of treatment. For example, study of the system where X = Br- should be relevant to the knotty question of the stereochemistry of HBr addition to olefins. The multiple time scale phenomenon in the radical decomposition of such unsymmetrical diacyl peroxides in solution, may be an almost universal tool for the study of radical intermediates.

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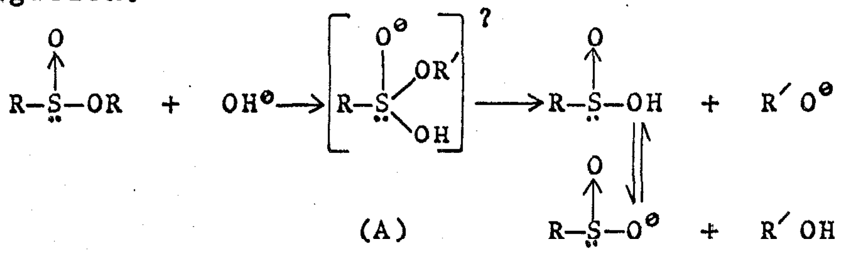
(6) This Dissertation, Part I.

PROPOSITION 4

d-ORBITAL EXPANSION OF SULFUR. NUCLEOPHILIC SUBSTITUTION AT SULFUR

Abstract: It is proposed that an attempt be made to determine whether *d*-orbital expanded sulfur species are involved as intermediates or as transition states in nucleophilic displacement reactions at sulfur. It is further suggested that the nucleophilic substitution reactions of esters of arenesulfinic acids, e.g., hydrolysis, appear particularly well suited for such a study.

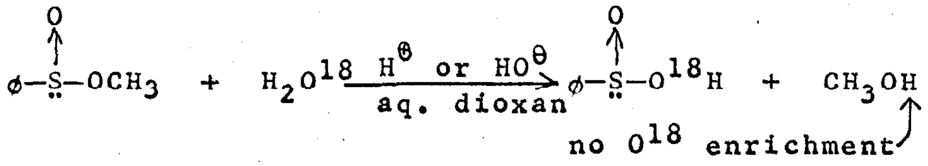
It has been suggested by various workers (1), that sulfur and other atoms have the ability to expand their valence shell when there are low lying vacant orbitals. In the case of sulfur these are the 3*d*-orbitals. The existence of compounds sulfur tetra- and hexafluoride and the nature of sulfur-oxygen "double" bonds demands that something akin to *d*-orbital expansion be invoked (2). In addition, it would be interesting to have some idea of the nature of the energy profile (3) for a process involving formation of a bond between two separate entities where valence shell expansion is required for bond formation. For example, the addition at sulfur of a nucleophile to a suitable sulfur compound, where the valence shell would be required to accommodate 10 electrons. Thus it might be informative to investigate a reaction where such a process could reasonably be expected to occur. Nucleophilic substitution reactions of arenesulfinate esters, especially basic hydrolysis (Eq. 1), appear admirably suited for such an investigation.



(1)

It has <u>not</u> been satisfactorily demonstrated whether nucleophilic substitution reactions of sulfinate esters are one step (S_N2) or two step (S_N1 or addition-elimination) processes (4). Demonstration of a two step, addition-elimination mechanism for the substitution process would suggest strongly that accommodation of extra electrons by expansion of sulfur's valence shell is an energetically favorable process.

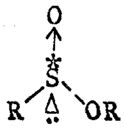
Hydrolysis of methyl benzenesulfinate (Eq. 2) has been shown by Bunton (5), using O^{18}-tracer techniques, to proceed exclusively <u>via</u> sulfur-oxygen bond cleavage (i.e. analogous to acyl-oxygen fission in carboxylic ester hydrolyses). The hydrolysis was carried out in O^{18} enriched water and the methanol formed was examined for O^{18} content. The absence



$$\phi-\overset{\overset{O}{\uparrow}}{\underset{\cdot\cdot}{S}}-OCH_3 + H_2O^{18} \xrightarrow[\text{aq. dioxan}]{H^{\oplus} \text{ or } HO^{\ominus}} \phi-\overset{\overset{O}{\uparrow}}{\underset{\cdot\cdot}{S}}-O^{18}H + \underset{\text{no } O^{18} \text{ enrichment}}{CH_3OH} \qquad (2)$$

of O^{18} enrichment in the methanol demonstrates exclusive sulfur-oxygen bond cleavage.

Stereochemistry can be included in the information collected concerning the reactions of sulfinate esters, since in contrast to planar carboxylic esters they are pyramidal (e.g. B) and have been resolved (6). Nucleophilic

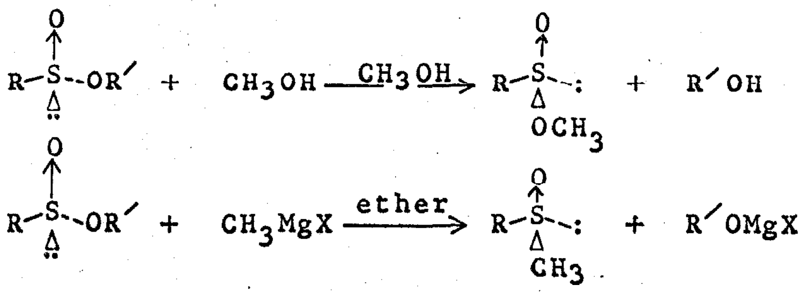


(B)

where: R = *p*-tolyl and R = *l*-menthyl

displacement reactions of these esters appear to consistently occur with *inversion* of configuration at sulfur, for example reaction with Grignard Reagents (7) and transesterification (8) proceed *via* inversion (Eq.s 3 and 4).

e.g.



$$R-\overset{\overset{O}{\uparrow}}{\underset{\Delta}{S}}--OR' + CH_3OH \xrightarrow{CH_3OH} R-\overset{\overset{O}{\uparrow}}{\underset{\underset{OCH_3}{\Delta}}{S}}--: + R'OH \qquad (3)$$

$$R-\overset{\overset{O}{\uparrow}}{\underset{\Delta}{S}}--OR' + CH_3MgX \xrightarrow{\text{ether}} R-\overset{\overset{O}{\uparrow}}{\underset{\underset{CH_3}{\Delta}}{S}}--: + R'OMgX \qquad (4)$$

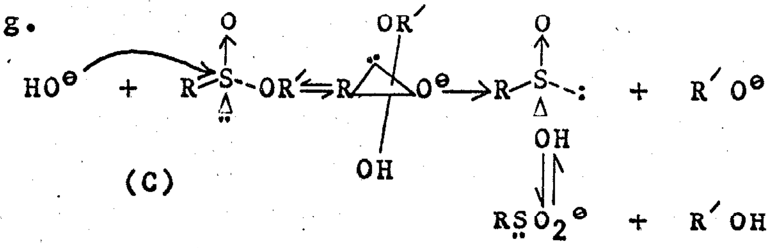
Reasoning by analogy the stereochemical course of hydrolysis is probably also *inversion* at sulfur, even though isomerization of the sulfinic acid *via* proton exchange makes it difficult to determine directly. Therefore, it would appear highly unlikely that hydrolysis or the reactions represented in equations 3 and 4 occurs by a dissociative pathway (S_N1) which should lose stereochemical distinctions; but involves attack by nucleophile on sulfur (however, the absence of dissociative processes in strong acid media (5) cannot be assured). Clearly basic hydrolysis of sulfinate esters occurs *via* nucleophilic attack on sulfur and if the nucleophile *adds* to the ester group, as is the case of carboxylic ester saponification (9), forming a discrete *intermediate* then d-orbital expansion will be required.

Having eliminated on S_N1 process there remains two other likely mechanism for basic hydrolysis, addition-elimination (Mechanism I) or S_N2 (Mechanism II). Here we

Basic Hydrolysis

Mechanism I:

e.g.

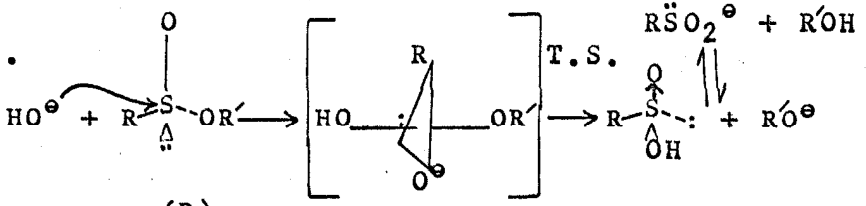


(C)

(5)

Mechanism II:

e.g.

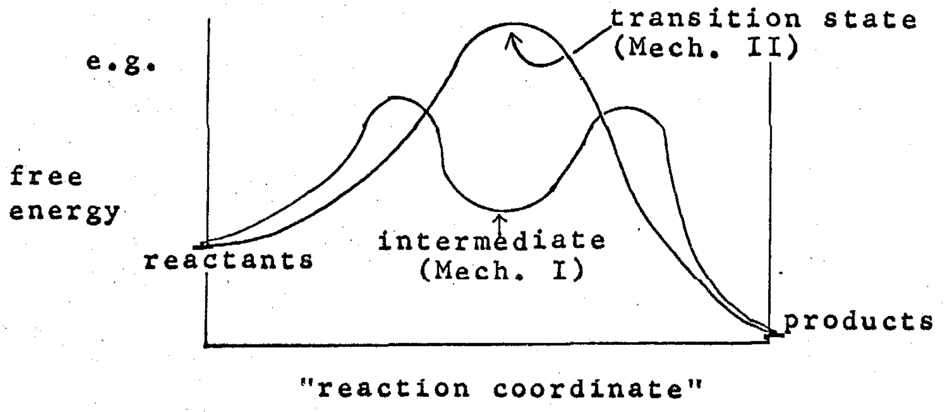


(D) (6)

have a system where it is highly probable that the bond making process involves valence shell expansion whether Mechanism I or II is in operation. Determination of which mechanism is operative would provide some idea of the energetics of a process where bond formation requires sulfur to accommodate extra electrons.

Mechanism II can be represented by a single peaked curve (Figure 1) which describes a steady increase in energy as the extent of bond formation increases up to a full bond. Little or no energy is gained as the extent of bond formation increases, where the expanded sulfur species is a transition state. However in Mechanism I, where an

e.g.



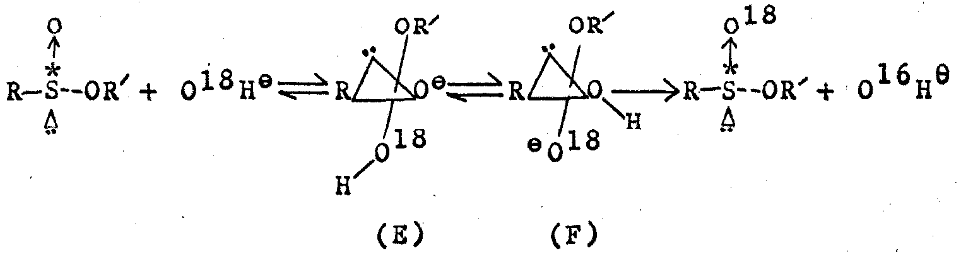
(Figure 1)

expanded sulfur intermediate is formed (Figure 1), some energy is gained as the extent of bonding between nucleophile and sulfur increases. As a result the energy does not increase monotonously with degree of bond formation and an intermediate, represented by the valley, is produced. Clearly a first order determination of the energetics of an expansion of sulfur can be obtained by ascertaining whether an intermediate is produced.

It is proposed that the basic hydrolysis of a sulfinic ester such as (l)menthyl (-)*p*-toluenesulfinate be studied in O^{18} enriched water. After extensive hydrolysis the remaining ester isolated and examined for incorporation of O^{18} and/or racemization.

Observation of O^{18} incorporation would strongly suggest an intermediate formed reversibly by hydroxide addition to ester, Mechanism I, since direct displacement would hardly be likely under basic conditions. As in the case of carboxylic ester saponification (8), only a fractional degree of competition between hydroxide and alkoxide elimination from the intermediate (e.g. C) and rapid proton transfer are required for O^{18} incorporation.

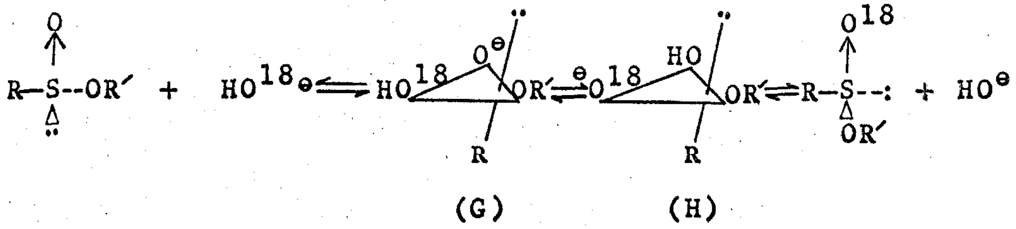
If O^{18} enrichment is observed then the stereochemical course of that process would be quite significant. Assuming the intermediate formed is represented by E, then proton transfer yields F where elimination of $HO^{16}\ominus$, from a radial position, would yield O^{18} enriched ester with



(7)

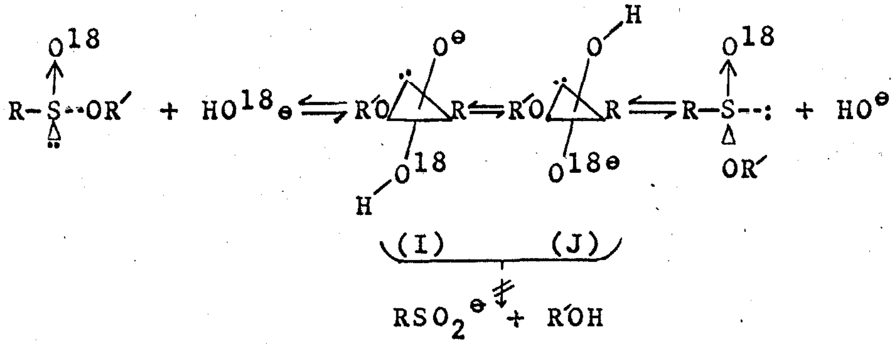
retention of configuration at sulfur. Thus by the principle of microscopic reversibility it would be expected that the addition process could equally well yield F (with O^{18}-label reversed) as E. Radial attack by nucleophile would occur with retention of configuration which is inconsistent with the results where the stereochemical course has been observed. Therefore, retention of configuration in the O^{18} incorporation process is not an expected result.

O^{18} incorporation with the expected inversion of configuration as the stereochemical course would require that HO^{18}-, R′O-, and $^{\ominus}O$- groups all occupy radial positions in the intermediate (G), that a mode of addition occurs which



(8)

does not even potentially lead to hydrolysis (Eq. 9), due to inappropriate geometry, or that the intermediate is not a trigonal bipyramide.



(9)

Having the results of the above studies, it should be possible to devise experiments, including substituent effects (resonance, inductive and steric) to elucidate the processes involved in detail.

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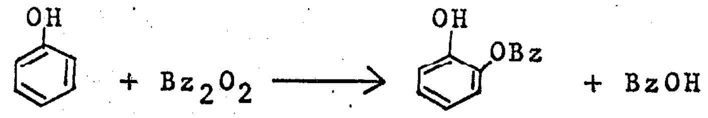
PROPOSITION 5

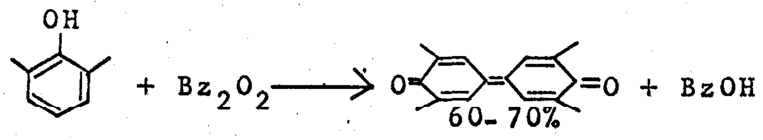
THE REACTION OF AMINES AND PHENOLS WITH ACYL PEROXIDES

Abstract: It is proposed that the reactions of acyl peroxides with amines and phenols be reinvestigated. Similarities in the reactions of these two classes of compounds with acyl peroxides suggests a basic mechanistic unity. Mechanisms are discussed.

The reaction of phenols and amines with acyl peroxide yield complex and varied products (Eq.s 1-10). Waters (1) studied the products from the reaction of various phenols with benzoyl peroxide (Eq.s 1-3) and interpreted the results



(1)



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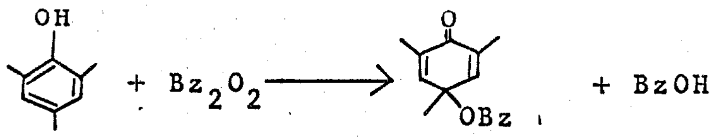
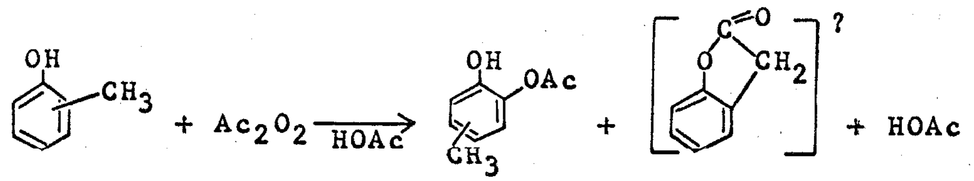


(3)

in terms of radical coupling and disproportionation reactions. Similar products were obtained from the reaction of acetyl peroxide with the isomeric cresol (Eq. 4) by Wesseley and Schinzel (2) and more recently by Walling and Hodgdon (3) for the reaction of phenol and acetyl peroxide (Eq. 5). Walling found no evidence of free radical formation in the reaction of acetyl peroxide with phenol. In fact the absence of effect on the kinetics and products of this reaction by scavenger, coupled with the absence of carbon dioxide evolution suggested to Walling that radicals are not involved. Observation of a small enthalpy of activation, a strongly negative entropy of activation, and a deuterium kinetic isotope effect (ϕOD-vs-ϕOH) on the rate, led Walling to suggest a "4-center" reaction mechanism for the first step (Eq. 6) and facile rearrangements to the observed product, B (Eq. 7). However, there is no direct evidence for the intermediacy of A. Bartlett (4) also studied the reaction of phenols (and amines as well) with benzoyl peroxide and even though addition of iodine, oxygen and vinyl monomer (e.g. stryene) to the reaction mixture



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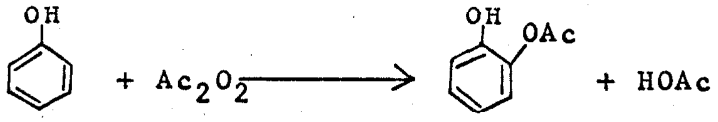
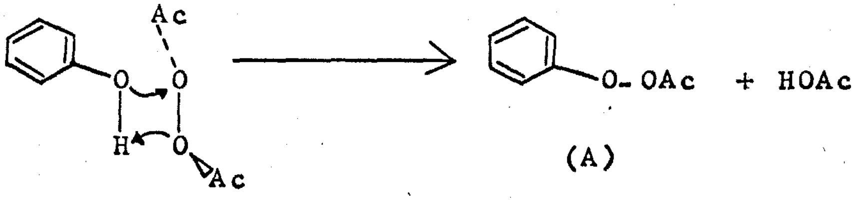


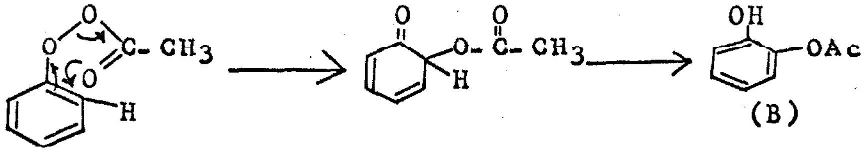
(5)

did not appear to greatly effect the rate, a radical-chain



(A)

(6)



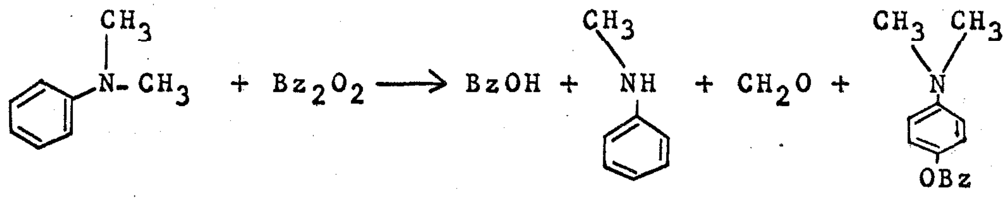
(B)

(7)

induced decomposition of benzoyl peroxide was proposed, explaining the absence of effect by scavengers on the basis of the amine and phenol derived radicals being unreactive (except towards peroxide).

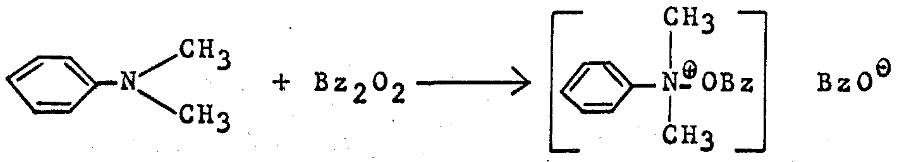
Walling (5) states that there is in general no evidence to demand the intermediacy of "free radicals" in any of the reactions of phenols and acyl peroxides.

In the case of the amine-induced decomposition of acyl peroxide there *is* evidence requiring the intermediacy of free radicals. Radical formation in the *t*-amine-peroxide systems has been clearly demonstrated, for example benzoyl peroxide and dimethyl aniline (6) initiate the polymerization of styrene. The efficiency of radical-chain initiation is however quite small, from 2 to 25% depending on the experimenter (7, 8). In dilute chloroform solution dimethyl aniline and benzoyl peroxide (Eq. 8) yield mainly benzoic acid, monomethyl aniline, formaldehyde, and small amounts of p-benzoyloxydimethylaniline and p,p'-di(dimethylamino)-diphenylmethane (9). Horner (8, 9) proposed

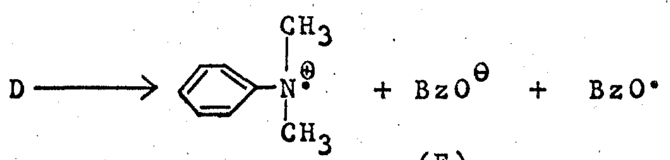

(C)

(8)

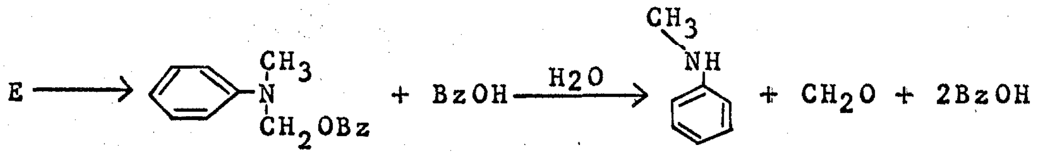
essentially the following reaction scheme for this process:


(D)

(9)


(E)

(10)



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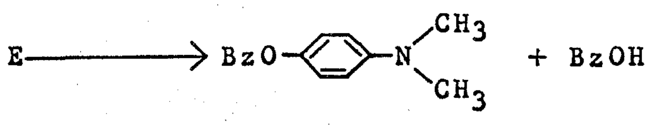
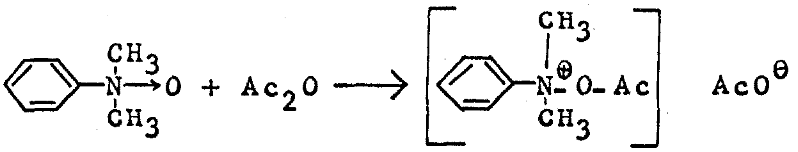


(12)

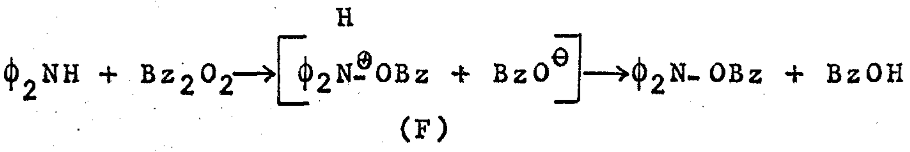
The rate is accelerated by electron-supplying groups on the t-amine and electron-withdrawing groups on the peroxide and *vice versa* (10). This system also rapidly absorbs oxygen and nitric oxide, as well as initiating polymerization, thus the production of radicals is clearly demonstrated. The reaction of dimethylaniline oxide and acetic anhydride which presumably produces a similar "intermediate" (Eq. 13) also initiates vinyl polymerization (11). The kinetics of the amine-peroxide reaction also fit a bimolecular process for the production of radicals. Solvent effects in this


(13)

reaction are interesting if not predicted by Horner's mechanism; it is slow in acetone, average in benzene, but rapid in pyridine (12, 7).

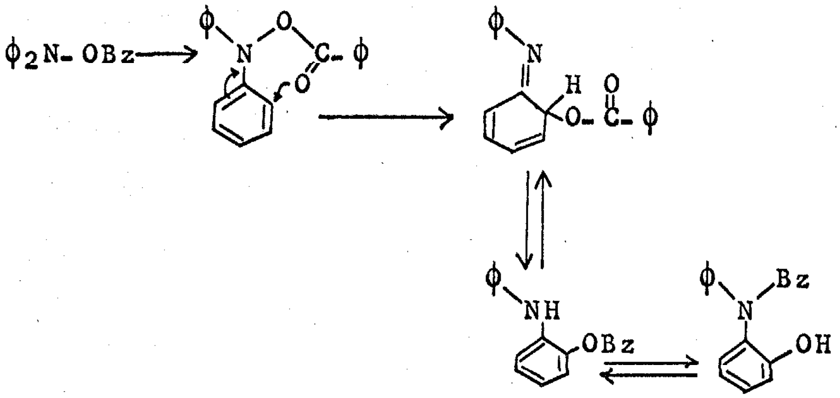
Product studies which have been carried out for primary and secondary amine reactions with peroxide (13), seem to indicate that hydroxylamine acylates (F) are very likely either intermediates or major products in the reactions (Eq. 14). It has been reported (14) that in general

e.g.



$$\phi_2NH + Bz_2O_2 \longrightarrow \underset{(F)}{\left[\phi_2\overset{H}{N}{}^{\oplus}\text{-}OBz + BzO^{\ominus}\right]} \longrightarrow \phi_2N\text{-}OBz + BzOH \qquad (14)$$

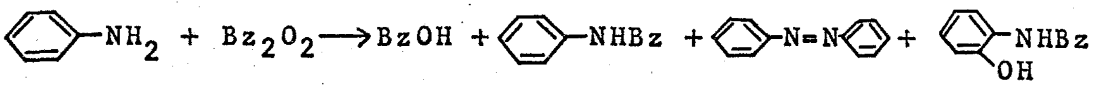
secondary amines neither absorb oxygen nor initiate polymerization. However, tetraphenyl hydrazine (4) has been reported as one of the products in diphenyl amine reaction with acyl peroxide and it has been reported (14) that the



(15)

diethyl amine-alkanesulfonyl acetyl peroxide system does initial polymerization and evolve carbon dioxide.

Primary amines have been less extensively studied; however, the results of the aniline-benzoyl peroxide system (Eq. 16) seem consistent with the pattern of other systems.



(16)

It is proposed that the reactions of these two classes of compounds*, amines and phenols, with acyl peroxides (and possible peroxides in general) be reinvestigated. The general direction of this reinvestigation would be toward

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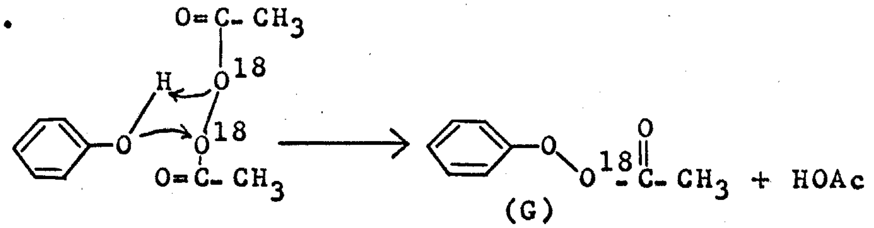
*It is not necessary that only phenols and amines can act in this fashion, e.g., iodobenzenes, sulfides, and possibly even thiols may react similarly.

obtaining comparable data from the different classes (e.g. amine and phenols) and sub-classes (e.g. 1°, 2°, and 3° amines) and careful documentation of the mechanism of a minimum number of representative examples of the reactions of each class or sub-class. Especially important would be evidence bearing on the factor(s) which make the extent of radical character in these reactions appear to vary from 0 to 100%.

A likely starting point might be reinvestigation of Wallings (5) proposed mechanism for the reaction of phenols with acetyl peroxide (Eq. 17). Since an analogous first and second step can be envisioned for primary and secondary amines, the reactions of acetyl peroxide with diphenyl amine and aniline might be studied in parallel experiments. There are two obvious approaches to obtaining more direct evidence for the intermediacy of species such as G: 1) Prepare the intermediate(s) analogous to G by some other route (Eq. 22) and compare the results. 2) Label the acyl peroxide with O^{18} in the peroxy-oxygens (or carbonyl) and examine the products for scrambling of label, since a definite prediction of no scrambling can be made on the basis of Walling mechanism (Eq. 17, 18, 19, and 20).

In the O^{18}-labeling experiments scrambling of label will suggest strongly the involvement of radical intermediates (Eq. 21).

e.g.



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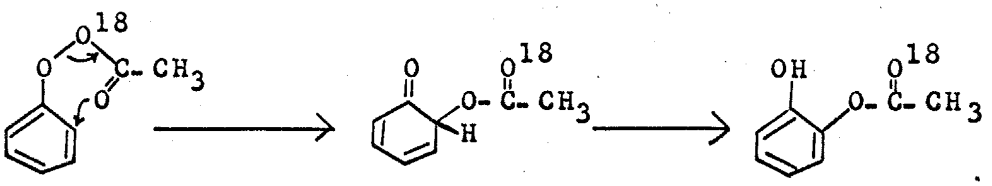

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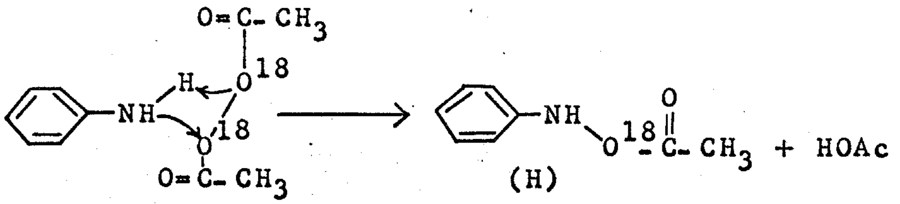

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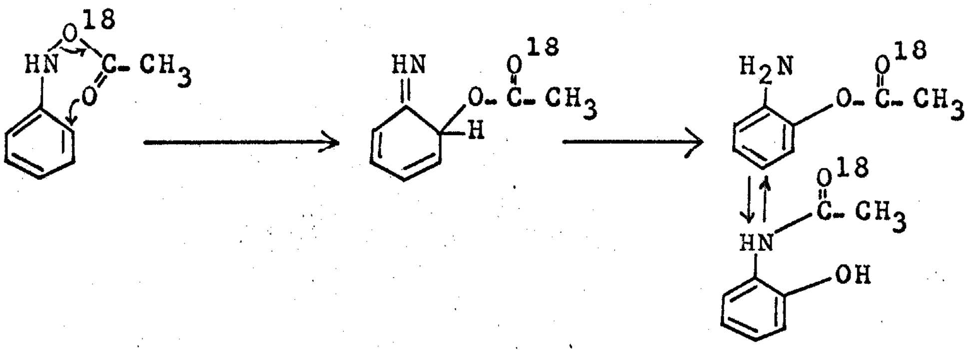

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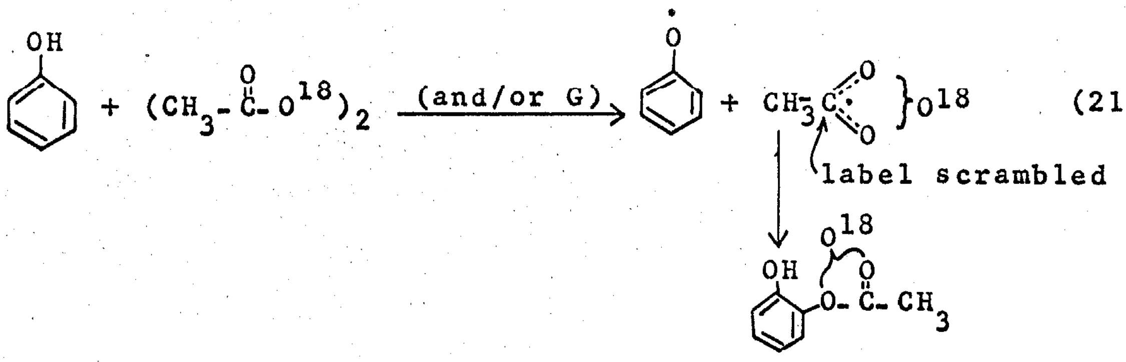
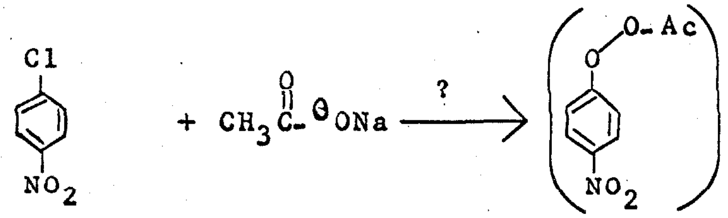


(21)

In addition, it may be possible to prepare a phenyl peracetate similar to G (Eq. 22). p-Nitrochlorobenzene is quite reactive toward chloride displacement by nucleophiles and if sodium peracetate will work, the supposed intermediate in p-nitrophenol-acetyl peroxide system (Eq. 23) will be available via an independent path. Comparison



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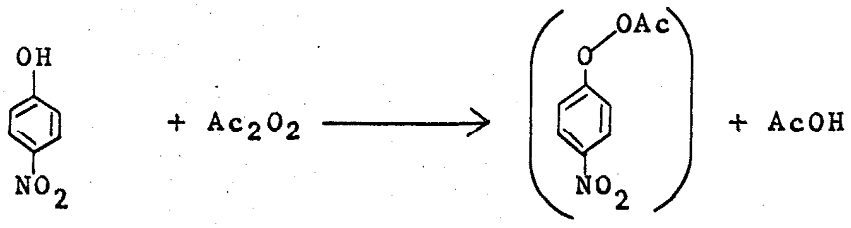
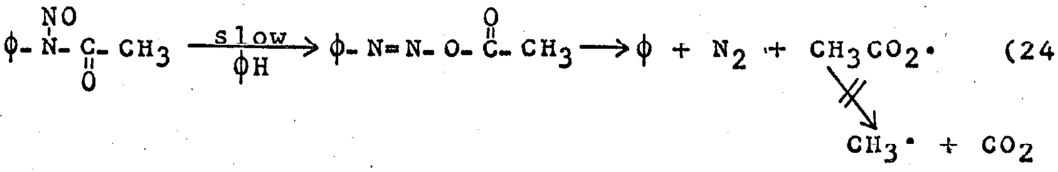


(23)

of the products from these reactions (Eq.s 22 and 23) could clearly be pertinent.

In so far as the extent of radical character of these reactions is concerned, we may just not be using the correct criteria for judging results of scavenging experiments. It is likely and certainly possible that the amine- and phenol-derived radicals will be unreactive toward oxygen, iodine, and vinyl monomer, the usual scavengers. In addition we expect, when acetoxyl radicals (AcO•) are involved that carbon dioxide must be produced to a finite extent; however, at room temperature, for example, the rate of (acetoxyl radical) decarboxylation should be considerably slower than at the higher temperatures at which they are normally generated from acetyl peroxide *via* thermolysis. In fact the supposed radical decomposition of N-nitrosoacetanilides (Eq. 24) yielding acetoxyl as intermediates at room temperature, produces a nearly quantative amount of acetic acid and little or *no* carbon dioxide in ϕH.

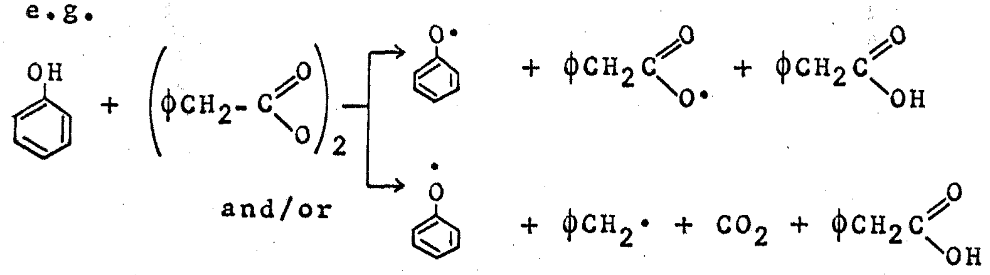


$$\phi\text{-}\overset{NO}{N}\text{-}\underset{O}{\overset{}{C}}\text{-}CH_3 \xrightarrow[\phi H]{slow} \phi\text{-}N{=}N\text{-}O\text{-}\overset{O}{C}\text{-}CH_3 \longrightarrow \phi + N_2 + \underset{\cancel{\searrow}\; CH_3\cdot + CO_2}{CH_3CO_2\cdot} \qquad (24)$$

If carbon dioxide evolution is to be an indicator of the intermediacy of acyloxy radicals then it must be definately demonstratable that decarboxylation of the acyloxy radical in question will compete with other possible reactions. It is known that phenylacetoxyl radical decarboxylation is probably concurrent with acyloxy radical formation (15), thus, in the experiment represented by Equation 25, the *absence* of carbon dioxide production would argue dramatically for the *absence* acyloxy radical intermediacy in the reaction. It must be kept in mind, however, that if the acyloxy radical decarboxylation step is too favorable that the mode of peroxide decomposition may be changed from non-radical to radical, or from bimolecular to unimolecular.

Thus choice of peroxide may be quite critical.

e.g.



(25)

One point in these processes of similarity is the bimolecular character of the first step in all of these reactions which have been investigated kinetically (5, 6). A first step consisting of essentially a nucleophilic attack by phenol or amine at a peroxy-oxygen could fairly well fit the results. Hydrogen transfer concurrent with nucleophilic attack could be accommodated in the case of phenols, primary amines, and secondary amines, without drastically effecting the argument for a basic mechanistic unity for the reactions of amines and phenols with acyl peroxides. Production of radicals could then be a secondary phenomenon and would depend on the stability of the intermediate thus formed. Thus, dimethyl analine would attack benzoyl peroxide nucleophilically to yield N-benzoyloxydimethylaniline which being relatively unstable would fragment into a cation radical and a radical.

Another attractive first step would involve one electron transfer, either to form a charge-transfer complex or two separate radical species (Eq.s 26-29). The charge-transfer

e.g.

$$\phi_2\ddot{N}H + Bz_2O_2 \underset{?}{\rightleftarrows} \underset{(I)}{\overset{\text{charge-transfer complex}}{\left[\phi_2\overset{\oplus}{\dot{N}}H \longrightarrow Bz_2\dot{O}_2^{\ominus}\right]}} \qquad (26)$$

where:

$$I\begin{cases} \xrightarrow{\text{either}} \phi_2N\cdot + BzO\cdot + BzOH \longrightarrow \phi_2N\text{-}OBz \\ \xrightarrow[\text{or}]{} \phi_2N\text{-}OBz + BzOH \end{cases} \qquad (27)$$

e.g.

$$\phi_2\ddot{N}H + Bz_2O_2 \longrightarrow \underbrace{\phi_2\underset{H}{\overset{\oplus}{\dot{N}}} + BzO^{\ominus} + BzO\cdot}_{(J)} \qquad (28)$$

$$J \longrightarrow \phi_2N\cdot + BzO\cdot + BzOH \longrightarrow \phi_2N\text{-}OBz \qquad (29)$$

complex (I) could collapse either <u>via</u> a radical pathway or <u>via</u> a non-radical pathway depending on the character of the species involved. In redox systems such as these, one-electron transfer processes would seem extremely propitious.

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