PART I

THE KINETICS AND MECHANISM OF ADDITION OF HYDROGEN CHLORIDE TO 2,3-DIMETHYLBUTADIENE-1,3 IN SYSTEMS OF APROTIC SOLVENTS

PART II

A THEORY OF VISCO-ELASTIC BEHAVIOR AND FLOW BIREFRINGENCE IN SOLUTIONS OF RIGID ROD-LIKE MACROMOLECULES

Thesis By

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ABSTRACT

The kinetics of addition of hydrogen chloride to 2,3-dimethylbutadiene-1,3 in systems of aprotic solvents has been investigated at 25° and 35°C. The reaction of one molecule of hydrogen chloride with one molecule of diene is reversible; the rate of the forward reaction is proportional to the first power of the diene concentration and the three halves power of the hydrogen chloride concentration, while the rate of the reverse reaction is proportional to the first power of the butene chloride concentration and to the one half power of the hydrogen chloride concentration. In a system of aprotic solvents the rate of addition is inversely proportional to the basicity of the reaction medium. A mechanism is proposed wherein the reacting species are a proton-diene complex and a hydrogen chloride molecule; thus, the addition of hydrogen chloride to conjugated dienes in aprotic solvents may be viewed as a proton catalysed reaction.

The general statistical mechanical theory of irreversible processes in solutions of macromolecules presented previously by John G. Kirkwood has been applied to solutions containing large rigid rod-like molecules. It has been found that orientational factors previously neglected contribute significant terms to the real part of the shear viscosity coefficient and give rise to a rigidity modulus in the presence of periodic shear waves. A simple theory of flow birefringence gives results previously obtained by other investigators.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

PART I

THE KINETICS AND MECHANISM OF ADDITION OF HYDROGEN CHLORIDE TO 2,3-DIMETHYLBUTADIENE-1,3 IN SYSTEMS OF APROTIC SOLVENTS

I. INTRODUCTION

Although the chemical literature is filled with ample discussion of the mechanism of addition of hydrogen halides to unsaturated hydrocarbons and of analogous electrophilic addition reactions[1], it is surprisingly void of any quantitative rate studies. The gas phase addition of hydrogen halides to olefins has been investigated by a number of workers[2], and the results of these studies indicate the absence of any simple homogeneous gas phase reaction. The liquid phase reaction between olefins and hydrogen halides tends to proceed much more readily and has been the subject of a number of qualitative investigations[3].

Only two notable attempts at quantitative rate studies have been made on the hydrogen halide-olefin system[4]. Hennion and his co-workers made a somewhat superficial rate study of the addition of hydrogen chloride and hydrogen bromide to 3-hexene and cyclohexene in various non-aqueous solvents. They concluded that the rate of addition was influenced largely by the basicity of their reaction medium and was nearly independent of the olefin concentration. Mayo and his co-workers concluded from their studies on the addition of hydrogen chloride to isobutylene and of hydrogen bromide to propylene in liquid pentane, that there was a competition between a catalyzed second-order reaction and an uncatalyzed reaction of higher order. A rate constant calculated on the basis of the equation

$$\frac{dx}{dt} = k[HX]^3[\text{Olefin}]$$

seemed to fit the experimental results better than constants calculated on the basis of any other integral reaction order. Mayo also reached the conclusion that some sort of molecular complex between the hydrogen halide and the olefin molecules played a decisive role in the mechanism of addition; such a postulate was made earlier by Maas[2].

No experimental rate data are available in the literature on the addition of hydrogen halides to conjugated dienes, although the reaction itself has been the subject of considerable investigation[5,6]. Most of the studies on these systems were concerned with establishing the mode of 1,4 and 1,2 additions to conjugated systems. Further discussion of this subject is deferred to a later part.

We chose to study the rate and mechanism of addition of hydrogen chloride to 2,3-dimethylbutadiene-1,3 for a number of reasons. Of the four hydrogen halides, hydrogen chloride is the simplest to study, since its addition reactions are not complicated by possible "peroxide" effects and it is easily handled in the anhydrous state. The 2,3-dimethylbutadiene-1,3 is one of the few readily available conjugated dienes which is easy to store and handle. Our original purpose in undertaking the present investigation was threefold: 1 - to study the mechanism of addition of hydrogen halides to unsaturated hydrocarbons; 2 - to study the mode of 1,4 and 1,2 additions to conjugated systems; and 3 - to compare the reactivities of conjugated systems with those of ordinary olefinic systems in simple electrophilic addition reactions.

II. THE PREPARATION OF MATERIALS AND THEIR ISOLATION

2,3-Dimethylbutadiene-1,3

The 2,3-dimethylbutadiene-1,3 was prepared according to the method described by Kyriakides[7]. Pinacol, Eastman white label #407, was heated in a round-bottom flask equipped with an efficient fractionating column. The temperature of the molten pinacol was maintained at 130°C. until any water of hydration present was removed. The temperature was allowed to drop to 94°C. and 1% of concentrated aqueous (48%) hydrobromic acid was introduced. The temperature was maintained at 94°C. until all of the pinacol was converted to diene and pinacolone. The organic phase of the distillate was separated from the aqueous, washed with two portions of cold water to remove any remaining pinacolone and pinacol, and dried over anhydrous potassium carbonate. The dried organic phase was distilled and the fraction boiling between 68.5° and 70.0°C. was collected. The purified 2,3-dimethylbutadiene-1,3 was stored over hydroquinone in order to prevent any subsequent polymerization.

Butene Chlorides

The 1-chloro-2,3-dimethylbutene-2 and the 3-chloro-2,3-dimethylbutene-1 were prepared simultaneously by treating a 50% by weight solution of 2,3-dimethylbutadiene-1,3 in glacial acetic acid with anhydrous hydrogen chloride. Enough hydrogen chloride was furnished to provide an equimolar ratio between it and the diene; the solution was kept at an ice-salt bath temperature for five hours. The reaction was then terminated, the solution washed with four portions of cold neutral water and finally with two portions of ice cold water with a small amount of potassium carbonate dissolved in it. The organic phase was then separated and dried over anhydrous magnesium sulfate. The mixture of the two chlorides was then distilled through an efficient distilling column, final portions being collected over a two degree range. A list of physical properties is given in Table I. It was found that separation at atmospheric pressure was not convenient, since at elevated temperatures some isomerization and polymerization occurred. These difficulties were removed when distillation was carried out below 40 mm. Hg. On storing it was found that both of the chlorides underwent polymerization on the action of sunlight and oxygen. Samples kept stored under nitrogen and hydroquinone and protected from sun light remained quite pure over a period of months.

The anhydrous hydrogen chloride used in our studies was obtained from cylinders provided by the Matheson Co.

Dioxane

Commercial dioxane obtained from the General Chemical Corp. was heated over sodium hydroxide pellets on a steam bath for 24 hrs. Subsequently the dioxane was refluxed over metallic sodium for several hours until no further discoloration occurred on the sodium particles. The dioxane was then distilled and the fraction collected between 99.0° and 100.1°C. was stored under nitrogen. Some samples of dioxane were prepared according to the method described by Fieser*; however, no differences in properties were noticed between these samples and the ones purified by the above simpler method.

Xylene

Commercial xylene obtained from the General Chemical Corp. and containing approximately 90-95% meta isomer was refluxed over metallic sodium for several hours and then distilled. The fraction boiling between 136° and 138°C. was collected and stored under air.

Di-n-Butyl Ether

The di-n-butyl ether was obtained from the preparations of the Junior Organic Laboratory course at the California Institute of Technology.** The student preparations were refluxed over potassium permanganate to remove any traces of alcohol, distilled, and then refluxed over metallic sodium and distilled. The fraction boiling between 141.5 and 142.5°C. was collected and stored under nitrogen.

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* L. Fieser - "Experiments in Organic Chemistry", Heath and Co. (1941), p. 368.

** See: H. J. Lucas and D. Pressman, "Principles and Practice in Org. Chem.", Wiley, (1949), p. 261.

Table I.

Physical Properties

Compound	B. P. °C		n_D^{20}		D_4^{20}	
	Observed	Reported	Observed	Reported	Observed	Reported
2,3-Dimethylbutadiene-1,3 (a)	68.7° to 68.9° @ 756 mm	68.9° @ 760 mm	1.4384	1.4386	0.7285	0.7263
3-Chloro-2,3-Dimethylbutene-1 (b)	112°-13° @ 756 19°-21° @ 30 mm	111°-112° @ 756 mm	1.4250	n_c^{19} 1.4315	0.8898	0.8895
1-Chloro-2,3-Dimethylbutene-2	125-26° @ 756 28°-30° @ 30 mm	--	1.4452	--	0.9330	--
2,3-Dimethylbutene-1-ol-3 (b)	--	116°-18° @ 760 mm	--	n_c^{19} 1.4248	--	0.08350

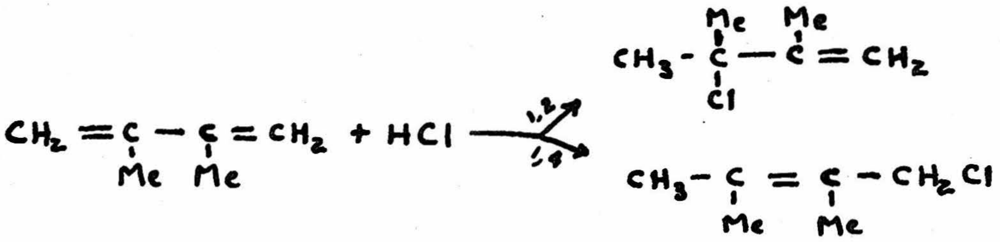
(a) Reported in Egloff, Phys. Prop. Hydrocarb., Vol. I.

(b) Tishchenko, C. A., 33, 4190 (1939). Huntress erroneously lists this compound as its isomer in Org. Chlorine Cpds., #3:752.

III. PRELIMINARY INVESTIGATIONS ON THE REACTION BETWEEN HYDROGEN CHLORIDE AND 2,3-DIMETHYLBUTADIENE-1,3

Thermodynamic considerations tend to rule out the possibility of adding hydrogen chloride to unsaturated hydrocarbons in the presence of hydroxylic solvents such as water and the lower aliphatic alcohols[8]. We therefore chose glacial acetic acid and dioxane as the reaction media for our preliminary investigations.

The results of our preliminary investigations in both of the solvent media mentioned were the same. The diene and hydrogen chloride react according to the following scheme.



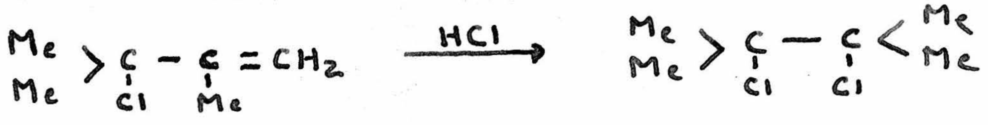
$$CH_2=\underset{Me}{C}-\underset{Me}{C}=CH_2 + HCl \xrightarrow{1,2} CH_3-\overset{Me}{\underset{Cl}{C}}-\overset{Me}{C}=CH_2$$

$$CH_2=\underset{Me}{C}-\underset{Me}{C}=CH_2 + HCl \xrightarrow{1,4} CH_3-\underset{Me}{C}=\underset{Me}{C}-CH_2Cl$$

The reaction was allowed to take place in moderately dilute solutions over a slight range of concentrations and at two different temperatures, 0°C. and room temperature (ca. 25°C.). Results of this phase of our investigation are summarized in Table II.

From Table II it is seen that initial addition of hydrogen chloride to the diene favors the 1,2 mode over the 1,4 mode. If a solution of the 1,2 isomer is allowed to remain in the presence of hydrogen chloride over a prolonged period of time, it will slowly isomerize to the 1,4 isomer. No carefully controlled quantitative studies were conducted on this phase of the problem since our objective was merely the determination of the course of the reaction. Our findings agree largely with those of Kharasch and his co-workers[6], who studied the system butadiene-1,3 and hydrogen chloride. They found that initial addition resulted in a mixture of 80% 1,2 and 20% 1,4 product. On heating the 1,2 isomer in the presence of hydrogen chloride and inorganic chlorides, it became converted to a mixture of 1,2 and 1,4 isomers. Some of their results are tabulated in Table IIa for the sake of comparison.

Under our experimental procedure no second molecule of hydrogen chloride was observed to add to the butene chlorides formed from the initial addition reaction. It must be concluded that in the absence of a large excess of hydrogen chloride the second molecule of hydrogen chloride adds much more slowly than the first. If any further reaction were to take place, we would expect it to follow the course



Further discussion on the question of 1,2 vs. 1,4 addition is deferred until a later part.

Table II.

Addition of Hydrogen Chloride to Diene

Diene Concen. Molality	Moles of HCl per Diene	Solvent	Temp. oC.	Time Hrs.	Diene Reacted in %	3-Chloro Isomer Formed in %
1.8	1.5	HOAc	0	24	60	75
2	1.5	HOAc	25	12	50	70
2.2	1	Diox	0	24	30	80
2.5	1.5	Diox	25	48	60	70

Table IIa

Addition of Hydrogen Chloride to Butadiene-1,3 (a)

1.5	HOAc	Room	24	50	78
1.5	HOAc	Room	48	61-79	78
1.5	Ether	80	24	None	
1.5	Ether	Room	24	None	

Equilib. mixt. in 1M HCl in HOAc is

70-75% of 1,4
30-25% of 1,2

(a) M. Kharasch, Kritchevsky, Mayo, J. Org. Chem., 2, 490 (1937-38).

IV. METHOD OF ANALYSIS AND SAMPLING

Preliminary

The usual method for following the rate of addition of hydrogen halides to unsaturated hydrocarbons is by titration of the unreacted acid with aqueous base. Early investigations by us indicated that this procedure would not be applicable to our system. The primary product formed in the addition of one molecule of hydrogen chloride to 2,3-dimethylbutadiene-1,3 is 3-chloro-2,3-dimethylbutene-1; this is a tertiary, as well as allylic, chloride and is therefore expected to be quite reactive. It was indeed found that the above butene chloride hydrolyzed slowly in neutral cold water; whereas in 0.1N sodium hydroxide solution at room temperature the hydrolysis was practically instantaneous. Obviously, another method for following the rate had to be devised.

Two avenues of investigation were open for following the rate of our reaction. The first possibility was to devise a method for following the rate of disappearance of the diene. Most unsaturated hydrocarbons may be titrated quantitatively in a bromine-bromate system with or without the use of catalysts (i.e. mercuric salts). Many investigators[9a] found that conjugated dienes did not react quantitatively with bromine under the conditions of normal titrations; some industrial methods were devised for titrating dienes with bromine quantitatively, but these were effective only if the sample to be titrated contained predominantly diene. The usual industrial method practiced today for determining quantitatively the amount of diene present in a given sample is based on infra-red spectrophotometric methods. The apparatus needed for such analysis was not available to us.

We investigated briefly the possibility of following the rate of disappearance of the diene by ultra-violet spectroscopic methods. It was found, however, that the addition compound formed from the diene and hydrogen chloride exhibited an ultra-violet absorption spectrum very similar to that of the original diene. Further work on devising a suitable method for the quantitative determination of dienes was abandoned and attention was focused on the second alternative.

Instead of following the rate of our reaction by quantitative titration of the diene, we may follow it by measuring the rate of disappearance of hydrogen chloride. The method to be devised had to be applicable to the non-aqueous, aprotic solvent systems used in our rate studies. We first investigated the possibility of determining acid concentrations by a method similar to the spectrophotometric-indicator method used by Lemaire[9b]. Among the indicators tried were: methyl red, methyl orange, bromthymol blue, thymol blue, and bromcresol purple. The absorption spectra of these indicators in the visible region have been determined by Brode[10], and for convenience are tabulated in Table III.

It was found that none of the above named indicators provided a system suitable for our purposes. In trying to calibrate concentration of hydrogen chloride vs. absorption curves, slow drifts with time and other anomolies were observed whenever traces of the diene or butene chloride were introduced. We concluded that some complexing or reaction must have occurred between the indicator and the diene or butene chloride. Furthermore, it was found difficult to control the temperature evenly during the spectral analyses or to correct for these fluctuations. An illustration of our indicator study is given in Tables IIIa and IIIb, wherein the above mentioned difficulties are demonstrated. We abandoned more detailed investigations on this phase of our study, concluding that a simple indicator method gave unreliable results.

Method of Analysis

A suitable method for following the rate of our reaction was finally arrived at upon discovering that in the absence of appreciable amounts of water or other hydroxylic solvents, hydrogen chloride could be titrated quantitatively with a strong organic base (e.g. triethyl amine) without any interference from the butene chloride. This observation is not surprising in view of the facts that in our systems of aprotic solvents solvolysis of the butene chloride is not possible, and that it has been observed that the rate of formation of quaternary ammonium salts is greatly influenced by the ionizing power, i.e. dielectric constant and ionic strength, of the solvent medium[11]. Dioxane solutions of the butene chlorides and amine were found to yield nice crystalline derivatives after a 48 hour period, however.

Table III.

Properties of Indicators

Name	λ max.	p_H range
Thymol Blue	544	1.2 - 3.4
Thymol Blue	596	7.4 - 10.2
Brom Phenol Blue	592	2.4 - 5.6
Methyl Red	530	3.4 - 7.0
Brom Cresol Purple	591	4.8 - 7.6
Brom Thymol Blue	617	5.8 - 8.4
Phenol Red	558	6.2 - 9.2
Cresol Red	572	6.8 - 9.6

Table IIIa.

Calibration with Thymol Blue

Temp. - 25.0°C.
λ = 544 m
[Ind] = 0.001%

[HCl] in ML^{-1}	5.35	2.68	1.86	1.32	0.78	0.05
Intensity % Trans.	27.0	69.8	80.1	84.3	97.0	100.0

Table IIIb.

[HCl]	1.340	1.350	1.326	1.318	1.250	1.245	1.238
% Trans	21.3	19.4	22.1	29.9	34.8	37.0	40.8
Time in Hrs.	0	0.33	0.60	1.25	2.00	2.33	3.00
Temp. in oC.	25.0	25.7	25.3	26.0	25.6	25.2	25.3

[Diene] = 0.614 M

[Ind] = 0.002%

Thymol Blue

λ = 544 m

The indicator most suitable for our purposes was found to be tetrabromo-m-cresol sulfonaphthalein (brom-cresol green). In aqueous systems this indicator is pale yellow in strongly acid solutions, turns faint green at a pH of approximately 5 and becomes intense blue at a pH of approximately 8. In solutions of ethers and aromatic hydrocarbons, the indicator assumes a dark brownish purple color in the basic region. Stock solutions of 0.5% by wt. of indicator ware made up in mixtures of 20% by vol. ethyl alcohol and 80% dioxane or xylene.

Titrations were carried out by introducing a sample approximately 1 ml. in volume into an erlenmeyer flask containing 25 ml. of the solvent being used as the reaction medium (i.e. either dioxane, xylene, or di-n-butyl ether). Five drops of a suitable solution of the indicator were then added and the sample was then titrated with a standardized solution of triethyl amine in the solvent being used as the reaction medium. The sample was titrated to a standardized end point.

Stock solutions of triethyl amine were made up to the approximate concentrations required in suitable solvents (i.e. dioxane, xylene, or di-n-butyl ether), and standardized against a standard solution of aqueous hydrogen chloride, using bromcresol green as the indicator. These stock solutions were periodically sampled and re-standardized. It was found that end points could be standardized with respect to color and intensity by taking solutions with known concentrations of diene, hydrogen chloride, and butene chlorides. When these solutions were diluted to the same concentrations as the samples to be titrated, the resulting end point was found to remain stable over a period of several hours.

The Method of Sampling

To prevent any possible loss in hydrogen chloride by vaporization during sampling, the rate studies were carried out in apparatus suitable for sampling in the absence of air. (See Fig. 1) When a sample was desired, a pipette calibrated for total delivery[12] was attached to the apparatus and the required amount of sample was displaced with a stream of nitrogen. The pipette was then withdrawn and the sample flushed into an erlenmeyer flask with the appropriate solvent.

Solutions for rate studies were prepared in the following manner. Freshly distilled 2,3-dimethylbutadiene-1,3 was carefully weighed into a calibrated volumetric flask containing the desired solvent. The volumetric flask was then filled nearly to the required level and immersed in a thermostat bath set for the reaction temperature. After the flask reached equilibrium temperature, the contents were finally adjusted to the required level. Solutions of hydrogen chloride were prepared by passing anhydrous hydrogen chloride gas into a flask containing the desired solvent and surrounded by an ice bath, suitable arrangements being made to safeguard the contents of the flask from moisture. The gas was dispersed into a fine stream by allowing it to bubble forth from a sintered glass plate. After the approximately desired amount of hydrogen chloride was weighed in, the flask was stoppered and immersed into a thermostat bath adjusted to the required temperature. When the solution of hydrogen chloride reached the desired temperature, aliquot samples were taken and titrated against standardized solutions of triethyl amine in the suitable solvent and against aqueous sodium hydroxide solutions, using bromcresol green as the indicator in both instances. It was found that the moderately dilute acid solutions required for our rate studies could be stored over a period of weeks without any appreciable change in concentration; nevertheless, it was our practice to use freshly prepared hydrogen chloride solutions for our rate determinations.

Samples for rate studies were prepared by pipetting required amounts of diene and hydrogen chloride solutions into the reaction vessel, using properly calibrated pipettes. Blanks containing hydrogen chloride and solvent were run over a period of several hours under conditions similar to the ones actually used in rate determinations. No appreciable fluctuations in hydrogen chloride concentration could be detected during these runs.

Early runs were carried out under an atmosphere of nitrogen. Upon discovering thatoxygen had no effect on the reaction rate, subsequent runs were carried out in the presence of air. (See Part I, Section V-F.)

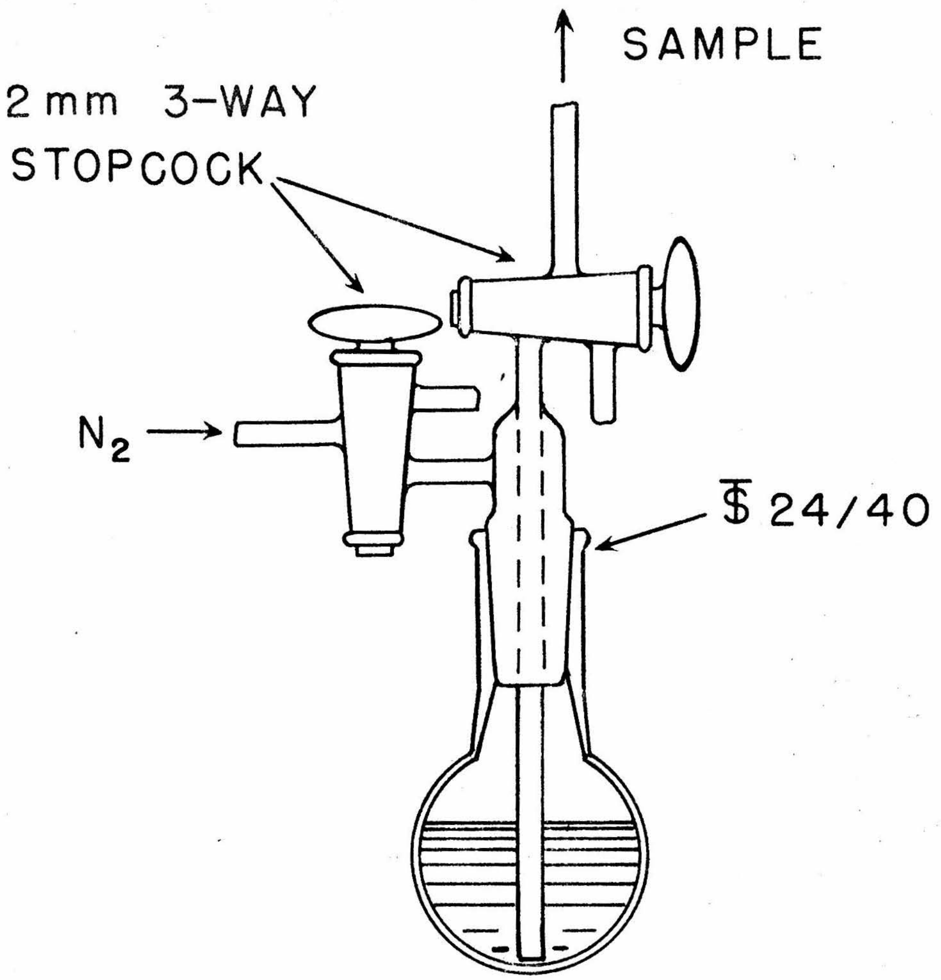


Figure 1

Apparatus for Sampling in Absence of Air

V. THE RATE AND MECHANISM OF ADDITION OF HYDROGEN CHLORIDE TO 2,3-DIMETHYLBUTADIENE-1,3.

A. Introduction

The kinetics of the addition of hydrogen chloride to the diene were studied at 25° and 35°C. in three different solvents; dioxane, di-n-butyl ether, and xylene. These three solvents were chosen in order to study how the basicity of the reaction medium affected the rate of addition. The basicity of the three solvents ranges from dioxane, being the highest, to xylene, being the lowest. All three have dielectric constants approximately equal (ca. 2), consequently any secondary solvent effects due to dielectric properties should cancel when comparisons between different solvent media are made.

In all of our studies only the rate of the first molecule of hydrogen chloride to add to the diene was determined. The shape of our kinetic plots indicated that after an appreciable concentration of butene chloride had built up a very slow second addition of hydrogen chloride took place. However, the rate of this reaction was considerably slower under our experimental conditions than the primary reaction between hydrogen chloride and diene. Under our mild experimental conditions no polymerization of the diene was ever observed.

The objectives of our rate studies were as follows. By measuring the rate of reaction between hydrogen chloride and diene at a given temperature and over a varied concentration range, we expected to determine the order of the reaction. By studying the effect of varying the basicity of the reaction medium and introducing various inorganic salts as catalysts, we hoped to determine the mechanism of the reaction. Finally we intended measuring the rate of the reaction at elevated temperatures and thus determining the activation energy of the reaction.

B. The Initial Rate of Reaction

The first step in analysing our rate data was the determination of the initial rate of reaction between hydrogen chloride and diene over a suitable range of concentrations. The initial rate was obtained in the following manner: the concentration of hydrogen chloride in the reaction mixture was measured during arbitrary time intervals; by plotting these concentrations against time a reasonably smooth curve was obtained and extrapolated back to zero time. A line was then drawn tangent to the concentration of hydrogen chloride vs. time curve at the point of zero time. The slope of this line represents the initial rate. The method is illustrated in Figure 2 for a representative run.

Although the graphical method is subject to a certain amount of error, it provides the simplest and most direct method of obtaining initial rates. The initial rates are important in determining at least approximately the order of the reaction since their values are uncomplicated by any subsequent reactions which may occur in the system at later times. The initial rate is related to the initial specific rate constant in the following manner:

$$\left[\frac{dx}{dt}\right]_{x=0} = v^{\circ} = k_1^{\circ} a^m b^n \qquad (1)$$

k_1^o is the initial specific rate constant

a is the initial concentration of HCl

b is the initial concentration of the diene

m and n represent the order of the reaction with respect to hydrogen chloride and diene respectively.

In Table IV are tabulated the initial rates of a number of representative runs along with values of k_1^o calculated on the basis of m = 1, 3/2, 2 and n = 1. From the tabulated results it is apparent that the best agreement is obtained with the experimental observations when m is chosen equal to 3/2 and n to 1. This indicates that the early part of our kinetic curves may be represented by the integrated form of the equation

$$\frac{dx}{dt} = k_1^{\circ} (HCl)^{3/2} (Diene) \qquad (2)$$

where x represents the concentration of butene chloride at a given time. If Eq. (2) were to describe adequately the rate of reaction between hydrogen chloride and diene, we would expect the plot of conc. of hydrogen chloride vs. time to approach zero concentration asymptotically. Fig. 2 shows that this is

Table IV.

Initial Rates of Addition

Run No.	Solvent	a	b	v^o Initial Slope	$k^{(o)}$ ab	$k^{(o)}$ $a^{3/2}b$	$k^{(o)}$ a^2b
1	Dioxane	0.400	1.050	2.92×10^{-2}	6.95×10^{-2}	0.110	0.174
2	Dioxane	0.582	1.050	4.15 "	6.80 "	0.089	0.117
3	Dioxane	0.892	1.050	7.88 "	8.42 "	0.089	0.0945
4	Dioxane	0.892	0.525	4.33 "	9.26 "	0.098	0.104
5	Dioxane	0.980	0.250	2.55 "	10.40 "	0.105	0.106
11	Xylene	0.115	0.117	1.68×10^{-2}	1.25	3.68	10.88
12	Xylene	0.0950	0.117	1.09 "	1.10	3.56	11.58
13	Xylene	0.0945	0.234	2.18 "	1.09	3.55	11.53
14	Xylene	0.0456	0.117	0.40 "	0.76	3.68	16.90
15	Xylene	0.0892	0.0585	0.565"	1.09	3.68	12.22
16	Xylene	0.1310	0.0350	0.638"	1.34	3.70	10.21
21	Bu Ether	0.645	0.500	4.68×10^{-2}	0.145	0.180	0.225
22	Bu Ether	0.645	0.250	4.99 "	0.155	0.193	0.241
23	Bu Ether	0.325	0.500	1.74 "	0.107	0.188	0.329
24	Bu Ether	0.750	0.685	8.52 "	0.166	0.192	0.221

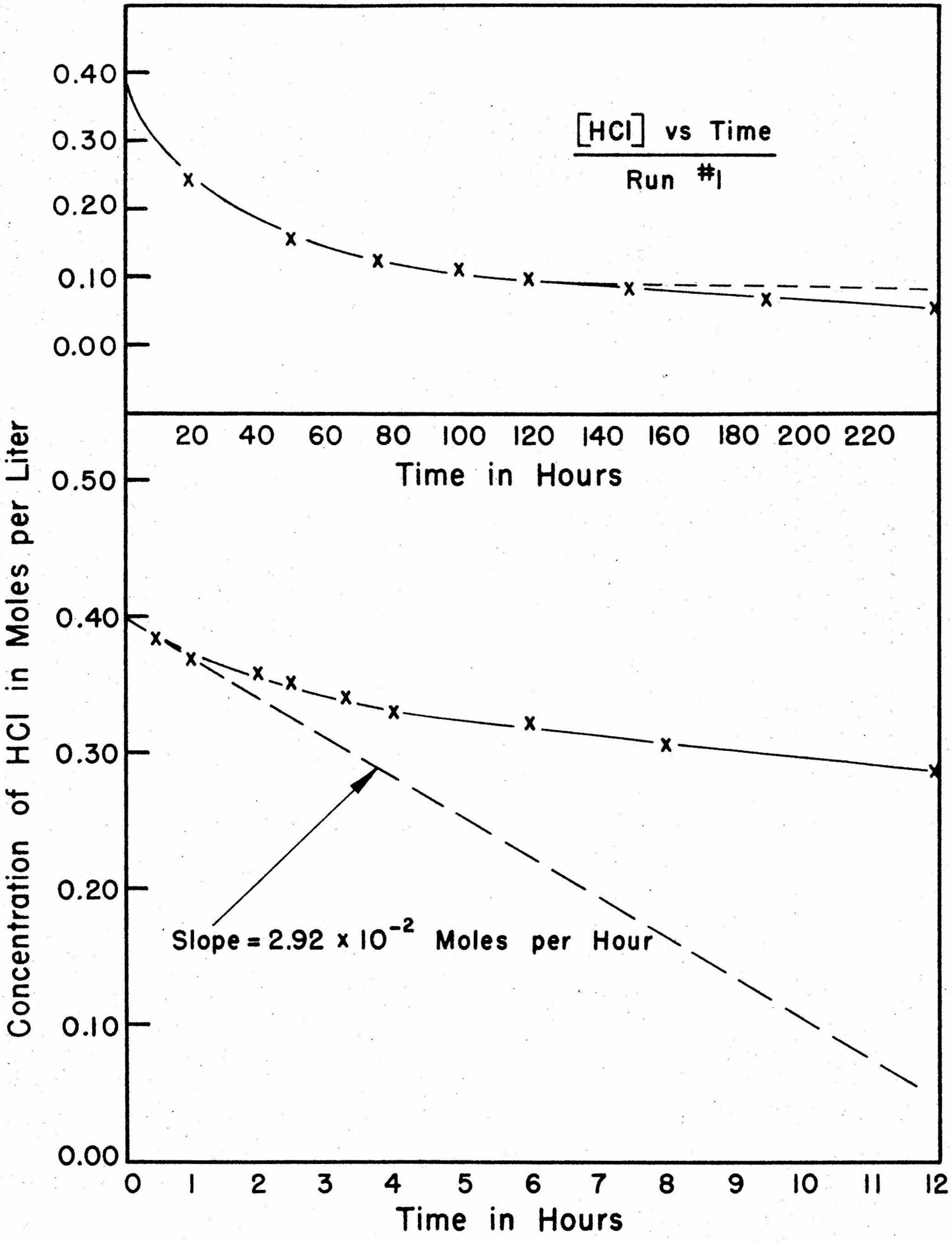

[HCl] vs Time
Run #1
0.40
0.30
0.20
0.10
0.00
20 40 60 80 100 120 140 160 180 200 220
Time in Hours
Concentration of HCl in Moles per Liter
0.50
0.40
0.30
0.20
0.10
0.00
Slope = 2.92 x 10^-2 Moles per Hour
0 1 2 3 4 5 6 7 8 9 10 11 12
Time in Hours

Figure 2

not the case; indeed, the shape of the curve depicted in Fig. 2 would indicate that the reaction between hydrogen chloride and diene is a reversible one approaching equilibrium. Unfortunately, this is not quite true either, for true equilibrium is never established between the diene and hydrogen chloride on account of the slow second addition of hydrogen chloride to the butene chloride formed from the first addition. The dotted line in Fig. 2 depicts the shape expected for true equilibrium. Consequently, accurate determinations of an "equilibrium" concentration could never be achieved experimentally. Nevertheless, the course of the reaction between hydrogen chloride and diene is best described by the equation

$$\frac{dx}{dt} = k_1 (HCl)^{3/2} (\text{Diene}) - k_2 x \qquad K = \frac{k_1}{k_2} \qquad \text{---- (3)}$$

where k_2 is the rate of the reverse reaction and K is the equilibrium constant of the reversible reaction

$$\frac{3}{2} HCl + \text{Diene} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Butene Chloride} + \frac{1}{2} HCl \qquad \text{---- (3a)}$$

We shall show below how approximate values of K may be obtained analytically.

C. The Integrated Rate Equation.

Eq. (3) may be rewritten in the form

$$\frac{dx}{dt} = k_1 (a-x)^{3/2}(b-x) - k_2 (a-x)^{1/2} x$$

$$= k_1 (a-x)^{1/2}\left[(a-x)(b-x) - K^{-1} x\right]$$

---- (4)

where a is the initial concentration of hydrogen chloride, b is the initial concentration of diene, and the other symbols have their previously given significance. Making the substitution

$$\rho = \tfrac{1}{2}\left[a + b + K^{-1} - \chi\right]$$

$$\chi = \left[(a+b+1/K)^2 - 4ab\right]^{1/2}$$

$$\sigma = \tfrac{1}{2}\left[a + b + K^{-1} + \chi\right]$$

Eq. (4) is converted into the following equation of partial fractions.

$$\frac{dx}{(a-x)^{1/2}}\left[\frac{1}{\chi(x-\sigma)} - \frac{1}{\chi(x-\rho)}\right]$$

---- (5)

Upon integration Eq. (5) yields four possible solutions subject to the conditions

$$(a-\sigma) > 0 \quad ; \quad (a-\rho) > 0$$

---- (6a)

$$(a-\sigma) < 0 \quad ; \quad (a-\rho) > 0 \qquad \text{---- (6b)}$$

$$(a-\sigma) > 0 \quad ; \quad (a-\rho) < 0 \qquad \text{---- (6c)}$$

$$(a-\sigma) < 0 \quad ; \quad (a-\rho) < 0 \qquad \text{---- (6d)}$$

Both conditions (6c) and (6d) require that $\kappa/2 < 0$, which can never be realized in our case. Condition (6a) requires that $(a-b) > (\kappa + K^{-1})$; whereas condition (6b) requires that $(a-b) < (\kappa + K^{-1})$. Actually, only condition (6b) is ever satisfied by the systems under study; and this leads to the integrated rate equation

$$k_1 \kappa t = \frac{2}{\sqrt{\sigma-a}}\left[\tan^{-1}\sqrt{\frac{a-x}{\sigma-a}} - \tan^{-1}\sqrt{\frac{a}{\sigma-a}}\right] + \frac{2.303}{\sqrt{a-\rho}}\log_{10}\left[\frac{\sqrt{a-x}+\sqrt{a-\rho}}{\sqrt{a-x}-\sqrt{a-\rho}}\cdot\frac{\sqrt{a}-\sqrt{a-\rho}}{\sqrt{a}+\sqrt{a-\rho}}\right] \qquad \text{---- (7)}$$

Eq. (7) has been used to calculate the forward specific rate constant, k_1, for a number of representative runs and the results are tabulated in Table V. It is seen that agreement in the rate constants during a time interval of several hours is quite good.

The only arbitrary parameter which has to be chosen in the integrated rate equation is the value of K, the equilibrium constant for the reaction. Values of K could not be determined directly on account of the slow addition of the second molecule of hydrogen chloride to the butene chlorides. However, reasonably good orders of magnitude may be assigned to K on the basis of Eq. (7). In Fig. 3 we show how the assigned values of K influence the plot of Eq. (7). To simplify matters we have chosen an illustrating run where the contributions of the arc tangent function in Eq. (7) may be neglected with respect to the contributions arising from the logarithmic function. Thus, we plot the function $\log_{10}\left[\frac{\sqrt{a-x}+\sqrt{a-\rho}}{\sqrt{a-x}-\sqrt{a-\rho}} - \frac{\sqrt{a}-\sqrt{a-\rho}}{\sqrt{a}+\sqrt{a-\rho}}\right]$ against time for three different values of K. It is seen that the value nearest to the true value gives a straight line plot with a slope equal to $k_1 \times \sqrt{a-\rho}/2.303$. Values of K differing appreciably from the true one do not yield straight line plots. If the plot of Eq. (7) with the correct value of K is carried out for long time intervals, deviations from the straight line will occur after a suitable length of time. These deviations occur at the point where the rate of addition of the second molecule of hydrogen chloride becomes appreciable.

In all cases we have chosen those values of K which yield the most consistent agreement in the k_1 values and conform with the above criterion of yielding straight line plots. However, the tabulated values of K should only be considered as approximate and merely indicate orders of magnitude. In Table VI we have summarized the average values of k_1 along with the values of the other rate constants for the representative runs listed in the previous table. Fluctuations in the average values of k_1 for different runs is random and well within the experimental error. Agreement with the graphically determined initial forward rate constants, k_1^o, is surprisingly good.

Table V.

Rates of Addition

Run No. 4

Temp. 25° a = 0.892 ML^{-1} K = 10
Solv. Dioxane b = 0.525 ML^{-1})(= 0.654

Time in hrs.	0.63	1.13	2.03	3.0	4.15	5.15
a-x in ML^{-1}	0.874	0.843	0.805	0.775	0.708	0.647
k_1 in hrs.$^{-1}$ M$^{-3/2}$	0.090	0.115	0.120	0.110	0.106	0.108

Run No. 6

Temp. 25° a = 0.892 ML^{-1} K = 10
Solv. Dioxane b = 0.350 ML^{-1})(= 0.743

Time in hrs.	0.7	1.5	1.9	2.9	4.0	5.0
a-x in ML^{-1}	0.880	0.858	0.836	0.809	0.790	0.775
k_1 in hrs.$^{-1}$ M$^{-3/2}$	0.094	0.117	0.115	0.105	0.105	0.106

Run No. 7

Temp. 25° a = 0.200 ML^{-1} K = 10
Solv. Dioxane b = 0.754 ML^{-1})(= 0.730

Time in hrs.	0.5	1.0	2.0	3.0	4	5
a-x in ML^{-1}	0.192	0.179	0.173	0.168	0.164	0.160
k_1 in hrs.$^{-1}$ M$^{-3/2}$	.115	0.108	0.102	0.110	0.105	0.112

Table V. (Continued)

Run No. 1

Temp. 25° a = 0.400 ML^{-1} K = 10
Solv. Dioxane b = 1.050 ML^{-1} χ = 0.850

Time in hrs.	0.5	1	2	2.5	2.75	3.33	4
a-x in ML^{-1}	0.384	0.369	0.359	0.353	0.346	0.339	0.330
k_1 in hrs.$^{-1}$ M$^{-3/2}$	0.114	0.116	0.098	0.090	0.100	0.107	0.106

Run No. 2

Temp. 25° a = 0.582 ML^{-1} K = 10
Solv. Dioxane b = 1.050 ML^{-1} χ = 0.752

Time in hrs.	0.1	1.25	2.4	3.1	4.75	5.0	5.5
a-x in ML^{-1}	0.577	0.538	0.515	0.490	0.457	0.456	0.445
k_1 in hrs.$^{-1}$ M$^{-3/2}$	0.100	0.101	0.101	0.118	0.114	0.108	0.109

Run No. 3

Temp. 25° a = 0.892 ML^{-1} K = 10
Solv. Dioxane b = 1.050 ML^{-1} χ = 0.651

Time in hrs.	0.8	1.05	1.55	2.25	3.5	4.55
a-x in ML^{-1}	0.844	0.815	0.775	0.736	0.687	0.642
k_1 in hrs.$^{-1}$ M$^{-3/2}$	0.100	0.080	0.102	0.099	0.100	0.100

Table V. (Continued)

Run No. 21

Temp. 25° a = 0.645 ML^{-1} K = 15
Solv. Bu Ether b = 0.500 ML^{-1})(= 0.422

Time in hrs.	.5	1	1.5	2	3	4
a-x in M	0.625	0.613	0.601	0.582	0.575	0.568
k_1 in hrs.$^{-1}$ $M^{-3/2}$	0.198	0.187	0.192	0.190	0.190	0.192

Run No. 22

Temp. 25° a = 0.645 ML^{-1} K = 15
Solv. Bu Ether b = 0.250 ML^{-1})(= 0.529

Time in hrs.	.5	1	1.5	2	3	4
a-x in M	0.632	0.625	0.619	0.615	0.608	0.602
k_1 in hrs.$^{-1}$ $M^{-3/2}$	0.195	0.190	0.192	0.185	0.190	0.187

Run No. 25

Temp. 25° a = 0.350 ML^{-1} K = 15
Solv. Bu Ether b = 0.800 ML^{-1})(= 0.600

Time in hrs.	0.4	1	1.5	2	3	4
a-x in M	0.340	0.331	0.320	0.316	0.304	0.293
k_1 in hrs.$^{-1}$ $M^{-3/2}$	0.193	0.186	0.188	0.188	0.190	0.195

Table V. (Continued)

Run No. 17

Temp. 25° $b = 0.0250\ ML^{-1}$ $K = 70$
Solv. Xylene $a = 0.1170\ ML^{-1}$ $\kappa = 0.1130$

Time in hrs.	0.53	1	2	3	4	5
a-x in M ×10[illegible]	0.108	0.102	0.0900	0.0802	0.0721	0.0683
k_1 in hrs.$^{-1}$ $M^{-3/2}$	3.82	3.76	3.85	3.88	3.80	3.91

Run No. 15

Temp. 25° $a = 0.0892\ ML^{-1}$ $K = 70$
Solv. Xylene $b = 0.0585\ ML^{-1}$ $\kappa = 0.0740$

Time in hrs.	0.05	0.33	0.75	1.8	3.0	5
a-x in M	0.0886	0.0875	0.0858	0.0805	0.0775	0.0720
k_1 in hrs.$^{-1}$ $M^{-3/2}$	3.68	4.05	3.50	3.98	3.66	3.85

Run No. 18

Temp. 25° $a = 0.0965\ ML^{-1}$ $K = 70$
Solv. Xylene $b = 0.1034\ ML^{-1}$ $\kappa = 0.0773$

Time in hrs.	0.5	1	2	4	6	8	10	12
a-x in M	.0904	.0860	.0785	.0670	.0575	.0525	.0495	.0467
k_1 in hrs.$^{-1}$ $M^{-3/2}$	3.90	3.87	3.87	3.85	3.95	3.92	3.94	3.95

Table V. (Continued)

Run No. 11

Temp. 25° $a = 0.1150$ ML^{-1} K = 70
Solv. Xylene $b = 0.1170$ ML^{-1})(= 0.0821

Time in hrs.	0.08	0.67	1.67	2.5	4.5	6.5
a-x in ML^{-1}	0.113	0.102	0.092	0.085	0.0695	0.0625
k_1 in hrs.$^{-1}$ M$^{-3/2}$	3.95	3.87	3.88	3.78	3.80	3.85

Run No. 14

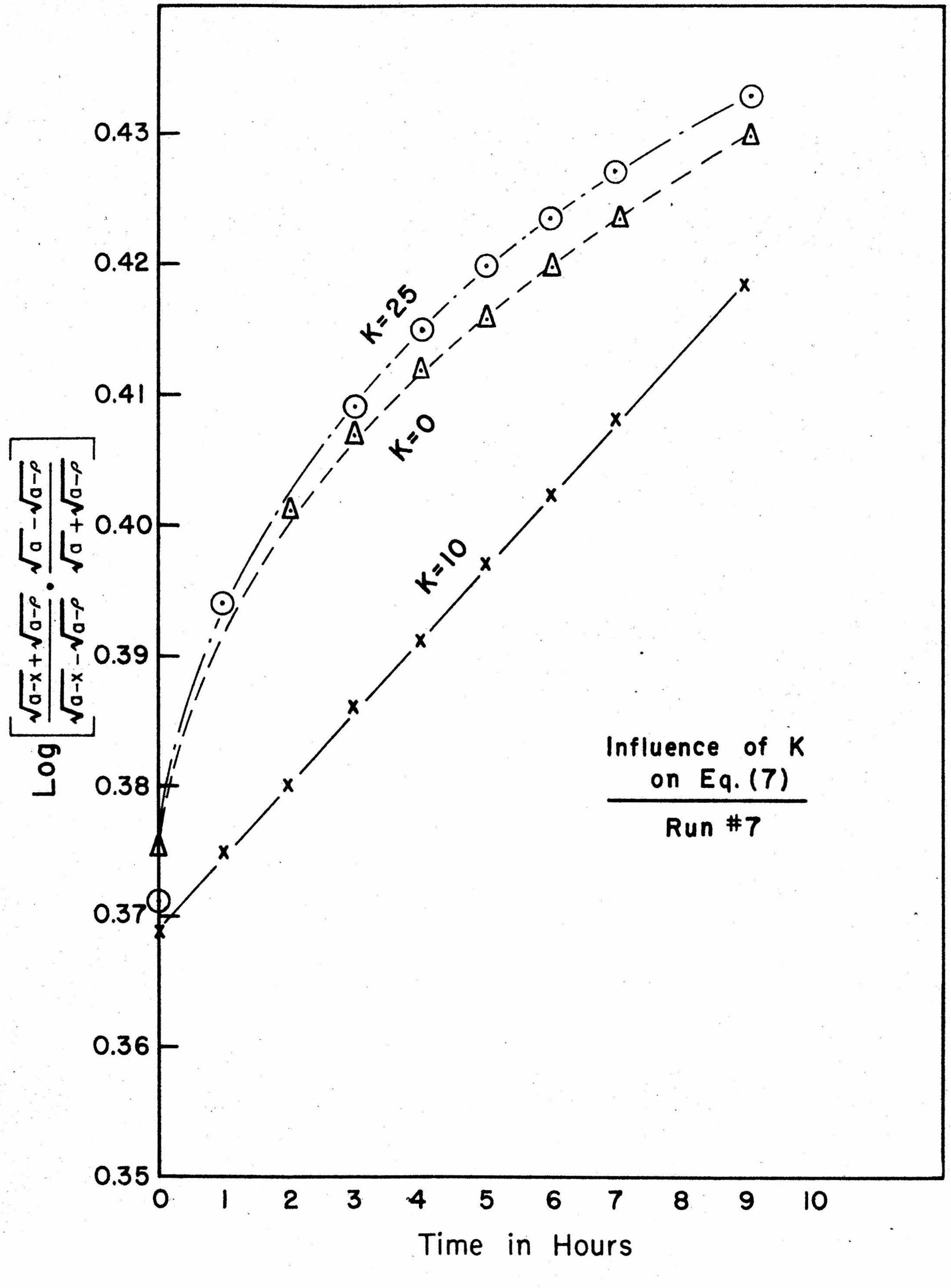
Temp. 25° $a = 0.0456$ ML^{-1} K = 70
Solv. Xylene $b = 0.1170$ ML^{-1})(= 0.1000

Time in hrs.	0.08	0.6	1.6	2.4	4.5	5.0	6.0
a-x in M	.0452	.0434	.0408	.0396	.0359	.0355	.0345
k_1 in hrs.$^{-1}$ M$^{-3/2}$	4.01	3.80	3.87	3.85	3.92	3.85	3.87

Run No. 13

Temp. 25° $a = 0.0945$ ML^{-1} K = 100
Solv. Xylene $b = 0.2340$ ML^{-1})(= 0.0775

Time in hrs.	0.07	0.6	1.6	2.4	4.5	5.0	6.0
a-x in M	.0934	.0829	.0700	.0608	.0502	.0477	.0425
k_1 in hrs.$^{-1}$ M$^{-3/2}$	3.91	3.89	3.96	4.09	3.66	3.65	3.80



$\text{Log}\left[\frac{\sqrt{a-x}+\sqrt{a-\rho}}{\sqrt{a-x}-\sqrt{a-\rho}}\cdot\frac{\sqrt{a}-\sqrt{a-\rho}}{\sqrt{a}+\sqrt{a-\rho}}\right]$
0.43
0.42
0.41
0.40
0.39
0.38
0.37
0.36
0.35
0
1
2
3
4
5
6
7
8
9
10
Time in Hours
K=25
K=0
K=10
Influence of K on Eq. (7)
Run #7

Figure 3

Table VI.

Summary of Rate Constants at 25°C.

Run No.	Solvent	HCl ML^{-1}	Diene ML^{-1}	$k_1^{(o)}$ $hr^{-1}M^{-3/2}$	Av. k_1 $hr^{-1}M^{3/2}$	Calc. K	Calc. k_2 $hr^{-1}M^{-1/2}$
3	Dioxane	0.892	1.050	0.089	0.100	10	0.0100
4	" "	.892	0.525	.098	.108	10	.0108
6	" "	.892	.350	.100	.105	10	.0105
2	" "	.582	1.050	.089	.106	10	.0106
1	" "	.400	1.050	.110	.103	10	.0103
7	" "	.200	0.754	.107	.110	10	.0110
11	Xylene	0.1150	0.1170	3.68	3.86	70	0.0526
18	" "	.0965	.1034	3.95	3.92	70	.0560
13	" "	.0945	.2340	3.55	3.89	100	.0389
15	" "	.0892	.0585	3.68	3.75	70	.0536
14	" "	.0456	.1170	3.68	3.86	70	.0551
17	" "	.0250	.1170	3.70	3.85	70	.0550
21	Bu Ether	0.645	0.500	0.180	0.192	15	0.0128
22	" "	.645	.250	.193	.190	15	.0127
25	" "	.350	.800	.186	.188	15	.0125

D. Mechanism of Reaction

It seems reasonable to postulate that when hydrogen chloride and diene are dissolved in a suitable solvent the following scheme of equilibria is established instantaneously:

a) $S + HCl = SH^{+} + Cl^{-}$

b) $D + HCl = DH^{+} + Cl^{-}$

c) $D + SH^{+} = DH^{+} + S$

where S denotes the solvent molecule, SH^{+} the protonated solvent molecule, D the diene molecule, and DH^{+} the protonated diene molecule. The protonated diene molecule used in our scheme should not be confused with the concept of carbonium ions. We consider a carbonium ion to be an activated intermediate with a very small life-time; whereas a protonated diene molecule is simply a molecular association complex between a proton and a double bond very similar in nature to protonated hydroxyl groups, etc.

Thus it is seen that the above scheme merely represents the distribution of proton in a system comprised of three basic constituents; the solvent molecules, the diene molecules, and the chloride ions. The tacit assumption is made that hydrogen chloride dissolved in solvents such as dioxane and xylene forms a mono-disperse system; although, the validity of such an assumption does not directly affect our conclusions.

The reaction between a molecule of hydrogen chloride and a molecule of diene may possibly proceed according to one of the four following steps:

i) $HCl + D \longrightarrow BuCl$

ii) $HCl + DH^{+} \longrightarrow BuCl + H^{+}$

iii) $Cl^{-} + DH^{+} \longrightarrow BuCl$

iv) $DH^{+} \longrightarrow \text{Carbonium ion} \xrightarrow{Cl^{-}} BuCl$

where BuCl denotes the butene chloride formed by adding one molecule of hydrogen chloride to the diene. Among the above listed possibilities we have included only those steps which proceed by a uni or bi-molecular mechanism. Other possible steps proceeding via higher molecular mechanisms would occur with a much smaller probability than the above mentioned and would require rate orders higher than the one observed experimentally.

If Eq. (i) were to describe the mechanism of our observed reaction, the rate would be proportional to the first power of both the hydrogen chloride and diene concentration; this is contrary to our observations. It will be shown that if Eq. (iv) were the correct mechanism, the observed rate would be proportional to the one-half power of the HCl concentration. Consequently, it remains to distinguish between (ii) and (iii) as possible mechanisms for our observed reaction.

We proceed to establish the correct mechanism by evaluating the concentrations of the various species in the scheme of equilibria, a), b), and c). Let <u>a</u> denote the initial concentration of hydrogen chloride and <u>b</u> denote the initial concentration of diene; then let x be the amount of hydrogen chloride dissociated in step a) and y be the amount dissociated in step b), and finally let z be the amount of protonated diene formed in step c). When equilibrium is established we have the following concentration of species present,

$$\begin{aligned} [HCl] &= a - x - y \\ [SH^+] &= x - z \\ [D] &= b - y - z \\ [DH^+] &= z + y \\ [Cl^-] &= x + y \,. \end{aligned}$$

And the following set of equilibrium relations must be satisfied:

$$\frac{[SH^+]\ [Cl^-]}{[HCl]\ [S]} = \frac{(x - z)\ (x + y)}{(a-x-y)\ (S)} = K_a$$

$$\frac{[DH^+]\ [Cl^-]}{[HCl]\ [D]} = \frac{(y + z)\ (x + y)}{(a-x-y)\ (b-y-z)} = K_b$$

$$\frac{[DH^+]\ [S]}{[SH^+]\ [D]} = \frac{(y + z)\ (S)}{(x - z)\ (b-y-z)} = K_c$$

The above represent three simultaneous equations in three unknowns; however, only two of the equations are independent since obviously $K_b/K_a = K_c$. Nevertheless, we may solve the set of equations, providing we make the assumption $\underline{x} > \underline{y}$. Since $\underline{x}$ represents the amount of hydrogen chloride dissociated through complexing with the solvent molecules while $\underline{y}$ represents the amount dissociated through complexing with diene molecules, and since solvent molecules in our system are present in large excess over diene molecules, the foregoing assumption is a reasonably valid one. An thus we arrive at the solutions,

$$x = \sqrt{a K_a [S]} = K' [HCl]^{1/2}$$

$$[DH^+] = (y + z) = \frac{K_c K'}{[S]} a^{1/2} b = K'' [HCl]^{1/2} [D]$$

$$[Cl^-] = (x + y) = \frac{K_b [S]}{K_c K'} a^{1/2} = K''' [HCl]^{1/2},$$

where we assume the concentration of the solvent to be constant.

Upon substituting the above solutions into Eqs. (ii) and (iii) of page 36, we find for Eq. (ii),

$$\frac{d}{dt}[HCl] = -k [DH^+][HCl] = -k K'' [HCl]^{3/2} [D]$$

and for Eq. (iii)

$$\frac{d}{dt}[HCl] = -k[DH^+][Cl^-] = -kK''K'''[HCl][D].$$

It is easily seen that for (iv) the rate would be proportional to $[HCl]^{\frac{1}{2}}$, as mentioned previously.

The above analysis indicates that Eq. (ii) is the one which describes correctly the observed rate order of the forward reaction, consequently we may depict the mechanism of reaction between one molecule of hydrogen chloride and diene in the following manner:

$$C_6H_{10} + HB^+ \rightleftharpoons [C_6H_{10}\cdot H]^+ + B \quad \text{(Rapid)}$$

$$[C_6H_{10}\cdot H]^+ + HCl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [C_6H_{11}Cl\cdot H]^+ \quad \text{(Slow)}$$

$$[C_6H_{11}Cl\cdot H]^+ + B \rightleftharpoons C_6H_{11}Cl + HB^+ \quad \text{(Rapid)}$$

where B is a base, such as chloride ion or solvent molecule, and is accordingly charged or neutral. In this scheme the second step is rate determining.

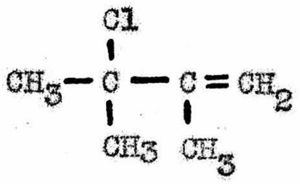
According to our postulated mechanism, the forward reaction between one molecule of hydrogen chloride and diene in aprotic solvents proceeds by a rapid complexing reaction between a diene molecule and a proton, followed by a slow attack on the protonated diene by a hydrogen chloride molecule. This mechanism is somewhat analogous to the ones proposed for the reaction between hydrogen chloride and olefins by Mayo and by Hennion[4]; however, the order of our observed reaction does not agree with the one proposed by these investigators.

The concept of terming a proton-double bond complex as the reactive species in hydrogen halide additions to unsaturated hydrocarbons did not originate with us. Similar schemes have been proposed by other workers; examples may be found among the works of Price[12b].

The mechanism proposed by us seems a rational one for the system under study. The addition of hydrogen halides to unsaturated hydrocarbons in solutions of aprotic solvents is not altogether different in behavior from such reactions as the acid catalyzed hydration of unsaturated hydrocarbons in water. In the systems under study the hydrogen chloride is present largely as the undissociated molecular species. This fact is indicated by the conductometric studies of Harned[13] on mixtures of water and dioxane. In this respect the systems under study resemble an aqueous acidic system, where the water molecule concentration is considerably greater than the hydroxyl ion concentration; it is the water molecule and not the hydroxyl ion, which adds to the protonated hydrocarbon during hydration. Consequently it is not at all surprising that in our system it is the relatively abundant hydrogen chloride molecule which adds and not the chloride ion. We must conclude that the forward reaction between one molecule of hydrogen chloride and diene is predominantly a simple acid catalysed addition reaction, very similar in nature to the acid catalysed hydration of unsaturated hydrocarbons; the striking difference between the two which should be kept in mind is the fact that whereas in aprotic solvents the concentration of such species as protonated dienes may be appreciable, their concentration in aqueous systems should be of a much lower order of magnitude.

Our discussion of the reverse reaction is limited to more or less superficial considerations since its characteristics have been inferred indirectly from the rate data for the forward reaction. In the previous section it was shown that the values of the reverse specific rate constant, k_2, were arbitrary to a certain extent, limited by the sensitivity of our analytic method. Nevertheless, the behavior of this reaction may be inferred from some general considerations and observations.

It seems reasonable to assume that the principal part of the initial addition reaction product is the 3-chloro isomer; we shall discuss the reverse reaction with respect to this compound, although the argument applies equally well to the 1-chloro isomer, with the allowance that the latter is somewhat less reactive than the former. From the structure of the 3-chloro compound it is easily seen that the chloride ion should be quite labile



$$CH_3-\overset{Cl}{\underset{CH_3}{C}}-\underset{CH_3}{C}=CH_2$$

since it is not only tertiary but also allylic. This fact was observed by us experimentally; in alcoholic solution the compound yields an immediate precipitate with silver nitrate, while in aqueous solutions at room temperature both isomers hydrolyse readily to the tertiary alcohol. In halide reactivity, it seems to us that this chloride should have an activity equal to or greater than that of tertiary butyl bromide.

Hughes, Ingold, and their co-workers have made an extensive study of the mechanism of olefin formation from alkyl halides[14]. Although their studies did not include aprotic solvents, their conclusions may be extrapolated to such systems. The findings of the above workers on molecules containing reactive halides, e.g. tertiary butyl chloride and bromide, indicate that these compounds tend to undergo primarily unimolecular elimination reactions, the rate determining step being a simple ionization of the halide, in systems not containing a large excess of basic constituent. The rate of such a reaction is largely the function of the ionizing power of the reaction medium. Our own observations on the butene chlorides formed during the course of the addition reaction fit in well with the above conclusions of the British group as elaborated upon by the more recent work of Swain[14a]. In a solution of pure dioxane a mixture of the butene chlorides developed no observable acidity over a prolonged period of time. However, our indicator studies and rate measurements indicate that in the presence of acid the butene chlorides do undergo an elimination reaction to form diene and hydrogen chloride. This is to be expected since aprotic solvents such as dioxane and xylene possess very poor ionizing powers. Upon introducing hydrogen chloride into the system, however, not only is its ionizing power improved, but the possibility of hydrogen-chlorine interaction facilitates greatly the elimination reaction.

Actually if the elimination reaction of our butene chloride be termed of the E_1 type, one should recognize the fact that the proton is instrumental in the reaction and that it is a protonated chloride complex which undergoes the "unimolecular" elimination. In this fashion the terminologies E_1 and E_2 become somewhat arbitrary. An E_2 reaction strictly requires a bimolecular collision followed by elimination. In one sense, the acid catalysed "E_1" differs from this only in that a loose molecular complex is first formed by chloride and proton and this complex then undergoes a "unimolecular" elimination reaction. Swain's opinions on the subject are quite similar.

In conclusion it must be stated that the mechanisms developed in this section are meant to apply strictly only to systems analogous to the ones investigated by us. It is quite conceivable that as the nature of the reaction system is changed the specific mechanism may also change.

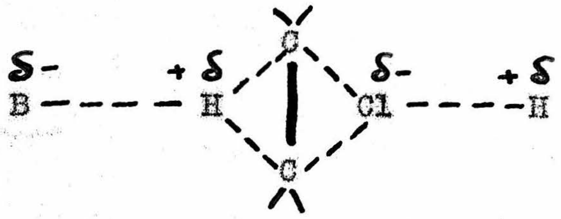
E. The Role of the Reaction Medium.

The effect of the solvent on the rate of ionic-type organic reactions may be surmised in a simple fashion by the use of the

Brønsted Theory of reaction rates. For the system under investigation, the theory gives the following relation for the specific rate constant of the forward reaction:

$$k_1 = k_1' \frac{\alpha_{HCl}\,\alpha_{DH^+}}{\alpha^*} \qquad \text{---- (8)}$$

where k_1' is the specific rate constant for the forward reaction in some chosen standard state and the α's denote the activity coefficients of the reacting species defined with respect to the same standard state; α^* is the activity coefficient of the activated complex formed during the reaction between the protonated diene molecule and the hydrogen chloride molecule. The structure of the complex leading to 1,2 addition is probably of the following nature:



where δ denotes partial charge and B is either a solvent molecule or a chloride ion and is accordingly either neutral or negatively charged. The structure of the complex leading to 1,4-addition is probably analogous; we shall elaborate on this question in a later part.

Our problem now is to determine what effect the solvent medium has on the values of the activity coefficients appearing in Eq. (8). In order to accomplish this we shall need to know how the activity coefficient of a solute species is related to the molecular properties of the solvent.

It is customary to define the activity coefficient of a solute species with respect to the infinitely dilute solution; i.e., the activity coefficient approaches unity as the concentration of the species approaches zero. Then roughly speaking the activity coefficient of a species in a given medium is inversely proportional to its solubility in that medium. It will be more instructive to look upon the activity coefficient of the solute species from the view point of order-disorder. An ideal solution is characterized by random distribution of molecules, i.e. disorder; and in such a solution the activity coefficient of the solute species is unity. As the amount of order increases in the solution, deviations from ideality increase and the activity coefficient of the solute species becomes different from unity by greater amounts. It is to be expected that in solutions of dilute and moderate concentrations, deviations from ideality will be negative leading to activity coefficient values less than unity. Furthermore, by applying Bjerrum's associated complex theory to our system, we would expect qualitatively that ordering in the solution due to solute-solvent interaction will lead to greater negative deviations than ordering due to solute-solute interaction.

In the light of the above discussion we may examine the effect of the solvent medium on the value of the activity coefficient of hydrogen chloride. The three solvents used in our rate studies range in order of basicity from dioxane to di-n-butyl ether to xylene. In none of these solvents do we expect the hydrogen chloride molecules to be considerably dissociated; however, the more basic the solvent the greater the amount of solvation which occurs. This solvation should take place largely through hydrogen bonding. The amount of order realized in the solution, and consequently the amount of deviation from ideality, should be directly proportional to the amount of solvation; i.e. solute-solvent interaction. Therefore, we shall expect that the activity coefficient of hydrogen chloride should increase as we go from dioxane to di-n-butyl ether to xylene. This variation in activity coefficient leads to increasing values for k_1 upon decreasing the basicity of the solvent.

The observed change in the rate constant upon variation of the basicity of the solvent medium may, however, not be ascribed solely to the change in the activity coefficient of hydrogen chloride; actually some of it is due to the variation in the ratio α_{DH^+}/α^* with change in solvent. Neglecting contributions from variation in dielectric constant and ionic strength, effects due to these being only secondary in the systems under investigation, we shall expect that the ratio α_{DH^+}/α^* will follow the same trend or the opposite trend as the hydrogen chloride activity coefficient, depending on whether the effective charge on the protonated diene molecule is greater or smaller than the one on the activated complex. This postulate is based on the supposition that the above species will be solvated in proportion to their effective charge and that the amount of solvation may in turn be related to the degree of order realized in the solution. It seems reasonable to assume that the protonated diene molecule will bear the larger effective charge and consequently the ratio α_{DH^+}/α^* will follow the same trend as α_{HCl} and contribute in similar fashion to the variation in k_1 with solvent.

It is somewhat difficult to ascertain precisely how large the relative contribution from the variation in α_{HCl} and α_{DH^+}/α^* is to the change in k_1 with solvent. However, since the system under investigation proceeds to a pseudo equilibrium, we may also examine the effect of solvent on the equilibrium constant. K as defined in our formulation is the concentration equilibrium constant; it is related to the thermodynamic equilibrium constant in the manner

$$K_{conc} = K_{thermo} \frac{\alpha_{HCl}\ \alpha_{Diene}}{\alpha_{BuCl}}$$

For two different solvents we then have the relation

$$\frac{K^1}{K^2} = \frac{\alpha^1_{HCl}}{\alpha^2_{HCl}} \cdot \frac{\alpha^1_{Diene}}{\alpha^2_{Diene}} \cdot \frac{\alpha^2_{BuCl}}{\alpha^1_{BuCl}} \qquad \text{----- (9)}$$

since K_{thermo} is independent of solvent properties. The ratio of diene activity coefficients should remain nearly constant, while the ratio of the butene chloride activity coefficients should not change appreciably with change in solvent. We may then expect the change in K to be due largely to the change in the hydrogen chloride activity coefficient. Comparing values of K and k_1 listed for the three solvents in Table VI, we see then that the change in k_1 with solvent is due more to the variation in α_{HCl} than in α_{DN^+}/α^*.

Application of the Bronsted Theory to the reverse reaction yields the expression

$$k_2 = k_2^1 \frac{\alpha_{HBuCl}}{\alpha^*} \qquad \text{---- (10)}$$

where HBuCl is the proton-butene chloride complex we postulate to be the reactive species in the reaction. This complex and the activated complex should have very similar structures and in theory k_2 should not be appreciably influenced by change in solvent medium. The data of Table VI bears this out to some extent; however, as we have pointed out previously, values of K and k_2 represent only orders of magnitude and should not be subject to rigorous analysis.

In the foregoing discussion we have used mainly quasi-thermodynamic arguments to explain the variation in specific rate constants with change in solvent medium. Under the section dealing with temperature effects, we shall mention another interpretation of this variation.

F. The Effect of Catalyst

A number of investigators have reported that the inorganic salts of a few heavy metals, such as mercury, silver, etc., act as catalysts in promoting the addition of hydrogen halides to olefins. Mayo[4] and his co-workers report that in the addition of hydrogen chloride to isobutylene in n-pentane solutions, water, phosphoric acid, and mercuric chloride acted as catalysts. In Table VII are listed a few rate determinations performed in the presence and absence of mercuric chloride. From our data it is seen that mercuric chloride does not act as a catalyst under the conditions of our experiments. The reason for this observation is quite evident. We have found the addition of hydrogen chloride to the conjugated double bond to be acid catalysed when carried out in solutions of aprotic solvents. In these solvents mercuric salts are not soluble enough to provide appreciable concentrations of mercury-diene complexes. If mercuric salts were to catalyse the reaction, they would probably act through the formation of such complexes. It is quite conceivable that in a system where the concentration of mercury-diene complexes becomes comparable to the concentration of proton-diene complex, it will be found that mercuric salts do act as catalysts. Other metallic salts were not tried since their solubilities are comparable or less than that of mercuric chloride in our solvent systems and their potential catalytic activity is probably lower. It is our belief that any agent capable of complexing with a system of conjugated double bonds or olefinic double bonds will catalyse the addition of hydrogen halides and similar reagents to these unsaturated bonds. This postulate is based on the supposition that complexing increases the polarizability of the unsaturated bond and consequently reduces the energy required to break open the double bond. Furthermore, if the complexing agent bears a charge, it will promote the attack of the double bond by an oppositely charged or polarized species. For example, the attack of the double bond in our diene molecule by hydrogen chloride molecules is rendered easier by the presence of a positive charge near the region of the double bond, the charge being due to the presence of the complexing proton.*

In addition to the effect of mercuric chloride on our system, we have also investigated the effect of oxygen. In Table VII are listed a few experiments carried out under conditions which carefully excluded the presence of any oxygen. It is seen that the rates obtained from these experiments compare with rates obtained in the presence of oxygen. These observations merely substantiate the well accepted theory that hydrogen chloride is not susceptible to "peroxide" effects, such as exhibited by hydrogen bromide.

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* It is interesting to note in connection with this discussion that recent investigations have shown silver salts to act as catalysts in promoting the polymerization of styrene [16] and vinyl ethers.

Table VII.

The Effect of Catalyst

Run No.	Solvent	HCl ML^{-1}	Diene ML^{-1}	$HgCl_2$ ML^{-1}	k_1 $hr^{-1}M^{-3/2}$
31	Dioxane	0.450	0.500	0.020	0.105
32	Dioxane	0.400	0.500		0.106
33	Dioxane	0.875	0.500	0.025	0.103
34	Dioxane	0.875	0.500		0.104
35	Dioxane	0.250	0.500	0.015	0.105
36	Dioxane	0.245	0.500		0.108
41	Dioxane	0.850	0.750		0.103
42	Dioxane*	0.850	0.750		0.104
43	Dioxane**	0.892	0.525		0.107
44	Xylene	0.0950	0.1050		3.90
45	Xylene*	0.0950	0.1050		3.92

* Carried out under N_2.

** Carried out under N_2 with 0.1% hydroquinone added to solvent.

G. The Effect of Temperature.

The rate of addition of hydrogen chloride to 2,3-dimethylbutadiene-1,3 was determined at 35°C. in dioxane and xylene. Using the data obtained at both 25° and 35°, we have calculated the activation energy for the reaction according to the Arrhenius equation,

$$\left(\frac{\partial \ln k}{\partial T}\right)_p = \frac{E^{\ddagger}}{RT^2}$$

$$k = A e^{-E^{\ddagger}/RT} \; ; \quad A = PZ \qquad \text{---- (11)}$$

We represent the constant term in the Arrhenius equation according to the simple collision theory, Z being the frequency of collision per second, per c.c. of solution, at unit concentration of reactants, and P being the probability factor. (Actually both P and Z are slightly temperature dependent, but over a ten degree change in temperature this variation is negligible.) The values of $E^{\ddagger}$ and PZ, along with the specific rate constants at the two temperatures, are listed in Table VIII.

It is seen that the value of the activation energy is the same in both dioxane and xylene, while the value of PZ is considerably higher in the latter. Since the value of Z is about the same in both solvents, the variation in PZ, and thus in k_1, may be ascribed solely to P. The significance in the variation of P is obvious; in the less basic solvent the probability of effective collisions should be greater than in the more basic.

By the term basic we are referring to solvating powers; solvation of the species hydrogen chloride and protonated diene results in a partial shielding of the reactants from each other and reduces the number of effective collisions between them.

From the tabulated values of the activation energy and frequency factors it is seen that the prime factor in the relatively slow rate of addition of hydrogen chloride to diene is the low value of P. We may conclude that the observed activation energy is characteristic for the reaction between a protonated diene molecule and hydrogen chloride molecule in a condensed system of aprotic solvents. The value of the probability factor, P, is largely a function of the basicity of the solvent medium. The order of magnitude of Z here[16b] is about 10^{11}, whereupon the order of magnitude of P becomes 10^{-7} for dioxane and 10^{-5} for xylene.

It is very interesting to observe that the values of P and E^{*} observed in our reaction system are very similar to the ones observed for Menschutkin type reactions[16] in systems of aprotic solvents. This fact is not too surprising when we realize that in Menschutkin type reactions we have a bi-molecular collision between the relatively negative nitrogen atom of the tertiary amine and the dipolar alkyl halide. The rate determining step here is the displacement reaction of the negative amine nitrogen on the alkyl halide. Similarly we may look upon our reaction as a displacement reaction on the hydrogen chloride

Table VIII.

The Effect of Temperature on Rate of Addition

Solvent	HCl ML^{-1}	Diene in Ml^{-1}	k_{25° in $hr^{-1}M^{-3/2}$	k_{35° in $hr^{-1}M^{-3/2}$	$E^{\ddagger}$ in K.cal.	PZ in $sec^{-1}c.c.^{-1}$
Dioxane	0.945	0.846	0.108	0.217	12.5	4.9×10^4
Dioxane	0.445	0.564	0.106	0.211	12.4	4.4×10^4
Dioxane	0.200	0.752	0.110	0.220	12.4	4.2×10^4
Xylene	0.0950	0.1200	3.82	7.65	12.5	165×10^4
Xylene	0.0450	0.1100	3.86	7.70	12.4	160×10^4
Xylene	0.0250	0.0860	3.85	7.72	12.5	165×10^4

Table VIIIa.

Heat of Addition

Temp. in°C	Solvent	K	ΔH in K cal/mole
25	Dioxane	10	-6.5
35	Dioxane	7	

molecule by the protonated diene molecule, which is carrying a diffused positive charge.

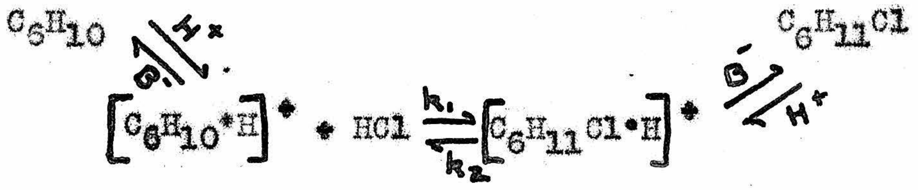
From the approximate values of the equilibrium constant, K, at 25°C. and 35°C. we can calculate the heat of the reaction, ΔH, using the integrated form of the van't Hoff equation,

$$\ln K_1/K_2 = -\frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right) .$$

Results are given in Table VIIIa.

VI. GENERAL DISCUSSION

From the analysis of the observed initial rates and the integrated specific rate constants* we have concluded that the addition of hydrogen chloride to 2,3-dimethylbutadiene-1,3 in the presence of aprotic solvents is a reversible reaction, the forward rate being proportional to the first power of the diene concentration and the three halves power of the hydrogen chloride concentration, and the reverse rate being proportional to the first power of the butene chloride concentration and the one half power of the hydrogen chloride concentration. The overall reaction is



$$\begin{tikzcd}
C_6H_{10} \arrow[d, shift left, "H^+"] & & C_6H_{11}Cl \arrow[d, shift left, "H^+"] \\
\left[C_6H_{10}\cdot H\right]^+ + HCl \arrow[u, shift left, "B^-"] \arrow[rr, shift left, "k_1"] & & \left[C_6H_{11}Cl\cdot H\right]^+ \arrow[ll, shift left, "k_2"] \arrow[u, shift left, "B^-"]
\end{tikzcd}$$

In our opinion the mechanism of this reaction bears a strong analogy to the mechanism of acid catalysed hydrations of olefins. The reactive species in both cases are a molecular complex between proton and unsaturated hydrocarbon on one part, and a dipolar molecule on the other part. We believe that the molecular complex is simply a proton coordinated with the unsaturated bond of the olefin or the system of conjugated double bonds of a diene.

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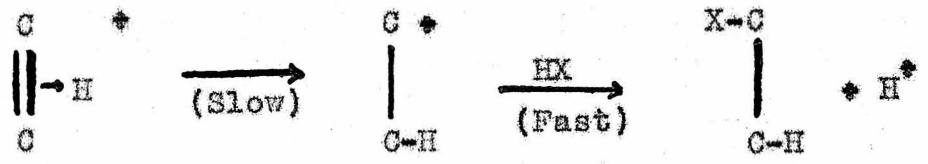
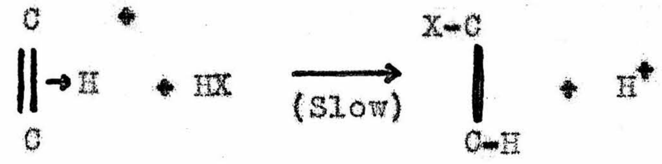
* See Section V, B, C.

In general a protonated unsaturated hydrocarbon may react with a dipolar molecule according to one of the following two schemes:

a)

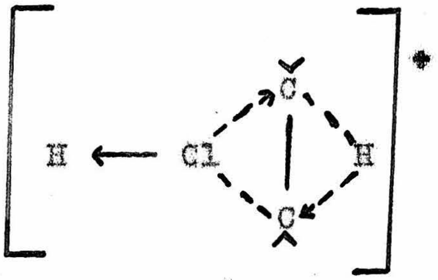


b)



The rate determining step in a) is unimolecular, whereas in b) it is bimolecular. The scheme depicted by a) is strictly analogous to the usual mechanisms given in textbooks for the addition of acids to unsaturated hydrocarbons; the rate determining step involves the formation of a carbonium ion which then reacts rapidly with a negative ion or the negative addendum of a dipolar molecule. The type of mechanism shown in a) should require a relatively small activation energy and may actually take place to some extent at lower temperatures. Our data indicates that at 25° and 35°C. the addition of hydrogen chloride to diene proceeds according to the scheme depicted in b). We do not believe that under the conditions of our experiments any significant amount of the addition reaction proceeds through a carbonium ion type of mechanism.

In our proposed mechanism a protonated diene molecule collides with a hydrogen chloride molecule, the chlorine part of the hydrogen chloride molecule becomes oriented with the protonated double bond, which at the same time repulses the hydrogen atom attached to the chlorine. Schematically this "push-pull" mechanism may be illustrated by



In the case of hydration, the HCl is to be replaced by HOH. The rate of hydration of simple olefins has been found proportional to the first power of the acid concentration and the first power of the olefin concentration[17]. Obviously in water the proton concentration will be proportional to the concentration of the strong acid used as proton source, and the concentration of the protonated olefin will then be proportional to the first power of this acid's stoichiometric concentration and the first power of the olefin concentration. Water being present as solvent and thus in large excess, the rate of hydration at a given acid concentration will be pseudo first order. In systems of aprotic solvents, acids which appear to be strong in water behave as if they were weak acids. In such cases the proton concentration is no longer proportional to the first power but to the one half power of the acid's stoichiometric concentration. This explains why the observed rate orders for hydration and hydrogen chloride addition are quite different, although their mechanisms are closely analogous.

One further analogy may be drawn between our system and the Menschutkin type reactions discussed previously. It has been pointed out[16] that the latter types of reactions are characterized by the fact that in aprotic solvents of low dielectric constant the observed slow rate of reaction is due primarily to a low value for the probability factor, P. As the solvent medium is changed to hydroxylic systems the value of the activation energy increases along with the value of P. We may observe that this trend also takes place when we go from the addition of hydrogen chloride to the double bond in aprotic solvents of low dielectric constant to the addition of water to the double bond in aqueous media[17].

It is our belief that in the acid catalysed addition reactions to unsaturated hydrocarbons the role of the solvent medium is two fold. One is of a specific nature dependent on the ability of the solvent molecules to interact with the reactant species. To this category belong the solvating properties of the medium due to specific chemical properties, such as hydrogen bonding, basicity, etc. The second role of the solvent medium depends on its electrostatic properties, that is, the dielectric constant, ionic strength, and van der Waals forces.

At this point it will be worthwhile to discuss briefly the question of 1,2 vs. 1,4 addition to conjugated systems. We are concerned here with electrophilic reactions of two types; in one we have a molecule of HB adding to one conjugated system, in the other we have a molecule of AB. By B we are denoting a Lewis type base, while in AB we simply denote by A the positive addendum of the species. In the first type of addition reaction we have a simple acid such as hydrogen chloride or hydrogen bromide reacting. It has been observed in this presentation and by other workers[15] that under normal conditions these simple acids always add predominantly 1,2 to alkyl substituted conjugated dienes. In the second case two alternatives have been observed. If A is a relatively small molecule, such as chlorine, then AB will add predominantly 1,2 regardless of the nature of B. Examples studied have been chlorine, hypochlorous acid, and alkyl hypochlorites.[18,19] However, if A is a larger molecule, such as bromine or iodine, the addition appears to be predominantly 1,4. Examples given are the addition of bromine, and iodine monochloride[20].

A reasonable explanation of these facts may be based on the following postulate. If the initially attacking positive species orients with one of the double bonds only, the resulting addition reaction will lead predominantly to the 1,2 isomer. However; if the positive species is large enough to orient with both of the conjugated double bonds; that is, complex with the entire conjugated system, then the addition reaction will lead to the 1,4 isomer. These two types of attacks have recently been termed terminal and frontal respectively. If 1,4 addition is due largely to a frontal attack by the positive addendum, then a certain amount of *cis* product is to be expected. This has indeed been found by the work of Johnson and Sweeting on the addition of bromine to 2,3-dimethylbutadiene-1,2[20]. Since we do not believe that most addition reactions of olefinic systems proceed by a carbonium ion mechanism, it is not justifiable to draw resonance structures for a postulated carbonium ion intermediate and explain 1,2 vs. 1,4 addition on this basis. This procedure is usually presented in most textbooks on organic chemistry. We simply assume that the negative addendum of the reacting species will add to that double bond which carries the largest share of the positive charge and that this will be located at the site of the complexed positive addendum. If we have a frontal attack and complexing by the positive addendum, the two positions will be *drained* of positive charge; whereas in a terminal attack and complexing it will be *fortified* with positive charge.

Although the original purpose of the present study included comparison of the reactivity of 2,3-dimethylbutadiene-1,3 with that of other simple olefins, the material presented in this work and available in the present literature does not allow us to do this. Unfortunately the studies carried out by Mayo and his co-workers[4] at 0°C. failed to include activation energies and leave us unable to compare our reaction studies with theirs. It seems imperative that similar studies to ours be carried out on simple olefinic substances, such as iso-butylene, for example.

The electronic theories relating nature of substituents to chemical reactivity have been carried out to a fairly successful state; however, no quantitative data exists relating the reactivity of conjugated systems with simple olefinic systems. It is to be expected that the conjugated system be somewhat more reactive to electrophilic reactions than the simple olefin; but quantitative data should be secured to justify such a generally accepted supposition.

It may also be worthwhile to re-investigate the entire question of carbonium ion mechanism in electrophilic addition reactions of unsaturated hydrocarbons. The additions of simple acids are invariably represented by carbonium ion mechanisms; we question the validity of this greatly.

VII. CONCLUSION

Analysis of kinetic data has shown that the reaction between hydrogen chloride and 2,3-dimethylbutadiene-1,3 in aprotic solvents of low dielectric constant proceeds predominantly by a simple acid catalysed reaction; the rate determining step involves the reaction of a protonated diene molecule with a hydrogen chloride molecule. In this respect our findings agree with the postulates of previous workers to some extent. Our rate data do not indicate any of the complications proposed by such workers as Mayo and his students, who studied the analogous addition reaction to isobutylene. Our kinetic data indicates that the reaction between one molecule of hydrogen chloride and diene is reversible, the reverse reaction being a simple elimination type reaction quite similar in nature to the ones studied by Swain, Hughes and Ingold, and other workers in the field.

The addition of the one molecule of hydrogen chloride to the diene yields predominantly the 1,2 isomer initially and in this respect agrees quite well with the findings of Kharasch and coworkers on the addition of hydrogen chloride to butadiene-1,3.

As expected, variation in the basicity of the solvent medium produced sharp variation in the rate of addition. Analysis of temperature effects showed this solvent effect to be expressed solely in the values of the probability factor, P, the value of the activation energy being largely independent of basicity properties. The effect of the solvent may be explained on the basis of solvating power.

In the system under study only proton donating compounds were found to act as effective catalyst. Oxygen and mercuric chloride had no effect on the rate of addition.

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I. INTRODUCTION

When a system consisting of macromolecules dispersed in a liquid medium of low molecular weight is set into motion, the velocity gradients produced in the fluid give rise to the irreversible processes of viscous flow and flow birefringence. The experimentally determined value of the shear viscosity coefficient of such a solution is due in part to the inherent viscosity of the solvent and in part to the presence of the dispersed solute. It has been common practice to define a quantitity, called the intrinsic viscosity, as the increment in the measured shear viscosity coefficient of the solution produced by the macromolecular solute at infinite dilution. More recently it has been reported[1] that when the velocity gradient in the fluid is not constant but a periodic function of time, the solution exhibits a rigidity modulus in addition to the shear viscosity.

It is the purpose of this presentation to give a detailed theory of the intrinsic viscosity, intrinsic rigidity, and flow birefringence of solutions of rod-like macromolecules.

The theoretical study of the effect of the presence of relatively large rigid particles upon the viscosity of the solution owes its origin to the work of A. Einstein[2], who calculated the relative increase in viscosity due to spherical particles. Einstein's pioneering work has been extended by many investigators to cover particles of ellipsoidal, cylindrical, and many other shapes. An excellent review of work in the field up to

1938 is given by J. M. Burgers[3]. The most notable recent achievement in this field is due to R. Simha[4], who has treated solute particles with prolate and oblate ellipsoidal and simple dumbbell-like shapes. In this presentation we shall not be concerned with theories of viscosity of solutions of flexible macromolecules; an authoritative review on this subject is given by R. F. Boyer[5] and R. Simha.

The phenomenon of flow birefringence was first observed by J. C. Maxwell[6] in 1870, who noted that Canada balsam, although isotropic at rest, became birefringent under shearing stress. Later workers found many more cases of flow birefringence, also termed double refraction of flow, exhibited by solutions of macromolecules[7]. The problem of flow birefringence received its first successful theoretical treatment from P. Boeder[8], who calculated the angle of birefringence and magnitude of birefringence for solutions of infinitely thin, needle-like particles. In later years A. Peterlin and H. A. Stuart[9] treated the case of prolate ellipsoids aided by the mathematical treatment of Jeffrey[10] on the rotary motion of ellipsoids subjected to a velocity gradient. A comprehensive review of existing theories of flow birefringence is now available[11].

The detailed theory of intrinsic viscosity, intrinsic rigidity, and flow birefringence of solutions of rod-like macromolecules presemted in this thesis is based on the general statistical mechanical theory of irreversible processes in solutions of macromolecules developed previously by J. G. Kirkwood[12]. It will be shown that our formulations lead to an improved theory of intrinsic viscosity and a new theory of intrinsic rigidity. Except for Simha[4], all other workers in the field[13,14] have failed to take into account adequately the influence of Brownian motion. It is found that when the hydrodynamic torques are equated not to zero but to the rotary diffusional torques, the statistical orientation of the macromolecule in the velocity field of the solvent, which is responsible for flow birefringence, contributes a linear as well as non-linear terms in the rate of shear to the stress, and thus to the Newtonian part of the viscosity. This term exhibits relaxation phase lags in the non-stationary case and imparts to the solution a rigidity modulus. Our calculations will show that for long rod-like particles inclusion of the orientational factor contributes a term to the intrinsic viscosity which is three times larger than the terms ordinarily considered.

Simha has shown[4] that in the limit of small velocity gradient new boundary conditions have to be satisfied by solutions of the Navier-Stokes equation. By this means he was able to account for the effect of Brownian motion on the statistical orientation of rigid prolate and oblate ellipsoids and rigid dumbells in the velocity field of the solvent. In a later part we shall compare our results with those of Simha and show his calculations to be the static limit of ours.

Application of our theories to flow birefringence yields results similar to the ones obtained by Boeder but including the definite determination of the diffusion constant.

II. PHYSICAL PRELIMINARIES

For the purposes of our present work we shall take as our model a set of 2n+1 groups, in which the hydrodynamic interactions of the monomeric elements composing the polymer chain are located, separated by 2n equidistant bonds of length b each, arranged so that the angle between successive bond vectors is equal to zero. This model is the same as the one used previously by Riseman and Kirkwood[13]. As in the general theory of Kirkwood, the configuration of the rigid "polymer" chain is specified by the 6n+3 dimensional vector $\vec{R}$,

$$\vec{R} = \sum_{l=-m}^{+m} \vec{R}^{(l)} \qquad \text{---- (1)}$$

The superscript l denotes a vector of magnitude R in the three dimensional sub-space of the lth. element of the rigid chain; vectors without superscripts denote vectors in the common three space of all elements. The chain space is spanned by two unitary vectors

$$\vec{a}_\theta = \sum_{l=-m}^{+m} \frac{\partial \vec{R}^{(l)}}{\partial \theta}$$

$$\vec{a}_\varphi = \sum_{l=-m}^{+m} \frac{\partial \vec{R}^{(l)}}{\partial \varphi} \qquad \text{---- (2)}$$

where θ and φ are respectively the polar and azimuthal angles formed by the vector $\vec{R}$ with respect to an external system of cartesian coordinates $\vec{e}_x$, $\vec{e}_y$, and $\vec{e}_z$. For the sake of convenience we place this external system of coordinates so that its origin coincides with the center of mass of the rigid "polymer" chain.

The covariant and contravariant components of the metric tensor of chain space are now given by

$$g_{\alpha\beta} = \sum_{\rho=-n}^{+n} \frac{\partial \vec{R}^{(\rho)}}{\partial q^{\alpha}} \cdot \frac{\partial \vec{R}^{(\rho)}}{\partial q^{\beta}}$$

$$g^{\alpha\beta} = \frac{|g|_{\alpha\beta}}{g}$$

$$q^{\alpha}, q^{\beta} = \vartheta, \varphi \qquad \text{---- (3)}$$

where g is the determinant formed by the elements $g_{\alpha\beta}$ and $/g/_{\alpha\beta}$ denotes the minor of this element.

For the rigid chain model previously described we find the following relations:

$$\vec{R} = b \sum_{-n}^{+n} l\, \vec{e}_R^{\,(\rho)} \quad ;$$

$$\vec{a}_{\vartheta} = b \sum_{-n}^{+n} l\, \vec{e}_{\vartheta}^{\,(\rho)} \quad ; \quad \vec{a}_{\varphi} = b \sin\vartheta \sum_{-n}^{+n} l\, \vec{e}_{\varphi}^{\,(\rho)} \quad ;$$

$$g_{\vartheta\vartheta} = b^2 \sigma \quad ; \quad g_{\varphi\varphi} = b^2 \sigma \sin^2\vartheta \, ;$$

$$g_{\vartheta\varphi} = 0 = g_{\varphi\vartheta} \quad ; \quad g^{\alpha\beta} = 1/g_{\alpha\beta}$$

$$g = b^4 \sigma^2 \sin^2\vartheta \quad ; \quad \sigma = \frac{n(n+1)(2n+1)}{3}$$

---- (4)

where $\vec{e}_R$, $\vec{e}_\vartheta$, $\vec{e}_\varphi$ are the three orthogonal unit vectors of spherical polar coordinates.

We suppose the macromolecule to be immersed in a fluid continuum of viscosity coefficient η_0. If the velocity $\vec{u}_1$ of chain element 1 differs from the velocity $\vec{v}_1$ the fluid would have if that element were absent from the chain, it is supposed to experience a frictional force, $\vec{F}_1$, of magnitude

$$\vec{F}_\ell = \zeta \, \vec{w}_\ell$$

$$\vec{W} = \vec{v}_\ell - \vec{u}_\ell \qquad \text{---- (5)}$$

where ζ is the Brownian motion friction constant, common to all chain elements. From the three dimensional vectors, $\vec{F}_1$, $\vec{u}_1$, and $\vec{v}_1$ we may construct 6n+3 dimensional vectors in the configuration space of chain elements:

$$\vec{F} = \sum_{\ell=-n}^{+n} \vec{F}^{(\ell)}$$

$$\vec{u} = \sum_{-n}^{+n} \vec{u}^{(\ell)}$$

$$\vec{v} = \sum_{-n}^{+n} \vec{v}^{(\ell)} \qquad \text{---- (6)}$$

It is to be noted that $\vec{u}$ has no components outside of chain space, while $\vec{F}$ and $\vec{v}$ my have outside components. Therefore,

$$\vec{u} = \sum_\alpha \vec{a}_\alpha \, \dot{q}^\alpha \qquad \text{---- (7)}$$

If the fluid is in a state of motion with velocity field $\vec{v}^{\,o}(\vec{R}_1)$ before introduction of the entire macromolecule, we may define a configuration vector

$$\vec{v}^{\,o} = \sum_{l=-n}^{+n} \vec{v}^{\,o(l)}$$

$$\vec{v}^{\,o}_{l} = \vec{v}^{\,o}(\vec{R}_{ol}) \qquad \text{---- (8)}$$

which will in general differ from $\vec{v}$ due to the hydrodynamic perturbations produced by the other chain elements of the macromolecule at the point of location of any given element $\underline{1}$. These perturbations are determined in the quasi-stationary case by the Oseen formula

$$\vec{v}_{l} = \vec{v}^{\,o}_{l} - \sum_{\substack{s=-n \\ \neq l}}^{+n} \underset{\sim}{T}_{ls} \cdot \vec{F}_{s}$$

$$\underset{\sim}{T}_{ls} = \frac{1}{8\pi\eta_0 R_{ls}}\left[\underset{\sim}{1} + \frac{\vec{R}_{ls}\vec{R}_{ls}}{R_{ls}^{2}}\right] \qquad \text{---- (9)}$$

Eq. (9) may be generalized to configuration space in the form

$$\vec{v} = \vec{v}^{\,o} - \underset{\sim}{T} \cdot \vec{F}$$

$$\underset{\sim}{T} = \sum_{\substack{l,s=-n \\ l \neq s}}^{+n} \underset{\sim}{T}^{(ls)}$$

$$\underset{\sim}{T}^{(ls)} = \frac{1}{8\pi\eta_0 R_{ls}}\left[\underset{\sim}{1}^{(ls)} + \frac{\vec{R}^{(l)}_{ls}\,\vec{R}^{(s)}_{ls}}{R_{ls}^{2}}\right] \qquad \text{---- (10)}$$

where $\vec{R}^{(1)}_{1s}$ denotes a vector in 1-space with direction and magnitude equal to that of R_{1s} in the common three space of all chain elements.

III. STATISTICAL ORIENTATION IN THE VELOCITY FIELD

We denote by $f(\vartheta, \varphi, t)$ the probability density in chain space of the ensemble from which the system is sampled in the act of making a macroscopic observation. The probability density is determined by the theory of Brownian motion in the manner described previously[12].

With neglect of inertial terms, the theory of Brownian motion gives the relations

$$\left[F_\alpha + X_\alpha - \frac{\partial V_0}{\partial q^\alpha}\right] f - kT \frac{\partial f}{\partial q^\alpha} = 0$$

$$F_\alpha f = \sum_\beta \zeta_{\alpha\beta} \left[v^{0\beta} f - j^\beta\right] \qquad \text{---- (11)}$$

$$J^\beta = f \dot{q}^\beta$$

where X_α is a covariant component of the external force, F_α and F^α are covariant and contravariant components of the frictional force respectively, j^β is a contravariant component of the probability current density in chain space, V_0 is the potential of the mean internal binding torques, and $\zeta_{\alpha\beta}$ is a covariant component of the friction tensor defined by the relation

$$F_\alpha = \sum_\beta \zeta_{\alpha\beta} \left(v^{0\beta} - \dot{q}^\beta\right) \qquad \text{---- (12)}$$

The probability current density satisfies the continuity equation,

$$\frac{1}{\sqrt{g}} \sum_{\beta} \frac{\partial}{\partial q^{\beta}} \left(\sqrt{g}\, j^{\beta} \right) + \frac{\partial f}{\partial t} = 0 \qquad \text{---- (13)}$$

Elimination of j^{β} between Eqs. (11) and (13) yields the partial differential equation

$$\sum_{\alpha,\beta} \frac{1}{\sqrt{g}} \frac{\partial \sqrt{g}}{\partial q^{\beta}} \left\{ D^{\alpha\beta} \frac{\partial f}{\partial q^{\alpha}} + \frac{D^{\alpha\beta}}{kT} \frac{\partial V_0}{\partial q^{\alpha}} f \right\} - \frac{\partial f}{\partial t}$$

$$= \sum_{\alpha,\beta} \frac{1}{\sqrt{g}} \frac{\partial \sqrt{g}}{\partial q^{\beta}} \left\{ \frac{D^{\alpha\beta}}{kT} X_{\alpha} f + g^{\alpha\beta} v_{\alpha}^{0} f \right\} \qquad \text{---- (14)}$$

$$D^{\alpha\beta} = kT \left(\zeta^{-1} \right)^{\alpha\beta}$$

with the boundary conditions that f be single-valued in the internal chain space coordinates, specifying the internal and external orientation of the macromolecule, supplemented by appropriate boundary conditions in the center of mass space determined by the experimental arrangements imposed by the observer. Except in the case of translational diffusion and sedimentation, the center of gravity coordinates are in general redundant, since f may be considered independent of them. $D^{\alpha\beta}$ of Eq. (12) is the diffusion tensor and is defined by the Einstein relation given above.

In the case of the rigid chain V_0 is zero; for the sake of simplicity we also set the external forces equal to zero. The general diffusion equation now takes the simple form

$$D_o \nabla^2_{\vartheta,\varphi} f - \frac{\partial f}{\partial t} = \vec{\nabla}_{\vartheta,\varphi} \cdot (\vec{r}^{\,\circ} f)$$

---- (15)

where D_o is a constant to be described later, and the operator $\vec{\nabla}$ contains only the angular terms ϑ, φ.

For low values of the velocity gradient the probability density f may be expanded in a power series of the rate of strain, $\dot{\varepsilon}$,

$$f(\vartheta,\varphi,t) = f_o\left[1 + \dot{\varepsilon} f_1 + \dot{\varepsilon}^2 f_2 + \text{----}\right]$$

---- (16)

The value of f_o is given by the equilibrium cannonical ensemble,

$$f_o = e^{\beta[A_o = V_o]}$$

$$\beta = 1/kT$$

---- (17)

where A_o is the internal configurational free energy of the macromolecule and V_o is as defined above and has the value zero for the rigid chain. The equilibrium value of f is normalized to unity, and consequently f_o has the value

$$1 = \int_v f_o \, d\,vol.$$

$$= \int_0^{2\pi}\int_0^{\pi} b^2 \sigma f_o \sin\vartheta \, d\vartheta \, d\varphi$$

$$f_o = (4\pi\sigma b^2)^{-1}$$

---- (18)

For laminar flow parallel to the x direction the unperturbed velocity of the fluid at a point $\vec{R}_{o1}$ from the origin is given by:

$$\vec{v}_\ell^{\,\circ} = \overset{\circ}{\mathcal{E}} \, (\vec{R}_{o\ell} \cdot \vec{e}_y) \, \vec{e}_x$$

$$\overset{\circ}{\mathcal{E}} = \overset{\circ}{\mathcal{E}}_0 \, e^{i\omega t}$$

---- (19)

Insertion of Eqs. (16) and (19) into Eq. (15), and performing a Fourier analysis upon the time component of f_1,

$$f_1(\vartheta, \varphi, t) = \int_{-\infty}^{+\infty} f_1(\vartheta, \varphi, \omega) \, e^{i\omega t} \, d\omega$$

---- (20)

leads to the following equation:

$$\frac{D_0}{\sigma b^2} \left\{ \frac{1}{\sin\vartheta} \left(\sin\vartheta \, \frac{\partial}{\partial\vartheta} f_1 \right) + \frac{1}{\sin^2\vartheta} \frac{\partial^2 f_1}{\partial\varphi^2} \right\} - i\omega f_1$$

$$= \frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \left(\sin\vartheta \, \vec{v}^{\,\circ} \cdot \vec{a}_\vartheta \right) + \frac{1}{\sin\vartheta} \frac{\partial}{\partial\varphi} \left(\vec{v}^{\,\circ} \cdot \vec{a}_\varphi \right)$$

$$= -\frac{3}{2} \sin^2\vartheta \, \sin 2\varphi$$

$$f_1(\vartheta, \varphi, \omega) = \frac{3/2}{\gamma + i\omega} \sin^2\vartheta \, \sin 2\varphi$$

$$\gamma = \frac{6 D_0}{\sigma b^2}$$

---- (21)

IV. THE DIFFUSION CONSTANT

The friction tensor has been defined above by the relation

$$F_\alpha = \sum_\beta \zeta_{\alpha\beta}(v^{0\beta} - \dot{q}^\beta) \qquad \text{---- (12)}$$

From the relations for $\vec{F}$, Eqs. (5), (6), (7), and (10), we obtain the system of equations

$$\zeta_{\alpha\beta} = \zeta g_{\alpha\beta} - \zeta \sum_\gamma T^\gamma_\alpha \zeta_{\gamma\beta} \qquad \text{---- (22)}$$

and by the methods of tensor analysis we arrive at the following equation for the inverse of the friction tensor:

$$(\zeta^{-1})^{\alpha\beta} = g^{\alpha\beta}/\zeta + T^{\alpha\beta} \qquad \text{---- (23)}$$

The diffusion tensor is then given by the Einstein relation,

$$\begin{aligned} D^{\alpha\beta} &= kT(\zeta^{-1})^{\alpha\beta} \\ &= kT\left\{\frac{g^{\alpha\beta}}{\zeta} + T^{\alpha\beta}\right\} \end{aligned} \qquad \text{---- (24)}$$

Eq. (24) thus determines the contravariant components of the generalized diffusion tensor in chain space.

We now define a constant, D_0, by the relation

$$D^{\alpha\beta} = D_0 g^{\alpha\beta} \qquad \text{---- (25)}$$

The value of this constant for the case of the rigid chain may be evaluated in the following manner:

$$T_{\alpha\beta} = \vec{a}_\alpha \cdot \underset{\sim}{T} \cdot \vec{a}_\beta$$

$$T^{\alpha\beta} = \sum_{\mu,\nu} g^{\nu\alpha} g^{\mu\beta} T_{\mu\nu}$$

$$T_{\theta\theta} = \frac{\lambda_0}{\zeta} \sum_{\substack{l,s=-n \\ l \neq s}}^{+n} \frac{R_{ol} R_{os}}{|l-s|}$$

$$T_{\varphi\varphi} = \frac{\lambda_0}{\zeta} \sum_{\substack{l,s \\ =-n \\ l \neq s}}^{+n} \frac{R_{ol} R_{os}}{|l-s|} \sin^2\theta$$

$$\lambda_0 = \zeta/8\pi\eta_0 b$$

$$D_0 = \frac{kT}{\zeta}\left\{1 + \lambda_0 \sum_{l \neq s} \frac{ls}{|l-s|} \Big/ \sum_l l^2\right\}$$

$$= \frac{kT}{\zeta}\left(1 + \rho/\sigma\right)$$

$$\rho = \lambda_0 \sum_{\substack{l \neq s \\ =-n}}^{+n} \frac{ls}{|l-s|} = 2\lambda_0 \sum_{\substack{l > s \\ =-n}}^{+n} \frac{ls}{|l-s|}$$

$$= 2\lambda_0 \int_{-n+1}^{n} \int_{-n}^{x-1} \frac{xy}{x-y}\, dx\, dy$$

$$= \frac{4\lambda_0 n^3}{3}\left(\ln 2n - \frac{4}{3}\right) + O(n^2)$$

$$D_0 = \frac{kT}{\zeta}\left[1 + 2\lambda_0\left(\ln 2n - 4/3\right)\right]$$

V. THEORY OF INTRINSIC VISCOSITY AND RIGIDITY

Two common methods exist for calculating theoretically the intrinsic viscosity of a solution of macromolecules. The first method was introduced by A. Einstein[2] and involves the calculation of the rate of dissipation of energy per unit volume of fluid. This is the method employed by R. Simha[4] and most other workers in the field. The second method involves the calculation of the effective rate of shear at the boundaries of flow and was used by Burgers[3] in his analysis of intrinsic viscosities of rigid particles. The second method is the more suitable to employ in the case of viscous flow between parallel plates, such as realised in a Couette viscometer apparatus.

The method of calculation of intrinsic viscosity employed below is based on the general theory of intrinsic viscosity developed by Kirkwood and Riseman[15] previously and follows the methods employed by Burgers. At this point only pertinent results of the Kirkwood Riseman method need to be quoted.

The perturbation in the flow, $\vec{v}'$, produced by the molecule as a whole at a point $\vec{R}$ from its center of mass is given by the Oseen formula as

$$\vec{v}'(\vec{R}) = \frac{1}{8\pi\eta_0} \sum_{l=-n}^{+n} \left\{ \frac{\vec{F}_l}{|\vec{R}-\vec{R}_{0l}|} + \frac{(\vec{R}-\vec{R}_{0l})(\vec{R}-\vec{R}_{0l}) - \vec{F}_l}{|\vec{R}-\vec{R}_{0l}|^3} \right\} \text{----} \quad (27)$$

When this velocity perturbation depending on the frictional forces, $\vec{F}_l$, is expanded in spherical harmonics and averaged over all configurations of the chain, one obtains at distances large relative to the linear dimensions of the chain

$$\langle \vec{v}\,' \rangle_{Av.} = -\frac{3\xi G\dot{\varepsilon}}{4\pi\eta_0 R^5}(\vec{R}\cdot\vec{e}_x)(\vec{R}\cdot\vec{e}_y)\vec{R}$$

$$G = -\frac{1}{\xi\dot{\varepsilon}}\sum_{l=-m}^{+m}\left\langle(\vec{F}_l\cdot\vec{e}_x)(\vec{R}_{0l}\cdot\vec{e}_y)\right\rangle_{Av.}$$

---- (28)

Following the methods of Burgers, the contributions at the parallel plane boundaries produced by all the solute molecules contained between the planes are summed; whereupon it is found that at constant shearing stress the velocity gradient is reduced by an amount which leads to the following expression for the intrinsic viscosity:

$$[\eta] = \lim_{c\to 0}\left[\frac{\eta-\eta_0}{\eta_0 c}\right] = \frac{N\xi G}{100\,M\,\eta_0} \qquad \text{---- (29)}$$

M is the molecular weight of the macromolecule, N is Avogadro's number, and c is the solute concentration in grams per 100 ml. Eq. (29) is strictly valid only if inertial terms in the Navier-Stokes equation are neglected.

If the rate of strain is not constant but a complex function of time, G and $[\eta]$ are also complex.

$$G = G' = i\,G'' \qquad [\eta'] = \frac{N\zeta G'}{100\,M\eta_0}$$

$$[\eta] = [\eta'] - i\,[\eta''] \qquad [\eta''] = \frac{N\zeta G''}{100\,M\eta_0}\ .$$

---- (30)

The intrinsic rigidity, $[\mu]$, is phenomenologically related to $[\eta'']$ in the following manner:

$$\begin{aligned}[\mu] &= \lim_{c\to 0} \mu/c \\ &= \omega\eta_0\,[\eta''] \\ &= \frac{N\zeta\omega G''}{100\,M}\ .\end{aligned}$$

---- (31)

The expression for the frictional force is as given before,

$$\vec{F}_l = -\zeta(\vec{v}^{\,0}_l - \vec{u}_l) - \zeta \sum_{\substack{l\neq s \\ = -n}}^{+n} \underset{\sim}{T}_{ls}\cdot\vec{F}_s$$

---- (32)

where $\vec{u}_l$ is the velocity of the <u>l</u>th. chain element. In order to determine $\vec{u}_l$ we return to Eq. (11) and find, since $\vec{u}$ has no components outside of chain space,

$$v^{0\alpha} - u^{\alpha} = \sum_{\beta} D^{\alpha\beta}\frac{\partial \ln f}{\partial q\beta}$$

$$\vec{v}^{\,0} - \vec{u} = \vec{v}^{\,0} - \sum \vec{a}_{\alpha}\left\{v^{0\alpha} - \sum_{\beta} D^{\alpha\beta}\frac{\partial \ln f}{\partial q\beta}\right\}$$ ---- (33)

In previous theories of intrinsic viscosity of solutions of macromolecules, it has been the practice to set the right hand side of the first of Eq. (33) equal to zero. Use of Eq. (33) after projection on the sub-spaces of the chain elements *1* in Eq. (32) yields

$$\vec{F}_l + \xi \sum_{l \neq s} \underset{\sim}{T_{ls}} \cdot \vec{F}_s = - \xi \dot{\varepsilon} \Big\{ (\vec{R}_{ol} \cdot \vec{e}_y)\, \vec{e}_x - \sum_{s=-n}^{+n} \sum_{\alpha,\beta} g^{\alpha\beta} \frac{\partial \vec{R}_{ol}}{\partial q^\alpha} (\vec{e}_y \cdot R_{os}) \Big(\frac{\partial \vec{R}_{os}}{\partial q^\beta} \cdot \vec{e}_x$$

$$- \xi \sum_{\alpha,\beta} D^{\alpha\beta} \frac{\partial \ln f}{\partial q^\beta} \frac{\partial \vec{R}_{ol}}{\partial q^\alpha} \,. \qquad \text{--- (34)}$$

Upon performing the summation over *s* and retaining only those terms which are linear in $\dot{\varepsilon}$, Eq. (34) simplifies, in the case of the rigid chain, to

$$\vec{F}_l + \xi \sum_{l \neq s} \underset{\sim}{T_{ls}} \cdot \vec{F}_s = - \xi \dot{\varepsilon} \Big\{ (\vec{e}_y \cdot \vec{R}_{ol})(\vec{e}_x - \vec{e}_R)\vec{e}_R + \sum_{\alpha = \vartheta, \varphi} D^{\alpha\kappa} \frac{\partial f_1}{\partial q^\alpha} \frac{\partial \vec{R}_{ol}}{\partial q^\alpha} \Big\} \qquad \text{---- (35)}$$

Eq. (34) along with Eq. (35) forms the basis of our present theory of intrinsic viscosity and rigidity of rod-like macromolecules in solution.

Eq. (35) represents a set of 2n+1 simultaneous vector equations, each of which may be divided into three equations involving the three components of $\vec{F}_1$:

$$(\vec{F}_l - \vec{e}_R) = - \xi \dot{\varepsilon} (\vec{e}_y \cdot \vec{R}_{ol})(\vec{e}_x - \vec{e}_R) - \xi \sum_{l \neq s} \vec{e}_R \cdot \underset{\sim}{T_{ls}} \cdot \vec{F}_s$$

$$= - \frac{\xi \dot{\varepsilon} b l}{2} \sin^2 \vartheta \sin 2\varphi - 2 \lambda_0 \sum_{l \neq s} (\vec{F}_s \cdot \vec{e}_R) / |l - s|$$

$$(\vec{F}_l \cdot \vec{e}_\vartheta) = -\zeta \dot{\varepsilon} D^{\vartheta\vartheta} \frac{\partial f_1}{\partial \vartheta} \left(\vec{e}_\vartheta \cdot \frac{\partial R_{0l}}{\partial \vartheta}\right) - \zeta \sum_{l \neq s} \vec{e}_\vartheta \cdot \underset{\sim}{T_{ls}} \cdot \vec{F}_s$$

$$= -\frac{5 \dot{\varepsilon} b l}{2} \frac{\gamma}{\gamma + i\omega} \sin\vartheta \cos\vartheta \sin 2\varphi - \lambda_0 \sum_{l \neq s} \frac{(\vec{F}_s \cdot \vec{e}_\vartheta)}{|l-s|}$$

$$(\vec{F}_l \cdot \vec{e}_\varphi) = -\zeta \dot{\varepsilon} D^{\varphi\varphi} \frac{\partial f_1}{\partial \varphi} \left(\vec{e}_\varphi \cdot \frac{\partial \vec{R}_{0l}}{\partial \varphi}\right) - \zeta \sum_{l \neq s} \vec{e}_\varphi \cdot \underset{\sim}{T_{ls}} \cdot \vec{F}_s$$

$$= -\frac{5 \dot{\varepsilon} b l}{2} \frac{\gamma}{\gamma + i\omega} \sin\vartheta \cos 2\varphi - \lambda_0 \sum_{l \neq s} \frac{(\vec{F}_s \cdot \vec{e}_\varphi)}{|l-s|}$$

---- (36)

Each of Eqs. (36) may be represented by an integral equation of the Kirkwood-Riseman type; however, in the present case solutions are rendered without having to make any assumptions on the fluctuations about mean values. As an example we set up the integral equation and solve for the $(\vec{F}_1 \cdot \vec{e}_R)$ component; solutions for the other two components follow readily.

Following methods presented previously[13], we may write

$$\phi(x) = f(x) - 2\lambda_0 \int_{-1}^{1} K(x,t)\, \phi(t)\, dt$$

$$\phi(x) = -{}^1/_\zeta\, \dot{\varepsilon}\, n\, (\vec{F}_l \cdot \vec{e}_R)$$

$$f(x) = \frac{b}{2} \sin^2\vartheta \sin 2\varphi\, x$$

$$x = l/n$$

$$K(x,t) = |x-t|^{-1}$$

$$= 0 \qquad x - \delta \leqslant t \leqslant x + \delta$$

$$\delta = 1/n$$

---- (37)

Solutions may now be constructed readily of the form

$$\Phi(x) = -\frac{b}{2}\sin^2\vartheta\,\sin 2\varphi\;\Phi(2\lambda_0)$$

$$\Phi(2\lambda_0) = \sum_{\substack{k=-\infty \\ \neq 0}}^{\infty} \frac{\left(\int_{-1}^{1} x e^{-i\pi k x}\,dx\right) e^{i\pi k x}}{1 - 4\lambda_0\,\mathrm{Ci}\{|k|\pi\delta\}}$$

$$\mathrm{Ci}(y) = \int_{\infty}^{y} \frac{\cos y}{y}\,dy \qquad \text{---- (38)}$$

Whereupon from Eqs. (36) and (37) it follows

$$\vec{F}_\ell = -\zeta\dot{\varepsilon}\,m\,b\,\vec{A}_\ell$$

$$2\vec{A}_\ell = \sin^2\vartheta\,\sin 2\varphi\;\Phi(2\lambda_0)\,\vec{e}_R + \frac{1}{1+i\omega\tau}\sin\vartheta\cos\vartheta\,\sin 2\varphi\;\Phi(\lambda_0)\,\vec{e}_\vartheta + \frac{1}{1+i\omega\tau}\sin\vartheta\,\cos 2\varphi\;\Phi(\lambda_0)\,\vec{e}_\varphi$$

$$\tau = 1/\gamma = \frac{\sigma b^2}{6D_0} \qquad \text{---- (39)}$$

Upon substituting Eq. (39) into Eq. (28) we obtain the following expression for G:

$$G = \frac{2m^3b^2}{3}\left\{\frac{F(2\lambda_0)}{4}\left\langle\sin^4\vartheta\,\sin^2 2\varphi\right\rangle_{Av.} + \frac{F(\lambda_0)}{4(1+i\omega\tau)}\left(\left\langle\sin^2\vartheta\cos^2\vartheta\,\sin^2 2\varphi\right\rangle_{Av.} - \left\langle 2\sin^2\vartheta\,\sin^2\varphi\,\cos 2\varphi\right\rangle_{Av}\right)\right.$$

$$F(\lambda_0) = \frac{3}{2} \sum_{\substack{k=-\infty \\ \neq 0}}^{\infty} \frac{2 I I^*}{1 - 2\lambda_0 \, Ci\{|k|\pi\delta\}}$$

$$= \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2(1-2\lambda_0 \, Ci\{k\pi\delta\})}$$

$$I = \frac{1}{2} \int_{-1}^{1} x \, e^{-i\pi k x} \, dx = \frac{(-1)^k}{\pi k}$$

$$I^* = \text{complex conjugate of } I.$$

---- (40)

Since we are interested only in the Newtonian contributions to the intrinsic viscosity, the averaging in Eq. (40) is performed with the equilibrium distribution function according to the scheme

$$\langle \Phi(\vartheta,\varphi) \rangle_{Av.} = \int_0^{2\pi}\int_0^{\pi} \Phi(\vartheta,\vartheta) \, f_0 \sqrt{g} \, d\vartheta \, d\varphi$$

---- (41)

Insertion of (40) into (30) and (31) after performing the averaging yields the following relations for the intrinsic viscosity and rigidity:

$$[\eta'] = \frac{N\zeta n^2 b^2}{4500 M_0 \eta_0} \left[F(2\lambda_0) + \frac{3}{2} F(\lambda_0) \frac{1}{1+\omega^2\tau^2} \right]$$

$$[\mu] = \frac{N\zeta n^2 b^2}{3000 M_0 \eta_0} \quad \frac{\omega^2 \tau}{1+\omega^2\tau^2} \; F(\lambda_0)$$

$$M/M_0 = 2n+1$$

---- (42)

The expression for the intrinsic rigidity may be put in the suggestive form

$$[\mu] = \frac{6 N \zeta}{1000 M} \quad \frac{\omega^2 \tau^2}{1+\omega^2\tau^2} \; D_0 F(\lambda_0)$$

$$= \frac{6 NkT}{1000 M} \quad \frac{\omega^2 \tau^2}{1+\omega^2\tau^2} \left(1 + \frac{\rho}{\sigma}\right) F(\lambda_0)$$

---- (43)

We shall now investigate the behavior of $F(\lambda_0)$ in the mathematical limits of small and large n, making use of the properties of the cosine integral

$$Ci(y) = \log \gamma y \quad (\text{small } y)$$

$$\gamma = 1.781$$

$$Ci(y) = \frac{\sin y}{y} \quad (\text{large } y)$$

---- (44)

Thus we find

$$\lim_{\substack{n\to 0\\ \text{or}\\ \lambda_0\to 0}} F(\lambda_0) = 1 = \lim_{\substack{n\to 0\\ \text{or}\\ \lambda_0\to 0}} F(2\lambda_0)$$

$$\lim_{n\to\infty} F(\lambda_0) = \frac{6}{\pi^2}\sum_{k=1}^{\infty}\left\{k^2\left(2\lambda_0\log\frac{n}{\pi\gamma k}+1\right)\right\}^{-1}$$

$$= \left[2\lambda_0\log\frac{n}{\pi\gamma}+1\right]^{-1}$$

$$\lim_{n\to\infty} F(2\lambda_0) = \left[4\lambda_0\log\frac{n}{\pi\gamma}+1\right]^{-1}$$

---- (45)

If we make the following alterations,

$L = nb$; $2L$ = length of rod

$\frac{N}{M} = 300/4\pi L a^2$ = sp. vol.$^{-1}$ of an ellipsoid,

Eq. (42) becomes in the limit of large n

$$[\eta'] = \frac{N\zeta L^2}{4500 M_0\eta_0}\left[\frac{1}{4\lambda_0\log\frac{n}{\pi\gamma}+1} + \frac{3}{4\lambda_0\log\frac{n}{\pi\gamma}+2} - \frac{1}{1+\omega^2\tau^2}\right]$$

$$= \left(\frac{L}{a}\right)^2\left[\frac{1}{15\left(\log\frac{n}{\pi\gamma}+\frac{1}{4\lambda_0}\right)} + \frac{1}{5\left(\log\frac{n}{\pi\gamma}+\frac{1}{2\lambda_0}\right)}\cdot\frac{1}{1+\omega^2\tau^2}\right]$$

---- (46)

The above expression for the intrinsic viscosity is to be compared with the one derived by Simha for the prolate ellipsoid of semi major axis L and semi minor axis a:

$$[\eta'] = \left(\frac{L}{a}\right)^2 \left[\frac{1}{15(\log\frac{L}{a} - \frac{3}{2})} + \frac{}{5(\log\frac{L}{a} - \frac{1}{2})}\right] + \frac{14}{15} .$$

It is seen that Simha's result corresponds quite nearly to our static limit with b $\sim$ 2a; or in other words, to a rigid chain composed of monomeric units whose effective shells of hydrodynamic interaction have a radius equal to one half the distance of separation between adjoining elements. (It is to be noted that for such a model $\lambda_0 = 3/4$.) In the limit of large n the expression for the intrinsic rigidity now becomes

$$[\mu] = \frac{6NkT}{1000\,M} \; \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \; \frac{1+2\lambda_0[\log 2n - 4/3]}{1 + 2\lambda_0 \log n/\pi\gamma} .$$

---- (47)

It is interesting to note that at high frequencies the intrinsic rigidity of a high molecular weight rod-like macromolecule is nearly inversely proportional to its molecular weight.

VI. INTRINSIC VISCOSITY AND RIGIDITY OF DUMBBELL-LIKE MACROMOLECULES IN SOLUTION.

For purposes of comparison we include calculations for the rigid dumbbell model, which is composed of two elements, wherein the seats of hydrodynamic interaction are located, joined together by an infinitely thin rod of length 2R, hydrodynamic perturbations due to the presence of the rod being negligible. For such a model, the sets of equations described in Eq. (36) become readily soluble by the common methods used to solve systems of linear simultaneous equations. At this point we need merely to quote the results of such calculations in order to compare them with the results obtained by Simha for a similar model.

The expressions for the intrinsic viscosity and rigidity now become

$$[\eta'] = \frac{N\zeta R^2}{1500\,M\eta_0}\left[\frac{2}{1-2K} + \frac{3}{(1-K)(1+\omega^2\tau^2)}\right]$$

$$[\mu] = \frac{6NkT}{1000\,M}\;\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\;\frac{1-2K}{1-K}$$

$$\tau = \zeta R^2/3kT(1-2K)$$

$$K = \zeta/16\pi\eta_0 R$$

---- (48)

If we take for our elements of hydrodynamic resistance two spheres of radius a, and if we assume that Stoke's Law is valid for our model ($\zeta = 6\pi\eta_0 a$), we may rewrite the expression for the intrinsic viscosity in the form

$$[\eta'] = \frac{3}{10}\,\frac{(R/a)^2}{1-2K}\left[1 + \frac{3}{2}\,\frac{1-2K}{1-K}\cdot\frac{1}{1+\omega^2\tau^2}\right]$$

$$\frac{N}{M} = 100\,\frac{3}{8\pi a^3}$$

---- (49)

Under the conditions $\omega = 0\,;\ K < 1,$ Eq. (49) may be expanded to yield

$$[\eta'] = \frac{3}{4}\left(\frac{R}{a}\right)^2\left[1 + \frac{21}{40}\,\frac{a}{R} + \cdots\right]$$

---- (50)

This is to be compared with the result obtained by Simha

$$[\eta] = \frac{3}{2}\left(\frac{R}{a}\right)^2\left[1 + \frac{9}{20}\,\frac{a}{R}\right] .$$

The reason for the discrepancy between Simha's result and ours is as follows. When placed in terms of our analysis, Simha's method of calculation is equivalent to stating

$$\vec{v}^{\,0}_{l} - \vec{u}_{l} = \vec{v}^{\,0}_{l} .$$

---- (51)

Upon substitution of this expression into Eq. (32) followed by substitution into Eq. (29), Simha's above result may be obtained with a more accurate determination of the Oseen correction term. However, Simha's treatment of the dumbbell model is incorrect for Eq. (51) does not hold. Indeed, for the case of constant rate of strain we obtain from Eq. (33) the expression

$$\vec{v}^{\circ}_{\ell} - \vec{u}_{\ell} = \vec{v}^{\circ}_{\ell} \cdot \left[\vec{e}_R \vec{e}_R + \frac{1}{2} \vec{e}_\varphi \vec{e}_\varphi + \vec{e}_\vartheta \vec{e}_\vartheta\right] + \frac{\dot{\varepsilon}}{2} (\vec{e}_x \cdot \vec{R}_{o\ell}) \vec{e}_y \cdot \vec{e}_\varphi \vec{e}_\varphi$$

$$= \vec{v}^{\circ}_{\ell} \cdot \underset{\sim}{1} + \frac{\dot{\varepsilon}}{2} (\vec{e}_z \times \vec{R}_{o\ell}) \cdot \vec{e}_\varphi \vec{e}_\varphi \qquad \text{---- (52)}$$

Substitution of Eq. (52) into Eq. (32) leads to the result given in Eq. (50). Simha's treatment amounts to neglecting the effect on the dumbbell of external torques caused by viscous drag.

VII. THE THEORY OF FLOW BIREFRINGENCE OF ROD-LIKE MACROMOLECULES IN SOLUTION.

A. Optical Part

We suppose the macromolecule to be bathed in a liquid continuum of dielectric, the dielectric tensor of such a system being given by the expression:

$$\underset{\sim}{\epsilon} - \underset{\sim}{1} = 4\pi\left[c_1\alpha_0\underset{\sim}{1} + c_2\underset{\sim}{\alpha}^{(2)}\right]\cdot\underset{\sim}{\sigma} \qquad \text{---- (53a)}$$

where $\underset{\sim}{\epsilon}$ is the dielectric tensor, α_0 is the polarizability constant of the liquid, $\underset{\sim}{\alpha}^{(2)}$ is the polarizability tensor of the macromolecule, c_1 and c_2 are respectively the concentration of solvent and of solute, and $\underset{\sim}{\sigma}$ is given by the following relations obtained from electrostatic theory:

$$\vec{F} = \underset{\sim}{\sigma}\cdot\vec{E}$$

$$\underset{\sim}{\sigma} = \left[1 + \frac{4\pi}{3}c_1\alpha_0\right]\underset{\sim}{1} + \frac{4\pi}{3}c_2\underset{\sim}{\alpha}^{(2)} \qquad \text{---- (53b)}$$

$\vec{F}$ is the local electric field acting within the dielectric continuum and $\vec{E}$ is the externally imposed electric field.

The polarizability tensor of the macromolecule is given by

$$\underset{\sim}{\alpha}^{(2)} = \sum_{l=-n}^{+n}\left\langle\underset{\sim}{\alpha}^{(l)}\right\rangle_{Av.} \qquad \text{---- (54)}$$

If we now assume that the polarizability tensor of the individual elements has cylindrical symmetry about the element, we may write

$$\alpha^{(l)} = \begin{pmatrix} \alpha_{xx}^{(l)} & \alpha_{xy}^{(l)} & 0 \\ \alpha_{yx}^{(l)} & \alpha_{yy}^{(l)} & 0 \\ 0 & 0 & \alpha_{zz}^{(l)} \end{pmatrix} .$$

---- (55)

The principal axes of $\underset{\sim}{\alpha}^{(2)}$ in the xy plane may be found by solving the secular equation

$$\begin{vmatrix} \overline{\alpha}_{xx}^{\,Av.} - \alpha & \overline{\alpha}_{xy}^{\,Av.} \\ \overline{\alpha}_{yx}^{\,Ar.} & \overline{\alpha}_{yy}^{\,Av.} - \alpha \end{vmatrix} = 0$$

---- (56)

The polarizability tensor is symmetric and $\alpha_{xy}^{(l)} = \alpha_{yx}^{(l)}$; consequently solution of Eq. (56) yields

$$\alpha_{11} = \frac{1}{2}\left\{ \overline{\alpha}_{xx}^{\,Av.} + \overline{\alpha}_{yy}^{\,Av.} + \sqrt{(\overline{\alpha}_{xx} - \overline{\alpha}_{yy})^2 + 4\,\overline{\alpha}_{xy}^{2}} \right\}$$

$$\alpha_{22} = \frac{1}{2}\left\{ \overline{\alpha}_{xx}^{\,Ar.} + \overline{\alpha}_{yy}^{\,Av.} - \sqrt{(\overline{\alpha}_{xx} - \overline{\alpha}_{yy})^2 + 4\,\overline{\alpha}_{xy}^{2}} \right\}$$

$$\underset{\sim}{\alpha}^{(2)} = \alpha_{11}\,\vec{e}_1\vec{e}_1 + \alpha_{22}\,\vec{e}_2\vec{e}_2 + \alpha_{22}\,\vec{e}_z\vec{e}_z$$

---- (57)

where $\vec{e}_1$ and $\vec{e}_2$ are the principal axes of $\underset{\sim}{\alpha}^{(2)}$ in the xy plane and correspond to the principal axes of $\underset{\sim}{\sigma}$ also.

The angle of extinction, χ, is defined as the angle between the stream lines and the optic axis of the flowing liquid; this angle corresponds to the angle formed by $\vec{e}_1$ and $\vec{e}_x$. Thus, we arrive at the expression

$$\tan\chi = \frac{\alpha_{11} - \overline{\alpha}_{yy}^{Av.}}{\overline{\alpha}_{xy}^{Av.}}$$

$$= \frac{\sqrt{4\overline{\alpha}_{xy}^{2} + (\overline{\alpha}_{xx} - \alpha_{yy})^{2} + (\overline{\alpha}_{xx} - \overline{\alpha}_{yy})}}{2\overline{\alpha}_{xy}}$$

$$= 1 + \frac{\overline{\alpha}_{xx} - \overline{\alpha}_{yy}}{2\overline{\alpha}_{xy}} + ----$$

$$\chi - \pi/4 = \frac{\overline{\alpha}_{xx} - \overline{\alpha}_{yy}}{2\overline{\alpha}_{xy}} + --- \qquad \text{---- (58)}$$

Upon transforming the components of the polarizability tensor to the principal axes, the expression for χ becomes

$$\chi - \frac{\pi}{4} = \frac{\langle \sin^2\vartheta \cos 2\varphi \rangle_{Av.}}{\langle \sin^2\vartheta \sin 2\varphi \rangle_{Av.}} \qquad \text{---- (59)}$$

Expressions for the magnitude of birefringence may be obtained through use of the Clausius-Mosotti equation,

$$\frac{n_1^2 - 1}{n_1^2 + 2} = \frac{4\pi}{3} c_1 \alpha_0 + \frac{4\pi}{3} c_2 \alpha_{11}$$

$$\frac{n_2^2 - 1}{n_2^2 + 2} = \frac{4\pi}{3} c_1 \alpha_0 + \frac{4\pi}{3} c_2 \alpha_{22}$$

And

$$\frac{n_1^2 - n_2^2}{(n_1^2+2)(n_2^2+2)} = \frac{4\pi}{9} c_2 (\alpha_{11} - \alpha_{22}) \qquad \text{---- (60a)}$$

where n_1 and n_2 are the values of the index of refraction of the solution in the principal directions. Retaining only terms which are first power in the concentration, Eq. (60a) may be converted by use of Eq. (58) to

$$\begin{aligned}\Delta n &= n_1 - n_2 \\ &= \frac{4\pi}{9} \frac{(n_0^2+2)^2}{n_0} c_2 \overline{\alpha}_{xy}^{Av.} \left\{ \tan\chi - \frac{\overline{\alpha}_{xx} - \overline{\alpha}_{yy}}{2\overline{\alpha}_{xy}} \right\}\end{aligned} \qquad \text{---- (60b)}$$

where n_o is the refractive index of the pure solvent. The expression in the brace in Eq. (60b) has the value unity in the first approximation.

B. Statistical Part.

We rewrite Eqs. (59) and (60b) in the form

$$\chi - \frac{\pi}{4} = \frac{\dot{\varepsilon}^2}{\dot{\varepsilon}} \frac{\int_v f_0 f_2 \sin^2\vartheta \cos 2\phi \, d\,\mathrm{vol.}}{\int_v f_0 f_1 \sin^2\vartheta \sin 2\phi \, d\,\mathrm{vol.}} \qquad \text{---- (61a)}$$

$$\Delta n = \frac{4\pi}{9} \frac{(n_0^2+2)^2}{n_0} c_2 \dot{\varepsilon} \int_v f_0 f_1 \alpha_{xy} \, d\,\mathrm{vol.} \qquad \text{---- (61b)}$$

Thus it is seen that the theory of flow birefringence requires knowledge of both f_1 and f_2, where these are the perturbation terms in the distribution function as defined by Eq. (16).

For constant rate of strain substitution of Eq. (16) into Eq. (14) and use of the results obtained in Eq. (21) yields

$$D_0 \nabla^2_{\vartheta,\varphi} f_2 = \vec{\nabla}_{\vartheta,\varphi}\cdot(\vec{v}^{\,0} f_1)$$

$$= \frac{\sigma_0 b^2}{4D_0}\nabla_{\vartheta,\varphi}\cdot(\vec{v}^{\,0}\sin^2\vartheta\sin 2\varphi)$$

$$= \frac{\sigma_0 b^2}{8D_0}\sin^2\vartheta\left[1-\cos 2\varphi+\sin^2 2\varphi(1-5\sin^2\vartheta))\right]$$

$$\sigma_0 = \frac{n(n+1)(2n+1)}{3}$$

---- (62)

Solutions to f_2 may now be constructed according to the following scheme. We let G represent the right hand side of the last of Eqs. (62). Then f_2 may be expanded in the form

$$f_2(\vartheta,\varphi) = \sum_{n=0}^{\infty}\left\{A_{n0}P_n(\mu)+\sum_{m=1}^{n}(A_{nm}\cos m\varphi+B_{nm}\sin m\varphi)\cdot P_n^m(\mu)\right\}$$

$$A_{n0} = \frac{3n+1}{4\pi}\,\frac{\sigma_0 b^2}{D_0}\int_0^{2\pi}\int_1^1 G\,P_n(\mu)\,d\mu\,d\varphi$$

$$A_{nm} = \frac{2n+1}{4\pi}\,\frac{(n-m)!}{(n+m)!}\,\frac{\sigma_0 b^2}{D_0}\int_0^{2\pi}\int_{-1}^{+1} G P_n^m(\mu)\cos m\varphi\,d\mu\,d\varphi$$

$$B_{nm} = \frac{2n+1}{4\pi}\,\frac{(n-m)!}{(n+m)!}\,\frac{\sigma_0 b^2}{D_0}\int_0^{2\pi}\int_{-1}^{+1} G P_n^m(\mu)\sin m\varphi\,d\mu\,d\varphi$$

$$G = \frac{\sigma_0 b^2}{8D_0}\sin^2\vartheta\left[1-\cos 2\varphi+\sin\vartheta(1-5\sin^2\vartheta)\right].$$

---- (63)

where $P_n^m(\mu)$ and $P_n(\mu)$ are the associated Legendre and Legendre polynomials in the variable $\mu = \cos\vartheta$ and the A's and B's are the corresponding expansion coefficients.

Since we make use of f_2 only in order to average the function $\cos 2\varphi$, we are only interested in the value of A_{22}; the other members of the series will not contribute to the average value of $\cos 2\varphi$ on account of the orthogonality properties of the Legendre polynomials. Carrying out the required integration we find

$$A_{22} = -\frac{1}{48}\left(\frac{\sigma_0 b^2}{D_0}\right)^2$$

$$f_2 = A_{22}\sin^2\vartheta\cos 2\varphi + ---$$

and from Eq. (21)

$$f_1(\vartheta,\varphi) = \frac{\sigma_0 b^2}{4}\sin^2\vartheta\sin 2\varphi$$

---- (64)

Whereupon substitution into Eq. (61a) leads to the result

$$\chi - \frac{\pi}{4} = -\frac{\dot{\varepsilon}}{12}\,\frac{\sigma_0 b^2}{D_0}$$

$$= -\frac{2\pi}{3}\cdot\frac{\eta_0\dot{\varepsilon}}{kT}\cdot\frac{L^3}{\left[\log 2n - \left(\frac{4}{3} - \frac{1}{2\lambda_0}\right)\right]}$$

---- (65)

where L is half the length of the rigid chain and λ_0 is the measure of hydrodynamic interaction between chain elements, defined before as $\lambda_0 = \zeta/8\pi\eta_0 b$.

The results of Eq. (65) are similar to those obtained by Boeder, who treated the infinitely thin rod undergoing two dimensional motion. Our results indicate the analysis is equally valid for three dimensions and the values so obtained correspond to the leading term in the expression derived by Peterlin and Stuart for the prolate ellipsoid. In order to obtain higher terms, our perturbation treatment would have to be carried further. Both Boeder and Peterlin and Stuart obtain expressions for the extinction angle in terms of an arbitrary diffusion constant. In our analysis, the value of this diffusion constant is given directly and is equal to $\frac{\sigma_0 b^2}{D_0}$.

The value of the magnitude of birefringence is now obtained by substituting the value of f_1 given in Eq. (21) into Eq. (61b). Upon performing the required integration it is found that

$$\Delta n = \frac{4\pi}{135} \frac{(n_0^2+2)^2}{n_0} c_2 (\alpha_{11} - \alpha_{22}) \frac{\dot{\varepsilon} \sigma_0 b^2}{D_0}$$

$$= \frac{32\pi^2}{135} \frac{(n_0^2+2)^2}{n_0} c_2 (\alpha_{11} - \alpha_{22}) \frac{\eta_0 \dot{\varepsilon} L^3}{kT\left[\ln 2n - \left(\frac{4}{3} - \frac{1}{2\lambda_0}\right)\right]}$$

---- (66)

Our results resemble to some extent those of J. J. Hermans[16] who calculates the magnitude of birefringence of flexible macromolecules undergoing Brownian motion.

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PROPOSITIONS

1\. a) Use of Kirkwood's theory of solutions of polar molecules[1] in conjunction with the Brønsted theory of reaction rates makes it possible to formulate a general theory predicting the electrostatic effects of the solvent medium on the rates of ionic-type organic reactions. Predictions of such a theory will correspond with predictions of the qualitative scheme proposed earlier by Hughes and Ingold[2]. When formulations based on our theory are applied to the unimolecular solvolysis of organic compounds, it is found possible to relate the empirical correlation functions of Grunwald and Winstein[3] to the electrostatic properties of the solvent medium and to the molecular parameters of the reactants.

b) The above mentioned formulations may be applied only when the electrostatic effects of the solvent medium outweigh the non-electrostatic. It is also to be expected that when our formulations do not apply, the empirical formulations of Grunwald and Winstein will break down. Deviations from simple correlation should occur in the region of low dielectric constants and in cases of specific interaction between solvent and reactant; the latter is usually due to hydrogen bonding.

1) J. G. Kirkwood, J. Chem. Phys. 2, 351 (1934).

2) E. D. Hughes and I. K. Ingold, J.C.S., 252 (1935).

3) E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948).

PROPOSITIONS (Continued)

2. a) A striking illustration of the difference in mechanism of bromination and hydrogen halide-type addition to olefinic hydrocarbons is the reversed rate order observed in the series isobutylene and trimethylethylene[1,2]. Olefin reactivity in bromination-type reactions is a function of pi electron availability and may be correlated with values of ionization potentials. Reactivity in hydrogen halide-type reactions, however, is a function of the polarity of the double bond. It is suggested that of the simple alkyl substituted olefins, isobutylene is the most reactive to hydrogen halide-type addition reactions.

1) A. Remick, "Elec. Interp. Org. Chem.", Wiley (1949), p. 80.

2) H. J. Lucas, et al., J. Am. Chem. Soc., 56, 460, 2138 (1934)

b) It is proposed that the principal initial product in electrophilic addition reactions of alkyl substituted conjugated diene hydrocarbons is the 1,2 isomer. In the case where the positive attacking group is large enough to form a 1,4 cyclic intermediate, exceptions to the above rule are to be expected and the principal product should be the 1,4 isomer. In the latter case, formation of cis products is also to be expected[1].

1) See this presentation, Part I., Section VI.

3. a) It is to be expected that a number of systems may be found wherein a given reaction occurring at a surface interface will differ markedly in its kinetics from the corresponding reaction occurring in the bulk phase. Such differences should

be due largely to orientational effects and may be correlated with the zeta potential of the double layer existing at the interface.

b) An example of a reaction exhibiting different kinetics at the surface interface from that in the bulk phase is the air catalysed polymerisation of unsaturated fatty acids. It is suggested that the difference in kinetics may be studied quantitatively by a combination of the techniques of monolayer casting and light scattering.

4. a) The unusually low yields obtained in reduction of alpha monochlor carboxylic acids with lithium aluminum hydride[1] may be ascribed to competitive reaction of the chloro and carboxyl groups. The increase in yield observed going from free acid to ester to acid halide and from monochlor to polychlor compounds[2] may be explained on the basis of resonance and provides an interesting example of how Pauling's resonance concepts apply to reactivities.

b) The kinetic data recently reported by Hine and Lee[3] on the hydrolysis of phenyl methyl halides indicates that differences in some of the observed rates may not be explained on the basis of resonance stablization, as proposed by the authors, but may be explained on the basis of steric considerations.

1) W. Fickett, private communication.

2) C. E. Sroog, et al., <u>J. Am. Chem. Soc.</u>, <u>71</u>, 1710 (1949).

3) J. Hine and D. E. Lee, Org. Abstracts, A.C.S. Meeting September 3, 1950., p. 45 N.

PROPOSITIONS (Continued)

5. It is widely recognized today that the simple Flory-Huggins theory is incapable of explaining many experimentally determined thermodynamic data on binary mixtures of polymer and solvent.[1,2] An order-disorder analysis following the Kirkwood theory[3] may be used to derive the Flory-Huggins formula. Such an analysis indicates that the theory is valid only for strictly regular solutions in the sense of Guggenheim. The shortcomings of the Flory-Huggins theory may be ascribed largely to the static lattice model employed. A more rational attack of the problem may be made through inclusion of vibrational considerations, following largely the method outlined previously by Kirkwood[4].

1) M. J. Schick, P. Doty, B. H. Zimm, J. Am. Chem. Soc., 72, 530 (1950).

2) P. J. Flory, J. Chem. Phys., 18, 1086 (1950).

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6. A successful explanation of the fine structure observed in Rayleigh scattering in liquids has been advanced by Brillouin[1]. A simpler, though more crude, explanation is proposed here based on the supposition that the scattering centers may be represented as damped harmonic oscillators. The damping term arises from Brownian motion. The fine structure may then be explained along lines similar to the ones given by Froehlich[2] in his

PROPOSITIONS (Continued)

explanation of "resonance absorption" of r.f. waves. The liquid model proposed by us is quite analogous to the vibrating crystal model proposed by Einstein.

1) L. Brillouin, Ann. Phys., 17, 88 (1922)

2) H. Froehlich, "Theory of Dielectrics", Oxford (1949).

7. In a recent paper S. Golden[1] claims to prove the "adiabatic hypothesis" from the Born-Oppenheimer zeroth order approximation and to prove the concept of microscopic reversibility from the first order Dirac time dependent perturbation theory. It is proposed that Golden's arguments on these points are circular and largely meaningless. A more rational attack of the problem would involve the conversion of Kramers' stochastic treatment[2] into quantum mechanics. It is to be expected that such an analysis would show the validity of the Eyring-Polyanyi transition state theory to be dependent largely on the nature of the interaction potential.

1) S. Golden, J. Chem. Phys., 17, 620, (1949).

2) H. A. Kramers, Physica, 7, 284 (1940).

8. In a recent note, J. Duchesne[1] suggests that the reactivity of a molecule is not only a function of the electronic distribution, as has been supposed in recent times, but also a function of the vibrational state. It seems to us that whereas vibrational considerations may actually become important at

PROPOSITIONS (Continued)

high temperature, their role is secondary in ordinary thermal reactions occurring near room temperature. The difference in reactivities between ethylene and acetylene which Duchesne explains on the basis of vibrational differences may be explained just as well, if not better, on the basis of electron distribution.

1) J. Duchesne, J. Chem. Phys., 18, 1120 (1950).

9. The system of simultaneous rate equations obtained in a system undergoing copolymerization may be represented by a general matrix equation and solved by the usual formal methods. In the simple case of binary copolymerization, the usual assumptions of steady state reciprocity and constancy of free radical concentrations should lead to the familiar monomer reactivity equations. The advantage of a matrix formulation is that explicit equations may be obtained for single constituents, whereas present methods yield equations for ratios only.

10. The specific viscosity per unit concentration of a solution of macromolecules is usually represented as an integral power series in the concentration. Suggestions have been made that the second term in such a power series should contain $c^{\frac{1}{3}}$ instead of c. It is proposed that for a solution consisting of large rigid spheres which are non-interacting at equilibrium,

PROPOSITIONS (Continued)

the Newtonian contributions to the specific viscosity may indeed be represented by an integral power series. It is quite conceivable, however, that non-Newtonian contributions will give rise to a term proportional to $c^{\frac{1}{2}}$.