It was learned while this research was being concluded that Davydov[21] had treated diphenyl by a method which makes explicit use of the dispersion force between the phenyls.

NOTE ADDED IN PROOF.—The interesting experimental results of Carmack and co-workers, in which interaction between nearby sulfur atoms in a molecule is demonstrated, seem to be capable of being nicely understood in terms of the discussion given in this paper.

Acknowledgment.—The writer wishes to thank Drs. D. S. McClure and Harvey Winston for reading the manuscript critically.

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[21] A. S. Davydov, *Zhur. Eksptl. Teoret. Fiz.*, **18**, 201 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

The Kinetics of the Ethyl Alcohol–Acetic Anhydride Reaction Using a Dielectric Constant Method[1]

BY ROBERT C. AXTMANN[2]

A kinetic study of the esterification of ethyl alcohol by acetic anhydride in carbon tetrachloride has been made by a semi-automatic, electronic method which follows decrements in the dielectric constant of the solution as the reaction progresses. Data collected indicate that the dielectric constant of multi-component solutions of polar molecules in a non-polar solvent is directly proportional to the concentrations of the individual solutes.

I. Introduction

The first measurements of the rate of esterification of ethyl alcohol by acetic anhydride in carbon tetrachloride and other solvents were made by Soper and Williams[3] who found that in accordance with an earlier theory[4] the various solvents might be arranged in an order of increasingly deactivating influence on this reaction. This arrangement conforms fairly closely with one of increasing internal pressure of the solvents involved. The order is also one of increasing dielectric constants.

The reaction has also been studied by Moelwyn-Hughes and Hinshelwood who found a sharp dependence of *k* on the initial concentrations of reactants, *i.e.*, the higher the concentration, the slower the reaction.[5] Soper and Williams also observed this and consistently ascribed the phenomenon to a medium effect of the reactants which raises the internal pressure of the entire system.

Soper and Williams report an effect not found in the later work, namely, a slowing-down of the reaction as it proceeds to completion in carbon tetrachloride. They attribute this to a specific inhibitory effect of the acetic acid which is produced in the reaction. Their proof lies in experiments where they add acetic acid to the original solution and observe lower values of *k*. On the basis of their explanation for the dependence of *k* on initial concentration, however, the medium effect of additional acetic acid (or any other polar substance) would be to raise the internal pressure of the solution and slow down the reaction. The proof, then, is at best circumstantial. In the absence of other effects, however, one would expect the reaction velocity to increase slightly as it progresses, since the products are of lower dielectric constant than the reactants and hence the over-all dielectric constant of the solution is decreasing.

The purpose of the following experiments, then, was to measure the velocity of the reaction by a method which would largely eliminate the possibility of systematic errors from an analytical procedure in an attempt to discover whether the slowing down of the reaction was real. A secondary aim was to demonstrate the usefulness of a new kinetic tool[6] which determines reaction velocities from dynamic measurements of the dielectric constant of the reacting solution.

II. Experimental

1. **Materials.**—The carbon tetrachloride was C.P. Reagent Grade which was fractionated in a 24-inch, lagged Vigreux column. Five-pound bottles were distilled collecting only the middle fraction which boiled within a 0.1° range. The anhydride was also C.P. Reagent Grade and was fractionated in the same apparatus, collecting over a 0.5° range. Weighed samples of anhydride hydrolyzed in water and titrated against standard base demonstrated that the substance was pure to well within 0.1%. The alcohol was anhydrous, prepared by a method described by Vogel.[7] Several standard solutions (about 0.1 *m*) were made up gravimetrically and stored in a cold room. The molarities of these solutions were in all cases known to 0.1%.

2. **Apparatus and Procedure.**—The instrument used for obtaining the kinetic data was a heterodyne beat assembly with an automatic timing circuit which will be described in another paper.[6] The power supplies for the oscillators and timing circuit were always turned on two hours before a run was started. The dielectric constant cell was also placed in the constant temperature bath at that time. Stability of the oscillators was checked by repeatedly resetting the micrometer capacitor to hear no beat in the loudspeaker of the receiver. When the same reading to ±0.002 mm. could be obtained at the beginning and end of a five-minute period, the circuits were judged to have come to a steady state.

150-ml. solutions of the two reactants in separate, stoppered erlenmeyer flasks were placed in the constant temperature bath one-half hour before the start of a run. When they had come up to temperature, they were poured simultaneously through a wide-mouthed funnel into the cell. To further ensure complete mixing of the two solutions, the magnetic stirrer in the bottom of the cell was allowed to run for five minutes.

No readings were taken until the mixing period was over.

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[1] This paper comprises a portion of the dissertation of R. C. Axtmann submitted to the School of Higher Studies of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Atomic Energy Division, E. I. du Pont de Nemours & Company, Inc., Argonne National Laboratory, Lemont, Illinois.

[3] F. G. Soper and E. Williams, *J. Chem. Soc.*, 2297 (1931).

[4] M. Richardson and F. G. Soper, *ibid.*, 1873 (1929).

[5] E. A. Moelwyn-Hughes and C. N. Hinshelwood, *ibid.*, 230 (1932).

[6] R. C. Axtmann, paper to be published soon.

[7] A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Company, New York, N. Y., 1948, p. 166.

The micrometer capacitor was set to a round-numbered figure such as 23.200 mm. (to afford easier calculations) by listening to the heterodyne beat signal in the loudspeaker. When the automatic timing circuit tripped, the micrometer was set ahead and the circuit reset. The procedure was repeated until the reaction reached 30 to 60% completion.

Usually three or four analytical samples were removed during the course of a run. These served a dual purpose. First they were used to establish the relationship between concentration of the anhydride and the micrometer readings, and second, they permitted a correction for the 0 time which was necessary in this reaction if *k*'s were to be calculated from the initial condition. The analytical samples were removed by means of a 10-ml. pipet and were immediately placed in 100 ml. of distilled water. They were allowed to hydrolyze for 24 hours and were then titrated against standard base using phenolphthalein as an indicator. The concentration of acetic acid in the hydrolyzed sample could then be used to calculate the concentration of anhydride at the time the sample was taken. The time at which the samples were removed was noted to the nearest minute on the recording clock.

III. Data and Results

Several preliminary experiments were performed to determine whether various factors not present in the earlier kinetic studies but present in this one would affect the reaction velocity.

1. **Effect of the Radio Frequency Field.**—Several workers have reported that ultrasonic frequencies may be used to accelerate certain reactions. These reactions include the decomposition of benzoylazide, diazobenzene chloride and diazotoluene chloride.[8] Two reactions, the mutarotation of glucose and the hydrolysis of sucrose, have been shown to be unaffected, leading one to suspect that non-free radical reactions may be free from this effect.

It must be remembered that ultra-sound contains both a sound and an r.f. field, whereas here we have only the latter. To check its effect, two runs were made: the reaction was performed with as nearly identical solutions and conditions as possible, both with and without the oscillators turned on. Analytical samples allowed calculations of *k*'s which were within the limit of error allowed by the analytical method (see Table I).

TABLE I

Run IV (no r.f. field): $Ac_2O = C_2H_5OH = 0.0969$, $T = 55.00°$.

Time, min.	77	240	306	598
$k \times 10^4$	4.18	4.12	3.98	4.15

Average $k = 4.16 \times 10^{-4}$

Run V (r.f. field) same concentrations and temperature

Time, min.	89.5	237.5	357.5
$k \times 10^4$	4.20	4.20	4.22

Average $k = 4.21 \times 10^{-4}$

2. **Effect of the Capacitor Plates. Inhomogeneity.**—The possibility of inhomogeneities in the reaction solution due to the presence of the capacitor was also checked in Run V, during which micrometer readings were taken. When the reaction had proceeded for eight hours the magnetic stirrer was turned on for five minutes. Following this more micrometer readings were taken. They were found to fall exactly on a smooth micrometer readings *vs.* time curve plotted from data taken before the stirrer was turned on, thus demonstrating that stirring had no effect.

3. **Additivity of Dielectric Constants.**—As indicated elsewhere,[6] data obtained from the heterodyne beat instrument might be treated most simply if the change in dielectric constant of the solution (indicated directly on the micrometer) were exactly proportional to the change in concentration of either a reactant or a product. Heston, Franklin, Hennelly and Smyth[9] have recently published an empirical relationship relating the real part of the dielectric constant, ϵ', of a solution of a polar solute in a non-polar solvent to c_2, the mole fraction of the solute in the following manner

$$\epsilon' = \epsilon'_1 + a'c_2 \qquad (1)$$

where the subscript 1 refers to the pure solvent. Now in the present system, the mole fraction of any one substance will be exactly proportional to its concentration since the total number of moles remains the same as the reaction progresses. If we may assume as a first approximation that there is no dielectric interaction between the various molecules, (1) becomes

$$\epsilon' = \epsilon'_2 + a_2c_2 + a_3c_3 + a_4c_4 + a_5c_5 \qquad (2)$$

where c_2 to c_5 are the mole fractions of the four products and reactants with the nessary condition that their sum is constant with $c_2 = c_3$ and $c_3 = c_4$. This relationship should hold whether ϵ' is measured or ϵ_0, the static dielectric constant. It is changes in the latter, actually, which are determined here since the wave length of the oscillators was 150 meters.

It may be seen from (2) that changes of concentration of any of the species in the reaction may be followed directly from the change in the over-all dielectric constant. In four runs this was done for acetic anhydride, since it was the compound most easily analyzed for. Micrometer readings, *R*, were plotted against time as were the analyses for anhydride. A second plot of *R vs.* anhydride concentration proved to be a straight line. For twelve analyses made in the four runs, deviations of the analytical values of anhydride from those calculated on the basis of least mean square lines averaged 0.38%. This was well within the experimental error of the volumetric apparatus in view of the fact that the time at which the analytical samples were removed from the reaction chamber could not be recorded very accurately. Mention should be made that absolute values of the dielectric constant are not necessary since changes in ϵ are directly proportional to changes in concentration.

Kinetic Experiments.—Two runs were made using solutions in which the reactant compounds were in equal concentration. *k*'s were calculated from Equation (2) given in the other paper.[6] R_0 and R_∞ were obtained from extrapolations of *R vs.* anhydride concentration plots. The extrapolated value obtained for 0 time was in each case about plus four minutes, *i.e.*, some cooling of the reactant solutions must have occurred between the times they were removed from the bath and poured into the cell. The time of mixing un-

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(8) L. Liboutry, *J. chim. phys.*, **41**, 173 (1944).

(9) W. M. Heston, A. D. Franklin, E. J. Hennelly and C. P. Smyth, THIS JOURNAL, **71**, 3443 (1950).

doubtedly contributed also to this value. Table II gives values of k in mole^{-1} sec.$^{-1}$ corresponding to the various micrometer readings. The k's are given to four significant figures although a, the original concentration of reactants, is not known this well. This procedure was followed since it demonstrates the precision of the data which may be obtained from the method. The absolute value of k, however, is known no more accurately than from other methods.

TABLE II

Run VI a = 0.0912	T = 55.00°	Run VII a = 0.0979	T = 49.90°
Time, sec.	$k \times 10^4$	Time, sec.	$k \times 10^4$
2519	4.334	4262	2.658
2869	4.335	4777	2.656
3229	4.335	6253	2.672
3607	4.324	9148	2.667
3967	4.345	9605	2.672
5592	4.337	11935	2.643
6045	4.323	12850	2.663
7389	4.443	13951	2.653
9972	4.340		
10562	4.330		
12443	4.307		
23093	4.208		
27684	4.113		

Table III compares the values for the second order velocity constant of the reaction between acetic anhydride and ethyl alcohol in carbon tetrachloride obtained in three different studies. The method by which both Soper and Williams and Moelwyn-Hughes and Hinshelwood followed the reaction was essentially the same as that in which analytical results were obtained in the present work.

TABLE III

	a	T, °C.	$k \times 10^4$
S. and W.[a]		50	1.88
M-H. and H.	0.101	49.9	2.60
	.100	55.0[b]	4.25
This work	.0979	49.90	2.66
	.0912	55.00	4.34

[a] Concentrations were not given in these authors' paper. Presumably they are above 0.2 M since all other experiments recorded in the paper for which concentrations are given range from about 0.250 to over 1 M. This accounts for the lower value of k observed by S. & W. [b] M.-H. & H. did not perform an experiment at this temperature. The value given was obtained by interpolation of their values obtained for experiments at 49.9, 60.2 and 70.6°.

The only detailed data which Moelwyn-Hughes and Hinshelwood present show k's whose average deviation is 1.57%. Examination of Table II in this work discloses that the average deviation for the first ten readings of Run VI is 0.12%. This clearly demonstrates the increased relative precision which may be expected from the present method. The agreement between the average values of k may be fortuitous in some degree since Moelwyn-Hughes and Hinshelwood observed k's differing by as much as 1% for the same reaction in different fractions of solvents.

The decreasing velocity of the reaction observed by Soper and Williams but not by Moelwyn-Hughes and Hinshelwood seems definitely to be confirmed. Whereas Soper and Williams observed a slowing-down of about 3% change in k between the time the reaction at 50° had progressed 30 and 50%, a decrease of about 4.5% was observed for the same period at 55° in this work. No slowing down was observed in the data of Run VII since the reaction was followed up to only about 30% completion.

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[CONTRIBUTION FROM THE HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

Condensation of Formaldehyde with Compounds Containing Activated Hydrogens

BY J. T. HAYS, G. F. HAGER,[*] H. M. ENGELMANN AND H. M. SPURLIN

This paper describes a method of reducing side reactions in the preparation of monomethylol derivatives by the reaction of formaldehyde with compounds containing activated hydrogens. The reaction is carried out in a fractionating column operated to maintain a large excess of activated compound over formaldehyde and to remove the initial product from the reaction zone by rectification. Yields higher than previously reported for liquid phase condensations are obtained.

The reaction of formaldehyde with compounds containing activated hydrogens, for example, ketones such as acetone and methyl ethyl ketone, is well known. Although the reaction may give the corresponding monomethylol derivative, complex mixtures have usually been obtained in actual practice.[1,2] A catalytic vapor-phase reaction of formaldehyde with acetone, methyl ethyl ketone and certain other ketones has been reported to give excellent yields of the corresponding unsaturated ketone, although large amounts of catalyst appear to be required for best results.[3] Landau and Irany[4] have recently studied the liquid-phase condensation of methyl ethyl ketone with formaldehyde; although they obtained high yields of crude condensation product (4-hydroxy-3-methyl-2-butanone), their over-all yields of methyl isopropenyl ketone were of the order of 50%, indicating that the crude condensation product was impure. It has been our experience that it is difficult to realize yields of greater than about 30% of monomethylol derivatives by the liquid-phase condensation of formaldehyde with acetone and with methyl ethyl ketone by methods previously

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