712.   *The Rate Constant of a Quaternisation in Methylene Dichloride between 35 and −71° and the Irrelevance of Dielectric Constant in Kinetics.*

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The Arrhenius plot for the reaction of methyl iodide with triethylamine in methylene dichloride was found to be accurately rectilinear between 35 and −71°, over which temperature range the dielectric constant increases from 8·5 to 14·3: $E_A = 8.78$ kcal./mole, $A = 5 \times 10^4$ l.mole^{-1} sec.$^{-1}$, $\Delta C^{\ddagger} = 2$ cal. mole^{-1} deg.$^{-1}$.

The implications of our results for the initiation and termination reactions in cationic polymerisations are discussed.

The argument is developed, that since in a single solvent at constant pressure the dielectric constant cannot be varied independently of temperature, and since in solvent mixtures its possible effects cannot be separated from specific solvent effects, it is meaningless to enquire into the influence of the dielectric constant as such on rate constants or activation energies.

THE application of transition state theory to reactions in solution lead to the conclusion that for reactions in which the products are more polar than the reactants (in particular, ionogenic reactions) the activation energy would be antibatically related to the solvating

power of the solvent; [1] and the dielectric constant or a function of it, appears as the relevant variable in the rate equations, such as that of Laidler and Landskroener.[2]   However, there is now much evidence that the dielectric constant, a macroscopic property, is in general not adequate to represent the effects of solvents on rates and equilibria.[3]

With respect to ionogenic reactions between dipolar molecules, of which the Menschutkin reaction has received most attention, the situation is particularly confused because both the activation energy, E_A, and the A-factor change from one solvent, or solvent mixture, to another (see for example the results of Grim, Ruf, and Wolff,[4] Hinshelwood *et al.*,[5a] Watanabe and Fuoss,[5b] and Rossell [5c]).   The fact that these changes frequently bring about a symbatic relation between the rate-constant at any one temperature and the dielectric constant of the solvents, or solvent mixtures, concerned has helped to conceal the fundamental complexity of the problem.[5c]

These and other considerations induced us to investigate how the rate of a Menschutkin reaction would behave in a single solvent over a temperature range so chosen that the change of dielectric constant with temperature should be as large as possible; curiously, this type of study does not appear to have been recorded.   As solvent we chose methylene dichloride, the dielectric constant of which [6] goes from 8·5 at 35° to 14·3 at −71°.   If the only effect of increasing dielectric constant were a reduction in E_A, one would expect to obtain an Arrhenius plot curved convex to the $1/T$ axis; the difficulty is to estimate the dielectric acceleration (the change in E_A) which a change of dielectric constant from 8·5 to 14·3 would produce.   Theory is of little help in this matter, and the results in the literature, which deal with series of solvents or solvent mixtures, are probably rather irrelevant; however, they are the only available guide and they suggest that a decrease in E_A of 0·5 to 2 kcal./mole might be expected.

EXPERIMENTAL

Materials.—Methylene dichloride was purified as described,[7] and had the physical constants quoted.[7]   Methyl iodide was purified by a method similar to Carson, Hartley, and Skinner's,[8] b. p. 42·5°/760 mm. (lit.,[9,10] 42·3—42·8°), n_D^{20} 1·5300 (lit.,[9,11] 1·5303—1·53152).   Triethylamine was refluxed for $\frac{1}{2}$ hr. with toluene-*p*-sulphonyl chloride, distilled off this, and then fractionally distilled from sodium hydroxide pellets through a 38-cm. column of Fenske rings; it had b. p. 89·0°/760 mm. (lit.,[10] 89·35—89·5°), n_D^{20} 1·4007 (lit.,[10] 1·40032—1·40101).   When analysed by vapour-phase chromatography with a Perkin-Elmer fractometer, each of the materials gave only a single, sharp peak.   Both reagents were charged into glass phials by vacuum distillation on a manifold; the content of the phials was determined by weighing.

Triethylmethylammonium iodide was prepared from the purified reactants in three purified solvents—methylene dichloride, ethanol, and benzene.   The salt was recovered from the solvent, and dried in a vacuum-desiccator.   The results obtained with the three specimens were identical.

Apparatus and Procedure.—The reactions were followed conductimetrically, and the concentration of reaction product corresponding to any observed value of the specific conductivity was read off on the previously constructed calibration graph for the particular temperature.

The conductivity cell, constructed from a 250-ml. conical flask of Pyrex glass, was fitted

[1] Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw-Hill, New York, 1941.
[2] Laidler and Landskroener, *Trans. Faraday Soc.*, 1956, **52**, 200.
[3] Bunton, *Nature*, 1957, **180**, 534; Venkataraman and Hinshelwood, *J.*, 1960, 4986, and references quoted therein.
[4] Grimm, Ruf, and Wolff, *Z. phys. Chem.*, 1931, B **13**, 301.
[5] (a) Raine and Hinshelwood, *J.*, 1939, 1378; Bose and Hinshelwood, *J.*, 1958, 4085; (b) Watanabe and Fuoss, *J. Amer. Chem. Soc.*, 1956, **78**, 527; (c) Rossell, *J.*, 1963, 5183.
[6] Morgan and Lowry, *J. Phys. Chem.*, 1930, **34**, 2385.
[7] Longworth, Plesch, and Rigbi, *J.*, 1958, 451.
[8] Carson, Hartley, and Skinner, *Proc. Roy. Soc.*, 1949, **195**, A, 500.
[9] Vogel, *J.*, 1943, 636.
[10] Weissberger, " Techniques of Organic Chemistry, Vol. VII—Organic Solvents," Interscience, London, 1955.
[11] Audsley and Goss, *J.*, 1941, 864.

with a pocket for insertion of a thermometer, and with bright platinum electrodes, 2×2 cm., which were sealed 2 mm. apart with lead glass beads. The leads were brought out by tungsten-through-Pyrex seals. The cell had a sidearm, carrying a greased tap and a B14 joint by which it could be attached to a vacuum manifold. The cell constant at 25° was obtained by Lind, Zwolenik, and Fuoss's [12] method; its value, 0·03901, was constant over a wide range of concentrations, and for all volumes of solution greater than 15 ml.

Resistance measurements were made with a Wayne-Kerr B221 universal bridge, working at 1592 C./sec; resistance (which could be measured to 0·1%) and capacitance were balanced separately.

Reactions were carried out at $+35$, $+25$, 0, -20, -40, -55, and $-71°$. For the first two of these temperatures a water thermostat controlled to $\pm 0·01°$ was used. The 0° temperature ($\pm 0·02°$) was obtained by a well stirred ice-in-distilled water bath. The lower temperatures were obtained with a " Minus Seventy Thermostat Bath " (Townson and Mercer Ltd.), filled with light petroleum (b. p. 100—120°). The temperature of the bath remained constant, to within $\pm 0·05°$, over the whole range of temperature for indefinite periods.

The temperature of the $+35$, $+25$, and 0° thermostats was measured to $\pm 0·01°$ with standardised mercury-in-glass thermometers. Temperatures below 0° were measured to $\pm 0·1°$ with an alcohol-in-glass thermometer, which had been calibrated against an N.P.L. standard. The temperature of the reaction mixture was measured by means of a platinum resistance thermometer inserted into the pocket of the conductivity cell.

The calibration curves. Approximately 0·3 g. of methyltriethylammonium iodide was weighed (to $\pm 5 \times 10^{-6}$ g.) into the conductivity cell. This was attached to the vacuum manifold, evacuated, and a volume of methylene dichloride (measured to $\pm 0·1$ ml.) was distilled into it from a burette; the manifold used for this was essentially the same as that of Longworth, Plesch, and Rigbi.[7]

The conductivity of the solution was measured at all the required temperatures. Then the cell was re-attached to the manifold, more solvent was distilled in, and the conductivity of the solution was again measured at the same temperatures. This procedure was repeated until the cell was full (*ca.* 200 ml.). During the measurements the cell was kept evacuated at all times.

From these measurements a curve relating specific conductivity to salt concentration was constructed for each temperature.

Measurement of reaction rate. The reaction mixtures were prepared by a similar procedure. A phial of triethylamine was broken in a special vessel attached to the vacuum manifold, and its contents were distilled into the cell before the methylene dichloride. When the distillation of the methylene dichloride was almost complete, the methyl iodide phial was broken and its contents were also distilled into the cell. The cell was removed from the vacuum line, thoroughly shaken, and placed in a thermostat; resistance readings were taken in most experiments until there was no further change, *i.e.*, the reaction was complete. The resistance readings were converted into salt concentration by means of the calibration graphs.

The phials used in each experiment were carefully matched so that in no experiment did the difference between the initial concentrations of the reagents exceed 1%. The results were plotted according to the equation for a second-order reaction with equal initial concentrations of reagents.

Special precautions and sources of error. We ascertained by separate experiments the following points: (1) Neither reagent alone gives a measurable conductivity in methylene dichloride.

(2) Neither of the reagents in the concentrations used by us affects the conductivity of the salt solution.

(3) At all the relevant temperatures the rate constant for the reaction between triethylamine and methylene dichloride is several powers of ten smaller than that of the reaction under study.

(4) In some experiments the final yield of salt was obtained (*a*) from the conductivity of the reaction mixture after 2 or 3 days, (*b*) by evaporating the solvent and weighing the salt, and (*c*) by titrating the iodide after dissolving the salt in water. The results of the three methods agreed to within $\pm 0·5\%$ with each other and with the value expected from the initial quantities of reagents.

(5) The conductivity of methylene dichloride freshly distilled from calcium hydride becomes

[12] Lind, Zwolenik, and Fuoss, *J. Amer. Chem. Soc.*, 1959, **81**, 1557.

appreciable if the liquid is exposed to the atmosphere. Although the rate of the quaternisation reaction appears to be unaffected, we preferred to use a vacuum technique.

(6) The results of preliminary " open " experiments in which the rate was followed by titrating the iodide formed, gave essentially the same results as the " vacuum conductivity " experiments, but there was a greater scatter of the k_2 values.

(7) Measurements of the density, d, at ·25° of solutions of triethylmethylammonium iodide in methylene dichloride at five concentrations, c, in the range 0—0·5 mole/l. showed that $d =$ 1·3166 + 0·0498c, with an uncertainty of $\pm 0·0003$. Therefore in the range of concentrations used in the kinetic experiments no appreciable error was introduced by using the density of the solvent, as given by Morgan and Lowry,[6] to calculate the concentration of the solutions at each temperature.

Correction for the quantity of solvent present in the vapour phase was only necessary at temperatures above 0° and when the volume of solvent was less than about 30 ml.

(8) The different parts of all the vacuum manifolds used in this work were separated by all-metal " BiPl " valves (Scientific Instrument and Model Co., Ross-on-Wye) the only greased tap being attached to the conductivity cell.

RESULTS

The plots of $1/(a - x)$ against t, where $a =$ initial concentration of reactants, $x =$ concentration of product, and $t =$ time, were accurately rectilinear up to at least 80% conversion.

TABLE 1.

The results of the non-vacuum experiments.

Expt.	Temp.	$10^2 a$ (mole/l.)	k_2 (l. mole^{-1} sec.$^{-1}$)	k_2 average
A	+30·0°	1·588	2·05 × 10^{-2}	
B	+30·0	1·588	2·07 × 10^{-2}	2·06 × 10^{-2}
C	+25·0	1·603	1·70 × 10^{-2}	
D	+25·0	1·603	1·70 × 10^{-2}	1·70 × 10^{-2}
E	0·0	38·7	4·85 × 10^{-3}	
F	0·0	3·242	4·60 × 10^{-3}	
G	0·0	0·837	4·69 × 10^{-3}	4·71 × 10^{-3}

TABLE 2.

The results of the vacuum experiments.

Expt.	Temp.	$10^2 a$ (mole/l.)	k_2 (l. mole^{-1} sec.$^{-1}$)	k_2 average
N18	35·0°	6·987	2·77 × 10^{-2}	
N1	25·0	6·682	1·72 × 10^{-2}	
N16	25·0	6·958	1·76 × 10^{-2}	1·74 × 10^{-2}
N14	0·0	7·108	4·74 × 10^{-3}	
N15	0·0	7·173	4·72 × 10^{-3}	4·73 × 10^{-3}
N12	−20·0	10·703	1·15 × 10^{-3}	
N17	−20·0	7·515	1·28 × 10^{-3}	1·21 × 10^{-3}
N6	−40·0	7·974	2·64 × 10^{-4}	
N10	−40·0	7·769	2·62 × 10^{-4}	2·63 × 10^{-4}
N4	−55·0	8·124	6·27 × 10^{-5}	
N13	−55·0	11·182	6·32 × 10^{-5}	6·30 × 10^{-5}
N2	−71·0	7·847	1·48 × 10^{-5}	
N7	−71·0	8·280	1·45 × 10^{-5}	1·47 × 10^{-5}

The values of the second-order rate constant, k_2, obtained from these plots for the preliminary non-vacuum experiments are listed in Table 1 and those for the vacuum experiments in Table 2.

The Arrhenius plot, shown in the Figure, gives an activation energy, E_A, of 8·78 $\pm$ 0·05 kcal./mole, and an A factor of (5·0 $\pm$ 1·0) × 10^4 l.mole^{-1} sec.$^{-1}$.

Experiments E, F, and G show that changing the concentration of the reagents by a factor of about 50 has no significant effect on k_2.

Arrhenius plot for the reaction between MeI and Et_3N in CH_2Cl_2.
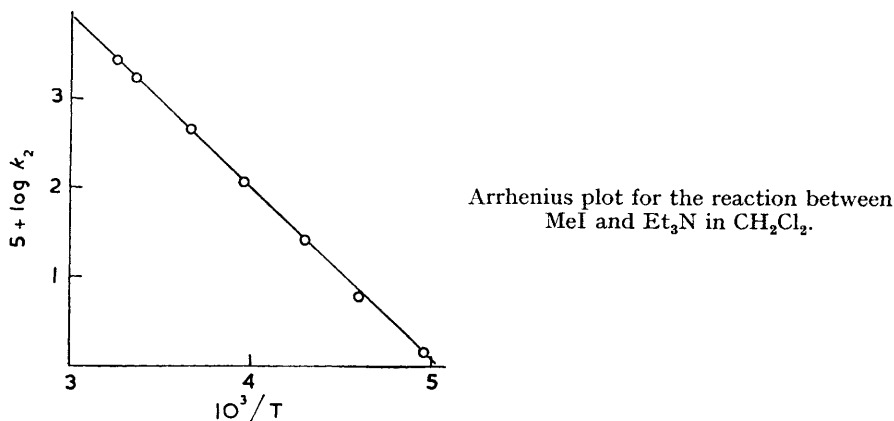
DISCUSSION

The Arrhenius Plot.—Since the Arrhenius plot is accurately rectilinear over more than 100° and over a 75% change in dielectric constant, it follows that there is no detectable change of activation energy in this system. Our results thus represent a further example of how difficult it is to detect the relevance of the dielectric constant in kinetic considerations.

The Entropy, Enthalpy, and Heat Capacity of Activation.—From our results, values of $\Delta S^{\ddagger}$ can be calculated by the usual equation, giving -36.88 ± 0.20 e.u. at 35° and -36.05 ± 0.20 e.u. at $-70°$. Since $d(\Delta S^{\ddagger})/dT$ is so very small, we have calculated an average value over the temperature range of 7.9×10^{-3} e.u. deg.$^{-1}$. Hence $\Delta C^{\ddagger}$, given by

$$\Delta C^{\ddagger} = d(\Delta H^{\ddagger})/dT = T d(\Delta S^{\ddagger})/dT$$

varies from 2.4 cal. mole^{-1} deg.$^{-1}$ at 35° to 1.6 cal. mole^{-1} deg.$^{-1}$ at $-70°$. In view of the uncertainty of our $\Delta S^{\ddagger}$ values, this variation can hardly be regarded as significant.

Absence of Primary Salt Effect.—In Experiment E the concentration of the ionic reaction product increased from 0 to 0.387 mole/l. at complete conversion. Yet the second-order plot is rectilinear throughout, showing the absence of a primary kinetic salt effect. The reason is undoubtedly that the salt is present predominantly in the form of ion-pairs and higher aggregates.[13]

Implications for Cationic Polymerisations.—Methylene dichloride and other alkyl chlorides have been widely used as solvents for cationic polymerisations. The initiation of these resembles the Menschutkin reaction, in that an ion-pair is formed from dipolar reagents, namely the catalyst (*e.g.*, perchloric acid or boron fluoride monohydrate) and the monomer. On the basis of the results presented here one may conclude that the Arrhenius plot for such initiation reactions is unlikely to depart significantly from linearity.

It follows from the principle of microscopic reversibility that for a reaction in which ions react to form a neutral molecule the Arrhenius plot will probably also be rectilinear, and since the termination reactions in cationic polymerisations are of this nature, they too will obey a rectilinear Arrhenius relation.

Temperature and Dielectric Constant.—Most current theories of reactions in solution treat temperature and dielectric constant as independent variables, and assume that for any given reaction at constant pressure these are the only relevant ones, the contribution of non-electrostatic effects to departures from ideality being generally neglected. Our results led us to examine the logical validity of this procedure which was the original basis of our study. The argument runs thus:

[13] Beard, Thesis, Birmingham, 1963: Beard and Plesch, *J.*, 1964, in the press.

Since experiments show that the dielectric constant is not the only relevant variable, and that indeed it may be much less important than " specific solvent effects," or perhaps even quite irrelevant, the endeavour to separate the effects of temperature and dielectric constant becomes scientifically meaningless. The reason is that the theoretical equations purporting to represent the rate constant as a function of temperature and dielectric constant only, cannot be tested even for the very simplest case, *i.e.*, with a single solvent, since in no conceivable experiment can one of these parameters be varied whilst the other is kept constant. Furthermore, since the change of dielectric constant is a necessary consequence of the change in temperature, inseparable from it, it is meaningless to enquire whether the change in dielectric constant, itself, has a distinguishable effect on the events taking place in the solution. (This same conclusion was reached independently by Pepper and Reilly.[14])

In other words, the attempt to separate the effect of dielectric constant from the effect of temperature, is meaningless, because for a series of solvents, or of binary solvent mixtures, the effect of dielectric constant cannot be separated from the specific solvent effects, and for a single solvent the dielectric constant is a unique function of temperature. This conclusion is of quite general validity.

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[14] Reilly, Ph.D. Thesis, University of Dublin, 1962.