BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 818—821 (1973) [Vol. 46, No. 3

Kinetics and Mechanism of the Reaction of Iodine Mono Chloride with Some Alcohols

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(Received December 14, 1971)

Kinetics of the reaction of ICl with some aliphatic alcohols, methanol to *n*-butanol and isobutyl alcohol and isopropyl alcohol, have been studied by the conductance method at five different temperatures. Arrhenius parameters have been determined. Plot of log *k* against the reciprocal of dielectric constant has been drawn to test the applicability of the Amis and Jaffé equation. Energy of activation has been correlated with polarity of alcohols. The IR analysis of the product shows a sharp peak at 1620 cm^{-1}, which confirms a (O–I) bond stretching in the product. From these results a reasonable mechanism has been suggested as follows:

$$\mathrm{ICl} \xrightarrow{\text{fast}} \mathrm{I^+ + Cl^-} \qquad (1)$$

$$\mathrm{R{-}O{-}H + I^+} \xrightarrow{\text{slow}} \mathrm{R{-}O{-}I + H^+} \qquad (2)$$

Iodination reactions by ICl have been studied by various workers.1–6) Lambourne and Robertson7) studied the kinetics of iodination of various aromatic compounds using glacial acetic acid or chloro benzene as solvents. Kinetics of iodination of *p*-Cl $C_6H_4NH_2$ with ICl in water containing excess of chloride and H^+ ions has been studied by Berliner.8) He suggested that the reaction involves free amine and hypo-iodous acidium ion (H_2OI^+). Irent'ev and Yanovskaya9) have found that iodo derivatives are formed in the case of reactions of acids and resorcinol with ICl.

In the present investigation kinetics of the reaction of ICl with aliphatic alcohols, methanol to *n*-butyl alcohol, isobutyl alcohol, and 2-propanol has been studied systematically. It has been found that the reaction takes place according to the equation, provided

$$\mathrm{R{-}O{-}H + ICl = R{-}O{-}I + H^+ + Cl^-}$$

no other complexities arise due to the impurities present either in alcohols or ICl. This has been confirmed in several ways. Infrared analysis confirms the presence of a (O–I) bond in the product. Gravimetric estimation of Cl^- ions confirms that Cl^- ions are not consumed during the course of the reaction. The aim of the present work is (a) to find out Arrhenius parameters, (b) to correlate rate constants with dielectric constant of the medium, (c) to find out the relationship between energy of activation (E) and polarity (μ) of the substance and (d) to suggest a reasonable mechanism for such reactions.

Experimental

(a) Materials. Iodine monochloride, E. Merck, E. P., was used for the experiment. It was kept in a vacuum desiccator to avoid moisture contamination.

The alcohols were of B. D. H. Analar quality. All the substances were dried with anhydrous calcium chloride and then distilled several times. Adequate precautions were taken to keep the sample dry.

Since ions were formed during the course of the reaction, kinetics was studied by conductance measurements most accurately with the help of a Beckman model RC 16 B 1 conductivity bridge and a cathod ray oscilloscope as a null point detector. This method was used in preference to the usual titriometric methods since it involves minimum number of operations and can be conveniently followed with the help of a small amount samples.

Fresh solutions were prepared every time before the experiment. First anhydrous alcohols were kept in glass stoppered tubes in a thermostat for one hour to attain the temperature of the bath. Calculated quantity of ICl was then taken by means of a perfectly dry syringe and accurately weighed inside the coloured glass conductivity cell as quickly as possible. 10 m*l* of the alcohol that had previously been kept in the thermostat was added to the cell. Thus a solution of ICl in alcohol of exactly 0.099M was immediately obtained in the cell. Rate of the reaction was then followed by measuring the resistance at different time intervals. Pseudo unimolecular rate constants were determined10) at five different temperatures ranging from 15 to 35°C by applying the least square method from which Arrhenius parameters were determined.

Test for I^+ Ion. The presence of I^+ in the reaction mixture after completion of the reaction was tested by the method adopted by Arotsu *et al.*11) When a drop of the reaction mixture was added to oleum, no blue colouration was observed, which proved the absence of I^+.

Effect of HCl. In order to find out if HCl has any catalytic effect, 0.05 ml of M/10 HCl was added to the reaction mixture of ICl and methanol, and then the rate of the reaction was followed by the conductance method. The rate constant was calculated. It was found that at 25°C

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6) F. M. Vainstein, E. I. Tomilenko, and E. A. Shilov, *Kinet. Katal.* **7**, 33 (1966).

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8) E. Berliner, *J. Amer. Chem. Soc.*, **78**, 3632 (1956).

9) A. P. Irent'ev and L. A. Yanovskaya, *J. Gen. Chem. USSR* **24**, 1251 (1954).

10) A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Edn. John Wiley and Sons Inc. N.Y. (1961), p. 36.

11) J. Arotsu, H. C. Mishra, and M. C. R. Symon, *J. Chem. Soc.*, **1961**, 12.

$k=35.97\times10^{-4}$ min^{-1} with HCl and $k=36.02\times10^{-4}$ min^{-1} at 25°C without HCl. The little difference was within experimental error.

Effect of Water. To find out whether water has any effect on the rate of the reaction, 0.05 ml of water was added to the reaction mixture at the beginning and then the rate was followed. It was found that a small amount of water had no effect.

Estimation of Cl⁻ Ion. The amount of Cl^- was estimated gravimetrically[12] as AgCl before and after the reaction. It was found that the amount of Cl^- after the reaction was the same as at the beginning. This proved that Cl^- was not consumed during the course of the reaction.

Results and Discussion

It is of interest that in all cases the reaction was completed when a reactant (*i.e.* -alcohol) was present in a large excess.

This was further verified by the method given by Arotsu *et al.* (loc. cit.), from the fact that no free I^+ (iodonium ion) remained after the reaction was over.

TABLE 1. VALUES OF μ, E, AND log PZ

Alcohol	μ	E (kcal/g mol)	log PZ (min)
Methanol	1.70	11060	5.61
n-Butanol	1.69	13200	7.65
Ethanol	1.68	14700	8.45
Propanol	1.67	16400	9.82
2-Propanol	1.60	26700	16.98
Isobutyl alcohol	—	20300	12.92

From the results given in Table 1, it is observed that the frequency factor (log PZ) and energy of activation (E) both vary in the case of reactions of methanol to *n*-butyl alcohol, 2-propanol, and isobutyl alcohol. The variation of frequency factor A can be explained in terms of collision theory. A is made up of two factors probability factor P and collision number Z. They may be identified in the following form as has been described by Stern and Eyring.[13]

$$P\approx(f_v/f_r)^5$$

$$\text{and } Z\approx kT/h(f_r^2/f_t^3)$$

where f_v, f_r, and f_t are the partition functions for vibrational, rotational, and translational degrees of freedom, respectively. At ordinary temperature f_v is of the order of unity while f_r may vary from 10 to 100 in case of complex molecules. If the molecules are less complex, the smaller will be the value of f_r and so the factor P will be high, which will help raise the values of 'PZ'. In the present case it can be seen from Table 1 that the higher values of PZ may be due to the increase in the probability factor P. But if the complexity of the molecules increases with solvation, P will have lower values and consequently factor A will be low. According to collision theory we have

$$Z=N^2\sigma_{AB}^2[8\pi RT(1/M_A+1/M_B)]^{1/2}C_AC_B \qquad (1)$$

In the present case, M_B the molecular weight of ICl is constant and M_A, the molecular weight of alcohols, does not vary much from methanol to *n*-butanol; so the factor 'Z' is constant.

Effect of Dielectric Constant on Reaction Velocity. Many equations[14] have been derived to correlate the dielectric constant of the medium with reaction velocity. Amis and Jaffé[15] gave the following equation for the ion-dipole interaction:

$$\ln k'=\ln k'_{r=0}+\frac{\xi Z_B\cos\theta_0}{DkTr_0^{\,2}}\left(\mu_0+\frac{\mu^*(1+Xr_0)}{e^{Xr_0}}\right) \qquad (2)$$

In the limiting case of the direct approach of an ion to a dipolar molecule, Eq. (2) was modified by Amis[16] as follows:

$$\ln k'_{D=D}=\ln k'_{D=\infty}+\frac{Zc\mu}{DkTr^2} \qquad (3)$$

According to this equation, the rate decreases with the increase of dielectric constant for a positive ionic reaction. Recently Laidler and Landskroener[17] developed the following general equation incorporating the corrections due to non-electrostatic forces.

$$\ln k=\ln k_0+\frac{\xi^2}{2kT}\left(\frac{1}{D}-1\right)\left[\frac{Z_A^{\,2}}{b_A}+\frac{Z_B^{\,2}}{b_B}-\frac{(Z_A+Z_B)^2}{b_{\neq}}\right]$$
$$+\frac{3\xi^2}{8kT}\left(\frac{2}{D}-1\right)\left[\frac{G_A}{b_A^{\,3}}+\frac{G_B}{b_B^{\,3}}-\frac{G_{\neq}}{b_{\neq}^{\,3}}\right] \qquad (4)$$

This also, predicts a linearity between log k and the reciprocal of the dielectric constant.

TABLE 2. VALUES OF $k_{25°C}$ AND $100/D$ FOR THE REACTION OF ICl WITH ALCOHOLS

Alcohol	$k_{25°C}\times10^4$ (min^{-1})	$100/D$
Methanol	36.02	3.062
Ethanol	54.81	4.110
Propanol	76.11	4.975
2-Propanol	92.12	5.464
n-Butanol	109.85	5.848
Isobutyl alcohol	132.10	6.330

In the present case of the reaction between ICl and alcohols, it has been found that log k increases with the decrease of the dielectric constant (Table 2) and the plot of log k against $100/D$ is a straight line (Fig. 1). This is in agreement with the Amis equation (2).

It can therefore be concluded that it is an ion-dipolar reaction.

Correlation of Polarity and Energy of Activation. Many equations have been derived by Amis,[16] Ingold and Nathan[18] and Evans, Gordon and Watson[19] connecting energy of activation and polarity of the solvents. Moelwyn-Hughes[20] has explained similar rela-

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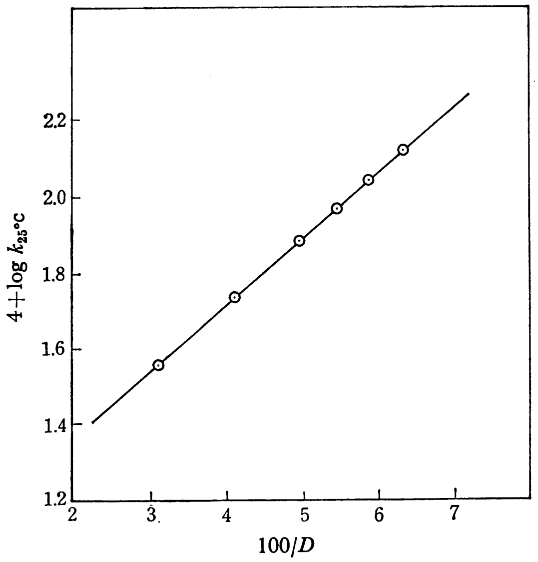

Fig. 1. Plot of log $k_{25°C}$ *vs*. 100/D for the reaction of ICl with alcohols.

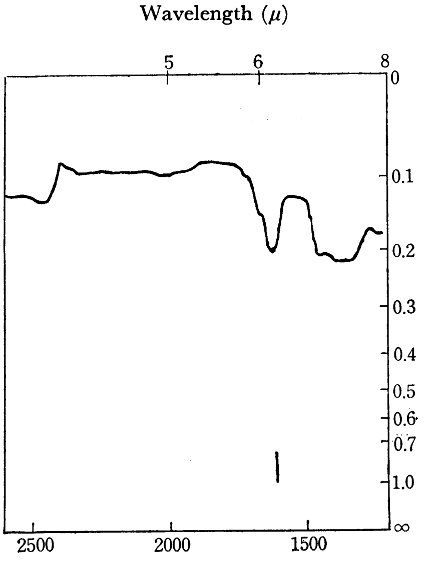

Fig. 3. IR spectrum.

tion ships in terms of electrostatic principles and for head on-alignment of ion and dipole, the equation becomes

$$E_s = E_\mu - \frac{N_Z \mu}{D_r^2} \qquad (5)$$

According to this equation, when the energy of activation is plotted against the dipole moment of dipolar molecules reacting with ions, the plot should be linear with a negative slope if the reacting ion is positive in charge, and with a positive slope if the ion is negative in charge.

In the present case, though the difference of dipole moments of alcohols is less, energy of activation has been plotted against 'μ'. It can be seen from that the plot is a straight line with a negative slope (Fig. 2), which means in this case the reacting ion is a positively charged I^+ ion reacting with a dipolar molecule like alcohol ($CH_3OH \rightleftharpoons CH_3O^- + H^+$). This also proves that in the case $ICl \rightleftharpoons I^+ + Cl^-$, a product like CH_3OI is expected not to be a chloride derivative. This has also been confirmed by the estimation of Cl^- ions, as AgCl, that no Cl^- ions are consumed during the course of the reaction.

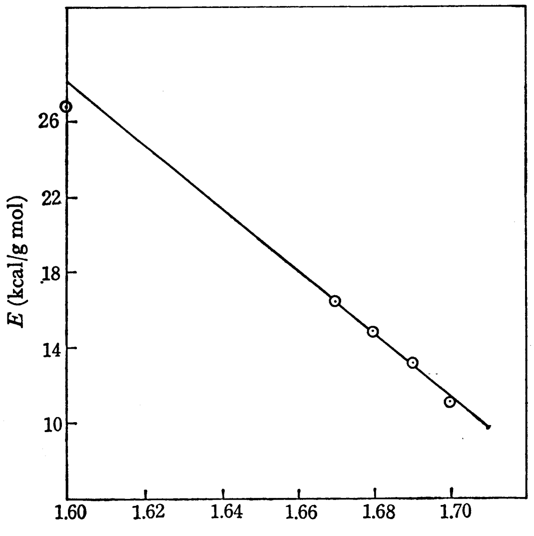

Fig. 2. Plot of E *vs*. μ for the reaction of ICl with alcohols.

Product Identification. The product in each case has been identified by IR spectrum (Fig. 3). A sharp peak at 1620 cm^{-1} confirms a (O–I) bond stretching[21] in the product. This confirms that iodo derivative of the type R–O–I is formed.

Mechanism. ICl being a highly reactive species and a polar compound, it is easily ionized in a medium of alcohols having high dielectric constants according to either of the following equations.

$$ICl \longrightarrow I^+ + Cl^- \qquad (1)$$

$$I_2Cl_2 \longrightarrow I^+ + ICl_2^- \qquad (2)$$

The interpretation will be the same whether ionization takes place according to Eq. (1) or (2). The iododichloride ion (ICl_2^-) has been ruled out, since the iodinating agent with the iodine in the middle of the structure of (ICl_2^-) has an unfavourable geometry for substitution.[22] Ionization (1) is favoured at high dielectric constants, as has been observed by Bearcraft and Nachtrich.[23]

Alcohols are also polar compounds and it is quite reasonable to predict that alcohols combine with highly reacting species like I^+ ions according to the reaction

$$CH_3OH + I^+ = CH_3OI + H^+ \qquad (3)$$

showing that this is an ion-dipole type of reaction.

If step (1) were the rate determining step of the present reaction, then the rate of the reaction would have increased with the increase of dielectric constant of the medium. In the present case (Table 2), however it was observed that as the dielectric constant decrease, from methanol to butanol, the rate of the reaction

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21) Nakanishi, "Infrared absorption spectroscopy practical" Holden day (1962).

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increases. This has also been confirmed from the straight line plot of log k against $100/D$.

It is also seen that addition of HCl does not change the specific reaction rate constant in these cases. Thus a reaction of the type $ICl+HCl=HICl_2$ is ruled out in this case, or if such a reaction takes place at all, the rate of reaction is extremely slow and indistinguishable kinetically.

The proposed mechanism is thus

$$ICl \xrightarrow{\text{fast}} I^+ + Cl^- \tag{1}$$

$$CH_3OH + I^+ \xrightarrow{\text{slow}} CH_3OI + H^+ \tag{2}$$

Step (2) is the rate determining step of the reaction as step (1) is an ionization process and very fast. A similar mechanism can be given for other alcohols.

The authors are grateful to Prof. E. Pickett, University of Missouri, U.S.A. and Prof. C. R. Kanekar of TIFR, Bombay, India for their kind help in carrying our IR analysis and supplying the pure ICl sample.