# 513. *Liquid-phase Reactions at High Pressures. Part XIV.*[1] *The Kinetics of Two Reverse Menschutkin Reactions*

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The kinetics of two reverse Menschutkin reactions have been investigated at 1 atm., by a conductivity method, as a preliminary to measurement of the reaction rates at high pressures. The conductance–concentration relationship for *N*-ethyl-*NN*-dimethylanilinium iodide in nitrobenzene indicates considerable association into ion-pairs, and dissociation constants for the ion-pair equilibrium have been calculated. The apparent rate constants for the reaction (to tertiary amine and methyl iodide) in nitrobenzene vary widely with salt concentration, but the first-order rate constants calculated with respect to the concentration of ion-pairs are independent of the initial concentration. *N*-Allyl-*N*-benzyl-*N*-methylanilinium bromide is almost wholly associated in chloroform and the rate constant was calculated from the salt concentrations.

THE large increases in the rate constants of reactions between tertiary amines and organic halides at high pressures have been extensively investigated.[1] The results have provided much information about the transition states of the reactions but very little data is available on the reverse reaction of the quaternary ammonium salts at high pressures. The kinetic study of two reverse Menschutkin reactions at 1 atm. described below was undertaken as a preliminary to the measurements at high pressures described in the next Paper.

Reverse Menschutkin reactions, in which the ions of the quaternary ammonium salt react to yield an organic halide and a tertiary amine, are often approximately first-order with respect to salt concentration over narrow ranges of concentration. This has been attributed to association of the reactant ions as ion-pairs, but there has been no quantitative study of the relation between the ion-pair equilibrium and the kinetics of the reaction. Ross *et al.*[2] have produced strong evidence that the analogous reaction of quaternary ammonium thiocyanates occurs *via* ion-pairs in moderately ionising solvents, while Hughes *et al.*[3] have argued that the halide ion must participate in the transition state of sulphonium halide decompositions because of the principle of microscopic reversibility, and the participation of the halide ion in the opposing bimolecular reaction.

[1] Part XIII, A. P. Harris and K. E. Weale, *J.*, 1961, 146.

[2] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Amer. Chem. Soc.*, 1961, **83**, 4853.

[3] E. D. Hughes, C. K. Ingold, and Y. Pocker, *Chem. and Ind.*, 1959, 1282.

The concentration-dependence of the apparent first-order rate constants for reverse Menschutkin reactions varies with the solvent. In chloroform they increase markedly with decreasing initial concentration,[4] whilst in nitrobenzene Laidler's results [5] indicate that the constants decrease with decreasing initial concentration.

## EXPERIMENTAL

Kinetic measurements of the reaction of *N*-allyl-*N*-benzyl-*N*-methylanilinium bromide in chloroform were made because the effect of pressure on the rate has previously been investigated.[6] The proportions of the various possible products formed are not known, and the high degree of association of the salt makes detailed interpretation difficult. Some other quaternary-halide decompositions, which were examined because the effect of pressure on the rates of the opposing reactions is known, proved either to be complicated by side-reactions or to proceed to a negligible extent under the conditions used.[7] The rate of decomposition of *N*-ethyl-*NN*-dimethylanilinium iodide in nitrobenzene at 65° was found to be convenient for measurement. Excellent separation of the mixed amines produced was obtained by argon chromatography (Apiezon M packing at 100°). 94·3 mol. per cent was *N*-ethyl-*N*-methylaniline, the remainder being *NN*-dimethylaniline. This reaction was selected for detailed measurement.

*Materials.*—AnalaR nitrobenzene, dried ($Na_2SO_4$), fractionated under dry nitrogen (100 mm.), stored over activated alumina, and filtered before use, had m. p. 5·7° (lit.,[8] 5·76°). The specific conductance, $1 \times 10^{-8}$ ohm$^{-1}$ cm.$^{-1}$, though higher than some recorded values, was negligible in comparison with the conductances of the reactant solutions.

AnalaR chloroform, purified by the method of Williams *et al.*[6] had b. p. 61·0—61·5°, and specific conductance $6{\cdot}7 \times 10^{-10}$ ohm$^{-1}$ cm.$^{-1}$. Methyl iodide (b. p. 42·5°), purified as in previous work,[1] and allyl bromide [6] (b. p. 70·2—70·5°) were kept over mercury. *N*-Ethyl-*N*-methylaniline, purified by the method of Evans *et al.*,[9] had b. p. 203—205° (lit.,[10] 200—204°) and chromatographic analysis showed no significant impurities. *N*-Benzyl-*N*-methylaniline (used to prepare the quaternary bromide) was twice distilled under nitrogen and had b. p. 161°/8 mm. (lit.,[11] 161—162°). As it rapidly became brown on contact with air it was used immediately.

The quaternary salts, prepared from equimolar quantities of amine and halide at ~35°, were washed with AnalaR light petroleum, recrystallised three times from methanol, dried *in vacuo* at room temperature, and stored *in vacuo* in the dark. *N*-Ethyl-*NN*-dimethylanilinium iodide (Found: I, 45·7. Calc. I, 45·75%) and *N*-allyl-*N*-benzyl-*N*-methylanilinium bromide (Found: Br, 24·8. Calc. Br, 25·11%), m. p. 143·5°, (lit.,[6] 144°) were both white crystalline solids.

*Reaction Rate and Conductance Measurements.*—Most rates were determined conductimetrically in glass cells immersed in oil-baths, with temperature control to ±0·02°. A few runs were followed by titration of halide ion, as in previous work.[1] The conductivity cells, of about 11 c.c. capacity, had platinum electrodes which were lightly platinised from solution, and they were flushed with reactant solution before each run. Conductances were measured with a Wayne–Kerr Universal bridge to within ±0·2%, and fresh solutions were made for each run. The quaternary bromide dissolved readily in chloroform but the iodide required warming to ~35° to dissolve completely in nitrobenzene at 0·05M. Most kinetic runs in nitrobenzene were at 0·05M, and in chloroform at 0·1M. Conversions were generally kept well below 20%. To obtain the absolute conductances necessary for calculations of ion-pair dissociation the cells were standardised with 0·1M-potassium chloride solution. It is estimated that the variation of the cell constants, which were all between 0·4 and 0·7 cm.$^{-1}$, was less than 0·1% over the temperature range of the work.

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[4] W. C. Davies and R. G. Cox, *J.*, 1937, 614.

[5] K. J. Laidler, *J.*, 1938, 1786.

[6] E. G. Williams, M. W. Perrin, and R. O. Gibson, *Proc. Roy. Soc.*, 1936, *A*, **154**, 684.

[7] J. M. Stewart, Ph.D. Thesis, University of London, 1962.

[8] A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, " Organic Solvents," 2nd edn., Interscience, New York and London, 1955.

[9] D. P. Evans, H. B. Watson, and R. Williams, *J.*, 1939, 1345.

[10] Y. Y. Makarov-Zemlyanskii, S. F. Filatov, and V. S. Velichkin, *J. Appl. Chem.* (*U.S.S.R.*), 1937, **10**, 660.

[11] I. M. Heilbron and H. M. Bunbury, " Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.

## CALCULATIONS AND RESULTS

*The Conductance–Concentration Relationship.*—A direct proportionality between conductance and ion concentration has sometimes been erroneously assumed, and some studies of forward Menschutkin reactions appear to be an instance of this.[12] The dependence of conductance on concentration was measured for the quaternary bromide in chloroform at 34·95°, and for the iodide in nitrobenzene at 25 and 65°. The decomposition, with a corresponding change in conductance, began as soon as the cells were immersed in the oil-bath, but values at zero time were extrapolated without difficulty from the curves. The results for the two salts are given in Table 1.

TABLE 1

Equivalent conductances of quaternary salt solutions

| Iodide in nitrobenzene | | | | Bromide in chloroform | |
|---|---|---|---|---|---|
| 25° | | 65° | | 34·95° | |
| $10^5$M | Λ | $10^5$M | Λ | $10^4$M | $10^3$Λ |
| 4970 | 16·75 | 4808 | 29·21 | 980·7 | 87·66 |
| 2485 | 21·10 | 2404 | 36·57 | 688·7 | 67·15 |
| 245·4 | 33·27 | 237·4 | 58·60 | 344·4 | 50·62 |
| 98·16 | 36·15 | 94·96 | 64·34 | 49·89 | 52·55 |
| 9·816 | 39·45 | 9·496 | 70·87 | 24·95 | 60·27 |
| | | | | 9·978 | 78·66 |

*Calculation of Ion-pair Dissociation for the Iodide in Nitrobenzene.*—In order to interpret the rate measurements for the quaternary iodide the results of Table 1 were used to calculate ion-pair dissociation constants. According to Robinson and Stokes [13] the equivalent conductance $\Lambda_i$ (mhos cm.$^2$) of a hypothetical fully-dissociated solution, at a concentration $\alpha c_s$, is given by

$$\Lambda_i = \Lambda_0 - \frac{B_1\Lambda_0 + B_2\sqrt{\alpha c_s}}{1 + Ba\sqrt{\alpha c_s}} \qquad (1)$$

where $\Lambda_0$ is the equivalent conductance at infinite dilution, $\alpha$ is the fraction dissociated, $c_s$ is the total salt concentration (mole. l.$^{-1}$), $B_1$ and $B_2$ are the Debye–Huckel constants, which depend on temperature and the dielectric constant of the solvent, $B$ is a constant which depends on temperature and the viscosity and dielectric constant of the solvent, and $a$ is the "ion-size parameter." This equation can be used up to ~0·1M with proper choice of the parameter $a$. Following the procedure of Monk,[14] the Bjerrum critical distance was calculated and used to derive a value of $a = 4{\cdot}95$ Å for nitrobenzene solution at 25°. The same figure was used at 65° since equation (1) is insensitive to small changes in $a$.

In conjunction with (1) the equation

$$\log f_\pm = (-A\sqrt{\alpha c_s})/(1 + Ba\sqrt{\alpha c_s}) \qquad (2)$$

was used, which defines the mean activity coefficient for a 1 : 1 electrolyte. The constant $A$ depends on temperature and the dielectric constant of the solvent. The equation for the dissociation constant is then

$$K_d = (\alpha^2 c_s f_\pm{}^2)/(1 - \alpha) \qquad (3)$$

(ignoring the negligible difference between $f_\pm$ and $\gamma_\pm$).

$A$, $B$, $B_1$, and $B_2$ were evaluated from the properties of the solvent. $K_d$ was then calculated by the iterative procedure of Robinson and Stokes [13] in which, using an initial value of $\Lambda_0$ from the data, assumed values of $\alpha$ are improved by successive approximations, and the process is then repeated for slightly different values of $\Lambda_0$ until the most consistent $K_d$ is obtained. The results for the iodide ($10^2$ $K_d$ in mole. l.$^{-1}$, over the concentration range 0·0001—0·025M) are 1·28 at 25°, and 1·02 at 65°.

*Apparent Rate Constants.*—As conversions were limited to less than 20%, corrections for the

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[12] W. J. McGuire, M.Sc. Thesis, Northwestern University, 1949. See also A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, 1953.

[13] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd edn., Butterworths, London, 1959.

[14] C. B. Monk, "Electrolytic Dissociation," Academic Press, London and New York, 1961.

opposing reaction were unnecessary. The conductance *vs.* concentration data show that it is justifiable to assume a linear relationship over the range covered in a run. The relationship was determined from the conductance at the initial reactant concentration (as found in the kinetic run), and from the conductance at a concentration corresponding to approximately 20% conversion of the salt, which was measured in a separate calibration run. The apparent first-order rate constant $k_1'$ is then given by

$$k_1' = \frac{2{\cdot}303}{t_2 - t_1} \log\left(\frac{c_1 - c_\infty}{c_2 - c_\infty}\right) \tag{4}$$

where $c_1$ and $c_2$ are the conductances at times $t_1$ and $t_2$, and $c_\infty$ is the hypothetical conductance at zero salt concentration, derived by extrapolation of the assumed linear relationship. Plots of $t_2 - t_1$ against the conductance term gave excellent straight lines and the values of $k_1'$ are given in Tables 2 and 3, together with values of apparent second-order constants, $k_2'$, obtained by dividing $k_1'$ by the corresponding mean concentration. This approximate procedure involves an error of $<1\%$ at the conversions employed. The two values in parentheses were obtained by titration of halide ion.

TABLE 2

Effect of concentration on the apparent rate constants for the quaternary iodide in nitrobenzene at 65°

| Initial concn. ($10^3$M) | Conversion (%) | Mean concn. ($10^3$M) | $10^6k_1'$ (sec.$^{-1}$) | $10^4k_2'$ (l. mol.$^{-1}$ sec.$^{-1}$) |
|---|---|---|---|---|
| 1·034 | 5 | 1·01 | 1·86 | 18·3 |
| 3·102 | 11 | 2·93 | 4·35 | 14·6 |
| 6·203 | 11·4 | 5·85 | 6·70 | 11·5 |
| 11·74 | 14·2 | 10·90 | 7·80 | 7·28 |
| 19·35 | 19·4 | 17·50 | 9·78(10·3) | 5·61 |
| 35·99 | 21·2 | 32·20 | 11·6(12·0) | 3·67 |
| 48·70 | 15·0 | 45·0 | 12·7 | 3·08 |
| 76·97 | 10·0 | 73·1 | 13·8 | 2·01 |

TABLE 3

Effect of temperature on the apparent first-order constant at constant concentration

| Temp. (°C) | Initial concn. $10^2$M | Conversion (%) | Mean concn. $10^2$M | $10^6k_1'$ (sec.$^{-1}$) |
|---|---|---|---|---|
| 52·5 | 4·893 | 10 | 4·65 | 2·55 |
| 58·75 | 4·843 | 10 | 4·60 | 5·63 |
| 65·0 | 4·870 | 15 | 4·50 | 12·7 |
| 71·25 | 4·841 | 18 | 4·41 | 28·0 |

In the case of the quaternary bromide in chloroform the apparent rate constant, which showed no drift with reaction time, was determined at a single temperature (34·95°) and for one initial concentration (0·1M). $10^5k_1'$ (sec.$^{-1}$) was found to be 2·40 by the conductance method, and 2·35 by halide ion analysis. Earlier work [6] gave 2·63.

## DISCUSSION

*The Reaction of the Quaternary Iodide in Nitrobenzene.*—The results of Table 2 show that, at 65°, neither first-order nor second-order rate constants, calculated on the basis of salt concentration, are satisfactory. Over the range 0·001—0·073M, $k_1'$ increases by a factor of ~7, and $k_2'$ decreases by a factor of ~9. In this moderately ionising solvent (dielectric constant 34·82 at 25°) the iodide is considerably associated to ion-pairs. New first-order constants, $k_1$, were therefore calculated from the expression

$$k_1 = k_1'/(1 - \alpha) \tag{5}$$

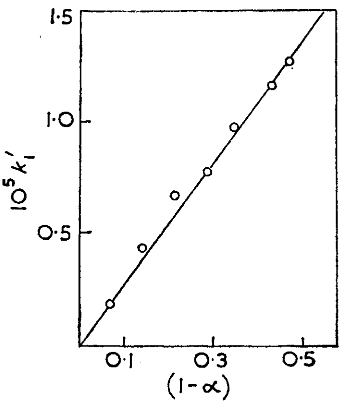
in which $(1 - \alpha)$ is the average fraction of the salt present as ion-pairs during a run. The implied assumption that the mean integrated $k_1'$ is equal to its instantaneous value at the mean concentration probably introduces no significant error, because $k_1'$ varies little over the restricted range of conversion at each concentration. At temperatures other than 65°, $K_d$ was calculated by assuming $\log K_d$ to vary linearly with $1/T$. The essentially linear relation between $k_1'$ and $(1 - \alpha)$ is shown in the Figure, and the calculated rate constants are given in Table 4.

TABLE 4

First-order rate constants (based on ion-pair concentrations) for the quaternary iodine in nitrobenzene

| Temp. (°C) | Mean salt concn. $10^3$M | Mean fraction of ion-pairs $(1 - \alpha)$ | $10^6 k_1$ (sec.$^{-1}$) |
|---|---|---|---|
| 65 | 1·01 | 0·0675 | 27·6 |
| 65 | 2·93 | 0·143 | 30·5 |
| 65 | 5·85 | 0·214 | 31·2 |
| 65 | 10·9 | 0·285 | 25·6 |
| 65 | 17·5 | 0·345 | 28·4 |
| 65 | 32·2 | 0·430 | 27·0 |
| 65 | 45·0 | 0·470 | 27·0 |
| 65 | 73·1 | 0·525 | 26·3 |
| 52·5 | 46·48 | 0·465 | 5·48 |
| 58·75 | 46·01 | 0·468 | 12·0 |
| 71·25 | 44·05 | 0·467 | 60·0 |

$k_1$ is reasonably constant at 65° over the whole concentration range, and the most probable value is $27{\cdot}2 \times 10^{-6}$ sec.$^{-1}$. The agreement is very satisfactory, since the rate constants are calculated from two sets of measurements ($k_1'$ and $K_d$), and the result confirms the view that the rate of the reverse Menschutkin reaction in this solvent depends on the equilibrium between ions and ion-pairs. It does not necessarily prove that the rate-determining step is the unimolecular decomposition of the ion-pair rather than the bimolecular reaction between cation and anion, since if $k_1$ is constant $k_2$ should also be independent of concentration. Some of the ion-pairs will have configurations close to that of the transition state and it appears more likely that they are the reacting species.



Variation of the apparent first-order rate constant of the quaternary-iodide reaction, at 65°, with the fraction of ion-pairs

*The Reaction of the Quaternary Bromide in Chloroform.*—In this very weakly ionising solvent (dielectric constant 4·806 at 20°) the low conductance at all concentrations (Table 1) indicates that most of the ions are associated. At the lowest concentrations the slope of the conductance–concentration curve tends to $-\frac{1}{2}$ and simple ions probably carry most of the current. At intermediate concentrations the conductance is a minimum, because of increased association into ion-pairs; and at higher concentrations the slope approaches $+\frac{1}{2}$ as ion-triplets are formed. It is likely that the decomposition of the quaternary bromide occurs *via* the ion-pairs and that their concentration is close to that of the salt, but rate measurements were confined to a single concentration. The decrease of the apparent first-order constant with increasing salt concentration, reported for a similar reaction in chloroform,[4] may be due to an increase in the concentration of the less-reactive ion-triplets.

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