514. *Liquid-phase Reactions at High Pressures. Part XV.*[1]
The Effect of Pressure on the Rates of Reverse Menschutkin Reactions

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The rates of reaction of *N*-allyl-*N*-benzyl-*N*-methylanilinium bromide in chloroform, and of *N*-ethyl-*NN*-dimethylanilinium iodide in nitrobenzene have been measured at pressures up to several thousand atmospheres by a conductivity method. In the case of the iodide the rate constants were corrected for the concentration of ion-pairs, and the rate of the opposing Menschutkin reaction has also been measured. The initial effect of pressure on the rates of reverse Menschutkin reactions is much greater than previously supposed. The combination of the differences in volume, ΔV^*, between reactants and transition state for the forward and reverse iodide reactions, is approximately equal to the overall volume change. The values of ΔV^* indicate that in the transition state the nitrogen and iodine atoms each carry only fractional charges. The entropies of activation and the pressure-dependence of ΔV^* are also discussed.

THE change in the rate constant of a liquid-phase reaction with pressure can be expressed by the equation

$$(\partial \ln k / \partial P)_T = -\Delta V^* / RT$$

where ΔV^* is the molar volume change when the reactants form the transition state. Menschutkin reactions between tertiary amines and organic halides are considerably accelerated by pressure. ΔV^* is therefore negative and the contraction is usually[2] at least -20 c.c./mole at 1 atm. There has been only one previous kinetic study[3] of a reverse Menschutkin reaction at high pressure, from which a mean ΔV^* of $+3 \cdot 4$ c.c./mole between 1 and 2884 atm. can be calculated. The contrast with ΔV^* for forward reactions has sometimes been considered to show that the transition state resembles the quaternary salt much more closely than the neutral reactants. However, the overall volume contraction for the formation of the quaternary salt from the initial reactants has been measured in a few instances,[2] and is approximately twice as large as the corresponding ΔV^*. This result, in conflict with the other evidence, suggests that the characteristics of the quaternary salt are only partially developed in the transition state. In order to investigate the discrepancy, the rate of reaction of *N*-ethyl-*NN*-dimethylanilinium iodide in nitrobenzene, which was studied in detail at 1 atm. (preceding Paper), has been measured at pressures up to 2000 atm. The rate of the corresponding forward reaction between methyl iodide and *N*-ethyl-*N*-methylaniline in the same solvent was also determined up to 1500 atm.; and the overall volume change for the reaction was measured at 1 atm. A further study of the effect of pressure on the rate of reaction of *N*-allyl-*N*-benzyl-*N*-methyl-anilinium bromide in chloroform has also been carried out. A preliminary account of some of the results has been published.[4]

<div align="center">EXPERIMENTAL</div>

Materials.—The two quaternary ammonium halides were prepared and purified as described in the preceding Paper. Nitrobenzene, chloroform, the amines, and the organic halides were also purified as before.

Reaction Rate and Conductance Measurements.—These were carried out in a steel vessel in which pressure was developed by means of a hand-pump and hydraulic intensifier. The internal temperature was controlled to within $\pm 0 \cdot 05°$. Pressure was measured with calibrated Bourdon

[1] Part XIV, preceding Paper.
[2] A. P. Harris and K. E. Weale, *J.*, 1961, 146.
[3] E. G. Williams, M. W. Perrin, and R. O. Gibson, *Proc. Roy. Soc.*, 1936, *A*, **154**, 684.
[4] J. M. Stewart and K. E. Weale, *Proc. Chem. Soc.*, 1961, 389.

gauges, the estimated accuracy being ± 5 atm. up to 1500 atm., and ± 25 atm. at higher pressures.   Conductance measurements, including rate determinations on the reverse Menschutkin reactions, were made with a Wayne–Kerr bridge, using a glass cell with platinum electrodes. A mercury seal, remote from the electrodes, allowed transmission of pressure to the cell contents from the surrounding oil.   The forward reaction was followed by titration of halide ion,[2] and was carried out in glass tubes having mercury seals.   The conductivity cell had a capacity of about 8 c.c. and it was standardised using 0·1M-potassium chloride solution.   Strauss[5] has calculated that pressures up to 3000 atm. cause negligible changes in the cell constants of glass conductivity cells.

Overall Volume Changes of the Reactions.—The overall volume changes accompanying the reactions were measured in a glass dilatometer having a bulb of approximately 25 c.c. capacity and two graduated stems, 10 cm. long, of 1 mm. precision-bore Pyrex tubing, which was calibrated by weight using distilled water.   Solution levels were observed through a telescope and the temperature of the dilatometer was controlled to within $\pm 0·05°$.   The volume change for the quaternary-iodide reaction was determined by measuring the densities of the salt solution and of the equivalent amine–iodide solution at 25° (at this temperature the reactions are too slow to interfere with the measurement).   As the reaction products from the decomposition of the quaternary bromide in chloroform were not determined, and the reaction proceeds at a significant rate even at 25°, the same procedure could not be used.   Instead, the salt was allowed to react in the dilatometer at 34·95° (the temperature of the rate measurements) and the solution levels were measured as a function of time. ΔV_0 was then calculated from the reaction rate, with a small correction for the equilibrium effect.

<div align="center">RESULTS</div>

The Conductance–Concentration Relationship for the Quaternary Iodide at High Pressures.— The conductances are given in Table 1 and have been corrected for the compression of the solvent (see below).

<div align="center">TABLE 1</div>

<div align="center">Equivalent conductance of N-ethyl-NN-dimethylanilinium iodide in nitrobenzene</div>
<div align="center">at 65°</div>

500 atm.		1000 atm.		2000 atm.	
10^4M	Λ	10^4M	Λ	10^4M	Λ
261·3	26·89	266·6	21·82	267·5	14·76
57·54	38·15	53·59	30·03	59·86	19·58
10·62	45·37	10·83	35·44	2·551	24·25
2·097	48·56	2·139	37·67		

A very similar decrease in conductance with increasing pressure, at approximately constant concentration, occurs for tetraethylammonium iodide in nitrobenzene.[6]

Dissociation Constants of the Quaternary Iodide at High Pressures.—Ion-pair dissociation constants, K_d, were calculated from Table 1 by the method described in the preceding Paper. The viscosities of nitrobenzene at high pressures were interpolated from the data of Kuss,[7] who determined values at 25 and 80° up to 2000 atm.   The only data on the pressure-dependence of the dielectric constant of nitrobenzene [8] cover the limited range 1—56 atm., at 25°.   The pressure coefficient was assumed to be independent of temperature (which is reasonable for a limited temperature range [9]), and was used to extrapolate values to 2000 atm. from the equation: [10]

$$(\varepsilon_p + 2)/(\varepsilon_p - 1) = mv_0 + b$$

in which ε_p is the dielectric constant, v_0 the specific volume and m and b are constants for the liquid.   The very accurate compression data of Gibson and Loeffler [11] was used to evaluate m and b, but Kuss's more extensive results [12] were used to calculate ε_p.

[5] W. Strauss, M.Sc. Thesis, University of Melbourne, 1956.
[6] E. W. Schmidt, *Z. phys. Chem.*, 1911, **75**, 305.
[7] E. Kuss, Erdöl u. Kohle, 1953, **6**, 266.
[8] M. Grenacher, *Ann. Physik*, 1925, **77**, 138.
[9] I. S. Jacobs and A. W. Lawson, *J. Chem. Phys.*, 1952, **20**, 1161.
[10] J. S. Rosen, *J. Chem. Phys.*, 1949, **17**, 1192.
[11] R. E. Gibson and O. H. Loeffler, *J. Amer. Chem. Soc.*, 1939, **61**, 2877.
[12] E. Kuss, *Z. angew. Phys.*, 1952, **4**, 201.

The dissociation constants at 65°, including that at 1 atm. from the preceding Paper, are given below. Values at other temperatures, and at 500 atm., were obtained by assuming log K_d to be a linear function of $1/T$, as in Part XIV,[1] with the same gradient at 500 atm. as at 1 atm.

P (atm.)	1	200	500	1000	2000
$10^2 K_d$ at 65° (mol. l.$^{-1}$)	1·02	1·22	1·51	1·91	2·43

The Rates of the Reverse Menschutkin Reactions at High Pressures.—Apparent first-order rate constants, k_1', based on salt concentration, were obtained in the same way as at 1 atm. In the preceding Paper it was shown that constants which do not vary with concentration are obtained for the quaternary iodide reaction in nitrobenzene if they are calculated with respect to the concentration of ion-pairs. Corrected first-order rate constants, k_1, were therefore calculated by dividing k_1' by $(1 - \alpha)$, the average fraction of the salt present as ion-pairs. The results appear in Table 2.

TABLE 2

First-order rate constants for the reaction of the quaternary iodide in nitrobenzene

Temp. (°c)	P (atm.)	Mean concn. (10^3 mole l.$^{-1}$)	Fraction of ion-pairs $(1 - \alpha)$	$10^6 k_1'$ (sec.$^{-1}$)	$10^6 k_1$ (sec.$^{-1}$)
52·5	500	48·6	0·404	1·66	4·11
58·75	500	47·8	0·403	3·57	8·86
65	200	46·2	0·435	9·60	22·1
65	500	47·4	0·404	8·10	20·1
65	1000	49·4	0·371	6·67	18·0
65	2000	50·4	0·338	5·92	17·5
71·25	500	46·6	0·405	1·83	45·2

The conductance–concentration data for the quaternary bromide in chloroform at 1 atm., indicate that it exists predominantly as associated ions. The concentration of associated ions is unlikely to be very pressure-dependent, and first-order rate constants at 34·95° were therefore calculated on the basis of salt concentrations. They are given in Table 3, the initial concentration for the runs being 0·1M.

TABLE 3

First-order rate constants for the reaction of the quaternary bromide in chloroform at 34·95°

P (atm.)	500	1000	2000	2884
$10^6 k_1'$ (sec.$^{-1}$)	20·2(19·3)	18·8(18·3)	17·0	15·8

The values in parentheses were determined by titration of halide ion.

The Rate of the Forward Menschutkin Reaction at High Pressures.—Second-order rate constants, k_2, for the reaction between methyl iodide and N-ethyl-N-methylaniline in nitrobenzene were determined by titration of halide ion. Concentrations were corrected for temperature and the compression of the solvent, and a small correction for the opposing reaction was made when necessary. The results are shown in Table 4.

TABLE 4

Second-order rate constants for the reaction between methyl iodide and N-ethyl-N-methylaniline in nitrobenzene

(Initial concn. [Iodide] = [Amine] = 0·05M at 1 atm., 20°)

| P (atm.)	$10^5 k_2$ (l. mole^{-1} sec.$^{-1}$) 30°	P (atm.)	$10^5 k_2$ (l. mole^{-1} sec.$^{-1}$) 50°
1	6·12	1	24·3
500	9·35	500	34·8
	40	1000	49·2
1	12·7 ^{a}	1500	65·0
1	12·6		60
1	13·1 ^{b}	1	44·8
500	18·5	500	63·6

^{a} 0·025M.　^{b} 0·1M.

The Overall Volumes of Reaction at 1 atm.—ΔV_0 for the reaction of the quaternary iodide in nitrobenzene (1 atm., 25°, initial concn. 0·028M) is +62·8 c.c./mole. (A previously reported value [4] was wrongly calculated.) For the quaternary-bromide reaction in chloroform (1 atm., 34·95°, initial concn. 0·1M, conversion ~40%) ΔV_0 is +36·1 c.c./mole.

DISCUSSION

The effect of pressure on the rate constants of the reverse Menschutkin reactions is shown in the Figure. The correction for ion-pair concentration in the quaternary-iodide reaction is considerable, but in both reactions there is a pronounced curvature at the lower pressures. The ratio of the rate constants of the bromide reaction at 2884 atm. and at 1 atm. is 0·66, in good agreement with the value of 0·67 found by Williams *et al.*[3] over the same pressure range.

The pressure-dependence of the first-order rate
constants:
(A) quaternary bromide in $CHCl_3$ at 34·95°.
(B) quaternary iodide in $PhNO_2$ at 65° (k_1 from
ion-pair concentrations).
(C) quaternary iodide at 65° (k_1' from salt concen-
trations)
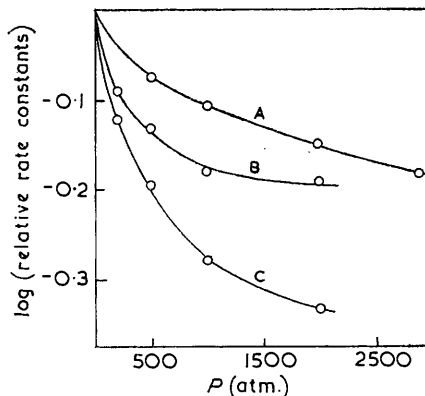
The initial slopes of the curves are much higher than are the mean slopes taken over a large pressure range. The activation volumes, ΔV^*, at 1 atm., of reverse Menschutkin reactions are therefore much higher than has been supposed from the mean value (+3·4 c.c./mole) derived from the previous work on the bromide reaction. The volumes at 1 atm. are difficult to estimate accurately and the uncertainty could be as high as ±20%. They are given in Table 5, together with values at higher pressures, and values for the forward

TABLE 5

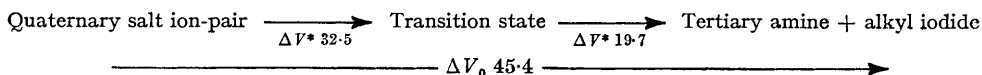ΔV^* (c.c./mole) for forward and reverse Menschutkin reactions

P (atm.)	1	500	1000	1500	2000
Quaternary bromide in $CHCl_3$ at 34·95° ...	13·6	5·1	3·3	—	2·2
Quaternary iodide in $PhNO_2$ at 65° *	32·5	8·5	3·2	1·0	—
Formation of iodide in $PhNO_2$ at 50°	−20·4	−18·4	−16·5	−14·4	—

reaction between methyl iodide and *N*-ethyl-*N*-methylaniline. ΔV^* for the forward reaction at 1 atm. is the same, within experimental error, as for the ethyl iodide–*NN*-dimethylaniline reaction in the same solvent at 52·5°, and the change in ΔV^* with increasing pressure is similar to that found for other forward Menschutkin reactions.[2] In the case of the quaternary-bromide decomposition part of the electrolyte exists as ion-triplets or quadrupoles and the rate constant may vary with concentration because of changes in the proportions of these higher aggregates. As these factors, and their pressure-dependence, have not been investigated, nor have the products of the reaction been determined, the exact significance of ΔV^* in relation to the reaction mechanism has not been established.

It is likely (preceding Paper) that the quaternary-iodide reaction takes place in the ion-pairs, and the relationship between ΔV^*, for the forward and reverse reactions, and ΔV_0 can be considered in more detail. ΔV^* for the forward reaction (corrected to 65° by means of the identity $\partial \Delta V^*/\partial T = -\partial \Delta S^*/\partial P$) is −19·7 c.c./mole at 1 atm., and that

for the reverse reaction (1 atm., 65°) is $+32.5$. The temperature correction for ΔV_0 is negligible but the measured value ($+62.8$) for the reaction: quaternary salt $\longrightarrow$ amine $+$ halide, at 1 atm., contains a substantial positive term due to the association of free ions into the less-polar ion-pairs, which then take part in the reaction. From the data of Table 2 the volume of association is calculated to be $+28.1$ c.c./mole at 1 atm. and 65°. The fraction α of free ions present in the salt solution used for the ΔV_0 determination is 0.619, so that the volume term attributed to the ion-association process is 17.4 c.c. The corrected overall volume change, ΔV_0, for the reaction: quaternary salt (ion-pairs) $\longrightarrow$ products, is therefore $+45.4$ c.c./mole.

The results for the molar volume changes at 1 atm. are shown schematically below:

Quaternary salt ion-pair $\xrightarrow[\Delta V^* \ 32.5]{}$ Transition state $\xrightarrow[\Delta V^* \ 19.7]{}$ Tertiary amine $+$ alkyl iodide

$\xrightarrow[\hspace{3cm} \Delta V_0 \ 45.4 \hspace{3cm}]{}$

There is a discrepancy of 6.8 c.c./mole between the sum of the activation volumes and the overall volume change, but this is within the possible errors. It is concluded that these findings are essentially consistent and that the volume difference between the ion-pair and the transition state (which probably contains most of the error) is substantially larger than that between the transition state and the tertiary amine $+$ methyl iodide molecules.

The Activation Volumes and the Reaction Mechanisms.—ΔV^* is generally considered as the sum of the terms $\Delta_1 V^*$ and $\Delta_2 V^*$. The first of these arises from changes in the configuration and the interatomic distances of the reacting molecules as they form the transition state, whilst $\Delta_2 V^*$ is attributed to the difference between the interactions of the initial reactants and of the transition state with neighbouring molecules. Data for forward Menschutkin reactions in different solvents [2,13] show that $\Delta_2 V^*$ is an important component of ΔV^*, which is to be expected when a polar transition state, carrying partial ionic charges, is formed from neutral molecules. An exact calculation of $\Delta_1 V^*$ would require accurate information about the geometry of the transition state, but a rough estimate of its magnitude for the reaction between methyl iodide and N-ethyl-N-methylaniline can be made. A cylinder enclosing the carbon and iodine atoms of the halide and the nitrogen atom of the amine will have an initial length of 5.3 Å, *i.e.*, the sum of the van der Waals radii of C (1.6 Å), N (1.6 Å), and of the C–I bond length (2.1 Å). In the transition state the length of the partial bonds is taken [14,15] as the covalent radius of carbon (0.77 Å) plus the mean of the covalent and ionic radii of the nitrogen atom or the iodine atom. The lengths of the partial N–C and C–I bonds are then respectively 1.92 and 2.52 Å so that there is a contraction along the axis of 0.86 Å. Assuming an effective cylinder diameter of 4 Å (diameters of I, 4.3 Å; CH_3, 4.0 Å; N, 3.2 Å) the volume contraction, $\Delta_1 V^*$, is 6.5 c.c./mole. In view of the approximate nature of the calculation it is concluded only that $\Delta_1 V^*$ for the forward reaction is of the order of -10 c.c./mole. From the experimental value of ΔV^* the magnitude of $\Delta_2 V^*$ must also be about -10 c.c./mole.

In the corresponding reverse Menschutkin reaction $\Delta_1 V^*$, arising from the approach of the two ions from the " touching " distance to the same transition state, is also estimated to be ~-10 c.c./mole. As the measured ΔV^* is $+32.5$ the volume change $\Delta_2 V^*$, which accompanies the release of solvating molecules, is probably within the range $+25$—45 c.c./mole. Born's theory relating solvation to the charge on the ions requires considerable modification,[16] particularly for ion-pairs and dipolar transition states, but a comparison of $\Delta_2 V^*$ for the forward and reverse reactions indicates that in the transition states the charges on the nitrogen and iodine atoms are only fractionally developed.

The effect of pressure on ΔV^* (Table 5) is much greater in the reverse reaction than in the forward reaction. Possibly $\Delta_2 V^*$, which is the dominant factor in the reverse reaction

[13] K. R. Brower, *J. Amer. Chem. Soc.*, 1963, **85**, 1401.
[14] I. Dostrovsky, E. D. Hughes, and C. K. Ingold, *J.*, 1946, 173.
[15] P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold, and J. D. H. Mackie, *J.*, 1955, 3200.
[16] E. Whalley, *J. Chem. Phys.*, 1963, **38**, 1400.

at 1 atm., is more sensitive to pressure than $\Delta_1 V^*$. If the solvating molecules are relatively incompressible the volume difference between them and unrestricted solvent will diminish fairly rapidly as the solvent is compressed. $\Delta_2 V^*$ is a less important component of ΔV^* in the forward reaction, and also has the same sign as $\Delta_1 V^*$.

Entropies of Activation.—ΔS^* for forward Menschutkin reactions is usually of similar magnitude to the overall entropy change ΔS_0 (although most determinations of ΔS_0 have not taken into account the partial association of the electrolyte to ion-pairs). The similarity has been cited as evidence that the transition state is almost as fully solvated as the product ions, but this conclusion ignores the complexity of the entropy terms. Values of the Arrhenius parameters and ΔS^* for the forward and reverse quaternary-iodide reactions are given in Table 6. The entropy of activation in the forward reaction is large and negative, and that for the reverse reaction is small and positive. The respective increase and decrease in solvation should contribute a corresponding decrease and increase in entropy

TABLE 6

Arrhenius parameters and entropies of activation for the quaternary iodide reactions in nitrobenzene

	P (atm.)	A (l. mole^{-1} sec.$^{-1}$)	E (kcal. mole^{-1})	ΔS^* (e.u.)
Forward reaction (50°)	1	$2 \cdot 2 \times 10^4$	$13 \cdot 2$	$-39 \cdot 5$
	500	$1 \cdot 6 \times 10^4$	$12 \cdot 7$	$-40 \cdot 0$
		(sec.$^{-1}$)		
Reverse reaction (65°)	1	$7 \cdot 2 \times 10^{13}$	$28 \cdot 5$	$4 \cdot 0$
	500	$5 \cdot 8 \times 10^{13}$	$28 \cdot 6$	$3 \cdot 6$

but for both reactions there are unknown differences between the " internal " entropies of the transition state and the reacting species, which, from calculations on simpler systems,[15] may be considerable. In the forward reaction there is also a loss of translational entropy as the two reacting molecules form the transition state. Until more detailed information is available about the activation entropies of Menschutkin reactions no useful correlation with the volumes of activation can be made.

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