235. "Borderline" Nucleophilic Substitution. Part II.[1]

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The Finkelstein substitution between diphenylmethyl chloride and bromide ions (as ammonium bromide) in dimethylformamide has been studied over a range of ionic concentrations at three temperatures. The rate constants for the first-order contribution to the substitution were found to be the same as those previously obtained for the exchange with chloride ions (as lithium chloride).

The isotopic exchange between lithium radio-chloride and diphenyl-methyl chloride has also been investigated in three further solvent media; the ratio between the first- and the second-order rate constants increases with increase in dielectric constant. The isotopic exchange between benzyl chloride and lithium radio-chloride has also been investigated in two further solvent media.

In a previous paper,[1] a clear example of concomitant first- and second-order nucleophilic substitution was described in an exchange reaction involving diphenylmethyl chloride and radio-isotopically labelled chloride ions in dimethylformamide. This reaction lends itself to further investigation regarding both the effect of change in solvent on the first- and the second-order rate constants as well as the effect of change in the substituting halide ion.

RESULTS

(1) *Reaction of Diphenylmethyl Chloride with Bromide Ions.*—If the interpretation of our previous results[1] is correct, the rate constant k_1 for the first-order S_N1 contribution to the overall exchange should be independent of both the cation and the anion of the halide salt provided that the necessary correction is made for partial ionisation. The halide exchange between diphenylmethyl chloride and bromide ions (as ammonium bromide) was accordingly investigated in an attempt to verify the constancy of k_1.

As pointed out by Farhat-Aziz and Moelwyn-Hughes,[2] it is not possible to integrate the differential rate equation for substitutions of this type directly since the degree of ionisation, α, of the halide salts changes continuously during the reaction. It was therefore necessary to make an approximation.

The most drastic approximation is that for small amounts of halide exchange, not only does α remain constant, but also the concentrations of diphenylmethyl chloride and ammonium bromide also remain sensibly constant, and that the reverse reaction may be neglected entirely. In these circumstances, the initial rate of exchange R (in mole l.$^{-1}$ sec.$^{-1}$) is given by the simple expression

$$R = x/t = (b/t)(x/b), \tag{1}$$

where x is the net number of moles that have exchanged at time t (sec.) and b is the initial concentration of the ammonium bromide.

A slightly less drastic approximation is to assume that, although the concentrations do change, α remains sensibly constant and the rate of the reverse reaction is small enough to be neglected. In these circumstances an equation analogous to that for a normal second-order reaction is applicable and the initial rate of exchange is given by

$$R = \frac{ab}{t\,(a-b)} \ln \frac{a - b(x/b)}{a - a(x/b)}, \tag{2}$$

where a is the initial concentration of the diphenylmethyl chloride.

A third method is to assume that, for small amounts of halide exchange, changes in α may be neglected and that as a first approximation the rate constants for the reverse reaction may

[1] Casapieri and Swart, *J.*, 1961, 4342; this paper is regarded as Part I of the series.
[2] Farhat-Aziz and Moelwyn-Hughes, *J.*, 1959, 2635.

be taken as equal to those of the forward reaction. In this case, the standard equation for isotopic exchange is applicable, *viz.*:

$$R = -\frac{ab}{t\,(a+b)}\ln\left(1 - \frac{x}{b}\cdot\frac{a+b}{a}\right). \tag{3}$$

The extent to which these approximations are valid depends on the relative rates of the forward and the reverse reaction as well as on the amount of exchange which has taken place at the time t. The reaction was therefore followed by means of ammonium radio-bromide in order to make it possible to measure small amounts of halide exchange with reasonable precision and thus keep the amount of exchange to less than 4%. The value of x/b in all three of these equations is then given by the ratio between the activity of the organic halide and the total radioactivity at the time t.

Further, although it was expected, by analogy with other results,[3] that the rate of the reverse reaction would be somewhat faster than that of the forward reaction, it was found that it did not swamp the forward reaction completely. Preliminary results obtained by potentiometric titration of the halide ions, according to Clark's method,[4] showed that at equilibrium 15—20% of the ammonium bromide was replaced by ammonium chloride, in the range of concentrations used for the kinetic runs.

The kinetic results obtained, at one set of concentrations and one temperature, by using each of the equations (1)—(3) are recorded in Table 1.

TABLE 1.

Apparent initial rates of substitution R (mole l.$^{-1}$ sec.$^{-1}$) between diphenylmethyl chloride and ammonium bromide at 30°.

$a = [Ph_2CHCl] = 0.0374M.$ $b = [NH_4Br] = 0.00435M.$

Time, t (hr.)	0 (by extrapn.)	4	9	14
$10^9 R$, equation (1)	5.45	4.94	4.25	3.58
$10^9 R$, equation (2)	5.45	4.97	4.31	3.63
$10^9 R$, equation (3)	5.45	4.97	4.33	3.66

Despite the small amount of substitution involved, the apparent rate of reaction shows a downward trend with time irrespective of the equation used. Extrapolation back to zero time, however, produces a curve that is very nearly linear and gives the same value of R for all three equations. We feel that the use of extrapolation is therefore justified and all our results have accordingly been obtained by this method with equation (3).

The values of R/a (sec.$^{-1}$) obtained in this way are recorded in Table 2, the degrees of ionisation α being obtained from conductivity data (see Appendix).

TABLE 2.

Kinetic data for the diphenylmethyl chloride–ammonium bromide substitution in dimethylformamide.

Temp.	$10^2 a$	$10^2 b$	$10^2 \alpha b$	$10^6 R/a$	Temp.	$10^2 a$	$10^2 b$	$10^2 \alpha b$	$10^6 R/a$
30°	2.11	2.01	1.21	0.282	50°	5.98	2.02	1.18	2.25
30	3.74	1.98	1.20	0.271	50	2.07	1.98	1.16	2.28
30	3.74	1.16	0.79	0.207	50	2.07	1.26	0.81	1.92
30	3.74	0.435	0.352	0.146	50	2.39	1.01	0.68	1.66
30	2.25	0.205	0.178	0.073	50	2.07	0.65	0.47	1.47
40	6.03	2.03	1.21	0.708	50	2.42	0.403	0.321	1.23
40	2.41	1.02	0.70	0.533	50	2.07	0.260	0.218	0.96
40	2.44	0.407	0.325	0.371	50	2.22	0.202	0.173	1.05
40	2.24	0.203	0.176	0.277					

The values of R/a were plotted against αb in order to obtain the first- and the second-order rate constants k_1 and k_2 (as before [1]); the results are recorded in Table 3, with the previous results for the first-order rate constants of the homogeneous exchange between diphenylmethyl chloride and chloride ions for comparison.

[3] de la Mare, Fowden, Hughes, Ingold, and Mackie, *J.*, 1955, 3200.
[4] Clark, *J.*, 1926, 749.

As can be seen from the Table, the values of the first-order rate constants k_1 are identical for the two substitutions within experimental error. This shows that the rate-determining step for the S_N1 contribution to the overall exchange is in both cases the rate of formation of free carbonium ions. The values of k_2, on the other hand, are significantly greater for the bromide-ion substitution with a correspondingly smaller activation energy.

This constancy of k_1 has previously been demonstrated by Pocker [5] for the exchange between diphenylmethyl bromide and chloride, bromide, and azide ions which confirms our contention

TABLE 3.

Rate constants and activation energies for the diphenylmethyl chloride–bromide ion substitution in dimethylformamide.

Reaction	$10^7 k_1$ (sec.$^{-1}$)			E_1	$\log_{10} A_1$
	30°	40°	50°		
$Ph_2CHCl + Cl^-$	0·63	2·30	7·76	24·4	10·4
$Ph_2CHCl + Br^-$	0·61	2·26	8·00	25·0	10·9
	$10^7 k_2$ (l. mole^{-1} sec.$^{-1}$)			E_2	$\log_{10} A_2$
	1·81	4·09	12·8	19·0	8·9

that for borderline nucleophilic substitutions of this type the overall rate of substitution may legitimately be regarded as the sum of unimolecular and bimolecular processes.

An attempt was made to study the diphenylmethyl chloride–iodide ion substitution as well, but this was unsuccessful as the organic iodide decomposed, with the production of free iodine, almost as fast as it was formed.

(2) *Reactions of Diphenylmethyl Chloride and Benzyl Chloride with Chloride Ions in Various Solvents.*—The reactions being studied by us are of charge type (1), according to the classification of nucleophilic substitutions adopted by Hughes and Ingold,[6] in which the nucleophile (Y^-) is initially negatively charged and the substrate (RX) initially neutral. The rate constant for the S_N2 contribution to the exchange would, therefore, be expected to decrease with increase in solvent polarity, whereas the rate constant for the S_N1 contribution would be expected to increase in similar circumstances. Since the polarity of a solvent normally increases with increase in dielectric constant it might be expected, therefore, that there would be a marked increase in the ratio between the first- and the second-order rate constants with increase in dielectric constant. It is even possible that a given exchange which is purely S_N2 in one solvent might become partially S_N1 in a solvent of higher dielectric constant.

In order to investigate these effects we have followed the diphenylmethyl chloride–chloride ion exchange as well as the benzyl chloride–chloride ion exchange in several different solvent media.

(a) *Dimethyl sulphoxide as solvent.* This solvent, which has a somewhat higher dielectric constant than dimethylformamide (46·6, as opposed to 36·7 at 25°), might well be expected to modify the absolute and relative rates of both the S_N1 and the S_N2 process.

The kinetic results for the diphenylmethyl chloride–lithium chloride exchange are recorded in Table 4. Values of α were obtained from conductivity measurements (see Appendix) and the values of R were calculated by means of equation (3). A reaction which was allowed to proceed to equilibrium (10 times the half-life) gave only 88% of the maximum theoretical exchange, showing that there was some side reaction. There was, however, no trend in the measured rates of reaction for the times of reaction used and the side reaction could therefore be ignored.

The values for the parameter R/a do not change appreciably with varying concentration of chloride ions, indicating the presence of a very considerable first-order component to the exchange. The values of the first- and the second-order rate constants were obtained from a plot of R/a against αb (a least-squares analysis was used) and the results are recorded in Table 5.

The kinetic results for the benzyl chloride–lithium chloride exchange are recorded in Table 6. In this case there was no detectable side reaction at all and a kinetic run which was allowed to go to completion gave 99% of the theoretical maximum exchange.

[5] Pocker, *J.*, 1959, 3939.
[6] Hughes and Ingold, *J.*, 1935, 244; see also Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 347.

TABLE 4.

Kinetic results for the diphenylmethyl chloride–lithium chloride exchange in dimethyl sulphoxide.

Temp.	10^2a	10^2b	$10^2\alpha b$	$10^5R/a$	Coeff. of variation	Temp.	10^2a	10^2b	$10^2\alpha b$	$10^5R/a$	Coeff. of variation
30·0°	7·14	2·22	2·13	0·243	3·4	50·0°	7·07	2·20	2·09	1·74	2·1
30·0	6·05	1·67	1·61	0·235	3·0	50·0	5·99	1·65	1·58	1·67	2·3
30·0	5·92	1·11	1·08	0·228	6·8	50·0	5·86	1·10	1·07	1·59	1·2
30·0	5·97	0·56	0·55	0·210	4·3	50·0	5·91	0·56	0·55	1·43	2·8
40·0	7·10	2·21	2·11	0·672	4·7	50·0	4·17	0·22	0·22	1·38	1·5
40·0	6·02	1·66	1·60	0·637	2·3						
40·0	5·89	1·11	1·08	0·620	3·1						
40·0	5·94	0·56	0·55	0·581	6·6						

TABLE 5.

First- and second-order rate constants for the diphenylmethyl chloride–chloride ion exchange in dimethyl sulphoxide.

Temp.	30·0°	40·0°	50·0°
10^5k_1 (sec.$^{-1}$)	0·202	0·542	1·34
10^5k_2 (l. mole^{-1} sec.$^{-1}$)	2·01	6·29	20·1

TABLE 6.

Kinetic results for the benzyl chloride–lithium chloride exchange in dimethyl sulphoxide.

Temp.	10^2a	10^2b	$10^2\alpha b$	$10^5R/a$	$10^5R/a\alpha b$	Coeff. of variation
30·0°	4·57	1·830	1·770	2·09	114	1·3
30·0	4·57	0·913	0·898	1·11	121	0·5
30·0	4·57	0·365	0·363	0·46	126	2·9
30·0	4·57	0·183	0·183	0·21	115	2·5
40·0	5·07	1·820	1·750	5·28	291	2·4
40·0	5·07	0·908	0·890	2·83	314	0·0
40·0	4·57	0·363	0·361	1·42	390	0·5
40·0	4·57	0·182	0·182	0·76	419	3·6
50·0	5·05	1·810	1·730	13·90	764	3·6
50·0	5·05	0·904	0·884	7·47	826	0·7
50·0	5·05	0·362	0·359	3·06	848	2·5
50·0	5·05	0·181	0·181	1·85	1022	4·3

If the exchange reaction proceeded solely by the S_N2 mechanism, the values of $R/a\alpha b$ (l. mole^{-1} sec.$^{-1}$) in the penultimate column of Table 6 should be constant at a given temperature. There appears, however, to be a definite increase in $R/a\alpha b$ with decrease in concentration, and the plot of R/a (sec.$^{-1}$) against αb does give a significant intercept, thus indicating some S_N1 character. This seems to be an example of a reaction which is purely of S_N2 type in one solvent (dimethylformamide [1]) but partly of S_N1 type in another solvent (dimethyl sulphoxide) of higher dielectric constant.

Both the first- and the second-order rate constants are recorded in Table 7, but the precision and accuracy of the results are not sufficient to justify an assumption as to the absolute value of the first-order rate constants. These must therefore be regarded as order of magnitude values only.

TABLE 7.

First- and second-order rate constants for the benzyl chloride–chloride ion exchange in dimethyl sulphoxide

Temp.	30·0°	40·0°	50·0°
10^5k_1 (sec.$^{-1}$)	0·02	0·3	0·4
10^5k_2 (l. mole^{-1} sec.$^{-1}$)	118	284	783

(b) *Dimethyl sulphoxide–dimethylformamide mixture as solvent.* The exchange between diphenylmethyl chloride and lithium chloride in 50% (w/w) dimethylformamide–dimethyl sulphoxide was also studied. Again no trend was observed in the measured rate of exchange and a reaction which was allowed to go to completion gave 95% of the expected exchange,

thus showing much less side reaction than in pure dimethyl sulphoxide. The rate constants which were obtained as above are recorded in Table 8.

<div align="center">TABLE 8.</div>

Rate constants for the diphenylmethyl chloride–chloride ion exchange in 50% (w/w) dimethylformamide–dimethyl sulphoxide.

Temp	$30 \cdot 0°$	$40 \cdot 0°$	$50 \cdot 0°$
$10^5 k_1$ (sec.$^{-1}$)	$0 \cdot 050$	$0 \cdot 151$	$0 \cdot 413$
$10^5 k_2$ (l. mole^{-1} sec.$^{-1}$)	$1 \cdot 28$	$3 \cdot 75$	$10 \cdot 8$

(c) *Methylformamide–dimethylformamide mixture as solvent.* An investigation of the diphenylmethyl chloride–lithium chloride exchange in the mixed solvent [10·5% (w/w) methylformamide in dimethylformamide] was approached with caution. Preliminary experiments showed that benzyl chloride reacted with pure N-methylformamide, probably by means of a Menschutkin-type reaction, and the greater reactivity of diphenylmethyl chloride led us to expect considerable side reaction even in the presence of small amounts of methylformamide.
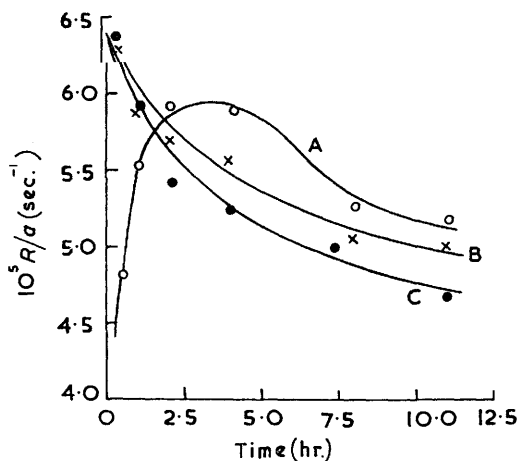
Exchange between diphenylmethyl chloride (0·0626M) and chloride ions (0·0165M) in 10·5% (w/w) methylformamide–dimethylformamide at 50°.

(A) Freshly prepared diphenylmethyl chloride solution. (B) Solution left for 24 hours. (C) Solution left for 48 hours.

To reduce the amount of side reaction to a minimum before commencement of exchange the organic halide solution was prepared immediately before use and, in these circumstances, peculiar " autocatalytic " effects were noted in the initial stages of the reaction; the rate of reaction first rose slightly and then fell steadily as the reaction proceeded further. An example of this is shown in the Figure. The initial rise was suppressed if the diphenylmethyl chloride solution was kept at room temperature for at least 14 hours before use (see the Figure).

It is relatively straightforward to explain the downward trend in rate of reaction as being due to the elimination of some of the organic halide from the solution as a result of its possible self-interaction and/or its reaction with methylformamide. It is much more difficult to account for the initial rise. Whatever the major side reaction, it results in an increase in the chloride-ion concentration during the exchange and this increase was followed argentometrically in a separate experiment in which the rate of exchange was followed by using lithium radio-chloride simultaneously. This increase in the concentration of chloride ions is obviously accompanied by an equal decrease in the concentration of the organic halide.

Table 9 records the results of this exchange in which the parameter R/a is calculated in the usual way without allowance for the decomposition of the organic halide; and R/a is the measured rate parameter, taking into account the changing concentration of the organic halide throughout the reaction. The Table also records the initial concentrations, and the mean between the initial and the measured concentrations at the time t (denoted $\bar{a}$ and $\bar{b}$). The value of R/a obtained by extrapolation to zero time is $6 \cdot 81 \times 10^{-6}$ sec.$^{-1}$, comparing favourably with the mean value of $R/\bar{a} = 7 \cdot 03 \times 10^{-6}$ sec.$^{-1}$ which appears to show no trend at all.

It should be noted that before this experiment the alkyl halide solution was allowed to " equilibrate " for about 14 hours at room temperature. This period of time was arbitrarily

TABLE 9.

Kinetic results of the exchange between diphenylmethyl chloride and chloride ions in 10·5% (w/w) methylformamide–dimethylformamide.

Reaction time (sec.)	10^2a	$10^2\bar{a}$	10^2b	$10^2\bar{b}$	$10^6R/a$	$10^6R/\bar{a}$
0	7·77	—	3·72	—	(6·81)	—
3600	7·77	7·67	3·72	3·82	6·75	7·03
7200	7·77	7·65	3·72	3·84	6·69	7·06
10,800	7·77	7·64	3·72	3·85	6·64	6·97
14,400	7·77	7·61	3·72	3·88	6·61	7·06

chosen as being sufficient to eliminate the initial increase in reaction rate. It is, perhaps, significant that the extrapolated value of R/a was the same for samples which had been kept for 24 and for 48 hours (see Figure).

Thus, although we do not know the nature of the " equilibration " we have completed a series of kinetic runs evaluating R/a by extrapolation back to zero time as in Table 9. Table 10 records the results of this series.

TABLE 10.

Kinetic data for the diphenylmethyl chloride–chloride ion exchange in 10·5% (w/w) methylformamide–dimethylformamide.

Temp.	10^2a	10^2b	$10^6R/a = 10^6k_1$	
30·0°	7·79	5·54	0·800	
30·0	7·45	4·15	0·828	Mean 0·812 ± 0·020
30·0	9·50	2·77	0·828	
40·0	7·72	5·49	2·50	
40·0	7·38	4·12	2·55	Mean 2·55 ± 0·04
40·0	9·42	2·75	2·59	
50·0	7·07	4·90	7·13	
50·0	7·77	3·72	6·81	Mean 6·8 ± 0·3
50·0	6·26	1·65	6·50	

Since the values of R/a showed no significant trend with change in the concentration of the halide ion, it follows that the reaction is predominantly of the first-order under these conditions and that the parameter R/a gives the value of the first-order rate constant.

It is difficult to decide whether or not extrapolation to zero time of the rates of exchange, with freshly prepared diphenylmethyl chloride solutions, would give more meaningful results than those obtained by the procedure outlined above, using " equilibrated " diphenylmethyl chloride solutions. Nor is it clear whether or not the unusual results are due to traces of impurities (*e.g.*, water) which might liberate hydrogen chloride. The deliberate addition of hydrogen chloride gave largely negative results: although it produced a small initial rise, the rate of reaction tended to drop to the same value as that obtained with " equilibrated " solutions.

An exchange between benzyl chloride and lithium chloride was also followed in the same solvent mixture (see Table 11). No side effects were observed and a reaction which was allowed to go to completion gave 101% of the maximum theoretical exchange.

TABLE 11.

Kinetic data for the benzyl chloride–chloride ion exchange in 10·5% (w/w) methyl-formamide–dimethylformamide.

Temp.	10^2a	10^2b	$10^5R/ab = 10^5k_2$	Coeff. of variation	Temp.	10^2a	10^2b	$10^5R/ab = 10^5k_2$	Coeff. of variation
30·0°	5·47	9·60	10·8	1·1	50·0°	5·62	9·44	83·6	1·0
30·0	5·47	4·80	10·6	1·0	50·0	5·62	4·72	84·4	1·2
30·0	5·72	1·92	10·5	1·1	50·0	5·38	1·89	83·8	2·2
30·0	5·72	0·96	11·3	5·4	50·0	5·38	0·94	84·7	4·9
		Mean 10·7					Mean 83·7		
40·0	5·67	9·52	30·3	1·0					
40·0	5·67	4·76	30·0	2·0					
40·0	5·42	1·90	30·6	1·8					
40·0	5·42	0·95	31·7	2·6					
		Mean 30·1							

No trend was observed in the value of R/ab with change in b, indicating that the reaction was predominantly of S_N2 type.   In addition, it appears that α-values are very close to unity and that no correction for partial ionisation is therefore necessary.   This is reasonable since the α-values for dimethyl sulphoxide (which has a slightly lower dielectric constant), obtained from conductivity measurements, were in the region of 0·95—1·00 over the same concentration range.

DISCUSSION

Table 12 correlates the information obtained for the benzyl chloride–chloride ion exchange in terms of the dielectric constants of the solvents used.   All rate constants are calculated for 25°.

The results show that for this reaction the bimolecular rate constant decreases with increase in solvent polarity.   On the basis of the Hammett ρ function,[9] it might be expected that there would be an approximately linear relation between the logarithm of the rate constant and the reciprocal of the dielectric constant.[10]   This relation would, of course, be disturbed by any specific interaction between solvent and solute or by preferential solvation by one type of solvent molecule in a mixed solvent.   Winstein and Smith [11]

TABLE 12.

Summary of kinetic data for the benzyl chloride–chloride ion exchange in various solvents.

Solvent	Dimethyl-formamide	Dimethyl sulphoxide	10·5% (w/w) methylformamide–dimethylformamide
$10^5 k_2$ (l. mole^{-1} sec.$^{-1}$)	152	68·4	6·1
*D (25°)	36·7	46·6	62·0
E_A (k cal.)	18·6	18·4	20·0
$\log_{10} A$	10·8	10·3	10·5

* See refs. 7 and 8 for dielectric constants.

have, for example, demonstrated an equilibrium between alkyl halides and dimethyl sulphoxide, with the formation of O-alkyl and S-alkyl salt-like compounds, due to the solvent's basic properties which result from the high electron density on the oxygen atom owing to the poor p–d overlap on the S–O bond.

Our results do not suffice to test this relation, even as a broad generalisation, but the bimolecular rate constant ($2·8 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$) obtained by de la Mare and Hughes [12] for the same reaction in acetone ($D = 19·0$) nevertheless appears to be abnormally low.   A similar discrepancy has been reported by Farhat-Aziz and Moelwyn-Hughes between their results [2] and those of Hughes, Ingold, and Mackie [13] for the halide-exchange between methyl iodide and lithium chloride in acetone.

The discrepancy is, in both cases, largely due to the fact that no meaningful comparison can be made between apparent second-order rate constants based on the stoicheiometric salt concentration and true second-order rate constants based on the actual ionic concentration.

It is true, as pointed out by Hughes, Ingold, and Parker [14] that " the door of dissociation (or ionisation) in acetone (or any other solvent) is not restricted to being shut or open but can be ajar to a continuous distribution of extents."   It is nevertheless equally true that the great majority of salt molecules in solution are to all intents fully ionised or un-ionised (except in the case of triple-ion formation which does not normally occur in solvents of

[7] Fuchs and Nisbet, *J. Amer. Chem. Soc.*, 1959, **81**, 2371.
[8] Leader and Gormley, *J. Amer. Chem. Soc.*, 1951, **73**, 5731.
[9] Hammett, " Physical Organic Chemistry," McGraw-Hill Co., New York, 1940, pp. 184—189.
[10] Swart and le Roux, *J.*, 1957, 406.
[11] Winstein and Smith, *Tetrahedron*, 1958, **3**, 317.
[12] de la Mare and Hughes, *J.*, 1956, 845.
[13] Hughes, Ingold, and Mackie, *J.*, 1955, 3177.
[14] Hughes, Ingold, and Parker, *J.*, 1960, 4400.

dielectric constant <10) and that the number for which the door is as it were ajar is very small indeed. Moreover, all the evidence on Finkelstein-type substitutions indicates that, except perhaps in rare instances at low dielectric constants,[15] such reactions take place predominantly between free ions and organic dipoles and that the rate of reaction with un-ionised salt molecules is too slow to be competitive.[1,16]

It would seem, therefore, desirable to distinguish between rate constants based on the actual concentration and rate constants based on the stoicheiometric concentrations by the use of some such term as " rate parameter " for the latter.

Unfortunately the ionisation constants for lithium chloride used by Farhat-Aziz and Moelwyn-Hughes [2] do not seem to be wholly reliable. On the basis of their data, however, the rate constant $k_2 = R/a\alpha b$ for the exchange between diphenylmethyl chloride and chloride ions in acetone at $25°$ would be about 140×10^{-5} l. mole^{-1} sec.$^{-1}$, which is only a little less than our value for this exchange in dimethylformamide.

Table 13 correlates the information obtained for the diphenylmethyl chloride–chloride ion exchanges in various solvents at $25°$.

The exchange in all four solvents shows considerable S_N1 character and there is a marked increase in the ratio k_1/k_2 with increase in dielectric constant. An increase in

TABLE 13.

Summary of kinetic data for the diphenylmethyl chloride–chloride ion exchange in various solvents.*

Solvent	DMF	50% (w/w) DMF–DMSO	DMSO	10% (w/w) NMF–DMF
$10^6 k_1$ (sec.$^{-1}$)	0·032	0·282	1·21	0·464
$10^5 k_2$ (l. mole^{-1} sec.$^{-1}$)	0·707	0·703	1·05	Not detectable
k_1/k_2 (relative)	1	9	26	Very large
E_1 (kcal. mole^{-1})	24·4	20·5	18·4	20·6
E_2 (kcal. mole^{-1})	21·1	20·8	22·3	—
D	36·7	41·6	46·6	52·0

* DMF = Dimethylformamide.   DMF–DMSO = Dimethylformamide–dimethyl sulphoxide. DMSO = Dimethyl sulphoxide.   NMF–DMF = Methylformamide–dimethylformamide.

the first-order rate constant k_1 is not, however, invariably accompanied by a decrease in the second-order rate constant k_2. It seems, therefore, that it is impossible to arrange a series of solvents in a fixed order of increasing polarity independently of the reaction mechanism.

APPENDIX

Degrees of ionisation were in all cases obtained from conductivity measurements according to the method of Shedlovsky.[17] The ionisation constant K, limiting conductance $\Lambda°$, and mean distance of closest approach of the ions d (in Ångstroms) which obtained are recorded in Table 14. Values of K at temperatures other than those recorded in Table 14 were deduced from Bjerrum's theory.[18]

TABLE 14.

Ionisation constants obtained from conductivity measurements.

Solvent	Solute	$\Lambda°$	K	d	Temp.
Dimethylformamide	NH$_4$Br	112·6	$0·796 \times 10^{-2}$	1·71	50°
50% w/w Dimethylformamide–dimethyl sulphoxide	LiCl	60·3	$5·29 \times 10^{-2}$	1·95	30
Dimethyl sulphoxide	LiCl	40·1	$25·9 \times 10^{-2}$	3·25	30

[15] Lichtin and Rao, *J. Amer. Chem. Soc.*, 1961, **83**, 2417.
[16] Sugden, *J. Chem. Phys.*, 1948, **45**, 147; *J.*, 1949, 270; le Roux and Swart, *J.*, 1955, 1475; Farhat-Aziz and Moelwyn-Hughes, *J.*, 1961, 1523; Winstein, Savedoff, Smith, Stevens, and Gall, *Tetrahedron Letters*, 1960, No. 9, 24.
[17] See Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 3rd edn., p. 288.
[18] Bjerrum, *Kgl. Danske Videnskab. Selskab*, 1926, **7**, No. 9.

EXPERIMENTAL

Dimethylformamide, benzyl chloride, diphenylmethyl chloride, and lithium radio-chloride were prepared as before.[1]

Dimethyl Sulphoxide.—Commercial dimethyl sulphoxide, dried ($CaSO_4$) and fractionated three times through a 20″ column packed with Fenske helices, had b. p. 90—92°/22—23 mm. Only the middle fraction was collected for use; it had d_4^{25} 1·097 (lit.,[19] 1·096), n_D^{25} 1·4768.

Methylformamide.—Commercial methylformamide, dried ($CaSO_4$) and distilled through the same 20″ column, had b. p. 99—100°/21—22 mm., d_4^{25} 0·9976 (lit.,[19] 0·9977), n_D^{25} 1·4310 (lit.,[8] 1·4309).

Ammonium Radio-bromide.—[82]Br was obtained from the Radiochemical Centre, Amersham, in 3-mc batches. The sample was evaporated to dryness, dissolved in the appropriate solvent, and diluted with Merck's ammonium bromide (assay 99·9% by potentiometric titration) to give a suitable specific activity.

Kinetic Measurements.—The reactions were carried out in the same way as before,[1] allowance being made, in the case of ammonium bromide, for decay during counting. The relevant correction factors by which the benzene activity had to be multiplied were as tabulated.

Solvent		Corrn. factor
50% (w/w) Dimethylformamide–dimethyl sulphoxide ...	Diphenylmethyl chloride	0·823
Dimethyl sulphoxide	Benzyl chloride	0·753
	Diphenylmethyl chloride	0·741
10·50% (w/w) Methylformamide–dimethyl sulphoxide ...	Benzyl chloride	0·886
	Diphenylmethyl chloride	0·904

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[19] Sears, Lester, and Dawson, *J. Phys. Chem.*, 1956, **60**, 1433.