

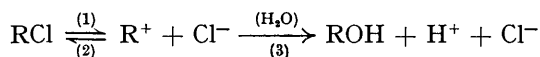
**470.** *Mechanism of Substitution at a Saturated Carbon Atom. Part XXXIII.\* Kinetic Effect of Common-ion and of Non-common-ion Salts on the Aqueous Solvolysis of Diphenylmethyl Halides. A Demonstration of the Unimolecular Mechanism of Solvolysis.*

By O. T. BENFEY, E. D. HUGHES, and C. K. INGOLD.

Our interpretation (1938—40) that certain retardations of solvolysis of alkyl halides by added salts (always salts whose anions were identical with those given by the alkyl halides) arose from reversal by the common anion of the initial stage in the unimolecular mechanism of substitution, was questioned (1942) on the ground that some salts might retard such reactions by modifying the solvent, for example, by combining with the water in an aqueous organic solvent. This theory would require the retardations to depend simply on the nature of the salt for a given solvent, and not, as demanded by our original interpretation, on the relation of the salt to the alkyl compound, in particular, on the identity or otherwise of the anions of the salt and the alkyl compound. We have now shown that the retardations cited do indeed depend on this relation: two salts, one retarding and the other accelerating with respect to a given alkyl compound, will interchange their kinetic effects when the potentially anionic part of the alkyl compound is suitably altered. The example relates to the effect of lithium chloride and bromide on the rate of hydrolysis by aqueous acetone of diphenylmethyl (benzhydryl) chloride and bromide. There are retardations when anions of salt and alkyl compound are the same, and accelerations when they are different. A new and concise demonstration of the reality of the unimolecular mechanism in solvolytic reactions is thus provided.

WE last discussed salt effects in nucleophilic substitution, both solvolytic and non-solvolytic, in 1940. It was shown then that salt effects could provide a method of diagnosis of mechanism of substitution, and could also fill detail into the picture of the unimolecular mechanism (*J. Amer. Chem. Soc.*, 1938, **60**, 3080; *J.*, 1940, 960 *et seq.*, 7 papers). These applications were especially useful in the field of solvolytic substitutions, where the problems arising are worthy of this powerful kinetic method. In the present three papers, the same applications are pursued further in the domain of solvolytic substitutions.

In this paper we again take up the determination of mechanism by means of salt effects. The possibility of such determination depends on the circumstance that the unimolecular mechanism has, typically, a somewhat complex kinetic form, which does not necessarily reduce to first-order form when the conditions become such that the bimolecular mechanism would have a first-order form, for instance, when the substituting agent is the solvent. The reason for this is the reversibility of the initial heterolysis in unimolecular reactions. For illustration, let us consider the unimolecular hydrolysis of an alkyl chloride in an aqueous solvent:



As larger chloride-ion concentrations are built up by reaction (3), reaction (2) gains in importance, so that the rate-determining ionisation becomes progressively retarded by its reversibility, without necessitating any reversal of the overall reaction, which might be a completely irreversible hydrolysis: the forward rate simply trails further and further behind the first-order rate, as reaction proceeds to its completion. This can be quantitatively expressed by specialising the typical kinetic equation for  $S_N1$  reactions, suitably for a substituting agent in constant excess:

$$dx/dt = k_1(a - x)(1 + \alpha x)^{-1}$$

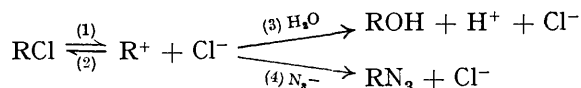
\* Part XXXII, *J.*, 1946, 173.

The factor  $(1 + \alpha x)^{-1}$  describes the progressive fall in the specific rate  $(dx/dt)/(a - x)$ . The constant  $\alpha$  measures the power of chloride ion to compete with water for the carbonium ion  $R^+$ .

An analogous effect is to be expected if, instead of relying on the formed hydrogen chloride, one adds some hydrogen chloride, or lithium chloride, or any other ionising chloride. The difference is only that the specific rate will now be depressed from the beginning, as indicated by the equation,

$$dx/dt = k_1(a - x)[1 + \alpha(c + x)]^{-1}$$

where  $c$  is the concentration of initially added chloride ion. These effects of salts on unimolecular reaction rate apply only to "common-ion salts," that is, salts having an anion identical with that given by the alkyl compound. "Non-common-ion salts," that is, salts with any other anion, *e.g.*, sodium azide in the example of the hydrolysis of an alkyl chloride, cannot produce a like effect, because such salts can intervene only after the rate-determining heterolysis:

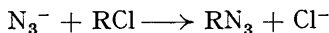


Thus mass-action gives these salts no effect on the initial rate of destruction of the alkyl halide, although, by supplying new competition for the carbonium ion, they should lessen the growing retardation produced by the developing chloride ion.

The bimolecular mechanism of substitution  $S_N2$  involves a different set of consequences. The irreversible aqueous solvolysis of an alkyl chloride by the mechanism,



should follow a first-order law. Mass-action can confer no kinetic effect either on the produced chloride ion, or on any added "common-ion salt." On the other hand, an added "non-common-ion" salt, such as sodium azide, supposing that it intervenes at all, must accelerate the destruction of the alkyl chloride from the outset, since it provides an additional mode of attack on that molecule:



The above consequences follow from the mass-law. Superposed on them all, there will be electrostatic effects dependent on ionic strength. They will be accelerative in reactions for which the transition state is more polar than the initial state. It is assumed that solutions are not so concentrated that one has to take account of ionic size.

Illustrating again by the unimolecular solvolysis of an alkyl chloride, we note that, on account of electrostatic effects only, the rise of ionic strength during reaction should produce a progressively rising specific rate, while any introduced salt, whether of "common-ion" type or of "non-common-ion" type, should increase rate from the outset.

In the corresponding bimolecular reaction, the various electrostatic effects should be qualitatively as described, but weaker.

TABLE 1. *Mass-law and ionic-strength effects on the unimolecular and bimolecular solvolysis of an alkyl halide.*

	MASS LAW		IONIC STRENGTH
$S_N1$	(Formed ions ..... <i>Progressive fall</i> in specific rate	+	Progressive rise in specific rate
	(Common-ion salt ..... <i>Retardation</i> ,	+	Acceleration
	(Non-common-ion salt ... No initial effect	+	Acceleration
$S_N2$	(Formed ions ..... No effect	+	Small progressive rise specific rate
	(Common-ion salt ..... No effect	+	Small acceleration
	(Non-common-ion salt ... Acceleration	+	Small acceleration

By assembling these deductions, as in Table 1, a basis for the diagnosis of unimolecular substitution can be made clear. The two kinetic effects entered in italics, *viz.*, the downward drift in specific rate in the absence of added salts, and the overall retardation produced by

added "common-ion" salts, but not by other salts, if they can be made dominating, and thus clearly observed, will demonstrate the unimolecular mechanism. The discussion summarised in Table 1 can, indeed, be put into a quantitative form.

In the papers of 1940, a number of unimolecular substitutions, both solvolytic and non-solvolytic, were demonstrated in this way. The alkyl compounds employed were mostly either simple or substituted diphenylmethyl (benzhydryl) halides. The solvolytic reactions were hydrolyses in aqueous acetone. The non-solvolytic substitutions included substitutions by various anions in this medium, and also a halide-ion exchange in sulphur dioxide as solvent.

In 1942 Lucas and Hammett suggested, with reference especially to the hydrolytic reactions, that our interpretation of the retardations, on the basis of the mass-law effect in the unimolecular mechanism of substitution, was not really well established, because of the possibility of another type of action through which salts might retard reactions in aqueous acetone (*J. Amer. Chem. Soc.*, 1942, **64**, 1928). Some salts, more than others, might attract water, rendering the aqueous acetone an effectively drier solvent, and in this way reducing the reaction rate. A salt with a low affinity for water would accelerate on account of its ionic-strength effect, while another salt of high affinity for water might retard because of its strong drying action. The relative kinetic effects of different salts would, according to this theory, depend simply on the salts, and not on their constitutional relation to the alkyl compound. It was, indeed, suggested that the relative kinetic effect of salts in partly aqueous media would follow the Hofmeister series of affinity of ions for water.

We shall see in the next paper what special observations caused Lucas and Hammett to introduce this type of hypothesis. In general principle, the suggested form of salt effect is entirely plausible. The only question was whether it was in fact responsible for the retardations which we had been observing. Even at the time of Lucas and Hammett's paper, we felt that the evidence was in favour of our interpretation. For in 1940 we had described the kinetic effects of 7 salts in all on 6 alkyl halides in all, some of them chlorides and some bromides, a total of 18 distinct salt effects, disregarding the many repetitions in aqueous-acetone solvents of different composition. These 18 kinetic effects included 7 retardations; and the significant point is that, in each of the latter, the anion of the salt was the same as that of the alkyl halide.

TABLE 2. *Initial specific rates ( $k_1^\circ$  in  $\text{sec.}^{-1}$ ) of reaction of diphenylmethyl chloride and bromide in "80%" aqueous acetone at 25°, without added salts, and in the presence of lithium chloride and bromide.*

[Alkyl halides, initially 0.1M. Added salts, 0.1M.]				
Added salt	Diphenylmethyl chloride		Diphenylmethyl bromide	
	$10^4 k_1^\circ$	Change	$10^4 k_1^\circ$	Change
None .....	7.00	—	153	—
LiBr .....	8.16	+17%	133	-13%
LiCl .....	6.09	-13%	194	+27%

However, the challenge which we accepted was to produce, not merely an argument, but a proof; and this was obviously possible. The criterion is that, according to the theory of Lucas and Hammett, the kinetic effect of a salt depends on the salt, whereas, on our interpretation, it depends on the relation of the salt to the alkyl compound, in particular, on the identity or otherwise of the anion of the salt with that given by the alkyl compound. We have, then, to solvolyse an alkyl compound  $\text{RX}_1$ , alone, and in the presence of two salts,  $\text{MX}_1$  and  $\text{MX}_2$ , such that the first retards and the second accelerates. Then we have to change the alkyl compound to  $\text{RX}_2$ , and observe whether the two salts preserve their relative kinetic effects, or whether they cross over, the formerly retarding salt becoming an accelerator, and the accelerating salt a retarder.

Using diphenylmethyl (benzhydryl) chloride and bromide as the alkyl compounds, lithium chloride and lithium bromide as the salts, and "80%" aqueous acetone as the solvent, we find that the salts do indeed cross over with respect to their kinetic effects. This

is illustrated in Table 2, in which initial specific rates are made the basis of comparison, because, as we have explained, unimolecular reactions have not a strict first-order form, owing to the kinetic effects of the produced ions. This must be one of the most concise demonstrations yet given of the reality of the unimolecular mechanism in solvolysis.

The rest of the present account relates to practical details. The rate of disappearance of diphenylmethyl chloride, alone, and in the presence of lithium chloride, and of diphenylmethyl bromide, alone, and in the presence of lithium bromide, can be measured, as has been found previously, with nearly equal ease, and with identical results, by following the

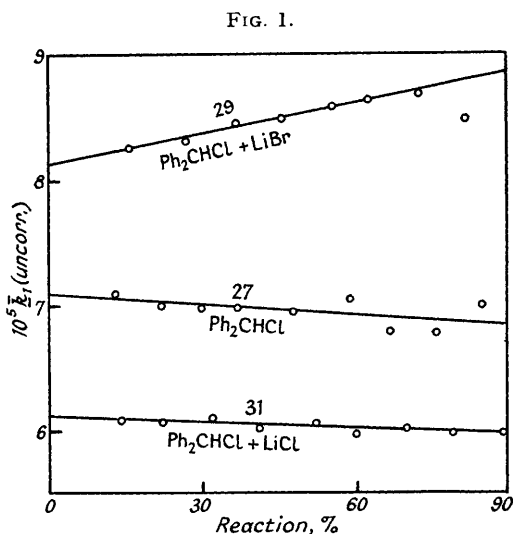


FIG. 1. Hydrolysis of diphenylmethyl chloride in "80%" aqueous acetone at 25°, alone, and in the presence of 0.1M-lithium chloride, and of 0.1M-lithium bromide. Integrated first-order rate constants,  $\bar{k}_1$  in  $\text{sec}^{-1}$ , plotted against percentage progress of reaction. The rate constants are not corrected for the slight reversibility of the reaction.

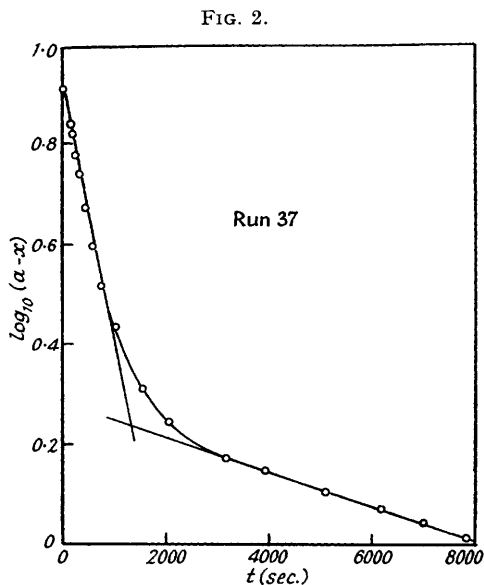


FIG. 2. Hydrolysis of diphenylmethyl bromide in "80%" aqueous acetone at 25° in the presence of 0.1M-lithium chloride. Logarithmic plot of the reaction progress, as followed by acid production ( $x$ ), against time ( $t$ ). The upper linear branch of the curve represents the hydrolysis of diphenylmethyl bromide. But about 20% of this substance is contemporaneously converted into diphenylmethyl chloride. We see the latter undergoing hydrolysis, along the lower linear branch of the curve, long after the reaction of diphenylmethyl bromide is over.

appearance either of acid or of halide ion. However, the two reactions which involve two different halogens require some special consideration.

The rate of reaction of diphenylmethyl chloride in the presence of lithium bromide can be measured conveniently, and with sufficient accuracy for our purpose, by following the production of acid. The reason is that, although the  $\text{RCl}$  is converted simultaneously into two first products,  $\text{RBr}$  and  $\text{ROH}$ , the  $\text{RBr}$  is hydrolysed relatively rapidly to  $\text{ROH}$  (see Table 2), thereby bringing the total production of acid at any given moment nearly up to equivalence with the liberated chloride ion. If we wished to be quite accurate, we ought to follow liberation of chloride ion; but this is technically more complicated on account of the presence of bromide ion; and therefore we took the easy course of following acid production. Because of the slight lag in the production of such acid as arises by the indirect route  $\text{RCl} \rightarrow \text{RBr} \rightarrow \text{ROH}$ , our observed rate, considered as a rate of decomposition of  $\text{RCl}$ , will be somewhat low; but, as is apparent from Table 2, it is still high enough to show the accelerative effect of the "non-common-ion" salt, in contrast to the retarding effect of the "common-ion" salt.

As to the measurement of the reaction rate of diphenylmethyl bromide in the presence

of lithium chloride, there is no escaping from the rigorous method. The halide RBr simultaneously gives two first products, RCl and ROH, but now RCl is hydrolysed relatively slowly, and thus acid production, which continues long after all the RBr has disappeared, is not an approximate measure of the destruction of RBr. This is clearly exhibited in Fig. 2 by the two linear branches of the logarithmic plot of reaction progress as measured by acid production. Therefore we have to measure bromide ions directly, despite the presence of chloride ions and of organic material. An electrometric method, carefully standardised, was elaborated for this purpose. The method confirms, as can be seen from Table 4, that chloride ion disappears during the earlier part of the reaction, and subsequently reappears as the formed diphenylmethyl chloride becomes hydrolysed.

TABLE 3. Runs followed by the production of acid.

$t$	$x_\infty - x_t$	$10^5 \bar{k}_1$	Reactn., %	$t$	$x_\infty - x_t$	$10^5 \bar{k}_1$	Reactn., %
Run 27: Initially, $[\text{Ph}_2\text{CHCl}] = 0.0981\text{M}$ .							
0	7.94	—	—	9,315	4.16	6.94	48
1000	7.39	(7.19)	7	12,560	3.28	7.04	59
1940	6.92	7.09	13	16,420	2.61	6.78	67
3490	6.22	6.99	22	21,110	1.90	6.77	76
5136	5.55	6.97	30	27,175	1.22	6.89	85
6638	5.00	6.97	37				
$k_1^\circ$ (uncorr.) = $7.08 \times 10^{-5} \text{ sec.}^{-1}$ .							
$k_1^\circ$ (corr.) = $7.00 \times 10^{-5} \text{ sec.}^{-1}$ .							
Run 29: Initially, $[\text{Ph}_2\text{CHCl}] = 0.0966\text{M}$ ; $[\text{LiBr}] = 0.1002\text{M}$ .							
0	7.80	—	—	9,490	3.49	8.58	56
980	7.31	(7.66)	7	11,590	2.90	8.63	63
2130	6.61	8.25	16	15,310	2.12	8.68	73
3860	5.72	8.30	27	19,980	1.45	8.47	82
5410	4.99	8.45	37	27,900	0.78	8.29	90
7280	4.28	8.48	46				
$k_1^\circ$ (uncorr.) = $8.12 \times 10^{-5} \text{ sec.}^{-1}$ .							
$k_1^\circ$ (corr.) = $8.09 \times 10^{-5} \text{ sec.}^{-1}$ .							
Run 31: Initially, $[\text{Ph}_2\text{CHCl}] = 0.0979\text{M}$ ; $[\text{LiCl}] = 0.1001\text{M}$ .							
0	7.96	—	—	12,260	3.79	6.05	52
1276	7.34	(6.38)	8	15,440	3.17	5.96	60
2520	6.83	6.08	14	20,160	2.37	6.01	70
4200	6.17	6.06	22	25,980	1.69	5.97	79
6240	5.44	6.10	32	37,080	0.87	5.97	89
8735	4.71	6.01	41				
$k_1^\circ$ (uncorr.) = $6.12 \times 10^{-5} \text{ sec.}^{-1}$ .							
$k_1^\circ$ (corr.) = $6.08 \times 10^{-5} \text{ sec.}^{-1}$ .							
Run 33: Initially, $[\text{Ph}_2\text{CHBr}] = 0.0974\text{M}$ .							
0	7.97	—	—	482	3.54	168	56
150	6.24	163	22	620	2.72	173	66
210	5.72	158	28	810	1.98	172	75
290	4.98	162	38	1,080	1.23	173	85
380	4.27	164	46	1,380	0.68	178	91
$k_1^\circ = 153 \times 10^{-5} \text{ sec.}^{-1}$ .							
Run 35: Initially, $[\text{Ph}_2\text{CHBr}] = 0.0979\text{M}$ ; $[\text{LiBr}] = 1.001\text{M}$ .							
0	8.01	—	—	500	3.89	144	51
150	6.60	(129)	18	642	3.11	147	61
202	6.07	137	24	840	2.33	147	71
270	5.54	137	31	1,100	1.62	145	80
370	4.73	142	41	1,620	0.72	149	91
$k_1^\circ = 133 \times 10^{-5} \text{ sec.}^{-1}$ .							
Run 37: Initially $[\text{Ph}_2\text{CHBr}] = 0.0987\text{M}$ ; $[\text{LiCl}] = 0.1000\text{M}$ .							
0	8.08	—	—	1,028	2.72	106	66
113	6.91	138	14	1,575	2.05	87.1	75
158	6.56	132	19	2,055	1.77	73.9	78
229	5.98	131	26	3,160	1.49	53.5	81.6
302	5.49	128	32	3,930	1.41	44.4	82.5
425	4.70	128	42	5,060	1.27	36.6	84.3
583	3.94	123	51	6,180	1.18	31.1	85.4
750	3.28	120	59	7,830	1.03	26.3	87.3
				9,540	0.84	23.7	89.6

## EXPERIMENTAL

Materials were purified as in the work described in 1940. All kinetic runs were conducted at 25-00° in "80%" aqueous acetone, *i.e.*, a mixture of 4 vols. of dry acetone with 1 vol. of water.

*Runs followed by Production of Acid.*—In Table 3, a sample run of each kind is recorded. Values of  $t$  are in sec., those of  $x_\infty - x_t$ , where  $x$  represents acid production, are in c.c. of 0.06146N-sodium hydroxide per sample of 5.03 c.c., and those of the integrated first-order rate constant,  $\bar{k}_1$ , and of the initial specific rate  $k_1^\circ$ , are in sec.<sup>-1</sup>. Values of  $\bar{k}_1$  are first computed, and are then extrapolated numerically to give  $k_1^\circ$ , to which, where necessary, the small correction for reversibility is applied. Each run which leads to a value of  $k_1^\circ$  is one of a pair, the other being unrecorded. The means of the pairs of values of  $k_1^\circ$  are in Table 2.

*Runs measured by following Halide Ion.*—Halide ion was followed by potentiometric titration with silver nitrate. The potentiometer could be read to 0.5 mv. A platinum-quinhydrone electrode served as standard, in a buffer of pH 3.0–3.3, which was made by adding 25 c.c. of 0.2N-sulphuric acid to 25 c.c. of 0.2M-potassium hydrogen phthalate, and diluting the whole to 100 c.c. A potassium nitrate bridge connected this half-cell to the solution undergoing titration, a silver wire acting as the second electrode. The method of operation was based particularly on the work of Clark, who showed that bromide and chloride could be individually estimated in a mixture, if 5% aqueous barium nitrate was used in the medium (*J.*, 1926, 749). For the accurate location of equivalence points on the titration curves, the recommendations of Flood and Slatton were followed (*Z. anal. Chem.*, 1938, 115, 30). Trials showed that the two halides could be individually estimated in a mixture, usually to within 0.5%, that acetone did not interfere, if it was first extracted with carbon tetrachloride, and that the carbon tetrachloride extract did not interfere, even if it was not separated, provided that the electrode and bridge did not dip into it. In kinetic runs, the withdrawn sample, 5.03 c.c., was delivered into 60 c.c. of carbon tetrachloride at -5°, and this solution was then shaken 3 times with 20 c.c. of 5% aqueous barium nitrate. The total aqueous extract was titrated as described.

In Table 4, the time  $t$  is in sec., and the integrated first-order rate constants,  $\bar{k}_1(\text{Br}^-)$ , based on bromide-ion liberation, as well as the corresponding constants,  $\bar{k}_1(\text{H}^+)$ , based on acid production, and the initial specific rate,  $k_1^\circ$ , obtained by numerical extrapolation of  $\bar{k}_1(\text{Br}^-)$ , are all in sec.<sup>-1</sup>. The concentrations  $[\text{Cl}^-]$  and  $[\text{Br}^-]$  are expressed in c.c. of 0.0600M-silver nitrate, and the concentration  $[\text{H}^+]$  in c.c. of 0.0600N-sodium hydroxide, required by a sample of 5.03 c.c.

TABLE 4. Run followed by the production of halide ions and acid.

Run 39: Initially,  $[\text{Ph}_2\text{CHBr}] = 0.0995\text{M}$ ;  $[\text{LiCl}] = 0.0994\text{M}$ .

$t$	Halide determination				Acid determination		
	$[\text{Cl}^-]$	$[\text{Br}^-]$	$\text{Br}^-/\text{Br}_\infty^-$	$10^5 k_1(\text{Br}^-)$	$[\text{H}^+]$	$\text{H}^+/\text{H}_\infty^+$	$10^5 k_1(\text{H}^+)$
0	8.33	0	—	—	—	—	—
105	7.75	1.52	18%	192	1.14	14%	140
155	7.68	2.19	26	197	1.67	20	144
225	7.48	2.93	35	192	2.34	28	146
310	7.25	3.77	45	194	2.86	34	135
410	7.15	4.58	55	194	3.53	42	134
512	7.26	5.18	62	190	—	—	—
642	6.91	5.96	71	195	—	—	—
840	6.67	6.74	81	197	5.40	65	124
1085	6.68	7.35	88	195	5.80	70	110
1455	6.71	7.75	93	—	6.23	75	94.7
3780	6.82	8.34	100	—	6.92	83	47.1
9960	7.30	8.33	—	—	7.47	90	22.8
$\infty$	8.33	8.33	—	—	8.33	100	—

$$k_1^\circ = 193 \times 10^{-5} \text{ sec.}^{-1}.$$

A second similar run gave  $k_1^\circ = 194 \times 10^{-5} \text{ sec.}^{-1}$ .

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,  
UNIVERSITY COLLEGE, LONDON, W.C.1.

[O. T. BENFEY, PRESENT ADDRESS:  
HAVERFORD COLLEGE, HAVERFORD, PA., U.S.A.]

[Received, March 1st, 1952.]