471. *Mechanism of Substitution at a Saturated Carbon Atom. Part XXXIV.** *Kinetic Effects of Hydroxide and Alkoxide Ions on the Rate-controlling and Product-forming Stages of Unimolecular Solvolysis of* tert.-*Butyl and Diphenylmethyl Halides.*

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Following an observation by Lucas and Hammett on the hydrolysis of *tert.*-butyl nitrate, a study has been made of the role of hydroxide ions in aqueous, and of alkoxide ions in alcoholic media, on the unimolecular solvolysis of *tert.*-butyl bromide, and of diphenylmethyl (benzhydryl) chloride and bromide. As to the initial slow step, such lyate ions are not accelerating like other " non-common " ions, and may be retarding. It is noted that an attack by a lyate ion on a proton of the solvation shell required for ionisation might account for these effects. As to the final fast step, lyate ions are poor competitors for the carbonium ion, the hydroxide ion being much outdone in this respect by the chloride or the azide ion. It is explained that chloride and azide ions can often penetrate the solvation shell around a carbonium ion, whereas an attacking lyate ion is usually waylaid by an exterior proton. The effect is thus connected with the selectively high reactivity of lyate ions for hydrogen, rather than for carbon, nuclei, and it is suggested that the charge on a lyate ion is normally distributed over some of the solvent, and has to be condensed on the nucleus attacked, condensation on the exposed hydrogen nucleus being more facile than on the shielded carbon nucleus.

Lucas and Hammett (*J. Amer. Chem. Soc.*, 1942, **64**, 1928) made the important observation that the solvolysis of *tert.*-butyl nitrate in " 60% " aqueous dioxan is not accelerated by the " non-common-ion " salt, sodium hydroxide, although it is accelerated by other salts, as illustrated for sodium perchlorate in Table 1, Section A. They suggested that the alkali selectively lowered the activity of the water in the aqueous organic medium.

We have confirmed Lucas and Hammett's finding; and we have made similar observations on solvolytic reactions of *tert.*-butyl bromide and of diphenylmethyl (benzhydryl) chloride, for which unimolecular mechanisms are otherwise established. For the solvolysis of *tert.*-butyl bromide we used the same aqueous dioxan, and also " 80% " aqueous ethyl alcohol (Table 1, Sections B and C). For that of diphenylmethyl chloride we employed anhydrous methyl alcohol as the solvent; and the " non-common-ion " salt which failed in this case to accelerate solvolysis was sodium methoxide (Table 1, Section D). Here, some early experiments by Ward (*J.*, 1927, 2285) may be recalled, which showed that the solvolysis of diphenylmethyl chloride in anhydrous ethyl alcohol is not accelerated in the smallest degree by sodium ethoxide, as illustrated in Table 1, Section E.

From these results two conclusions may be drawn. First, the condition for non-acceleration seems to be that the anion of the salt, OH^-, OMe^-, and OEt^-, in the examples cited, shall be identical with the anion of the solvent. Such anions are often called lyate ions, so that we may term the salts " lyate-ion " salts. Secondly, the failure of these salts to accelerate solvolysis cannot depend on a differential activity effect on solvent components, because the same failure arises in single-component solvents.

We have to decide whether the non-acceleration is to be regarded simply as an enfeeblement of the electrostatic accelerating effect general to " non-common-ion " salts, or whether it discloses, superposed on the (possibly modified) electrostatic effect of " lyate-ion " salts, some special mechanism of retardation. This question is answered by the result that net retardations by " lyate-ion " salts, although not general, can be realised. This was first established by Lucas and Hammett with respect to the effect of sodium hydroxide on the hydrolysis of *tert.*-butyl nitrate: the net retardation, although small, was definitely in excess of their experimental error. In the example of the hydrolysis of diphenylmethyl

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* Part XXXIII, preceding paper.

bromide, we have observed a fairly large retardation by sodium hydroxide, as is recorded in Table 2. Hence we conclude that "lyate-ion" salts provide a special mechanism of retardation.

TABLE 1. *Unimolecular solvolysis: kinetic effects of salts, especially of salts having anions in common with the solvent.*

(Integrated first-order rate constants $\bar{k}_1$, and initial specific rates k_1°, both in sec.$^{-1}$.)

(A) *tert.*-Butyl nitrate in "60%" aqueous dioxan at 10° (Lucas and Hammett):

$[Bu^tNO_3]_0$	$[Salt]_0$	$10^5 k_1^\circ$	Change, %
0·124	none	21·9	—
0·127	NaOH, 0·107	21·2	−3
0·124	$NaClO_4$, 0·112	25·8	+18

(B) *tert.*-Butyl bromide in "60%" aqueous dioxan at 10° (this paper):

$[Bu^tBr]_0$	$[Salt]_0$	$10^5 k_1^\circ$	Change, %
0·103	none	28·9	—
0·106	NaOH, 0·104	28·7	−1

(C) *tert.*-Butyl bromide in "80%" aqueous ethyl alcohol at 25° (this paper):

$[Bu^tBr]_0$	$[Salt]_0$	$10^5 k_1^\circ$	Change, %
0·097	none	35·8	—
0·100	NaOH, 0·105	36·1	+1

(D) Diphenylmethyl chloride in dry methyl alcohol at 15° (this paper):

$[Ph_2CHCl]_0$	$[Salt]_0$	$10^5 k_1^\circ$	Change, %
0·094	none	25·2	—
0·101	NaOMe, 0·113	25·1	± 0
0·094	NaBr, 0·100	30·6	+21
0·095	NaI, 0·100	31·0	+23

(E) Diphenylmethyl chloride in dry ethyl alcohol at 25° (Ward):

$[Ph_2CHCl]_0$	$[Salt]_0$	$10^5 \bar{k}_1$	Change, %
0·074	none	5·75	—
0·097	NaOEt, 0·130	5·75	±0

TABLE 2. *Unimolecular hydrolysis of diphenylmethyl bromide in "60%" aqueous dioxan at 8°. Effect of sodium hydroxide alone and with other salts.*

(Initial specific rates, k_1°, measured by acid development, are in sec.$^{-1}$

$[Ph_2CHBr]_0$	$[Salt]_0$	$10^5 k_1^\circ$	Break in curve at
0·088	none	190	—
0·088	LiCl, 0·089	152	82%
0·087	NaOH, 0·092	152	—
0·088	LiCl, 0·089 NaOH, 0·111	124	82%

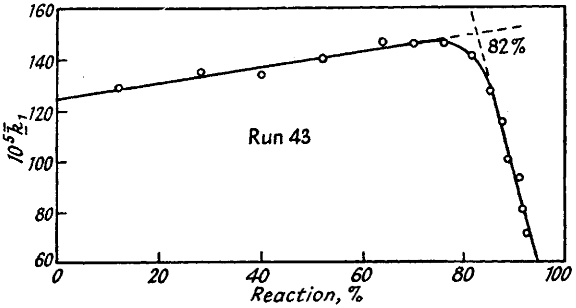
Note. The two equal rates, 152 × 10^{-5} sec.$^{-1}$, are equal only by coincidence. The first measures hydrolysis only in simultaneous hydrolysis and halide-ion exchange (see preceding paper). The second is the rate of a total reaction, which is nothing but hydrolysis.

It is an obvious suggestion that this mechanism depends on the ability of a lyate ion to distribute its charge by intermolecular proton displacement over a group of solvent molecules, all of which then share the proton defect. However, if this is an important factor, then it is also important that the shared charge should be a negative one. For the hydrogen ion can similarly co-opt solvent molecules to share its proton excess, and yet the hydrogen ion has been shown to have just the same salt effects as other univalent cations. Thus in the papers of 1940, it was shown that hydrogen chloride is equivalent in its salt effects to sodium chloride. Lucas and Hammett found that perchloric acid is similarly equivalent to sodium perchlorate. In further experiments, not recorded because of their similarity to those just mentioned, we have found nearly identical kinetic effects of hydrogen bromide, sodium bromide, and potassium bromide.

We base our picture of the retarding action of lyate ions on the conclusion of 1940 that many water or alcohol molecules are electrostatically involved in the initial stage of ionisation of an alkyl halide undergoing unimolecular solvolysis. We have to assume that the distributed proton defect in a solvent containing lyate ions impairs the solvation of the forming halide ion more than it aids that of the developing carbonium ion. The difference in the detailed condition of the molecules composing the solvation shell of the transition state would then be likely so to influence the energy and entropy of activation as to reduce reaction rate. We have to assume also that hydrogen ions, on the contrary, do not, in dilute solution, disturb the solvation shells of forming halide ions except through their electrostatic effect, just as, in dilute solution, they do not, otherwise than through their charge, affect fully formed halide ions. We do not claim more for this picture than that it seems plausible as an outline.

Our further concern has been with the influence of lyate ions on the final stage of unimolecular solvolysis. The question here is whether a lyate ion is an effective competitor for an already formed carbonium ion. One can, of course, guess that, since lyate ions do not observably assist the formation of a carbonium ion, they are unlikely to show much tendency to combine with it. We have, indeed, found that in comparison with the chloride ion or the azide ion, for example, the hydroxide ion is a very poor competitor for the diphenylmethyl cation.

We record below some experiments relating to the hydrolysis in " 60% " aqueous dioxan of diphenylmethyl bromide, in the presence of lithium chloride, without and with added sodium hydroxide. As illustrated in the preceding paper, the proportion in which introduced chloride ion competes with solvent water for the diphenylmethyl cation, as formed from diphenylmethyl bromide, can be judged from the percentage extent of hydrolysis at the point at which a break in the rate curve indicates that all the diphenylmethyl bromide has been destroyed, although most of the formed diphenylmethyl chloride still remains to be hydrolysed. Thus in one of a pair of experiments with equimolecular amounts of initially taken diphenylmethyl bromide and lithium chloride, the break occurred at 82% of hydrolysis; and in the comparison experiment, in which, additionally, rather more than one equivalent of sodium hydroxide was present, the break still occurred at 82% of hydrolysis, as indicated in Table 2 (and in the figure).



Plot of integrated first-order rate constants against the percentage progress of hydrolysis of diphenylmethyl bromide by alkaline aqueous dioxan in the presence of lithium chloride. The break occurs when the original diphenylmethyl bromide is consumed, and only the diphenylmethyl chloride, formed from it by the intervention of chloride ion, remains to be hydrolysed.

Experiments on the hydrolysis of diphenylmethyl bromide in " 60% " aqueous dioxan in the presence of sodium azide, conducted as described in the next paper, have similarly shown that the extent to which the azide ion intervenes to form the unhydrolysed product, diphenylmethyl azide, is not diminished by the additional presence initially of an equivalent of sodium hydroxide.

Clearly, then, the hydroxide ion is a poor competitor for the solvated carbonium ion, being much outdone in this respect by both the chloride ion and the azide ion. Probably this is a particular case of the general relation, noticed before in a number of connexions, that hydroxide and alkoxide ions, although they are strongly nucleophilic towards hydrogen (strongly basic), are relatively weakly nucleophilic towards carbon. This suggests that the charge on a lyate ion is normally distributed over some of the solvent, as already mentioned, and therefore has to be condensed on the nucleus under attack; and that such electrical condensation would occur with greater intensity on an exposed hydrogen nucleus than on a well-screened carbon nucleus. In the particular reaction under discussion, we can offer a molecular picture, based on the conclusion of 1940 that the carbonium ion in unimolecular solvolysis is formed within a solvation shell, which ends its life by internal collapse, unless it is previously pierced by an attacking anion. We assume that, whereas a chloride ion or an azide ion can often penetrate the water shell round a carbonium ion, a hydroxide ion is nearly always waylaid by an external proton of the shell.

TABLE 3. *Examples of kinetic runs.*

Run 4: In "60%" aqueous dioxan at 10·00°. Initially [Bu^{t}Br] = 0·1026M. Values of $x_\infty - x_t$, where x measures acidity, are in c.c. of 0·05958N-NaOH per sample of 5·02 c.c.

t	$x_\infty - x_t$	$10^5\bar{k}_1$	Reactn., %	t	$x_\infty - x_t$	$10^5\bar{k}_1$	Reactn., %
0	8·66	—	—	2995	3·39	31·3	61
210	8·15	28·9	6	3605	2·77	31·6	68
630	7·20	29·3	17	4350	2·19	31·6	75
1185	6·85	30·3	30	5150	1·69	31·7	80
1790	5·01	30·6	42	6005	1·24	32·4	86
2320	4·22	31·0	51	6930	0·92	32·4	89

$k_1^\circ = 28{\cdot}9 \times 10^{-5}$ sec.$^{-1}$.

Run 5: In "60%" aqueous dioxan at 10·00°. Initially [Bu^{t}Br] = 0·1061M, [NaOH] = 0·1039N. Values of $y_t - y_\infty$, where y measures alkalinity, are in c.c. of 0·09756N-HCl per sample of 5·02 c.c.

t	$y_t - y_\infty$	$10^5\bar{k}_1$	Reactn., %	t	$y_t - y_\infty$	$10^5\bar{k}_1$	Reactn., %
0	5·46	—	—	3380	1·98	30·0	64
330	4·94	(30·4)	10	3955	1·66	30·1	70
945	4·15	29·0	24	4615	1·33	30·6	76
1575	3·45	29·2	37	5200	1·11	30·6	80
2190	2·88	29·2	47	5745	0·92	31·0	83
2775	2·39	29·8	56	7030	0·61	31·2	89

$k_1^\circ = 28{\cdot}7 \times 10^{-5}$ sec.$^{-1}$.

Run 19: In "80%" aqueous ethyl alcohol at 25·00°. Initially [Bu^{t}Br] = 0·0968M. Values of $x_\infty - x_t$ in c.c. of 0·06656N-NaOH per 5·02 c.c.

t	$x_\infty - x_t$	$10^5\bar{k}_1$	Reactn., %	t	$x_\infty - x_t$	$10^5\bar{k}_1$	Reactn., %
0	7·30	—	—	2200	3·22	37·2	56
488	6·12	36·1	16	2835	2·52	37·5	65
826	5·42	36·1	26	3515	1·97	37·3	73
1220	4·68	36·4	36	4410	1·38	37·8	81
1675	3·95	36·7	46	6260	0·68	37·9	91

$k_1^\circ = 35{\cdot}8 \times 10^{-5}$ sec.$^{-1}$.

Run 20: In "80%" aqueous ethyl alcohol at 25·00°. Initially [Bu^{t}Br] = 0·1000M, [NaOH] = 0·1046N. Values of $y_t - y_\infty$ in c.c. of 0·06838N-HCl per 5·02 c.c.

t	$y_t - y_\infty$	$10^5\bar{k}_1$	Reactn., %	t	$y_t - y_\infty$	$10^5\bar{k}_1$	Reactn., %
0	7·34	—	—	2195	3·27	36·8	55
555	6·00	36·3	18	2845	2·55	37·2	65
852	5·37	36·7	27	3700	1·83	37·5	75
1200	4·77	35·9	35	4580	1·33	37·3	82
1655	3·98	37·0	46	6325	0·69	37·4	91

$k_1^\circ = 36{\cdot}1 \times 10^{-5}$ sec.$^{-1}$.

Run 40: In "60%" aqueous dioxan at 8·00°. Initially [Ph_2CHBr] = 0·0878M. Values of $x_\infty - x_t$ in c.c. of 0·06264N-NaOH per 5·03 c.c.

t	$x_\infty - x_t$	$10^5\bar{k}_1$	Reactn., %	t	$x_\infty - x_t$	$10^5\bar{k}_1$	Reactn., %
0	7·05	—	—	465	2·60	215	63
107	5·71	197	19	565	2·06	218	71
155	5·23	193	26	673	1·53	227	78
220	4·59	195	35	790	1·14	231	84
298	3·85	203	45	960	0·71	239	90
371	3·20	213	55				

$k_1^\circ = 190 \times 10^{-5}$ sec.$^{-1}$.

Run 42: In "60%" aqueous dioxan at 8·00°. Initially [Ph_2CHBr] = 0·0879M, [LiCl] = 0·0887M. Values of $x_\infty - x_t$ as in Run 40.

t	$x_\infty - x_t$	$10^5\bar{k}_1$	Reactn., %	t	$x_\infty - x_t$	$10^5\bar{k}_1$	Reactn., %
0	7·06	—	—	1092	1·34	162	81·0
153	5·52	161	22	1391	1·02	139	85·6
220	4·93	163	30	1682	0·93	121	86·8
308	4·23	166	40	2012	0·82	107	88·4
410	3·51	170	50	2292	0·74	96	89·6
525	2·79	177	60	2785	0·67	84	90·5
662	2·23	174	68	3266	0·65	73	90·8
882	1·63	166	77	3900	0·57	64	91·9

$k_1^\circ = 152 \times 10^{-5}$ sec.$^{-1}$.

TABLE 3. (*continued*).

Run 41 : In " 60% " aqueous dioxan at 8·00°. Initially $[Ph_2CHBr]$ = 0·0873M, [NaOH] = 0·0920N. Values of $y_t - y_\infty$ in c.c. of 0·06620N-HCl per 5·03 c.c.

t	$y_t - y_\infty$	$10^5\bar{k}_1$	Reactn., %	t	$y_t - y_\infty$	$10^5\bar{k}_1$	Reactn., %
0	6·63	—	—	572	2·14	198	68
92	5·75	155	13	725	1·51	204	77
201	4·75	166	28	857	1·02	218	85
329	3·75	173	43	1005	0·71	222	89
461	2·78	189	58	1125	0·55	221	92

$k_1^\circ = 152 \times 10^{-5}$ sec.$^{-1}$.

Run 43 : In " 60% " aqueous dioxan at 8·00°. Initially $[Ph_2CHBr]$ = 0·0877M, [LiCl] = 0·0887M [NaOH] = 0·113N. Values of $y_t - y_\infty$ as in Run 41.

t	$y_t - y_\infty$	$10^5\bar{k}_1$	Reactn., %	t	$y_t - y_\infty$	$10^5\bar{k}_1$	Reactn., %
0	6·66	—	—	1196	1·23	141	81·5
102	5·84	129	12	1500	0·99	127	85·1
242	4·80	135	28	1810	0·83	115	87·5
378	4·02	134	40	2180	0·76	100	88·6
532	3·17	140	52	2600	0·60	93	91·0
688	2·43	147	64	3080	0·56	80	91·6
832	1·97	146	70	3705	0·49	70	92·6
971	1·61	146	76				

$k_1^\circ = 124 \times 10^{-5}$ sec.$^{-1}$.

EXPERIMENTAL

Some kinetic runs are recorded in Table 3. No examples of runs with diphenylmethyl chloride are included, because most of these are nearly of first-order form, so that the course of the reaction is represented fairly well by the already quoted rate constants. The " 60% " aqueous dioxan was made from 3 vols. of dry dioxan and 2 of water, and the " 80% " aqueous ethyl alcohol from 4 vols. of dry ethyl alcohol and 1 of water. For runs whose rates were to be compared, the solvent was drawn from a single stock. All the runs in the Table were followed either by the development of acid, or by the disappearance of alkali. Times, t, are in sec., and integrated first-order rate constants, $\bar{k}_1$, and initial specific rates, k_1°, are in sec.$^{-1}$. The latter constants, here and in earlier tables, are corrected for reversibility when necessary.

The plot of $10^5\bar{k}_1$ against the percentage of reaction in Run 43 is shown in the figure. It is from this plot that the already given figure, 82%, for the position of the break in the rate curve is derived. The corresponding plot for Run 42 is quite similar, and the break occurs in the same position.

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[*Received, March* 1*st*, 1952.]