187. *Mechanism of Substitution at a Saturated Carbon Atom. Part XXII. A Kinetic Demonstration of the Unimolecular Solvolysis of Alkyl Halides. (Section D) Kinetics of, and Salt Effects in, the Hydrolysis of* pp'*-Dimethylbenzhydryl Chloride in Aqueous Acetone.*

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Still following the lines of the abstract on p. 960, the kinetics of the hydrolysis of *pp'*-dimethylbenzhydryl chloride have been studied in a range of acetone–water mixtures. So strong in this example is the mass-law effect arising from the unimolecular mechanism, that even in solutions of considerable dilution the kinetics bear no resemblance to first-order kinetics. The effect of adding an ionised chloride is on a corresponding scale: whilst salts other than chlorides raise the reaction rate, chlorides depress it strongly. A special study has been made of the extent to which added azide ions intervene in the decomposition, side-tracking the hydrolytic process. The extent is found to be independent of the alkyl halide concentration, independent of the proportion of water in the medium over the range 10—50 vols. %, but dependent on the concentration of azide ions. Conclusions are drawn concerning the molecularities of the competing processes. Detailed discussion is reserved to p. 979.

In this final example, the hydrolysis of *pp'*-dimethylbenzhydryl chloride in aqueous acetone, we find mass-law effects displayed much more prominently than in the hydrolysis of any of the alkyl halides discussed in the preceding papers. This has permitted the investigation of certain matters of detail, in relation both to the kinetic form of hydrolysis and to the effect of added salts on the reaction rate.

(1) *Kinetic Form of Hydrolysis.*

Even at low concentrations, at which the previously described hydrolyses follow the first-order rate law more or less accurately in "90—80%" aqueous acetone (acetone containing 10—20 vols. % of water), this hydrolysis exhibits appreciable deviations; and in the still fairly small concentrations, 0·04—0·05M, its kinetics show no resemblance at all to first-order kinetics, the calculated instantaneous first-order constants dropping to less than half their initial values before the reactions have proceeded half-way, although in all the solvents this hydrolysis is quite irreversible.

As the hydrolyses are rather rapid, we have studied them at 0°, and in "90%", "85%" and "80%" aqueous acetone. The accuracy of measurement decreases in the order of naming the solvents, because the hydrolyses become successively faster; but we have taken particular care to trace the kinetic forms of the reaction as exactly as possible, because in the next paper we shall account for these quantitatively, and derive conclusions concerning the life history of the intermediate alkyl cation; we shall also treat the differences between one solvent and another in a quantitative manner. In Table I we record three illustrative runs, one for each solvent; the recorded runs are well confirmed, and were carried out after considerable experience of the best ways of starting and stopping the reactions sharply and with the least possible thermal disturbance. As heretofore, we tabulate integrated first-order rate constants, $\bar{k}_1$, rather than instantaneous constants, k_1, although the former, because of the averaging effect of integration, show the kinetic deviations in a less striking manner; our reason is the usual one, *viz.*, that integrated constants are exactly determined by the experimental observations, and do not involve the arbitrary element which is difficult to avoid completely in the graphical smoothing necessary for the estimation of instantaneous rate constants. The important qualitative points are that the integrated constants fall steadily throughout reaction (*i.e.*, without passing through a maximum or minimum), and fall relatively more sharply in more aqueous solvents.

TABLE I.

Integrated First-order Rate Constants ($\bar{k}_1$ *in sec.*$^{-1}$) *of Hydrolysis of* pp'-*Dimethylbenzhydryl Chloride* (RCl) *in Aqueous Acetone at* 0·0°.

(1) Solvent, " 90% " aqueous acetone. Initially, [RCl] = 0·0463.

Time (mins.)	16·0	35·4	68·8	103·9	152·7	212·6	286·8	340·3	396·0
ROH formed (%)	8·0	16·2	27·6	37·5	48·9	57·0	69·2	74·9	79·7
$10^5\bar{k}_1$	8·68	8·30	7·83	7·53	7·33	7·05	6·87	6·77	6·70

(2) Solvent, " 85% " aqueous acetone. Initially, [RCl] = 0·0430.

Time (mins.)	5·00	10·5	31·0	46·6	67·3	90·9	118·3
ROH formed (%)	12·0	21·5	47·4	60·9	73·0	82·7	88·9
$10^5\bar{k}_1$	42·7	38·5	34·5	33·5	32·5	32·2	30·8

(3) Solvent, " 80% " aqueous acetone. Initially, [RCl] = 0·0439.

Time (mins.)	2·00	3·05	4·60	6·55	9·70	13·8	18·0	26·0
ROH formed (%)	15·0	21·9	29·7	38·2	49·1	59·0	68·5	79·8
$10^5\bar{k}_1$	135	135	124	122	116	108	100	102

(2) *Salt Effects on the Rate of Hydrolysis.*

In the experiments described in this Section we have employed the same three solvents, " 90%," " 85% " and " 80% " aqueous acetone, and four salts, lithium chloride, lithium bromide, sodium azide and tetramethylammonium nitrate; " 85% " aqueous acetone was made the common solvent for the comparison of the salts, and sodium azide the common salt for comparison of the solvents. The salts were employed in about 0·05M-concentration, which is quite sufficient to show a large mass-law effect and a considerable ionic strength effect. With the alkyl halide also initially in about 0·05M-concentration, all the investigated hydrolyses were irreversible to within the accuracy of analysis. In the experiments with lithium chloride and lithium bromide, we followed the development of acidity, *i.e.*, the production of dimethylbenzhydrol: for reasons similar to those given in the preceding papers (this vol., pp. 966 and 971) the rates thus obtained are, in both cases, the rates of total decomposition of the dimethylbenzhydryl chloride. In the experiments with sodium azide and tetramethylammonium nitrate we measured the total decomposition of the dimethylbenzhydryl chloride directly by following the development of chloride ions. It is these total rates that we consider in the present Section, their analysis, where possible, into their component parts being reserved for discussion in Section 3. The temperature for all measurements was 0°.

In " 85% " aqueous acetone, lithium bromide, sodium azide and tetramethylammonium nitrate in the similar concentrations employed (0·051M) were found to increase the initial rate of decomposition of the alkyl halide by the factors 1·46, 1·50, and 1·53 respectively. This is clearly an ionic strength effect, dependent, in sufficiently dilute solution, essentially on the concentration of the uni-univalent electrolyte, and not on its nature—provided the anion is not identical with that of the alkyl halide. On the other hand, lithium chloride in similar concentration reduced the initial rate of hydrolysis by the factor 0·49. We may take it, therefore, that the common-ion effect arising in the presence of 0·05M-lithium chloride is reducing the rate to only one-third of the value which, in the absence of a common-ion effect, would be appropriate to a solution of the ionic strength employed. An alternative method of expression is that, in the presence of lithium chloride, approximately (1·50 — 0·49)/1·50 or 67% of the dimethylbenzhydryl cation formed is reacting with chloride ions and only 33% of it with water molecules. We shall see below that (at the ionic strength used) azide ions have nearly the same activity in relation to water molecules.

Table II records two runs in detail, and a summary of the remaining rate data, together with some numerical material to be considered in Section 3. In the experiment with lithium chloride the integrated rate constant shows a just perceptible downward drift : the qualitative reason for this is the partial buffering of the chloride-ion concentration by the added salt, and calculation shows that the downward drift should be very small. All the other rate constants show strong downward drifts, similar qualitatively to those illustrated for certain experiments with salts in the preceding papers : this is because the added salts partly buffer the ionic strength of the solution, and therefore its accelerating influence, but do not buffer the concentration of the retarding chloride ions that are formed in the course of hydrolysis. The effect is greatest with azide ions, because the buffering of the ionic strength is greatest in this case, owing to an actual disappearance of azide ions, which largely compensates the contribution to the ionic strength made by the generated chloride ions.

In " 90%," " 85%," and " 80% " aqueous acetone, sodium azide in the nearly uniform concentrations stated in the Table increased the rate of decomposition by the factors 1·71, 1·50 and 1·40. There is thus a distinct solvent influence on the salt effect, and this also we shall account for quantitatively in the next paper.

TABLE II.

Integrated First-order Rate Constants ($\bar{k}_1$ *in sec.*$^{-1}$) *of Hydrolysis and Total Reaction of* pp'-*Dimethylbenzhydryl Chloride* (RCl) *in Aqueous Acetone at* 0·0° *in the Presence of Salts.*

(A) " 90% " *Aqueous acetone.*

(1) Initially, [RCl] = 0·0463, $[NaN_3]$ = 0·0512 = *c*. Rate : $10^5k_1^{(c)}$ = 15·5.

Reaction (%)		10	20	40	60	80	100
Proportions	ROH (%)	34	34	36	37	38	39·7
	RN_3 (%)	66	66	64	63	62	60·3

(B) " 85% " *Aqueous acetone.*

(2) Initially, [RCl] = 0·0479, [LiCl] = 0·0555.

Time (mins.)	5·1	12·2	20·0	28·0	38·5	52·0	73·0	110
ROH formed (%)	6·7	15·3	24·1	32·0	40·2	50·2	60·4	75·0
$10^5\bar{k}_1$	23·0	22·7	23·0	22·9	22·2	22·2	21·2	21·0

(3) Initially, [RCl] = 0·0486, [LiBr] = 0·0504.

Time (mins.)	6·45	9·7	13·0	18·5	26·5	38·0	60·0
ROH formed (%)	19·6	27·0	33·1	42·4	52·7	64·7	77·4
$10^5\bar{k}_1$	57·0	54·0	51·5	49·7	47·2	45·0	41·3

(4) Initially, [RCl] = 0·410, $[NaN_3]$ = 0·0512 = *c*. Rate : $10^5k_1^{(c)}$ = 70·5.

Reaction (%)		10	20	40	60	80	100
Proportions	ROH (%)	35	35	38	—	40	40·4
	RN_3 (%)	65	65	62	—	60	59·6

(5) Initially, [RCl] = 0·466, $[NMe_4NO_3]$ = 0·0506 = *c*. Rate : $10^5k_1^{(c)}$ = 72·0.

Reaction (%)		10	20	40	60	80	100
Proportions	ROH (%)	88	90	95	—	100	100
	RN_3 (%)	12	10	5	—	0	0

(C) " 80% " *Aqueous acetone.*

(6) Initially, [RCl] = 0·0403, $[NaN_3]$ = 0·0540 = *c*. Rate : $10^5k_1^{(c)}$ = 224.

Reaction (%)		10	20	40	60	80	100
Proportions	ROH (%)	35	35	36	37	38	38·8
	RN_3 (%)	65	65	64	63	62	61·2

(3) *The Proportion of Intervention of Added Anions.*

As indicated in Table II, we have taken advantage of the stability of dimethylbenzhydryl azide to measure the proportions in which azide ions have intervened in the various stages of the decompositions carried out in the presence of sodium azide, the method being our usual one of following separately the liberation of chloride ions and hydrogen ions. We can conveniently consider either the proportion in which dimethylbenzhydryl azide is formed in the initial stages of hydrolysis, or the proportion in which it is found in the completed reaction mixture: the latter value is always lower because it represents the integrated effect of intervention by a concentration of azide ions which is diminishing during the course of reaction.

To within the limits of experimental error, the proportion in which azide ions in the concentrations used intervene in the initial stages of hydrolysis in " 90%," " 85% " or " 80% " aqueous acetone is 66%, whilst the proportions in which they are found to have intervened in the completed reaction mixtures are very close to 60% for the same three solvents; thus, for a nearly constant concentration of azide ions, the proportions in which water and azide ions participate to form their respective products remain substantially constant over a 2-fold change in the water concentration.

Experiments with " 50% " aqueous acetone have shown that the same is true over a 5-fold change of water concentration. Although in this medium the reaction (*i.e.*, the total reaction and each of its constituents) is much too rapid to permit of kinetic measurements, we can still determine the composition of the final product; and, with approximately the concentration of azide ions used previously, we find, once again, 60% of dimethylbenzhydryl azide. This shows clearly that, over the investigated range, the rate of the individual process which directly produces dimethylbenzhydrol is approximately independent of the water concentration. The data are summarised in Table III, lines 1—4. In the next paper we shall show that this is consistent with the broader conclusions that can be derived from a quantitative discussion of the common-ion effects illustrated in the preceding Sections of this paper.

On the other hand, there is no doubt that the rate of the individual process which leads directly to dimethylbenzhydryl azide is dependent on the azide-ion concentration. This is shown most clearly by some further experiments with " 50% " aqueous acetone, which are recorded in Table III, lines 5—8: when we increase the concentration of azide ions, we obtain an increased proportion of dimethylbenzhydryl azide. The observed increases can be fairly well accounted for if we assume that, whilst the rate of the dimethylbenzhydrol-forming process is independent of the concentration of azide ions, that of the azide-ion intervention is proportional to their concentration. The calculation is made by the rough but simple method which neglects activity corrections and correlates the proportion of benzhydryl azide found in the final product with the " average " concentration of azide ions, *i.e.*, the arithmetic mean of the initial and the final concentration. The values thus obtained are given in the last column of the Table, and the agreement with the observed figures is sufficient to make it highly probable that the individual process which leads directly to dimethylbenzhydryl azide is unimolecular with respect to azide ions. In the next paper we shall establish an analogous conclusion for halide ions in the course of our discussion of common-ion influences on the reaction kinetics.

A comparison of the experimental results recorded in lines 7 and 8 of Table III shows that the proportions in which dimethylbenzhydrol and dimethylbenzhydryl azide are formed are substantially independent of the initial concentration of dimethylbenzhydryl chloride. This means that dimethylbenzhydryl chloride and any intermediates derived from it must enter in an identical way into the simultaneous processes that lead to the separate products—a general inference which, in the next paper, will be specialised in the conclusion that each process is unimolecular with respect to the dimethylbenzhydryl cation.

We have also examined the intervention of the nitrate ion, although this could not be studied in detail, because dimethylbenzhydryl nitrate does not survive the conditions of hydrolysis. However, the nitrate ion was shown to intervene to a small extent, a perceptible amount of dimethylbenzhydryl nitrate being produced in the initial stages of hydrolysis (Table II, run 4; Table III, line 9). The nitrate ion is evidently much less effective for intervention than the azide ion.

TABLE III.

Proportions in which Anions intervene in the Hydrolysis of pp′-*Dimethylbenzhydryl Chloride* (RCl) *in Aqueous Acetone at* 0·0°.

	Aqueous acetone.	Initial RCl.	Salts added.	Initial [salt].	Initial RN_3 formed (%).	Final RN_3 formed (%).	
						Found.	Calc.
			(A) *Azide ions.*				
(1)	" 90% "	0·0463	NaN_3	0·0512	67	60·3	(Mean 60·3) *
(2)	" 85% "	0·0410	,,	0·0512	66	59·6	
(3)	" 80% "	0·0403	,,	0·0540	66	61·2	
(4)	" 50% "	0·0572	,,	0·0519	—	60·0	
(5)	,,	0·0461	,,	0·1001	—	75·8	76·5
(6)	,,	0·0467	,,	0·2002	—	85·8	87·7
(7)	,,	0·0540	,,	0·4867	—	95·8	94·8
(8)	,,	0·0267	,,	0·4867	—	95·7	94·9
			(B) *Nitrate ions.*				
(9)	" 85% "	0·0466	NMe_4NO_3	0·0506	~12	—	—

* This figure is taken as the basis for the calculation of the figures given underneath it.

EXPERIMENTAL.

pp′-*Dimethylbenzhydryl Chloride.*—*pp*′-Dimethylbenzophenone, prepared from *p*-toluoyl chloride and toluene by the Friedel–Crafts reaction, was reduced by means of zinc dust and sodium hydroxide in ethyl-alcoholic solution to the carbinol, m. p. 70·5° after crystallisation from light petroleum. This carbinol (10 g.), dissolved in a mixture of dry ether (80 c.c.) and light petroleum (50 c.c.), was saturated with hydrogen chloride in the presence of calcium chloride. After 2 hours, the solution was poured on fresh, dry calcium chloride and again saturated with hydrogen chloride. After 2 days, the solution was concentrated under slightly reduced pressure until crystals began to be formed; it was then cooled to 0°. The *pp*′-dimethylbenzhydryl chloride, after crystallisation from light petroleum, with use of a little norit, had m. p. 45° (cf. Norris and Blake, *J. Amer. Chem. Soc.*, 1928, **50**, 1808).

Methods.—These were essentially as described in the preceding papers. A large Dewar vessel containing a stirred mixture of ice-shavings and water served as a thermostat. Ice-cold solvents were used to stop the reactions in the samples taken for analysis, and the washing necessary in chloride-ion estimations was expedited as much as possible.

Products.—*pp*′-Dimethylbenzhydrol was isolated in good yield by extraction with ether in a completed reaction solution in " 80% " aqueous acetone. It had m. p. 70·5°, and the same mixed m. p. with an authentic specimen. The formation of *pp*′-dimethylbenzhydryl azide in the experiments with sodium azide was proved by extracting the product of a reaction in " 50% " aqueous acetone with pentane, and reducing it in methyl-alcoholic solution with hydrogen and Adams's platinum catalyst to *pp*′-dimethylbenzhydrylamine. The crude hydrochloride of this base (Found: Cl, 15·2. Calc.: Cl, 14·3%) was converted into the *picrate*, which, first obtained in an amorphous form, was crystallised with some difficulty from ethyl alcohol. It had m. p. 228° (Found: C, 57·2; H, 4·6. $C_{15}H_{17}N,C_6H_3O_7N_3$ requires C, 57·3; H, 4·5%).

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