

185. Mechanism of Substitution at a Saturated Carbon Atom. Part XX.
A Kinetic Demonstration of the Unimolecular Solvolysis of Alkyl Halides. (Section B) Kinetics of, and Salt Effects in, the Hydrolysis of Benzhydryl Halides in Aqueous Acetone.

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Continuing the investigation on the lines explained in the abstract at the head of the preceding paper, a study has been made of the kinetics of hydrolysis of benzhydryl chloride and bromide in various acetone-water mixtures at various temperatures. An examination has been made also of the effect of the added "salts," hydrogen, lithium, and sodium chlorides, lithium bromide and sodium azide, on the rates of reaction. The combined results show that, although the accelerating electrostatic effects of ionised salts in general are larger with the benzhydryl halides than with *tert.*-butyl bromide, the special retarding mass-law effect associated with the unimolecular mechanism is also larger, and by a much greater amount, with the consequence that the latter effect determines the qualitative results under appropriate conditions. Detailed discussion is deferred to p. 979.

In the present kinetic studies of the hydrolysis of benzhydryl chloride and bromide in aqueous acetone, we meet with the first definite, though still not numerically very striking, evidence of the presence, and even dominance, of the special mass-law effect belonging to the unimolecular mechanism. The mass-law effect acting alone should produce deviations from first-order kinetics such that the calculated first-order rate constants fall with the progress of reaction. The ionic strength effect, which should produce a progressive rise in the calculated constants, such as was observed with *tert.*-butyl bromide, is inevitably present also (and, actually, is larger than with the latter halide); but what we find is a partial or complete neutralisation, or even slight over-compensation, of this expected rise in the specific rate. On carrying out these hydrolyses in the presence of added salts, we observe the large ionic strength acceleration of the decomposition, when the anion of the added salt is not identical with the anion formed from the alkyl halide; but, when it is identical, then despite the large ionic strength effect, the mass-law effect may dominate and produce a small depression of rate.

(1) *Kinetics of Hydrolysis of Benzhydryl Chloride and Bromide.*

(a) *Benzhydryl Chloride.*—The hydrolysis of benzhydryl chloride was followed by measuring the development of acidity. In quite dilute solution ($<0.02M$) in either "90%" or "80%" aqueous acetone (*i.e.*, acetone containing either 10 or 20 vols. % of water) the hydrolysis obeys the first-order rate law very accurately; and, consistently, the addition of an ionised chloride such as sodium chloride in similarly small concentration makes no detectable difference to the reaction rate. At higher concentrations ($\sim 0.1M$), however, we find small but systematic departures from the first-order rate law. This is illustrated for "90%" aqueous acetone as solvent and for the temperature 50° , by the integrated rate constants, \bar{k}_1 , of the first run recorded in Table I. The deviations are in part due to the circumstance that, in this solvent and at the concentrations employed, the reaction is slightly reversible, the equilibrium amount of benzhydrol being 97.8% of the theoretical. This hydrolysis is considerably more strongly reversed than are those of *tert.*-butyl bromide

(preceding paper) or benzhydryl bromide (below) under similar conditions as to solvent, temperature and concentration. The reversibility diminishes sharply if we use smaller initial concentrations (<0.05M) of benzhydryl chloride, or a more aqueous solvent such as "80%" aqueous acetone, but then the deviations from first-order kinetics shown by the forward reaction also diminish. As these deviations are not very large and the degree of reversibility is small, we can correct for reversibility, and exhibit the kinetics of the isolated forward reaction, by the approximate method indicated in the preceding paper: the usual formula, $\bar{k}_1 = (1/t) \log_e \{a/(a-x)\}$, is changed to $\bar{k}_1(r) = (1/t) \log_e \{x_\infty/(x_\infty-x)\}$, and then \bar{k}_1 (corr.) is taken as 0.978 $\bar{k}_1(r)$. These corrected constants are also tabulated, and it can be seen that their relative rise during the progress of reaction is little more than half as steep as the relative rise of the constants for *tert.*-butyl bromide.

According to the theory that this diminished rise in the constants represents a partial compensation of the ionic strength effect by a superposed mass-law effect, the rise should be still further reduced if we work in more aqueous solvents. For it is shown experimentally in the preceding paper and in Section (2) of this paper (the theoretical reason is given later—this vol., p. 979) that the ionic strength effect, although not very sensitive to moderate changes of temperature, is very sensitive to the water content of the solvent, and is much diminished in more aqueous solvents. On the other hand, the mass-law effect is probably not very sensitive to the solvent changes contemplated, because we shall see that, in the case in which this effect was studied in greatest detail, it was found to be quite insensitive to such changes (*ibid.*). It follows that, as we pass to more aqueous solvents, the ionic strength effect will be considerably reduced whilst the opposing mass-law effect will be relatively little altered, wherefore the balance in favour of the ionic strength effect will be reduced. This has been found, and is illustrated in the second run of Table I, which refers to "80%" aqueous acetone at 25° (the reduction of temperature was necessary to permit accurate measurement because the rates are higher in more aqueous solvents). The reaction is now completely irreversible. It will be seen that the constants, \bar{k}_1 , are now almost steady, evidently because, in this solvent, the opposing effects nearly compensate each other. We shall later account quantitatively for the difference between the kinetics of the reaction in the two solvents (*ibid.*).

TABLE I.

Integrated First-order Rate Constants (\bar{k}_1 in sec.⁻¹) of Hydrolysis of Benzhydryl Chloride and Bromide (RCl and RBr) in Aqueous Acetone.

(a) *Benzhydryl Chloride.*

(1) Solvent, "90%" aqueous acetone; temperature, 50.0°. Initially, [RCl] = 0.0968. At equilibrium, ROH = 97.8%.

Time (mins.)	30.0	60.0	105	135	195	246	360
ROH formed (%)	10.1	19.5	31.7	39.5	50.4	61.5	76.0
10 ⁵ \bar{k}_1	5.94	6.03	6.04	6.00	6.19	6.49	6.58
10 ⁵ \bar{k}_1 (corr.)	5.94	6.05	6.07	6.05	6.30	6.67	6.83

(2) Solvent, "80%" aqueous acetone; temperature, 25.0°. Initially, [RCl] = 0.1015. At equilibrium, ROH = 100%.

Time (mins.)	32.9	55.9	80.9	110	141	176	219
ROH formed (%)	13.3	21.8	30.0	28.0	46.2	53.5	62.0
10 ⁵ \bar{k}_1	7.24	7.32	7.34	7.24	7.32	7.35	7.36

(b) *Benzhydryl Bromide.*

(3) Solvent, "80%" aqueous acetone; temperature, 25.0°. Initially, [RBr] = 0.1001. At equilibrium, ROH = 100%.

Time (mins.)	2.00	3.25	4.50	5.00	10.5	13.0	16.5	21.0
ROH formed (%)	19.2	28.6	38.0	46.2	65.7	73.8	80.8	88.1
10 ⁵ \bar{k}_1	178	173	174	172	169	172	167	170

(b) *Benzhydryl Bromide.*—In "90%" aqueous acetone at 50°, benzhydryl bromide is hydrolysed about 30 times faster than the chloride. The hydrolysis of the bromide, as measured by the development of acidity, is not detectably reversible, even with an initial

concentration of 0.1M. In very dilute solution the reaction follows the first-order law accurately, and with an initial concentration as high as 0.1M the deviations are still very small, as is illustrated in the third run in Table I. Reviewing the whole of the evidence, including that which relates to the effect of added salts, we believe this to indicate, not an absence of disturbances, but an approximate compensation of the ionic strength and mass-law effects, each of which is considerable. The conditions of the hydrolysis mentioned are those under which the first-order rate constants for the hydrolysis of benzhydryl chloride rose with the progress of reaction; and, as we shall show (Section 2), by reference to the influence of those salts which have not an anion in common with the halide, that ionic strength effects are at least as great for benzhydryl bromide as for the chloride, the steady rate constant for benzhydryl bromide means that the mass-law effect of the developed bromide ions must be greater than that of the chloride ions formed in the hydrolyses of benzhydryl chloride. This difference between bromide and chloride appears again when we consider the influence of added salts which have an anion in common with the halide (Section 2).

(2) *Salt Effects in the Hydrolyses of Benzhydryl Chloride and Bromide.*

(a) *Benzhydryl Chloride.*—Three salts have been used, sodium chloride, lithium bromide, and sodium azide. The last two, whose anions are different from that of the alkyl halide, increase the initial rate of reaction. The experiments with salts in 0.1M-concentration in "90%" aqueous acetone at 50° can be compared directly with corresponding experiments on the hydrolysis of *tert.*-butyl bromide in the presence of lithium chloride and sodium azide, which also have anions different from that of the alkyl halide. We find that the factor by which the initial rate is increased is considerably greater for benzhydryl chloride than for *tert.*-butyl bromide, the mean factor being 1.93 for the former halide and 1.39 for the latter. We interpret these increases of rate as an effect of ionic strength, and shall advance a reason later showing why the effect is greater for benzhydryl chloride (and, indeed, throughout the series of simple and substituted benzhydryl halides) than for *tert.*-butyl bromide (*ibid.*). It has already been observed that ionic strength effects are characterised by a strong solvent influence, being much reduced in more aqueous solvents. As a further illustration we may note that, whilst in "90%" aqueous acetone at 50° the initial rate of reaction of benzhydryl chloride is increased by the factor 2.13 in the presence of 0.1M-sodium azide, the same concentration of the salt in "70%" aqueous acetone at 25° increases the reaction rate only by the factor 1.31. We shall account quantitatively for the difference later (*ibid.*).

In marked contrast to the accelerating effects produced by salts other than chlorides, added sodium chloride and hydrogen chloride slightly reduced the rate of hydrolysis of benzhydryl chloride. In "80%" aqueous acetone at 25° the initial rate was changed by 0.02M-sodium chloride by the factor 0.97, and by 0.1M-hydrogen chloride by the factor 0.93. This is interpreted—and the interpretation will later be made quantitative—as a mass-law effect due to the identity of the added anion with the anion of the alkyl halide, the retarding influence being rather more than sufficient to neutralise the general accelerating effect of salinity.

The details of a number of experiments are shown in Table II. In the run with lithium bromide in "90%" aqueous acetone at 50°, the reaction was followed by the development of acidity: this measures the total decomposition of the original benzhydryl chloride, since any benzhydryl bromide formed from it by the intervention of bromide ions would be so rapidly hydrolysed that its formation would be kinetically indistinguishable from an equivalent amount of direct hydrolysis of the chloride. The reaction is perceptibly reversible and a correction for reversibility is applied to the constants by the method already described. The constants are very uniform owing to the partial buffering of the ionic strength, and to the relatively small nett effect of the developed hydrogen chloride.

The second run recorded in Table II relates to an experiment with added 0.1M-sodium azide in 90% aqueous acetone at 50°. The special interest of the use of this salt is that any intervention by azide ions produces benzhydryl azide, which is not hydrolysed and can therefore be directly estimated. We have followed the development of chloride ions, *i.e.*,

the total decomposition of benzhydryl chloride, and have also determined the proportions in which benzhydrol and benzhydryl azide are present in the product by a combination of measurements of the chloride ion and of the acidity. Contrary to our experience with *tert.*-butyl bromide, we find that azide ions intervene to a large extent in the hydrolysis of benzhydryl chloride, some 34% of benzhydryl azide being present in the final product. This explains why, in contrast to the experiments with *tert.*-butyl bromide and sodium azide, and also in contrast to the hydrolysis of benzhydryl chloride in the presence of lithium bromide, the rate constants for the total decomposition of benzhydryl chloride in the presence of sodium azide fall markedly with the progress of reaction. The reason is evidently that the extensive intervention by azide ions to form a stable product is progressively replacing an accelerating salt (sodium azide) by a retarding salt (sodium chloride). In the case of *tert.*-butyl bromide and sodium azide the intervention is not extensive, and in that of benzhydryl chloride and lithium bromide intervention does not form a stable product, so that the added salt does not disappear.

The third and fourth runs illustrate the effect of sodium chloride and hydrogen chloride on the hydrolysis in "80%" aqueous acetone at 25°. The constants are uniform, just as they are in the above-mentioned experiment with lithium bromide, and for substantially the same reasons.

TABLE II.

Integrated First-order Rate Constants (\bar{k}_1 in sec.⁻¹) of Hydrolysis and Total Reaction of Benzhydryl Chloride (RCl) and Benzhydryl Bromide (RBr) in the Presence of Salts.

(a) Benzhydryl Chloride.										
(i) Solvent, "90%" aqueous acetone. Temperature, 50.0°.										
(1) Initially, [RCl] = 0.0979, [LiBr] = 0.0964. At equilibrium, ROH = 97.5%.										
Time (mins.)	12.0	30	45	60	80	105	180	225	360	
ROH formed (%)	7.1	16.0	24.2	30.5	39.0	47.9	66.3	77.0	85.5	
$10^5 \bar{k}_1$	10.2	10.1	10.6	10.5	10.7	10.8	10.7	10.3	9.9	
$10^5 \bar{k}_1$ (corr.)	10.2	10.1	10.7	10.5	10.8	10.9	10.9	10.7	10.7	
(2) Initially, [RCl] = 0.0915, [NaN ₃] = 0.1009. At equilibrium, RCl destroyed = 100%.										
Time (mins.)	15	30	60	90	135	240	330	510		
RCl destroyed (%)	10.6	19.3	34.5	44.2	54.5	69.8	78.1	87.8		
$10^5 \bar{k}_1$	12.5	12.0	11.7	10.8	9.7	8.3	7.6	6.8		
(ii) Solvent, "80%" aqueous acetone. Temperature, 25.0°.										
(3) Initially, [RCl] = 0.0169, [NaCl] = 0.0190. At equilibrium, ROH = 100.0%.										
Time (mins.)	17.9	37.9	86.8	112	142	172	245	362		
ROH formed (%)	7.5	15.1	31.5	38.3	46.0	52.4	65.1	71.9		
$10^5 \bar{k}_1$	7.25	7.21	7.25	7.20	7.23	7.21	7.20	7.25		
(4) Initially, [RCl] = 0.0995, [HCl] = 0.0955. At equilibrium, ROH = 100%.										
Time (mins.)	13.0	33.0	56.0	110	141	176	219	435		
ROH formed (%)	5.2	13.0	20.8	36.5	43.7	51.0	59.3	83.9		
$10^5 \bar{k}_1$	6.87	7.04	6.95	6.87	6.79	6.76	6.85	6.98		
(b) Benzhydryl Bromide.										
(i) Solvent, "90%" aqueous acetone. Temperature, 50.0°.										
(5) Initially, [RBr] = 0.0974, [NaN ₃] = 0.1007. At equilibrium, RBr destroyed = 100%.										
Time (mins.)	1.00	3.25	6.00	11.00	18.0	22.0	27.0			
RBr destroyed (%)	19.6	46.0	64.9	81.0	91.0	94.4	96.9			
$10^5 \bar{k}_1$	365	317	290	352	225	218	211			

Note.—The last three readings of Expt. 2 are affected by a partial precipitation of sodium chloride. The expected effect of this is to render the calculated constants corresponding to these readings a little too low.

(b) *Benzhydryl Bromide.*—We have studied the hydrolysis of this substance in the presence of salts in "90%" aqueous acetone at 50°. The salts used were lithium bromide and sodium azide. We did not closely investigate the action of any ionised chlorides, because anion intervention, which preliminary experiments showed to be considerable, produces benzhydryl chloride, which is hydrolysed more slowly than the original bromide, so that the developed acidity measures no simple process, but only a combination of

consecutive hydrolyses in shifting proportions; and the estimation of developed bromide ions, which would have measured the total rate of destruction of the original alkyl halide, is not sufficiently simple in the presence of chloride ions.

Under the conditions mentioned, 0.1M-sodium azide increased the initial rate of decomposition of benzhydryl bromide by the factor 2.07, which is slightly greater than the corresponding factor expressing the effect of the same salt on the reaction rate for benzhydryl chloride. We shall find that a small difference in the observed direction would be expected theoretically (*ibid.*).

Lithium bromide, which, having no ion in common with benzhydryl chloride, accelerated its hydrolysis, retards the hydrolysis of benzhydryl bromide, consistently with the idea that this and similar retardations are due to the over-compensation of the normal accelerating effect of salts by a mass-law effect which can arise only when the alkyl halide and the salt have a common anion. With the salt in 0.1M-concentration the initial rate was decreased by the factor 0.80, and this represents a considerably larger retardation than that produced by chlorides on the hydrolysis of benzhydryl chloride.

The reaction with added sodium azide is illustrated in the fifth run of Table II. The integrated first-order constants representing the total rate of destruction of the alkyl halide fall with progress of reaction owing to the large degree of intervention by the azide ions, and the consequential replacement of the accelerating salt, sodium azide, by the retarding salt, sodium bromide. The extent of this intervention is measured by the observation that the final product contained 34.5% of benzhydryl azide.

EXPERIMENTAL.

The methods are generally similar to those of the experiments described in the preceding paper.

We record a few additional first-order constants ($k_1^{(o)}$ or $k_1^{(c)}$ in sec.⁻¹) relating to the initial rate of hydrolysis of benzhydryl chloride (RCl) and benzhydryl bromide (RBr) in various solvents, with or without added salts. The third and fourth of the following series directly measure the salt effect of sodium azide on the hydrolysis of benzhydryl chloride in "70%" aqueous acetone at 25°. The rate constant for the fourth experiment is that of the total reaction of the benzhydryl chloride, as measured by the liberation of chloride ions. The fifth experiment, in conjunction with the third of those recorded in Table I, measures the salt effect of lithium bromide on the hydrolysis of benzhydryl bromide in "90%" aqueous acetone at 50°:

(1)	" 90% "	Aqueous acetone at 25°; initially [RCl] = 0.0182	$10^5 k_1^{(o)} = 0.460^*$
(2)	" 80% "	" " " 0°; " " = 0.0179	$10^5 k_1^{(o)} = 0.282$
(3)	" 70% "	" " " 25°; " [RCl] = 0.1143	$10^5 k_1^{(o)} = 32.0$
(4)	" " "	" " " " ; " " = 0.1110, [NaN ₃] = 0.0999 = <i>c</i>	$10^5 k_1^{(c)} = 41.8$
(5)	" 90% "	" " " 50°; " [RBr] = 0.1042, [LiBr] = 0.1013 = <i>c</i>	$10^6 k_1^{(c)} = 161$

In connexion with all the experiments involving sodium azide it was necessary to prove (i) that benzhydryl azide is not hydrolysed, and (ii) that benzhydryl is not "esterified" by hydrazoic acid, under the conditions of the experiments. The first point was established by the constancy of the "infinity" values for the development of acidity. The second was settled by special experiments in which benzhydryl and hydrazoic acid replaced respectively the benzhydryl halide and the sodium azide of the hydrolytic runs: determinations of acidity over periods of time sufficient to complete the corresponding hydrolyses showed that no esterification was taking place.

The material of this paper originated in preliminary measurements which were carried out by Dr. N. A. Taher in these Laboratories in 1937. These were the first observations to suggest to us that the mass-law ("common-ion") effect in the unimolecular mechanism could be observed with ease in certain cases.

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* The medium used in this experiment was part of a different batch from that employed for the comparative experiments, recorded in the introduction, on benzhydryl chloride in "90%" aqueous acetone, with or without added salts.