186. *Mechanism of Substitution at a Saturated Carbon Atom. Part XXI. A Kinetic Demonstration of the Unimolecular Solvolysis of Alkyl Halides. (Section C) Kinetics of, and Salt Effects in, the Hydrolysis of* p-*Monoalkylbenzhydryl Halides in Aqueous Acetone.*

By Mervyn G. Church, Edward D. Hughes, Christopher K. Ingold, and Nazeer Ahmed Taher.

In a further investigation in accordance with the scheme explained in the abstract on p. 960, the kinetics of the hydrolysis of *p-tert.*-butylbenzylhydryl and *p*-methylbenzhydryl chlorides in acetone–water mixtures have been studied. These compounds show relatively strong deviations from first-order kinetics, of the kind attributable to the special mass-law effect associated with the unimolecular mechanism. The influence of added " salts ", such as hydrogen and sodium chloride, lithium bromide and sodium azide, on the reaction rate also shows the importance of this mass-law effect. Taken altogether, the experiments show that, although the accelerating electrostatic effect of electrolytes in general is larger with these alkylbenzhydryl halides than with simple benzhydryl halides, the retarding mass-law effect, which distinguishes the unimolecular mechanism, is larger by a greater margin, and therefore controls the qualitative results more strikingly and over a wider range of conditions. Detailed discussion is deferred to p. 979.

In this paper we record experiments on the kinetic form of the hydrolysis in aqueous acetone of the two monoalkyl compounds, *p-tert.*-butyl- and *p*-methyl-benzhydryl chloride, as well as on the effects of various salts on the rate of reaction. In " 90% " aqueous acetone the opposing ionic strength and mass-law effects would appear to be of the same order of magnitude, as the deviations from the kinetic form of the first-order rate law are relatively small. In " 80% " aqueous acetone, however, the ionic strength effect becomes reduced (preceding two papers), and now the mass-law effect dominates strongly for both alkyl chlorides. The predominance of the mass-law effect is greater for the alkylbenzhydryl chlorides than for unsubstituted benzhydryl chloride, and greater for the methyl than for the *tert.*-butyl compound. Consistently with the previous paper we find that, whilst salinity in general increases the reaction rate, the addition of ionised chlorides decreases it. Under comparable conditions the depressions of rate produced by added chlorides are more marked than for unsubstituted benzhydryl chloride (preceding paper), and more marked for the *p*-methyl than for the *p-tert.*-butyl derivative.

(1) *Kinetics of Hydrolysis of* p-tert.*-Butyl- and* p-*Methyl-benzhydryl Chloride.*

(a) p-tert.*-Butylbenzhydryl Chloride.*—In very dilute solution (< 0·02M) in either " 90% " or " 80% " aqueous acetone (acetone containing 10 or 20 vols. % of water), this compound is hydrolysed completely, and the reaction accurately follows the first-order rate law. In somewhat more concentrated solution (*e.g.*, 0·05M) in " 90% " aqueous acetone, the hydrolysis is still substantially irreversible, the equilibrium proportion of *p-tert.*-butylbenzhydrol being at least 99·8%, but the integrated first-order rate constants rise slowly with the progress of reaction. An experiment illustrating this is included in Table I. In " 80% " aqueous acetone the hydrolysis is quite irreversible, even with an initial concentration of alkyl halide as high as 0·1M; but now the integrated first-order constants fall considerably as the reaction progresses. This is exemplified in the second experiment in Table I.

(b) p-*Methylbenzhydryl Chloride.*—At great dilutions (< 0·02M) the hydrolysis of this substance follows the first-order rate law very exactly in both " 90% " and " 80% " aqueous acetone. At larger concentrations the first-order rate law is still approximately obeyed in the " 90% " solvent, but in the " 80% " solvent it is not, the first-order rate constants now falling rather steeply with the progress of reaction, as illustrated in the third experiment of Table I, notwithstanding that the reaction is quite irreversible under these conditions. The results for benzhydryl chloride and its *p-tert.*-butyl and *p*-methyl derivatives are consistent: in the " 90% " solvent in which the first-order rate constants for the first rise strongly, those of the second rise slightly, and those of the third remain nearly steady; and in the " 80% " solvent for which the constants of the first remain steady, those of the second fall, and those of the third fall more steeply. This agrees with the idea of an ionic strength effect which diminishes from " 90% " to " 80% " aqueous acetone, and a mass-law effect which increases from benzhydryl chloride through its *tert.*-butyl to its methyl derivative.

TABLE I.

Integrated First-order Rate Constants ($\bar{k}_1$ *in sec.*$^{-1}$) *of Hydrolysis of* p-tert.-*Butyl- and* p-*Methyl-benzhydryl Chloride in Aqueous Acetone.*

(a) p-tert.-*Butylbenzhydryl Chloride.*

(1) Solvent, " 90% " aqueous acetone; temperature, 50·0°; initially, [$Bu^{\gamma}\cdot C_6H_4\cdot CHPhCl$] = 0·0471.

Time (mins.)	7·2	12·0	24·0	36·0	45·0	55·0
ROH formed (%)	21·2	33·1	55·5	69·9	78·2	82·9
$10^5\bar{k}_1$	54·9	56·0	55·5	55·8	56·9	57·6

(2) Solvent, " 80% " aqueous acetone; temperature, 25·0°; initially, [$Bu^{\gamma}\cdot C_6H_4\cdot CHPhCl$] = 0·0794.

Time (mins.)	3·03	5·58	13·45	17·5	22·5	35·0
ROH formed (%)	12·5	21·7	43·5	51·7	60·5	76·3
$10^5\bar{k}_1$	73·2	73·0	70·5	68·5	68·8	68·5

(b) p-*Methylbenzhydryl Chloride.*

(3) Solvent, " 80% " aqueous acetone; temperature, 25·0°; initially, [$Me\cdot C_6H_4\cdot CHPhCl$] = 0·1005.

Time (mins.)	0·55	3·62	5·37	7·63	10·09	14·4	18·9
ROH formed (%)	5·0	25·5	35·1	44·5	53·5	64·9	73·9
$10^5\bar{k}_1$	155	136	135	129	127	122	118

(2) *Salt Effects in the Hydrolysis of* p-tert.-*Butylbenzhydryl Chloride and* p-*Methylbenzhydryl Chloride.*

(a) p-tert.-*Butylbenzhydryl Chloride.*—Comparisons have been carried out in " 90% " aqueous acetone at 50°, and in " 80% " aqueous acetone at 25°. Under the first-named conditions ionic strength effects were observed with lithium bromide and sodium azide, which in 0·1M-concentration increased the initial rate of the total reaction by the factors 1·95 and 2·88 respectively. These factors are substantially greater than those which represent the effect of the same two salts on the initial rate of reaction of unsubstituted benzhydryl chloride. In the case of sodium azide the effect of halving the concentration of the salt was examined: this reduced the factor by which the initial rate is increased from 2·88 to 1·70. It will be noticed that the former factor is equal to the square of the latter, and this is in accordance with the theory of the ionic strength effect given in the next paper but one. Using " 80% " aqueous acetone as solvent, we have examined the effect of sodium chloride: in 0·1M-concentration this reduces the initial rate of hydrolysis by the factor 0·75, the mass-law effect due to the anion common to the salt and the alkyl halide overcoming the normal acceleration due to salinity.

The details are illustrated in Table II. In the experiment with lithium bromide in " 90% " aqueous acetone we have applied the small correction for reversibility. The constants are fairly steady: as we have reduced the initial concentration of alkyl halide to about 0·05M in all these experiments, the ionic strength is on the whole better buffered by the added salts than in the corresponding experiments of the two preceding papers. In the experiments with sodium azide the fall in the integrated first-order rate constants for the total reaction indicated a large intervention by azide ions, leading to an extensive replacement of sodium azide by sodium chloride as reaction progresses. The results of direct measurement of this intervention are shown in run 2. Taking account of the dependence of the rate of intervention on concentration (following paper), it can be shown that the data represent a perceptible increase of intervention over that found for unsubstituted benzhydryl chloride. This is what we should expect from our knowledge that the *p-tert.*-butyl substituent causes an increased mass-law retardation of hydrolysis, which we interpret as due to an analogous intervention of chloride ions.

TABLE II.

Integrated First-order Rate Constants ($\bar{k}_1$ *in sec.*$^{-1}$) *of Hydrolysis and Total Reaction of* p-tert.-*Butylbenzhydryl Chloride* (RCl) *in Aqueous Acetone in the Presence of Salts.*

(A) *Solvent,* " 90% " *aqueous acetone ; temp.*, 50·0°.

(1) Initially, [RCl] = 0·0478, [LiBr] = 0·1035. At equilibrium, ROH = 98·7%.

Time (mins.)	1·5	3·0	6·5	12·0	15·0	19·0	24·0	30·0	39·0
ROH formed (%)	10·0	18·4	34·1	53·8	62·0	68·0	76·0	83·8	88·2
$10^5\bar{k}_1$ (corr.)	107	107	106	107	107	106	102	105	96

(2) Initially, [RCl] = 0·0483, [NaN$_3$] = 0·0501. At equilibrium, RCl destroyed = 100%.

Time (mins.)	5·0	8·0	16·5	19·0	24·0	29·0	36·0	45·0	60·0	90·0
RCl destroyed (%)	21·1	32·4	53·2	60·2	67·0	73·3	77·7	84·2	92·0	93·9
$10^5\bar{k}_1$	87·5	84·7	81·7	77·5	73·2	70·1	64·5	60·2	59·3	51·8

Time (mins.)	3·0	6·0	10·5	15·0	20·0	27·5	35·0	50·0	70·0	105	∞
ROH formed (%)	7·3	15·2	25·1	33·0	39·5	46·0	50·0	57·5	62·3	67·0	66·7

Total reaction (%)	10	20	40	60	80	100
Proportions ROH (%)	60	61	62	63	64	64·5
Proportions RN$_3$ (%)	40	39	38	37	36	35·5

(3) Initially, [RCl] = 0·0466, [NaN$_3$] = 0·1000. At equilibrium, RCl destroyed = 100%.

Time (mins.)	1·5	3·1	5·0	8·0	12·0	15·0	19·0	24·0	29·0	36·0	45·0	60·0
RCl destroyed (%)	12·0	23·6	33·1	46·0	57·6	63·0	70·4	76·0	81·9	89·6	90·8	93·2
$10^5\bar{k}_1$	143	146	132	128	120	111	107	100	97	83	88	75

(B) *Solvent,* " 80% " *aqueous acetone ; temp.*, 25·0°.

(4) Initially, [RCl] = 0·0825, [NaCl] = 0·1000. At equilibrium, ROH = 100%.

Time (mins.)	1·1	2·6	3·5	5·7	8·0	10·6	14·3	17·9	22·9	35·0
ROH formed (%)	3·0	6·9	9·4	14·5	20·2	25·8	32·0	39·0	47·2	58·5
$10^5\bar{k}_1$	47·7	46·3	46·8	45·8	46·8	46·9	45·9	45·9	46·4	44·8

(b) p-*Methylbenzhydryl Chloride.*—This example was investigated less fully than the preceding one because the change of structure is comparatively slight and the effect of a more drastic change in the same direction was being studied (following paper). Using "80%" aqueous acetone at 25°, conditions under which hydrolysis is not perceptibly reversible, we found that added sodium chloride and added hydrogen chloride produced diminutions of rate agreeing approximately in magnitude with the deviation from first-order kinetics which was observed in the hydrolysis of *p*-methylbenzhydryl chloride without added substances. Typical experiments are recorded in Table III.

TABLE III.

Integrated First-order Rate Constants ($\bar{k}_1$ *in sec.*$^{-1}$) *of Hydrolysis of* p-*Methylbenzhydryl Chloride* (RCl) *in* " 80% " *Aqueous Acetone at* 25·0° *in the Presence of Chlorides.*

(1) Initially, [RCl] = 0·0355, [NaCl] = 0·0365.

Time (mins.)	1·10	2·35	3·70	5·50	8·10	11·1	15·2
ROH formed (%)	7·6	15·2	23·6	33·3	43·6	54·8	66·0
$10^5\bar{k}_1$	120	118	120	122	118	119	118

(2) Initially, [RCl] = 0·0314, [HCl] = 0·0385.

Time (mins.)	1·4	2·4	3·7	5·6	8·0	11·1	15·2	20·3
ROH formed (%)	10·1	16·2	24·8	34·5	45·5	57·3	68·3	77·9
$10^5\bar{k}_1$	127	123	128	126	126	128	127	123

EXPERIMENTAL.

p-Methyl- and *p*-*tert.*-butyl-benzhydryl chlorides were prepared as described in an accompanying paper (this vol., p. 949).

The kinetic methods and auxiliary experiments were similar to those described in the two immediately preceding papers (this vol., pp. 960 and 966).

Two additional rate constants seem worth recording, one to show the effect of solvent composition on the rate of hydrolysis of *p*-methylbenzhydryl chloride (RCl), and the other to illustrate the relatively small dependence on salt concentration of the effect of added hydrogen chloride on the rate of this hydrolysis. As was shown in the experiments with sodium azide, the ionic strength effect is largely dependent on the salt concentration; and so also is the mass-law effect, as was illustrated by the proportion of intervention by azide ions. These two effects lead to a relatively small nett effect of concentration where, as in the case of added chloride ions, they both occur together. The rate constants [$k_1^{(0)}$ and $k_1^{(c)}$ in sec.$^{-1}$] are given below together with data for comparison.

" 90% " Aqueous acetone, 25·0°; initially, [RCl] = 0·0160 .... $10^5k_1^{(0)}$ = 9·46
" 80% " ,, ,, ,, ,, ,, = 0·0152 .... ,, = 157
,, ,, ,, ,, ,, ,, = 0·1005 .... ,, = 160
,, ,, ,, ,, ,, ,, = 0·0314, [HCl] = 0·0385 = *c* ... $10^5k_1^{(c)}$ = 126
,, ,, ,, ,, ,, ,, = 0·0854, [HCl] = 0·0950 = *c* ... ,, = 117

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

[*Received, April 18th,* 1940.]