

184. *Mechanism of Substitution at a Saturated Carbon Atom. Part XIX. A Kinetic Demonstration of the Unimolecular Solvolysis of Alkyl Halides. (Section A) Kinetics of, and Salt Effects in, the Hydrolysis of tert.-Butyl Bromide in Aqueous Acetone.*

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The statement that both the bimolecular and the unimolecular mechanism of substitution require essentially first-order kinetics for substitutions in which the reagent is a sufficiently important constituent of the solvent to have a buffered concentration is substantially true for bimolecular substitution (S_N2); but for unimolecular substitution (S_N1) it is only true as a limit, from which large deviations of a highly characteristic nature are possible. These deviations arise essentially from the reversibility of the rate-determining ionisation. This reversibility gives rise to a distinctive type of retardation in what may be a completely irreversible substitution. For the same reason those added salts whose anions are identical with that given by the alkyl halide will, in contradistinction to all other salts, depress the rate of substitution. These special effects are opposite in direction to the general effect, due to electrostatic causes, of all electrolytes, which is to increase reaction rate. All these influences are capable of quantitative theoretical treatment. The effects which sharply distinguish the unimolecular mechanism are expected to vary in intensity with the alkyl group in such a way as to require the investigation of a graded series of those alkyl halides which, on less direct evidence, are already believed to undergo solvolysis by the unimolecular mechanism.

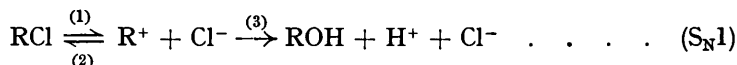
In order to provide data for the application of the kinetic criterion mentioned, such an investigation is here commenced with the hydrolysis of *tert.*-butyl bromide in aqueous acetone, at two temperatures and in two acetone-water mixtures, since theory predicts quantitatively how the deviations from first-order kinetics should vary with temperature and solvent composition. The addition of three salts was studied, one "common-ion" salt, lithium bromide, and two "non-common-ion" salts, lithium chloride and sodium azide. The reason for using sodium azide was that any intervention by azide ions in the substitution process, in contrast to intervention by bromide or chloride ions, leads to a stable substitution product (*tert.*-butyl azide), so that the extent of intervention can be directly checked. Detailed discussion of the results is deferred to p. 979.

Introduction to a Group of Papers.

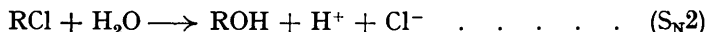
THIS is the first of a small group of connected papers within the main series. The conclusions reached are set out in the fifth and last paper of this internal group (this vol., p. 979). We therefore confine our preliminary statement to the general plan underlying this section of our work.

We have repeatedly emphasised the distinction between mechanism and reaction order in aliphatic substitution, pointing out that, although bimolecular substitutions are usually of second order and unimolecular of first, the correlation is not general. The familiar example is that in which the reagent is the solvent, and the usual statement is that, as the bimolecular mechanism now requires first-order kinetics, the reaction order provides no criterion of mechanism. We are going to consider, however, whether it is not possible even in this case to devise a kinetic criterion of mechanism; and we shall find that this is possible, because, although it remains true that bimolecular solvolytic substitutions must belong to the first-order type, unimolecular solvolytic substitutions need not do so. Our conclusion will, indeed, be that it is only under limiting conditions, which in general are not satisfied, that unimolecular substitutions should be of first order, and that therefore a study of the predictable deviations from this kinetic form provides a highly distinctive criterion for the unimolecular mechanism.

As a simplified illustration let us consider the unimolecular hydrolysis of an alkyl chloride in an aqueous solvent. We may suppose, either that the reaction is experimentally irreversible, or that, the hydrolysis being reversible, the forward reaction has been kinetically isolated from its inverse. The component processes being labelled (1), (2), and (3) as follows,



the usually mentioned condition for first-order kinetics is the rate inequality $v_1 \ll v_3$, where the v 's are instantaneous rates. However, there is really a second condition; for, with $v_1 \ll v_3$ only, the observed rate is $v_1 v_3 / (v_2 + v_3)$; this leads to a complicated time-law, which reduces to the first-order law, corresponding to the rate, v_1 , of ionisation, only if, in addition, $v_2 \ll v_3$. The nature of the deviations which obtain on removing this second restriction can be deduced by application of the mass law. The formula shows that calculated first-order rate constants should diminish with the progress of reaction, and should diminish more steeply the higher the original concentration of the alkyl chloride. Furthermore the whole rate should be decreased if we add an ionised chloride (but not any other ionised salt) initially, because this increases v_2 , and therefore decreases $v_1 v_3 / (v_2 + v_3)$. None of these quantitative deductions will apply to the bimolecular mechanism,



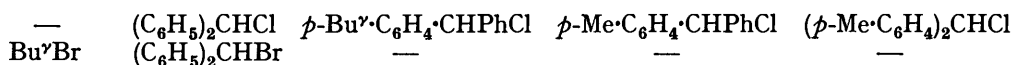
In this case, if the hydrolysis is irreversible or kinetically isolated from its inverse, it should proceed at a first-order rate which is uniform, independent of the initial concentration of alkyl chloride, and independent of initially added chloride ions.

The above is an over-simplified description, because in all real cases the varying ionic strengths of the solutions cause departure from classical kinetic forms. It can, however, be shown both theoretically and experimentally that this universal disturbance is qualitatively

opposite to the special deviation which arises under the mass-law in the unimolecular mechanism when the limiting situation, represented by $v_2 \ll v_3$, does not obtain. We shall find that, independently of mechanism, the ionic strength effect leads to calculated first-order constants which rise with progress of reaction, and rise more steeply the higher the initial concentration of alkyl chloride. Moreover, the whole rate should be increased by this effect if we add initially either an ionised chloride, or any other ionised salt. The only difference between the unimolecular and the bimolecular mechanism is that the former should be much more sensitive to these effects than the latter.

The position is then, that whilst the bimolecular mechanism of hydrolysis requires an ionic strength disturbance only, the unimolecular mechanism requires a superposition of two opposite disturbances, one of which, the ionic strength effect, is applicable universally, whilst the other, the mass-law effect, applies only in those cases in which there is an appreciable departure from the limiting situation $v_2 \ll v_3$. The object of these researches was to seek the mass-law effect, because it is characteristic for the unimolecular mechanism; and we naturally sought it in examples of a type for which, on other evidence, a unimolecular mechanism had previously been assumed. Amongst these, it was possible to indicate in advance the types of alkyl halide in which the mass-law disturbance should be weakest and the types in which it should be strongest. As we shall show, the rule is that the mass-law effect should increase as we change the alkyl group in such a way as to facilitate ionisation of the alkyl halide, *e.g.*, $\text{Bu}^\gamma\text{Cl} < \dots < \text{Ph}_3\text{CCl}$. Therefore, if we fill intermediate members into such a series, the left-hand members should show the universal ionic strength effect in a most nearly pure form, whilst the right-hand members should reveal a pronounced, and, with good fortune, dominating, mass-law effect. We shall find that in fact the dominance of the mass-law effect occurs at quite an early stage of progress through such a series. We need not develop these preliminary considerations further here, but it will emerge later that the mass-law effect is definitely distinguishable, not only by its direction, and by the special part played amongst ionised salts by those salts whose anions are identical with that formed from the alkyl halide, but also by several other criteria, qualitative and quantitative. A certain detection of the mass-law effect is an equally certain proof of the unimolecular mechanism—a direct kinetic proof, such as we used to think it would be difficult to provide for solvolytic reactions.

With this picture of the situation in mind, a number of parallel investigations were instituted on alkyl halides forming a series of the general nature indicated above. For experimental reasons we did not go so far as to include triphenylmethyl halides, which are inconveniently reactive, but instead introduced alkyl groups in order to increase ionising tendency in the benzhydryl series. This gave us all we wanted. The compounds were



and their investigation is described in the sequel. The reason for the serial order of the two monoalkyl benzhydryl chlorides will become clear on reference to a preceding paper (this vol., p. 949).

(2) Kinetics of the Hydrolysis of *tert.*-Butyl Bromide.

tert.-Butyl bromide is the simplest case in which to establish the ionic strength effect. As ionic strength effects are expected to be more pronounced in not too highly aqueous solvents, we used mainly "90%" aqueous acetone as solvent, but also, for contrast, "70%" aqueous acetone, *i.e.*, acetone containing 10 and 30 vols. % of water respectively. A much drier acetone solvent than "90%" aqueous acetone might (for all that we know at present) have caused some departure from the pure unimolecular mechanism; and it would certainly have introduced experimental difficulties into the work described in section (3). It has been shown before that *tert.*-butyl halides initially in dilute solution (<0.05M) give good first-order rate constants in aqueous solvents; we now used rather larger initial concentrations (~0.1M), large enough to bring out the ionic strength effect, yet not so large as to render the quantitative theory of the effect (this vol., p. 979) unmanageable.

Table I shows how the integrated first-order rate constant, $\bar{k}_1 = (1/t)\log_e\{a/(a-x)\}$ (the bar denotes integration), rises steadily with the percentage progress of reaction, which is here followed by the development of acidity. An indirect indication is obtained in the next section that this rise is an almost pure ionic strength effect. Probably if the mass-law effect were entirely absent the drifts illustrated would be very slightly steeper, but this is not important in relation to the experimental error.

TABLE I.

Integrated First-order Rate Constants (\bar{k}_1 in sec.⁻¹) of Hydrolysis of tert.-Butyl Bromide in Aqueous Acetone.

(1) Solvent, "90%" aqueous acetone. Temperature, 50.0°. Initially, [Bu ^ν Br] = 0.1056.												
Time (mins.)	9.0	18.0	27.0	40.0	54.0	72.0	105	135	180			
Bu ^ν OH formed (%)	9.9	18.9	27.3	38.9	49.2	59.0	74.4	83.5	91.6			
10 ⁵ \bar{k}_1	19.3	19.4	19.7	20.5	20.5	21.2	21.7	22.2	23.0			
(2) Solvent, "90%" aqueous acetone. Temperature, 25.0°. Initially, [Bu ^ν Br] = 0.1039.												
Time (hrs.)	3.15	4.10	6.20	8.20	10.00	13.50	18.3	26.0	30.8	37.3	43.8	
Bu ^ν OH formed (%)	13.7	17.4	25.3	32.5	38.5	49.1	66.0	74.0	80.1	86.3	90.3	
10 ⁵ \bar{k}_1	1.30	1.30	1.31	1.34	1.36	1.40	1.44	1.45	1.47	1.49	1.50	
(3) Solvent, "70%" aqueous acetone. Temperature, 25.0°. Initially, [Bu ^ν Br] = 0.1049.												
Time (mins.)	1.10	3.20	8.40	12.50	17.40	23.95	31.30	41.45	52.0	65.9	84.4	
Bu ^ν OH formed (%)	3.4	9.4	23.0	32.6	42.5	54.1	64.0	74.1	81.9	88.8	94.1	
10 ⁵ \bar{k}_1	52.0	51.5	51.9	52.7	53.1	54.4	54.5	54.7	54.9	55.3	56.2	

Three runs are recorded because we shall require this amount of illustration in the eventual discussion (*ibid.*). It will appear that the ionic strength effect is distinguished by a definite, quantitatively predictable, variation with the temperature and solvent-composition; wherefore a comparison of the kinetic deviations observed under different conditions of temperature and solvent-composition affords a means of identifying the effect, and of assessing its freedom from other disturbances.

Special experiments showed that the degree of reversibility of the reaction under all the conditions used was below the limits of certain measurement: the proportion of *tert.*-butyl alcohol ultimately produced even in "90%" aqueous acetone was at least 99.8% of the stoichiometric quantity, and, of course, it must have been still higher in the "70%" solvent. The point is not important for this example considered alone, but it becomes important in the discussion of mass-law effects, for which *tert.*-butyl bromide is to be treated as the control case.

(3) Salt Effects in the Hydrolysis of *tert.*-Butyl Bromide.

In these experiments we have used "90%" aqueous acetone throughout, the temperature being 50.0°. Three neutral salts were investigated, one, lithium bromide, having an anion identical with that formed from the alkyl halide; the other two salts were lithium chloride and sodium azide. The salt concentrations and the initial concentration of *tert.*-butyl bromide were all of order 0.1M.

The effect of added lithium bromide is illustrated in the upper part of Table II. In the first place, the whole rate of reaction, which is again followed by the development of acidity, is considerably raised, the initial rate being increased by the factor 1.44. This also is a nearly pure ionic strength effect, and we shall find (*ibid.*) that the increase of rate is nearly of the value to be expected on the basis of the deviations from first-order kinetics in the absence of added salts. Secondly, the calculated first-order constant is steadier than in the absence of the salt. This is attributed in part to the smaller proportionate change of ionic strength during reaction, and in part to the known limitation placed on ionic strength effects in more concentrated solutions by the finite size of the ions. Thirdly there is now a small but definite degree of reversibility, the directly measured equilibrium proportion of *tert.*-butyl alcohol being 99.5%. In order to correct for this we replace the usual formula, $\bar{k}_1 = (1/t)\log_e\{a/(a-x)\}$, for irreversible hydrolysis, by the

formula, $\bar{k}_1(r) = (1/t) \log_e\{x_\infty/(x_\infty - x)\}$, for a reversible first-order process, because the forward reaction is very nearly of first order as shown by the relative steadiness of the constant \bar{k}_1 , and, although we do not know the kinetics of the back-reaction, the proportionate change in the concentrations of its reactants between complete hydrolysis and the equilibrium point is very small. The corrected constants for the "kinetically isolated" forward reaction are then 0.995 times these composite "reversible" constants. In the present case the correction does not exceed experimental error, but corrected constants, \bar{k}_1 (corr.), are listed in Table II.

The effects observed with added lithium chloride are illustrated in the middle part of Table II. The position here is somewhat more complicated, and it is necessary to note that we again followed hydrolysis by the development of acidity. It will be seen that the

TABLE II.

Integrated First-order Rate Constants (\bar{k}_1 in sec.⁻¹) for the Hydrolysis and Total Reaction of tert.-Butyl Bromide in the Presence of Salts. Solvent, "90%" Aqueous Acetone. Temperature, 50.0°.

(1) Initially: [Bu ν Br] = 0.1056, [LiBr] = 0.1065. At equilibrium, Bu ν OH = 99.6%.

Time (mins.)	6.0	12.0	27.0	36.0	48.0	60.0	84.0
Bu ν OH formed (%)	9.6	18.3	37.4	45.9	56.0	64.6	76.7
10 ⁵ \bar{k}_1 (corr.)	27.8	28.1	29.0	28.6	28.7	29.1	29.1

(2) Initially: [Bu ν Br] = 0.1016, [LiCl] = 0.1005. At equilibrium, Bu ν OH = 100%.

Time (mins.)	6.00	12.0	19.0	27.0	36.0	48.0	60.0	78.0	100	128	180	240
Bu ν OH formed (%)	9.1	17.5	26.2	35.0	43.2	53.7	61.0	69.7	77.8	83.9	89.0	91.7
10 ⁵ \bar{k}_1	26.5	26.7	26.7	26.7	26.0	26.7	26.2	25.5	24.3	23.2	20.3	16.6

(3) Initially: [Bu ν Br] = 0.1049, [NaN₃] = 0.1000. At equilibrium Bu ν Br destroyed = 100%.

Time (mins.)	12.0	19.0	27.0	36.0	48.0	60.0	84.0	110	135	225		
Bu ν Br destroyed (%)	14.7	26.3	36.5	45.4	55.5	61.5	73.6	81.9	87.1	97.0		
10 ⁵ \bar{k}_1	25.8	26.5	27.8	27.7	27.3	26.2	26.2	25.3	25.3	—		
Time (mins.)	6.00	12.0	19.0	27.0	36.0	48.0	60.0	84.0	108	135	210	∞
Bu ν OH formed (%)	9.1	16.5	24.8	32.5	39.3	47.5	54.9	66.2	73.0	79.0	86.5	93.9
10 ⁵ \bar{k}_1	26.3	25.0	24.9	24.2	25.2	24.0	23.8	23.5	22.5	19.2	15.7	—

lithium chloride produces a general increase of rate of the same order of magnitude as that caused by lithium bromide; the initial rate is now raised by the factor 1.39. The integrated first-order rate constants, as calculated from the formula for irreversible hydrolysis, are steady as compared with those obtained in the absence of salts, but towards the close of reaction there is a rather marked fall in these constants. No doubt a small part of this fall is due to the slight back-reaction we observed with lithium bromide, partly replaced in the present case by an analogous interaction between *tert.*-butyl alcohol and hydrogen chloride. But this is not the whole cause, for, if it were, the reaction should cease in approximate accordance with an exponential time-law, whereas actually it ceases very much less abruptly. We account for this partly on the internal evidence, and partly on the indirect evidence given in the next paragraph. Our conclusion is that, although the ionic strength effect is by far the most important kinetic disturbance in the hydrolysis of *tert.*-butyl bromide, anions such as bromide and chloride do intervene in hydrolysis to a small extent. We are not here considering the mechanism of the intervention, which might be bimolecular or unimolecular; *i.e.*, the anion might attack either the *tert.*-butyl bromide molecule or the pre-formed *tert.*-butyl cation. In either case, bromide ions will regenerate *tert.*-butyl bromide; and, if the mechanism is bimolecular, this will be completely without chemical consequences (except such as might be checked by isotopic indicator methods); whilst, if it is unimolecular, the only result will be a mass-law depression of rate, which we cannot hope directly to detect (except possibly by isotopic indicator methods) in the presence of the large ionic strength acceleration. On the other hand, chloride ions will produce *tert.*-butyl chloride, which is hydrolysed considerably more slowly than the bromide (the factor representing the difference has not been determined, but may be assumed to be about 33); and we have followed, not the liberation of bromide ions, but the development of

acidity, that is, the combined hydrolysis of the *tert.*-butyl bromide and any *tert.*-butyl chloride formed from it in the course of reaction. The formation of a few units % of *tert.*-butyl chloride would, of course, reduce the total hydrolysis rate considerably when, towards the end of reaction, the chloride has become an important constituent of the still unhydrolysed alkyl halides.

The direct intervention of anions can be more simply established by means of experiments with sodium azide, because *tert.*-butyl azide, when once formed, is not hydrolysed under the conditions used; so that, both the total rate of destruction of *tert.*-butyl bromide, and that part of the rate which represents hydrolysis to *tert.*-butyl alcohol, can be separately evaluated by following both the liberation of bromide ions and the development of acidity. Data of this type are shown in the bottom part of Table II. The total decomposition of *tert.*-butyl bromide has again an enhanced rate, the increase being of the same order as the increases produced by lithium bromide and lithium chloride. The initial rate is increased by the factor 1.40, and the integrated rate constant is again fairly steady. On the other hand, the part of the decomposition which results in the production of acidity gives rate constants which fall towards the end of reaction more markedly than the corresponding constants obtained in the experiments with lithium chloride: indeed the rate falls to zero when 94% of the theoretical quantity of *tert.*-butyl alcohol has been produced. This means that 6% of *tert.*-butyl azide is formed, and the conclusion that azide ions intervene in approximately this proportion right through the reaction is confirmed by a comparison of the initial rates obtained by the two methods of measurement; for the absolute initial rate as measured by the development of acidity is smaller by about 5% than the corresponding rate given by the determination of bromide ions. Since we shall show in the following papers that the proportions in which chloride, bromide, and azide ions intervene in the hydrolysis of other alkyl halides are all roughly of the same order of magnitude (for the same alkyl halide and the same concentration of added anions), we are confirmed in our conclusion that a few units % of *tert.*-butyl chloride are formed and subsequently destroyed during the hydrolysis of *tert.*-butyl bromide in the presence of added lithium chloride. The above argument is also the basis of our assumption that an analogous small intervention by bromide ions is present in the hydrolysis with added lithium bromide; and even to a still smaller degree in the hydrolysis of *tert.*-butyl bromide alone, though the methods we have used cannot directly detect the effects in these cases.

EXPERIMENTAL.

The results having been sufficiently illustrated, this section is restricted to a description of methods. Acetone was purified and dried as usual (Conant and Kirner's method). The "90%" aqueous acetone used for many of the experiments was from a single batch containing 99.43 g. of water per litre. For some experiments the medium was made up specially by volumes, the "90%" and "70%" aqueous acetone of experiments (2) and (3) of Table I, for example, containing 100 and 300 c.c. of water per litre respectively.

For runs with *tert.*-butyl bromide in the absence of salts the halide (*ca.* 1.25 c.c.) was made up to 100 c.c. with the medium at 0°, and portions (5 c.c.) were separately enclosed in tubes, and heated at the required temperature (25.0° or 50.0°). The tubes were then broken under acetone (*ca.* 100 c.c.), and the acidity determined, lacmoid being used as indicator. Initial values were determined by shaking the tubes in the thermostat for 1 min., and then estimating the acidity, this value and the corresponding time being treated as the zero point of the reaction. "Infinity values" were determined on tubes which had been kept in the thermostat for at least 10 times the period of half-change. The degree of reversibility was determined by adding to an "infinity tube" an equal volume of water, which rapidly completes hydrolysis if it is incomplete at equilibrium. This datum also gave the initial concentration of *tert.*-butyl bromide.

Lithium bromide and lithium chloride were dried at 250°, and sodium azide was dried in air at 100° and then over phosphoric oxide in a vacuum at room temperature. For the determinations of hydrolysis alone (acidity development) in the presence of their salts, the procedure was that described above, except that in experiments with sodium azide bromothymol-blue was used as indicator in place of lacmoid. For the determination of total decomposition of *tert.*-butyl bromide (bromide ion liberation) the tubes were broken under cooled carbon tetrachloride (*ca.* 75 c.c.), and the solution was rapidly extracted twice with ice-cold water (25 c.c.). The

aqueous solution was treated with concentrated nitric acid (10 c.c.), ferric alum (as indicator), ether (25 c.c.) and standard silver nitrate solution, the excess of silver ion being determined as usual by titration with standard thiocyanate. The nitric acid is added in order to destroy the brown colour produced by azide ions and ferric alum. The addition of the ether was found to improve the end-point.

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