*Mechanism of Substitution at a Saturated Carbon Atom. Part XL.** *Unimolecular Nucleophilic Substitution and Elimination of* tert.*-Butyl Bromide with Anionic Reagents in Nitromethane Solvent; with some Remarks on the Addition of Acids to Olefins.*

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The reactions of *tert.*-butyl bromide with bromide ions, with chloride ions, and with nitrite ions have been studied kinetically in nitromethane solution. The reaction with bromide ions is stoicheiometrically mainly one of substitution, though strongly reversed elimination occurs concurrently. The reaction with chloride ions is mainly one of elimination, which is much less strongly reversed. The reaction with nitrite ions consists of two substitutions, together with an elimination. The total reactions in all these cases are of first order in the alkyl bromide, and of zero order in the anionic reagent. The reactions show a positive salt effect, but their absolute rates at low reagent concentrations are almost identical with one another and with common limiting rate of the reactions of *tert.*-butyl bromide in nitromethane with pyridine, and with the hydroxylic reagents, examined in the preceding paper. It is concluded that all these reactions of substitution and elimination have the unimolecular mechanism.

The additions of hydrogen bromide and of hydrogen chloride to *iso*butylene in nitromethane are retarded by bromide ions and by chloride ions, respectively. It is inferred that the halogen acids cannot as such protonate the olefin, but must first set their protons relatively free in pre-equilibrium. An extension of this conclusion to the acid hydration of olefins in aqueous solution is considered.

The nature of the unimolecular mechanism of nucleophilic substitution and elimination has long been a subject of controversy, partly for the reason that the first investigations of it (1933—1940) related mainly to solvolytic substitution, for which the most elementary kinetic criterion of mechanism is unavailable. Therefore special interest attaches to the study of the unimolecular mechanism in those aprotic solvents which are polar enough to sustain it. Here we continue the study of the substitution and elimination reactions of *tert.*-butyl bromide in solvent nitromethane. The simple idea of the investigation is that which was applied in the first work of this kind in solvent sulphur dioxide (*J.*, 1940, 1011), *viz.*, that in the unimolecular mechanism all nucleophilic reagents should react with a common substrate at the same rate, whereas in the bimolecular mechanism they should react at very different rates. We know (preceding paper) the rates at which *tert.*-butyl bromide undergoes unimolecular elimination through the action of pyridine, and unimolecular substitution with the reagents, water, ethyl alcohol, and phenol, in solvent nitromethane. We now report on its reactions with bromide ions, chloride ions, and nitrite ions in that solvent. Our investigation has so developed that it bears not only on the mechanism of unimolecular substitution and elimination, but also on that of the reversal of the latter process in the addition of acids to olefins.

(1) *Reactions of* tert.*-Butyl Bromide with Bromide Ion.*—These reactions were studied over a range of temperature, and for one temperature over a range of reagent concentrations, the basic measurement being that of isotopic exchange between ordinary bromine of *tert.*-butyl bromide and bromine made radioactive with ^{82}Br of half-life 36 hr., supplied in the form of tetraethylammonium bromide. The results are in Table 1. They are calculated by a method (p. 2938) which allows for radioactive decay and dilution, and for any reaction which occurs during warming to the reaction temperature, as well as for the concomitant expansion of the solvent. The counting rates C, $C - X_1$, and $C - X_2$ measure specific radioactivities of the tetraethylammonium bromide, initially, at a time t_1

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* Part XXXIX, preceding paper.

soon after the solution has attained reaction temperature, and at a later time t_2, respectively. The spread of the calculated first-order rate constants, k_1, for each temperature and reagent concentration, is typical of such experiments, and arises almost entirely from random fluctuations in counts measured within finite time intervals. Usually counts of about 10,000 were recorded on each sample, and it can be computed that this number should lead to a probable error of 3% in resulting rate-constants. The fact that the standard deviation in all the groups of more than three rate-constants lies in the range 4·2—5·6% (corresponding to a formal probable error of 2·8—3·7%) shows that no other casual kinetic errors are of comparable importance.

The near-identity of mean rate-constants at a fixed temperature, when the reagent concentration is varied, shows that the recorded first-order constants are indeed measuring unimolecular reactions.

TABLE 1. *Rate constants (k_1 in sec.$^{-1}$) of bromine exchange between* tert.*-butyl bromide and tetraethylammonium radio-bromide in nitromethane.*

			Counting rates					
Temp.	[Bu^{t}Br]	[NEt$_4$Br]	C	C–X_1	C–X_2	$t_2 - t_1$ (min.)	10^5k_1	10^5k_1, mean
49·7°	0·0511	0·0220	1191	1142	988·3	29·7	6·12	6·54
					903·8	35·5	6·49	
					853·3	45·6	6·60	
					767·9	49·7	6·54	
					698·1	60·2	6·96	
40·6	0·0466	0·0479	382·8	387·6	318·4	122·2	3·03	2·88
					322·8	124·7	2·74	
					305·6	161·4	2·87	
40·6	0·0470	0·0239	382·8	393·0	235·9	193·3	2·56	2·56
					233·0	197·5	2·59	
					234·4	200·2	2·52	
40·6	0·0470	0·0120	382·8	380·6	220·4	106·9	2·45	2·62
					114·9	257·3	2·80	
40·5	0·0488	0·0243	1012	1020	780·2	91·5	2·60	2·51
					744·0	123·0	2·31	
					685·3	143·0	2·59	
					589·6	206·0	2·66	
25·0	0·0497	0·0248	409·3	406·0	255·8	997·0	0·452	0·448
					259·6	1013	0·428	
					262·1	1015	0·416	
					244·3	1031	0·492	
					250·3	1050	0·454	
					251·3	1057	0·447	
21·7	0·0529	0·0228	571·5	566·7	336·2	1448	0·305	0·298
					318·6	1548	0·321	
					327·3	1646	0·284	
					323·5	1706	0·282	
					306·3	1766	0·306	

With the aid of unpublished work by P. J. C. Fierens, and by one of us (P. B. D. de la M.) on bimolecular halogen exchanges in acetone and in nitromethane, we can derive further support for this conclusion from solvent effects on reaction rate. The bromide-ion exchanges of primary alkyl halides are bimolecular, both with lithium bromide in acetone and with tetraethylammonium bromide in nitromethane; and reaction in the latter, more polar, solvent is appreciably the slower, as we should expect from the theory of kinetic solvent effects for a bimolecular reaction of this charge-type. Thus for *n*-propyl bromide, reacting at 25°, with a salt concentration 0·024M, the second-order rate-constants are 108 × 10^{-5} sec.$^{-1}$ mole^{-1} l. in acetone, and 24 × 10^{-5} sec.$^{-1}$ mole^{-1} l. in nitromethane. For the reaction of *tert.*-butyl bromide with lithium bromide in acetone, the second-order rate-constant can also be determined: in similar conditions, this rate-constant has the value 0·52 × 10^{-5} sec.$^{-1}$ mole^{-1} l. A bimolecular reaction of *tert.*-butyl bromide with tetraethylammonium bromide in nitromethane should be slower: the comparable rate-constant would be of the order of 0·1 × 10^{-5} sec.$^{-1}$ mole^{-1} l. In fact, the absolute rate of the reaction of *tert.*-butyl bromide in nitromethane is much greater, its rate-constant for the above conditions, computed as a second-order constant for comparison, being

18×10^{-5} sec.$^{-1}$ mole^{-1} l. This would be expected if, in the highly polar solvent, the slow bimolecular substitution is being overlaid by a much more rapid unimolecular exchange.

The temperature dependence of the rate of the *tert.*-butyl bromide exchange in nitromethane satisfies the equation $k_1 = Be^{-E/RT}$ sec.$^{-1}$, with the substitutions $\log_{10} B = 9{\cdot}76$ and $E = 20{\cdot}6$ kcal./mole, values to which we shall refer in Section (4).

Table 1 contains an indication, in the results of experiments at 40·6°, of an increase in the rate of exchange with increasing concentration of the ionic bromide. This effect is in excess of the experimental error. It can be classed as a salt effect, as we shall see in more detail in Sections (2) and (4).

It has been shown that, although the stoicheiometric reaction is essentially one of substitution, concurrent elimination occurs: the latter process has been followed by measuring the development of acidity. Initially, acid is formed at nearly the rate of the bromide exchange; but the amount of acid ultimately developed is quite small. Thus at 25·0°, for which the rate constant for bromide exchange is $0{\cdot}448 \times 10^{-5}$ sec.$^{-1}$ and represents 50% of conversion in 14·3 hr., the rate of development of acid during the first 15 min. was about $0{\cdot}41 \times 10^{-5}$ sec.$^{-1}$; but within 2 hr. the rate had fallen to zero; and the total amount of acid formed, by then 1%, thereafter remained constant. The obvious conclusion is that *iso*butylene adds hydrogen bromide rapidly and almost completely in these conditions; and this has been directly confirmed. In a solution, made up at 25° to contain 0·0174M-*iso*butylene and 0·0126M-hydrogen bromide, the additive process reached 98% of completion in 2·5 min. and 99·4% in 30 min.; and it later attained completion to within the analytical error. The addition was, however, retarded by the presence of tetraethylammonium bromide. Thus, in an experiment closely comparable to that just mentioned, except that the salt was also present in 0·02M concentration, the addition process reached 98% of completion only after 3 hr.; and the ultimate extent of reaction was only 99·4%. This kinetic effect can be interpreted as a repression, by the added bromide ions, of the ionisation of hydrogen bromide, and thus of the production of protons in a sufficiently free condition to be accepted by the olefin. In other words, we assume that the covalent acid HBr cannot as such protonate the olefin, but must first set its proton relatively free in pre-equilibrium. In the absence of definite knowledge as to just what the free state is, we shall write it in equations given later in the simple form H^+. As will be noted in Section 2, chloride ions have a similar repressing effect on the addition of hydrogen chloride to *iso*butylene, and we interpret this similarly.*

It is interesting to compare these results and conclusions with Taft's result (*J. Amer. Chem. Soc.*, 1952, **74**, 5372) that the rate of acid hydration of olefins in aqueous solution follows Hammett's acidity function rather than the hydrogen-ion concentration, and with his conclusion, derived therefrom, that the adding proton must first leave the covalent acid H_3O^+, and get into some more available condition in pre-equilibrium, before it can participate in the slow process of forming the carbonium ion. If we leave aside the special form in which Taft cast his interpretation (he assumed slow isomerisation of a π-bond complex), it is, in its essentials, similar to that which we have given for acid addition to an olefin in our aprotic solvent. The correspondence suggests that, even in aqueous solution, there may possibly be some freer form of protons than the normal electronic state of covalent H_3O^+. Pending further clarification, we could write this freer form simply as H^+, thereby obtaining a system of chemical equations for the acid hydration of olefins, which, whilst they omit unproved details, do express the kinetic findings:

$$H_3O^+ \xrightleftharpoons{\text{Fast}} H_2O + H^+ \qquad \text{Olefin} + H^+ \xrightleftharpoons{\text{Slow}} \text{Carbonium ion}$$

To return to the reactions in nitromethane, we have already concluded that the mechanism of the substitution process is unimolecular, and therefore no critical question of mechanism is raised by the observation that *iso*butylene is simultaneously produced in low concentration, but at an initial rate nearly equal to the steady rate of substitution. The consistent interpretation is that the elimination, like the substitution, is part of the total

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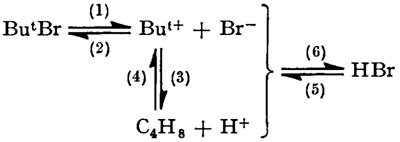
* The results cited are taken from a more general study soon to be reported, of the kinetics of the addition of acids to olefins in aprotic solvents.

unimolecular process, the carbonium ion, formed in the common rate-controlling stage, undergoing relatively rapid, but strongly reversible, proton loss, besides back-conversion with bromide ions into the alkyl bromide. By adding to this our conclusion that the reversal of the elimination depends on prior proton loss from hydrogen bromide, the complete system of equations may be represented as follows :



[Rates : (1) $\ll$ (2) $\ll$ (3) $\ll$ (4) $\ll$ (5) $\ll$ (6)]

We have, for kinetic reasons, to describe the formation of the olefin as dependent on unimolecular proton-loss by the carbonium ion, and not on bimolecular extraction of the proton by a bromide ion; and, for independent kinetic reasons, we have had to describe the protonation of the olefin as being effected by previously liberated protons, and not by direct attack of the proton-carrier, hydrogen bromide. Actually these two conclusions are correlated by theory, and either could have been deduced from the other by the principle of microscopic reversibility.

(2) *The Reactions of* tert.*-Butyl Bromide with Chloride Ion.*—These reactions were studied at one temperature only, 25·0°. The chloride ion was supplied as tetraethylammonium chloride. The kinetics of the reactions which ensued were more involved than those of the reactions just described, but when unravelled showed that the reactions with chloride ion follow quite similar mechanisms. The main difference is that the elimination, which was a minor reaction before, now constitutes the main part of the process. Thus, after the commencement of reaction, both hydrogen bromide and hydrogen chloride are present in quantity, and it is this which produces the more complex kinetics.

The kinetics were studied in four ways : (*a*) by following the development of bromide ion, which measures substitution plus elimination, (*b*) by following the production of acid, which measures the elimination only, (*c*) by determination of chloride ion, which should isolate the substitution, and (*d*) by determination of the formed *iso*butylene, which provides a direct check on the amount of elimination. The bromide and chloride ions were separately determined by electrometric titration, the acid by titration with alkali, and the *iso*butylene by its uptake of bromine.

When the rate of the total reaction, as measured by bromide-ion development, was expressed as first-order rate constants, these were found to remain steady over the first 10% of reaction, but thereafter to fall away. Because of the mathematical difficulties involved in elucidating a system of interlocked reactions on the basis of the precise forms of drift shown by drifting rate-constants, it was decided to study in detail only the initial steady period of reaction by various methods, and in various sets of initial conditions.

During this initial period, the bromide-ion concentration rises, but the chloride-ion concentration does not fall comparably, while the acid concentration, and equally the olefin concentration, both rise nearly as rapidly as does the concentration of bromide ions. This is illustrated by the three runs compared in Table 2, from which it appears that at least 90% of the initial reaction consists of elimination. It was confirmed that no elimination is apparent in the absence of tetraethylammonium chloride.

Despite the need for tetraethylammonium chloride, the rates of reaction depend only slightly on its concentration, within the range of our experiments. This is shown both for bromide-ion development, and for acid production, in Table 3. In the measurements on bromide ions, the concentration of tetraethylammonium chloride could not be taken up to very high values, because the determination of bromide ion in the presence of the chloride ion then becomes too inaccurate. However, the rates are seen to rise by only 30% for a 3-fold increase in the concentration of the chloride. The measurements of acid involve no such analytical difficulty, and accordingly the concentration of supplied chloride was taken up to relatively high values. The rate now increased 3½ times for a 29-fold increase in the concentration of chloride.

In considering the kinetic situation revealed by the results described, it is convenient at first to neglect as a detail the slow variations of rate with changing concentration of the tetraethylammonium chloride: it is a point to which we shall return. Such details apart, our conclusions are that the main reaction is one of elimination, that it becomes observable only in the presence of the tetraethylammonium chloride, but that its rate is approximately independent of the concentration of that reagent. These conclusions can only be reconciled on the assumption that the elimination is unimolecular, depending for its rate on that of the ionisation of the *tert.*-butyl bromide, and that the tetraethylammonium chloride acts by retarding the retrograde reaction of addition to the formed olefin. Certainly it might be expected to do so. We know that, under our experimental conditions, hydrogen bromide adds to *iso*butylene rapidly and almost completely. The expected first effect of the tetraethylammonium chloride would be to replace most of the formed hydrogen bromide by less ionising, and presumably less rapidly adding, hydrogen chloride. And a supporting second effect is expected: for, just as the rate of addition of hydrogen bromide to *iso*butylene is depressed in the presence of bromide ions, so the presumably smaller rate of addition of hydrogen chloride should be further reduced by the presence of chloride ions. These retarding effects could allow the elimination to go forward a considerable distance, but still at a rate essentially controlled by that of the ionisation of the alkyl bromide.

TABLE 2. *Initial rate-constants* (k_1 *in sec.*$^{-1}$) *of formation of bromide ions, hydrogen ions, and olefin, from* tert.*-butyl bromide and tetraethylammonium chloride in nitromethane at* 25·0°.

Run	$[\mathrm{Bu^tBr}]_0$	$[\mathrm{NEt_4Cl}]_0$	Method	10^5k_1
86	0·0202	0·0204	$d[\mathrm{Br^-}]/dt$	0·56
87A	0·0202	0·0200	$d[\mathrm{H^+}]/dt$	0·52
87B	0·0202	0·0200	$d[\mathrm{Olefin}]/dt$	0·51

TABLE 3. *Initial rates* (k_1 *in sec.*$^{-1}$) *of production of bromide ions, and of hydrogen ions, from* tert.*-butyl bromide in nitromethane at* 25·0°, *as a function of the concentration of added tetraethylammonium chloride.*

Run	$[\mathrm{Bu^tBr}]_0$	$[\mathrm{NEt_4Cl}]_0$	Method	10^5k_1
83	0·0200	0·0110	$d[\mathrm{Br^-}]/dt$ *	0·45
84	0·0200	0·0128	,, *	0·48
86	0·0202	0·0200	,, †	0·56
81	0·0197	0·0290	,, *	0·60
29A	0·0200	0·0049	$d[\mathrm{H^+}]/dt$	0·40
8A	0·0201	0·0111	,,	0·45
87A	0·0202	0·0200	,,	0·52
7A	0·0202	0·0506	,,	0·74
6A	0·0200	0·0730	,,	0·89
18A	0·0200	0·0983	,,	1·10
19A	0·0200	0·1410	,,	1·43

* Extraction method (cf. p. 2938). † Evaporation method (cf. p. 2938).

The general validity of this interpretation has been checked by a direct examination of the rate of addition of hydrogen chloride to *iso*butylene in nitromethane, in the absence, and in the presence of added tetraethylammonium chloride. In our conditions, hydrogen chloride, in the absence of added salt, adds to *iso*butylene some hundreds of times more slowly than does hydrogen bromide, though ultimately the addition goes almost to completion. In the presence of 0·02M-tetraethylammonium chloride, the rate of addition of hydrogen chloride is reduced by a further factor of a similarly large order. Two runs are recorded for illustration in Table 4: they were followed by measuring the disappearance of acid.

Returning to the slow increase in the rate of elimination with increasing concentration of tetraethylammonium chloride, it is easy to exclude the hypothesis that this is connected with the increased suppression by this salt of the back-reaction of addition of halogen-acids to the olefin. For first, the observed rates are initial rates. And secondly, an upper limit to the possible effect of reducing the additive reactivity of hydrogen halides can be set by removing them completely, by the addition, not of tetraethylammonium chloride, but of pyridine, or triethylamine. However, as the preceding paper shows, the rate of elimination in the presence of excess of pyridine ($k_1 = 0{\cdot}39 \times 10^{-5}$ sec.$^{-1}$ at 25·0°) is not above the lowest of the rates recorded in Table 3 (run 29A) for elimination in the presence of tetraethylammonium chloride, and is therefore very far from being an upper limit to a range of rates which run up to values more than three times higher. A similar statement holds for the reaction in the presence of triethylamine. We can almost as definitely excluded the hypothesis that the slow increase of rate with increasing salt concentration arises from a minor bimolecular component of the reaction. If any of the investigated eliminations of *tert.*-butyl bromide could show a bimolecular component, the reactions with amines should do so. Yet it was noted in the preceding paper that the rate of elimination in the presence of pyridine is independent of the concentration of pyridine up to 0·11M; and the same point has been verified for elimination in the presence of triethylamine over the concentration range 0·01—0·06M. Therefore, we conclude that the slow rate change with increasing salt concentration represents a long-range interaction, classifiable as a salt effect. We shall refer to it again in Section (4).

TABLE 4. *Rate of addition of hydrogen chloride to* iso*butylene in nitromethane at* 25·0° *in the absence and in the presence of tetraethylammonium chloride.*

Run 2A: Initially, $[C_4H_8] = 0{\cdot}017$M; [HCl] = 0·0169M; $[NEt_4Cl] = 0{\cdot}0000$M.

t (min.)	HCl (%)	*t* (min.)	HCl (%)
0	100	150	20·2
30	41·5	180	17·6
60	32·7	210	16·4
95	26·4	270	12·6
120	22·6	1260	1·9

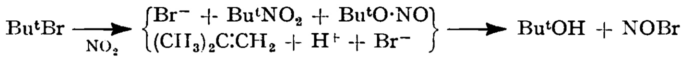
Run 4A: Initially, $[C_4H_8] = 0{\cdot}0210$M; [HCl] = 0·0207M; $[NEt_4Cl] = 0{\cdot}0200$M.

t (min.)	HCl (%)	*t* (min.)	HCl (%)
0	100	150	93·9
30	99·0	180	92·8
60	97·9	1440	75·5
90	95·9	2880	66·3
120	94·9		

The remaining detail of the kinetics of the reaction of chloride ions with *tert.*-butyl bromide relates to the minor process of substitution; but, as to this, we cannot make any precise statement from direct observation, for the reason that there is too little substitution to be treated accurately by the not very exact techniques available for determining chloride and bromide ions in the presence of each other in our reaction system. Our conclusions concerning this part of the reaction rest on analogy with the bromide-ion reaction. This granted, a scheme can be written for the chloride-ion reaction which is similar to that given on p. 2933, except for the complication of including chloride ion and hydrogen chloride, and the changes in relative rates already discussed.

(3) *Reactions of* tert.*-Butyl Bromide with Nitrite Ion.*—The nitrite ions were supplied as either tetraethyl- or tetramethyl-ammonium nitrite, and the rate of the total reaction, as given by electrometric titration of the formed bromide ions, was studied for a range of salt concentrations at one temperature, and for a range of temperatures at one salt concentration.

A qualitative examination of the reaction product showed that substitution and elimination were both taking place. There were two substitution products, *tert.*-nitro*iso*butane and *tert.*-butyl nitrite. The elimination product was *iso*butylene. At a later stage of these primary reactions, the *tert.*-butyl nitrite, and the formed bromide ion, began to disappear, and some nitrosyl bromide was produced. The *tert.*-nitro*iso*butane, once formed, underwent no further reaction. In the following summary of these chemical changes, it is assumed, though it was not directly proved, that *tert.*-butyl alcohol is produced along with the nitrosyl bromide: *



$$\mathrm{Bu^tBr} \xrightarrow[\mathrm{NO_2}]{} \left\{\begin{matrix} \mathrm{Br^- + Bu^tNO_2 + Bu^tO{\cdot}NO} \\ \mathrm{(CH_3)_2C{:}CH_2 + H^+ + Br^-} \end{matrix}\right\} \longrightarrow \mathrm{Bu^tOH + NOBr}$$

It was found that the first 80% of the primary reactions, which liberate bromide ions from *tert.*-butyl bromide, could be kinetically followed, without interference from the

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* We are still uncertain whether any appreciable addition of nitrosyl compounds to the olefin occurs in our conditions, but hope to settle the point in a current investigation of olefinic additions.

subsequent reaction of *tert.*-butyl nitrite with bromide ion to give nitrosyl bromide. Up to this point, all the runs were accurately represented by the first-order rate law. A summary of the rate constants is given in Table 5.

TABLE 5. *First-order rate constants (k_1 in sec.$^{-1}$) of decomposition of* tert.*-butyl bromide in the presence of tetraethyl- or tetramethyl-ammonium nitrite in nitromethane: variation with salt concentration and with temperature.*

Run	Temp.	$[Bu^tBr]_0$	Salt	$[Salt]_0$	10^5k_1
31A	25·0°	0·0200	NEt_4NO_2	0·0048	0·391
16A	,,	0·0202	,,	0·0916	0·519
17A	,,	0·0201	,,	0·0306	0·556
63	25·1	0·0155	NMe_4NO_2	0·0323	0·557
62	45·0	0·0155	,,	,,	5·24
64	62·6	0·0155	,,	,,	29·0

From the first-order character of the rates, and the fact that the rate constants rise only slightly during a proportionately large increase in the reagent concentration, it can be concluded that the observed reactions are unimolecular, having a common rate-governing step, the ionisation of the alkyl bromide.

The temperature dependence of the rate is represented by the equation $k_1 = Be^{-E/RT}$ sec.$^{-1}$ with the substitutions $\log_{10} B = 9·86$ and $E = 20·6$ kcal./mole.

The slow increase in the rate of the total nitrite-ion reaction with increasing concentration of the saline reagent, *viz.*, about 40% of rate change for a 6-fold concentration change, is roughly the same as that found both for the elimination induced by chloride ions, and for the total chloride-ion reactions; and it is of the same order of magnitude as that observed for the bromide-ion exchange, although the larger errors inherent in the radioactive measurements, and also the temperature difference, preclude close comparison with this case. It seems clear therefore that the effect for the nitrite-ion reactions should be classified as a salt effect, just as for the other reactions.

The demonstration here given of a unimolecular mechanism for the reaction of an alkyl halide with nitrite ions is taken from a wider series of investigations by one of us (Y. P.), which show that both bimolecular and unimolecular substitutions (S_N2 and S_N1) as well as catalysed forms, such as the silver-ion mechanism (S_N1–Ag), can occur with this substituting agent, according to the alkyl halide, the solvent, and the catalyst. The question of the bearing of the mechanism of substitution on the nature of the products, whether they are nitro-compounds or alkyl nitrites, will be discussed in a forthcoming publication. Parallel investigations of the relation of mechanism to products in the reactions of alkyl halides with thiocyanate and with cyanide ions have shown that similar considerations are fundamental in these cases also.

(4) *Comparison of the Rates of Reaction of* tert.*-Butyl Bromide with Various Reagents.*—This comparison was the original object of the present work. In the results of this and the preceding paper, rate data can be found for seven reagents. Table 6 assembles the directly determined rates at 25·0° for the lowest concentration of each reagent used in measurements at this temperature. Though the concentrations are not ideally low, and are not even equal, all the rates are within 15% of the common value $0·45 \times 10^{-5}$ sec.$^{-1}$. If we use the rate data for higher reagent concentration to effect an asymptotically linear extrapolation to zero concentration, all the extrapolated rates are within 5% of the common value $0·38 \times 10^{-5}$ sec.$^{-1}$. This is strong evidence that, whatever may be the stoicheiometry of the reactions, all of them, substitutions and eliminations, are rate-controlled by a common process in which the reagent plays no part. Bearing in mind also the first-order forms of the reactions, we conclude that the mechanism throughout is unimolecular, the common slow step being the ionisation of the alkyl halide.

This demonstration of the essential identity of the rates of reaction of *tert.*-butyl bromide with different reagents at 25·0° is extended to other temperatures in three cases by determination of the Arrhenius parameters, which are compared in Table 7.

As far as our experiments show, the rates of the reactions with tertiary amines are independent of the amine concentration. The rates of the reactions with the other reagents vary with the concentration of reagent. For the three hydroxylic reagents the variation is discussed in the preceding paper. It remains to discuss rate variation with the concentration of the three anionic reagents. We have provisionally concluded, by the exclusion of other alternatives (Section 2), that these rate variations arise from long-range interactions of the general nature of salt effects. However, the physical mechanism is not fully clear, because, although the ionic character of these reagents must be an important factor, the curves of rate against concentration do not steepen exponentially at higher concentrations, as is required for salt effects on unimolecular reactions by the simple theory which treats the ions as point charges (*J.*, 1940, 893). Possibly the deviations indicate, in addition to long-range effects of ionic strength, an appreciable incursion of medium-range interactions, either of a non-specific type depending on mutual interference between the outer solvation layers of the transition state of ionisation and of the reagent ions, or of the more specific type recently considered in connexion with certain unimolecular reactions in sulphur dioxide (*J.*, 1954, 634).

TABLE 6. *Rate constants* (k_1 *in sec.*$^{-1}$) *of reactions of* tert.*-butyl bromide in nitromethane at* 25·0°.

Reagent	Concn. of reag. (c)	Obs. 10^5k_1 $^{(c)}$	Extrap. 10^5k_1 $^{(c)}$	Stoicheiometric reactions
C_5H_5N	0·02	0·39	0·39	$E1$
H_2O	0·035	0·43	0·40	Mainly S_N1
EtOH	0·11	0·45	0·40	Mainly S_N1
PhOH	0·06	0·52	0·40	Mainly S_N1
Br^-	0·025	0·45	(0·41) *	S_N1 + a little $E1$
Cl^-	0·01	0·45	0·36	$E1$ + a little S_N1
,,	0·005	0·40	0·37	$E1$ only
NO_2^-	0·005	0·39	0·36	S_N1 (two products) + $E1$

* Estimate based on results obtained at a higher temperature.

TABLE 7. *Parameters of the equation* $k_1 = Be^{-E/RT}$ *sec.*$^{-1}$ *for reactions of* tert.*-butyl bromide in nitromethane.*

Reagent	Temp. range	[Reagent]	$\log_{10} B$	E (kcal./mole)
H_2O	0—40°	0·125	9·8	20·6
Br^-	22—50	0·023	9·8	20·6
NO_2^-	25—63	0·032	9·9	20·6

EXPERIMENTAL

Materials.—The methods of preparation or purification of the materials used are standard, or have been described in other papers from this laboratory, except for tetramethyl- and tetraethyl-ammonium nitrite, which were made both from the tetra-alkylammonium iodide and silver nitrite in acetonitrile, and from the tetra-alkylammonium sulphate, prepared through the hydroxide, and barium nitrite in dry methyl alcohol. In either case, the filtered solution was evaporated to dryness at room temperature, and the nitrite, which formed pale yellow crystals, was purified by crystallisation from acetonitrile–diethyl ether, and dried at 60° in a good vacuum. For tetramethylammonium nitrite, made by the " silver " method, found, NO_2^- = 38·15; and, made by the " barium " method, found, NO_2^- = 38·2; calc., 38·3%. For tetraethylammonium nitrite, made by the barium method, found, NO_2^- = 26·05; calc., 26·1%.

Reaction of tert.*-Butyl Bromide with Tetraethylammonium Bromide in Nitromethane.*—Radioactive ammonium bromide, supplied by the Atomic Energy Research Establishment, Harwell, was evaporated almost to dryness with an equivalent of tetraethylammonium hydroxide, and the product was then finally dried in a vacuum over phosphoric oxide at the temperature of boiling chloroform. The filtered solution of the residue in nitromethane was standardised by Volhard's method.

Known volumes of solutions of *tert.*-butyl bromide and of tetraethylammonium radiobromide in nitromethane were mixed in small tubes, which were sealed and immersed in the thermostat. After suitable intervals, tubes were removed and chilled, and the solvent and organic bromide were rapidly evaporated under reduced pressure. The remaining tetraethylammonium bromide was dissolved in water, and its radioactivity was measured, employing the type of counter usual for liquid samples and standard scaling equipment. Each sample was counted at least twice. From the decay curves, which corresponded to within experimental error, with those expected for ^{82}Br as the only radioactive species, values were read to give counts for each sample at the same arbitrary time. The bromide content of each sample was also determined, and thus the activities, as measured, were corrected to give specific activities, referring in each experiment to the same arbitrary concentration of bromide ion.

If a and b are respectively the concentrations of alkyl bromide and tetraethylammonium bromide, and if C and $C - X$ are respectively the specific activities of the initial solution of tetraethylammonium bromide, and of a solution of the salt recovered from a reaction stopped after a time t, then the first-order constant is given by the equation (cf. le Roux and Sugden, *J.*, 1939, 1279),

$$k_1 = \frac{2{\cdot}303b}{(a+b)t} \log_{10} \left\{1 - \frac{X}{C}\left(1 + \frac{b}{a}\right)\right\}^{-1}$$

This formula is valid, and was used, when no appreciable exchange occurred during the time taken by the reaction mixtures to reach the temperature of the thermostat, as was true for all but the highest of the temperatures employed. When it was not true, then specific activities, X_1 and X_2 were measured at two times, t_1 and t_2, after the experimental temperature had been attained, and accordingly the equation was used in its difference form :

$$k_1 = \frac{2{\cdot}303b}{(a+b)(t_2 - t_1)} \log_{10} \left[\left\{1 - \frac{X_1}{C}\left(1 + \frac{b}{a}\right)\right\}\left\{1 - \frac{X_2}{C}\left(1 + \frac{b}{a}\right)\right\}^{-1}\right]$$

The results are in Table 1.

Reaction of tert.*-Butyl Bromide with Tetraethylammonium Chloride in Nitromethane.*—For the determination of halide ions by potentiometric titration with silver nitrate, a calomel half-cell was connected by a potassium nitrate bridge to the solution to be titrated, a silver wire acting as the second electrode. The method of operation was based on the work of Clark (*J.*, 1926, 749), who showed that bromide and chloride could be individually estimated in a mixture, if 5% of barium nitrate was present in the solution. Equivalence points were located following the recommendations of Flood and Slatten (*Z. analyt. Chem.*, 1938, **115**, 30). Two methods were used for the preparation for titration of samples withdrawn from the kinetic runs. In the first (the " extraction " method), the sample (10 c.c.) was delivered into carbon tetrachloride (60 c.c.) at −10°, and this solution was shaken three times with 20 c.c. of ice-cold water. Barium nitrate (3 g.) was added to the total aqueous extract. In the second (the " evaporation ") method, the sample was run into a flask immersed in a freezing mixture, and evaporated with the aid of a high-capacity pump; and the residue was dissolved in 5% aqueous barium nitrate. For the determination of acid, the sample (10 c.c.) was run into dry acetone (70 c.c.) at −30°, and titrated with standard sodium methoxide, with lacmoid as indicator. For the determination of olefin, the sample (10 c.c.) was added to dry methyl alcohol (70 c.c.) at −30°, and, after addition of excess of methyl-alcoholic bromine, solid potassium iodide was introduced, and the liberated iodine was titrated with thiosulphate. Table 8 records two runs in illustration of these kinetic measurements.

TABLE 8. *Reaction of* tert.*-butyl bromide with tetraethylammonium chloride in nitromethane at* 25·0° : *illustrative kinetic runs.*

Run 86. Initially, $[\mathrm{Bu^tBr}] = 0{\cdot}0202$M; $[\mathrm{NEt_4Cl}] = 0{\cdot}0204$M; $[\mathrm{Br^-}]$, as given by evaporation method, is in c.c. of 0·01N-AgNO$_3$ per 10 c.c. sample.

$k_1 = (2{\cdot}303/t) \log_{10} \{0{\cdot}202/(0{\cdot}202 - x)\}$ sec.$^{-1}$.

t (min.)	[Br$^-$] (c.c.)	10^5k_1
30	0·20	0·563
60	0·40	0·557
90	0·65	0·610
120	0·80	0·569
150	1·00	0·565
180	1·10	0·517
240	1·60	0·574
330	2·00	0·526
	Mean	0·56

Run 8*A*. Initially, $[\mathrm{Bu^tBr}] = 0{\cdot}0201$M; $[\mathrm{NEt_4Cl}] = 0{\cdot}0111$M; $[\mathrm{H^+}]$ is expressed in c.c. of 0·0543N-NaOMe per 10 c.c. sample.

$k_1 = (2{\cdot}303/t) \log_{10} \{0{\cdot}0201/(0{\cdot}0201 - x)\}$ sec.$^{-1}$.

t (min.)	[H$^+$] (c.c.)	10^5k_1
60	0·61	0·454
90	0·90	0·456
120	1·15	0·438
150	1·50	0·461
180	1·68	0·431
240	2·23	0·432
	Mean	0·45

Reaction of tert.*-Butyl Bromide with Tetramethyl- or Tetraethyl-ammonium Nitrite in Nitromethane.*—These reactions were followed by determination of the liberated bromide ion by potentiometric titration with silver nitrate in 1% aqueous sulphuric acid. Samples withdrawn from the kinetic runs were prepared for titration by the " extraction method " described in the preceding paragraph. An illustrative run is recorded in Table 9.

TABLE 9. *Reaction of* tert.*-butyl bromide with tetramethylammonium nitrite in nitromethane at* 62·6° : *illustrative kinetic run.*

Run 64. Initially, $[Bu^tBr] = 0{\cdot}0155$M; $NMe_4NO_2 = 0{\cdot}0323$M. Sealed tube technique used. $[Br^-]$ expressed in c.c. of 0·01N-$AgNO_3$ per sample of 5·48 c.c. $[Br^-]_{corr.}$ is the value of[Br^-] corrected for reaction before the first measurement at time $t = 0$, and for the separately determined, small amount of hydrolysis, which occurs during preparation of the samples for titration. The rate constant is calculated from $k_1 = (2{\cdot}303/t) \log_{10} \{7{\cdot}6/(7{\cdot}6 - [Br^-]_{corr.}\}$ with t in sec. and $[Br^-]_{corr.}$ in the above units.

t (sec.)	$[Br^-]_{corr.}$	10^5k_1	t (sec.)	$[Br^-]_{corr.}$	10^5k_1
300	0·65	29·8	840	1·65	29·1
400	0·85	29·7	900	1·75	29·1
420	0·85	28·2	1800	3·03	28·3
460	0·95	29·0	1920	3·23	28·6
600	1·20	28·7	2100	3·43	28·8
600	1·23	29·4			
				Mean	29·0

Incidentally to a larger programme, preliminary work on the chloride-ion reaction, which disclosed the difficulties later overcome, was done by Dr. Paul J. C. Fierens, now of the University of Brussels. We also received material help in the present experiments from Messrs. P. J. Collins and A. Spiers.

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