46. *Mechanism of Substitution at a Saturated Carbon Atom. Part XXVIII. The Rôle of Steric Hindrance. (Section C) A Comparison of the Rates of Reaction of Methyl, Ethyl, n-Propyl, isoButyl, and neoPentyl Bromides with Aqueous Ethyl Alcohol.*

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A comparison has been made of the rates of solvolysis of the halides, named in the title, in " 50% " aqueous ethyl alcohol at 95°. The rate sequence is again found to be Me > Et > *n*-Pr > *iso*Bu $\gg$ *neo*pentyl, but the rate differences (relative rates : Me 2·0, Et 1, *n*-Pr 0·57, *iso*Bu 0·080, *neo*pentyl 0·0065) are smaller than those observed for the bimolecular reaction with sodium ethoxide, the difference between *iso*butyl and *neo*pentyl being very much smaller (cf. p. 157). It is shown that the solvolytic reactions of the first four halides are largely bimolecular, but the results for *neo*pentyl bromide support an ionisation mechanism (cf. following paper). On the basis of the duality of mechanism, the rate data for the solvolytic process can be explained, both in relation to the alkyl series, and by comparison with the results for the bimolecular reaction with sodium ethoxide. Some special aspects of the results are discussed further in Part XXXII (p. 173).

Having obtained a comparison of the reactivity of *neo*pentyl and other primary bromides in their bimolecular reactions with sodium ethoxide in absolute ethyl alcohol (this vol., p. 157) and with sodium iodide in acetone (this vol., p. 161), it was of interest to institute a similar comparison with respect to other conditions of reaction, particularly those more favourable to a preliminary ionisation of the alkyl halides. Relatively to the bimolecular process, an ionisation mechanism should be facilitated by an increase in the ionising capacity of the solvent and by a decrease in the nucleophilic activity of the reagent (Hughes and Ingold, J., 1935, 244, and later papers). We therefore examined the solvolytic reactions of the bromides named in the title, in " 50% " aqueous alcohol † in the absence of alkali or any other reagent of high nucleophilic activity. The results are now described.

The first-order rate coefficients (in sec.⁻¹) at 94·85° are listed in Table I; the second-order rate coefficients (in sec.⁻¹ g.-mol.⁻¹ l.) at 95° for the reactions with sodium ethoxide in absolute alcohol (*loc. cit.*) are included for comparison.

<div align="center">TABLE I.</div>

(1) = Bimolecular reaction with NaOEt in EtOH.   (2) = Solvolytic reaction in " 50% " H₂O–EtOH.

Alkyl bromide.	10⁴k for (1).	(2).	Alkyl bromide.	10⁴k for (1).	(2).
Me	9650	2·86	*iso*Bu	26·2	0·113
Et	647	1·41	*neo*Pentyl	0·00649	0·00910
n-Pr	181 *	0·803			

* Estimated from results at 55° (this vol., p. 157), the ratio $k_{\mathrm{EtBr}}/k_{n\text{-}\mathrm{PrBr}}$ being assumed to be independent of temperature.

If we imagine the sodium ethoxide concentration to be buffered to N, the figures of the first and the second row become directly comparable, the former now becoming first-order constants under the mass law. The kinetic order of the solvolytic reaction gives by itself no information concerning mechanism. If, however, the solvolytic reaction followed a bimolecular course throughout the series of halides, the change of conditions from (1) to (2) should cause a large decrease of rate in all cases, because of the decrease in the nucleophilic activity of the substituting agent. For the first four members of the series the observed rates do decrease from (1) to (2). We also have independent evidence that the solvolytic reactions of these four compounds are largely bimolecular. Of the four, *iso*butyl should be most prone to react by the unimolecular mechanism ; yet we have shown that added alkali produces a large increase in the rate of its hydrolysis in 50% aqueous ethyl alcohol (experimental section). An analysis of the results by the method previously used to demonstrate that the solvolytic reactions of methyl bromide and ethyl bromide in aqueous ethyl alcohol are bimol-

* Senior, Hetrick, and Miller (*J. Amer. Chem. Soc.*, 1944, **66**, 1987) have recently referred to the inaccuracy of Andrews's similar method in the presence of acetone.

† See Experimental section.

ecular (Bateman, Cooper, Hughes, and Ingold, J., 1940, 925) shows that the reaction of *iso*butyl bromide is predominantly of the same type.* For *neo*pentyl bromide the rate constant for reaction (2) is slightly greater than that for reaction (1). This could be explained if the bimolecular mechanism, operative for reaction (1), has here been replaced by a unimolecular mechanism in the case of reaction (2). Evidence in support of an ionisation mechanism for the solvolysis of *neo*pentyl bromide in aqueous ethyl alcohol is contained in the following paper.

On the basis of the duality of mechanism, the results for the solvolytic reaction can be explained, both in relation to the alkyl series, and by comparison with the results for the bimolecular reaction with sodium ethoxide. The rate variation among the members of the series is similar in type in both cases, except that the rate differences for the solvolytic process are smaller than those for the reaction with sodium ethoxide, and that the difference between *iso*butyl bromide and *neo*pentyl bromide is very much smaller; so much so that the latter compound, although still the slowest of the halides, is much less peculiar with respect to its behaviour in solvolysis than in the reaction with ethoxide ions. The rate relationships for the solvolytic reactions of the first four halides are consistent with the evidence that these reactions are predominantly, though probably not wholly, bimolecular (cf. Part XXVI). However, for the last member of the series, the rate, instead of dropping to an immeasurably small value, as it would were the reaction bimolecular, drops only to about one-twelfth of that for *iso*butyl bromide, this value representing, according to our explanation, the unimolecular rate (rate of ionisation) of *neo*pentyl bromide. It should be emphasised that this unimolecular rate is observed in a highly aqueous solvent, and that it would be much smaller in dry ethyl alcohol, the solvent used for the study of the alkaline reaction. Some further aspects of these results, particularly the absence of any large steric effect in the unimolecular reaction of the *neo*pentyl halide, are discussed in accompanying papers (see, especially, this vol., p. 173).

<div align="center">EXPERIMENTAL.</div>

Materials.—*n*-Propyl bromide was obtained by fractionation of a commercial sample through a 15-plate column; the fraction used for the measurements had b. p. 70·9—71·1°/760 mm. In the case of the other halides, samples obtained as described in the preceding papers were used. The solvent labelled " 50% " aqueous ethyl alcohol was obtained by mixing, at room temperature, equal volumes of dry ethyl alcohol (this vol., p. 160) and distilled water.

Rate Measurements.—The technique employed was similar to that described in Part XXVI (this vol., p. 157), but, with two exceptions, the halides were always examined in initially neutral solution. One exception was *neo*pentyl bromide, for which it was generally convenient to dissolve in the medium sufficient sodium hydroxide to maintain the solution alkaline throughout the runs. The presence of the base has no influence on the rate of solvolysis of this halide, and it prevents the incursion of a reaction between the medium and hydrogen bromide, which in this case becomes troublesome in initially neutral solutions (following paper). The other exception was *iso*butyl bromide, for which it was necessary to determine the magnitude of the effect of added alkali through a comparison of the rates in basic, and in neutral or acidic, solutions (cf. below, and the theoretical section of this paper). The initial concentrations of the alkyl halides were approximately 0·05N throughout.

Rates of Solvolysis of Alkyl Halides in " 50% " Aqueous Ethyl Alcohol at 94·85°.—In the following record of detailed experiments (Table II), which are typical of the series of solvolytic reactions studied, the concentrations of the alkyl halides are expressed in equivalent ml. of 0·010N-silver nitrate per 5 ml. of solution, and the first-order rate coefficients are in sec.$^{-1}$.

<div align="center">TABLE II.</div>

<div align="center">(a) isoButyl bromide.</div>

t (hrs.) ...	0	1·0	2·0	3·25	4·0	4·25	5·25	7·0	14·6	17·0	19·75	23·5
[RBr] ...	24·41	23·36	22·48	21·23	20·70	20·45	19·73	18·50	13·33	12·63	10·99	10·32
$k_1 \times 10^5$	—	1·22	1·15	1·19	1·15	1·16	1·13	1·10	1·15	1·08	1·12	1·02

<div align="center">(b) Ethyl bromide.</div>

t (mins.)	0	5	11	14	16·5	19	25	33	46	61	75	95
[RBr] ...	22·75	21·79	20·72	20·30	19·91	19·38	18·34	17·08	15·70	13·20	12·26	9·96
$k_1 \times 10^4$	—	1·44	1·42	1·36	1·35	1·41	1·44	1·45	1·37	1·49	1·38	1·45

Rate of Hydrolysis of iso*Butyl Bromide with Alkali in " 50% " Aqueous Ethyl Alcohol at* 94·85°.—In order to show that the rate of hydrolysis of *iso*butyl bromide is influenced by alkali, a kinetic run was carried out in the presence of 0·11M-sodium hydroxide. The mean second-order rate coefficient of the total reaction was found to be $2·73 \times 10^{-3}$ sec.$^{-1}$ g.-mol.$^{-1}$ l. Under these conditions an elimination reaction leading to olefin formation accompanies the substitution process, and olefin determinations, carried out on the products of a completed hydrolysis, as described in Part XXVI (this vol., p. 161), indicated that the elimination process accounts for 37·5% of the total reaction. The second-order rate coefficient for the substitution reaction is thus $(62·5/100) \times 2·73 \times 10^{-3} = 1·71 \times 10^{-3}$ sec.$^{-1}$ g.-mol.$^{-1}$ l. Comparing this result with the determined first-order rate coefficient of the solvolytic reaction ($k_1 = 1·13 \times 10^{-5}$ sec.$^{-1}$), it is obvious that the rate of hydrolysis of *iso*butyl bromide is greatly increased by alkali.

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* Taking account of the concentration of the solvent for the purpose of an order-of-magnitude calculation, it was shown (Bateman, *et al., loc. cit.*) that the specific rate which would have to represent the activity of water and alcohol in an assumed bimolecular reaction with the methyl and ethyl halides is about 10^{-5} times smaller than the corresponding rate for the reaction with hydroxide and ethoxide ions; and this is consistent with the known relationships between specific rate and basic strengths established by Brönsted and others. The rate disparity for *iso*butyl bromide is smaller (factor *ca.* 10^{-4}), and this may indicate a slight tendency towards unimolecular solvolysis in the case of this halide. However, we may conclude that the reactions of the first four members of the halide series under discussion are largely bimolecular.