

49. *Mechanism of Substitution at a Saturated Carbon Atom. Part XXXI. The Rôle of Steric Hindrance. (Section F) A Comparison of the Rates of Reaction of Methyl, Ethyl, n-Propyl, and neoPentyl Bromides with Wet Formic Acid.*

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A comparison of the rates of reaction of the four halides named in the title with slightly aqueous formic acid gave the sequence $\text{Et} > \text{Me} \sim n\text{-Pr} \sim \text{neoPentyl}$, the relative rates being Me 0.64, Et, 1.0, *n*-Pr 0.69, *neo*Pentyl 0.57. Since the *neo*pentyl reaction undoubtedly pursues the unimolecular mechanism (see Abstracts, pp. 164 and 166), the evidence of the rates suggests that this form of reaction is also important for the other halides under these conditions. However, the rate sequence is not the theoretical one for the inductive effect in the unimolecular mechanism, $\text{Me} < \text{Et} < n\text{-Pr} < \text{neoPentyl}$: the main inequality $\text{Me} < \text{Et}$ is, indeed, in the direction of the observed rate difference, but the other inequalities, which should be smaller, are not reflected in the data. This may mean that the use of formic acid has greatly diminished, but not eradicated, the bimolecular mechanism, which enters as a complicating influence into the reactions of the first three members of the series; or it may be due merely to the finite heat contents of the interacting species.

THE study of the solvolytic reactions of the primary halides in aqueous ethyl alcohol (Part XXVIII, this vol., p. 164) failed to fulfil one of the main objects of our investigations, namely, to obtain a comparison of unimolecular reaction rates for a series of primary halides. This paper records an attempt to secure such a comparison.

In aqueous ethyl alcohol, the reaction of *neo*pentyl bromide undoubtedly followed a unimolecular mechanism (this vol., p. 166), but the other halides, named in the title, reacted mainly by the alternative bimolecular route. In order to minimise the incursion of a bimolecular reaction, it is advisable to decrease the concentration of the nucleophilic reagent (*e.g.*, water or alcohol) and to employ a good ionising medium (Hughes and Ingold, J., 1935, 244 and later papers). We therefore examined the reaction with a comparatively small concentration

of water in formic acid solution, conditions which, in the case of the methyl and ethyl halides, had previously been shown to be favourable to the unimolecular mechanism (Bateman and Hughes, J., 1940, 945).

The first-order rate constants for the reactions of the four halides in "Kahlbaum" formic acid (which contains about 0.5% of water) are recorded in Table I; the constants for the reactions in aqueous ethyl alcohol are included for comparison. In both cases, the temperature was 95°, and k_1 is in sec.⁻¹.

TABLE I.

Comparison of First-order Rate Coefficients for the Reactions of Alkyl Bromides with 50% Aqueous Ethyl Alcohol and with "Kahlbaum" Formic Acid.

Alkyl bromide	Me.	Et.	<i>n</i> -Pr.	<i>neo</i> Pentyl.
$10^5 k_1$ for (1) the reaction with 50% H ₂ O-EtOH	286	141	80.3	0.910
(2) the reaction with "Kahlbaum" formic acid	1.74	2.70	1.85	1.53

We first note that for *neopentyl* bromide the rate is slightly greater in formic acid than in 50% aqueous ethyl alcohol. This fact recalls the similar behaviour of *tert.*-butyl chloride (Bateman and Hughes, J., 1940, 941), and may be regarded as further evidence in favour of our view that in both media the reaction of the primary halide, like that of the tertiary compound (for which the mechanism is well established), depends essentially on a rate-determining ionisation. Doubtless, the reaction in formic acid leads to the rearrangement of the *neopentyl* structure (cf. this vol., p. 166), though this has not been experimentally proved. In the case of the other three bromides, the rates in "Kahlbaum" formic acid are much smaller than those in aqueous ethyl alcohol, and this is consistent with our previous conclusion that the reactions of these halides in the latter medium are largely bimolecular (this vol., p. 164).

The chief point which emerges from the results of Table I is that in "Kahlbaum" formic acid the reactivity of *neopentyl* bromide is of the same order of magnitude as that of the other halides. Since the *neopentyl* reaction must be unimolecular, the evidence of the rates suggests that the reactions of the other alkyl halides largely pursue this mechanism. The main difference, Me < Et, to be expected on account of the inductive effect, is in the observed direction. The other theoretical differences, Et < *n*-Pr < *neo*Pentyl, which should be much smaller, are the reverse of the observed differences. This may mean that the finer theoretical differences become modified from what they would be if we could work with less energised molecules, *i.e.*, closer to the absolute zero of temperature. It is an equally reasonable interpretation, however, that even in formic acid, the bimolecular contribution to the rate, which by itself would lead to the sequence Me > Et > *n*-Pr > *neo*Pentyl, is by no means negligible in the case of the first three compounds (cf. Bateman and Hughes, J., 1940, 946). It could then be concluded that the rates for a reaction which is entirely and uniformly unimolecular throughout the series will exhibit the theoretical sequence (S_N1 :—Me < Et < *n*-Pr < *neo*pentyl) to be expected from the operation of the inductive effects of the alkyl groups; but that, owing to the great tendency for the incursion of a bimolecular contribution to the reaction rate in the simpler structures, it is difficult to test the validity of this conclusion. Some confirmation for the view that an alkyl halide containing a "neopentyl" structure may exhibit quite normal reactivity in unimolecular reactions is, however, provided by available data for the rates of solvolysis of three tertiary halides, one of which is a substituted *neopentyl* compound, under comparable experimental conditions. These are contained in Table II.

TABLE II.

First-order Rate Constants for the Solvolysis of Tertiary Alkyl Halides in 80% Aqueous Ethyl Alcohol at 25°.

Alkyl chloride	<i>tert.</i> -Butyl (CH ₃ ·CMe ₂ Cl).	<i>tert.</i> -Amyl (CH ₃ ·CH ₂ ·CMe ₂ Cl).	<i>aa</i> -Diethyl <i>neopentyl</i> (CMe ₃ ·CEt ₂ Cl).
$10^5 k_1$ (sec. ⁻¹)	0.854 *	1.50 †	11.7 ‡

* Cooper, Hughes, and Ingold, J., 1937, 1280.

† Hughes and MacNulty, J., 1937, 1283.

‡ Bartlett and Knox, *J. Amer. Chem. Soc.*, 1939, **61**, 3184.

In the tertiary halides, the ionisation mechanism is well developed and easy to isolate from accompanying bimolecular substitution, and it is clear that the "neopentyl" structure in the last compound has not introduced any abnormality in its reactivity towards unimolecular solvolysis. A further discussion of the results herein recorded is contained in the following paper.

EXPERIMENTAL.

Materials.—The quality of the halides used was the same as in the foregoing papers.

Kinetic Measurements.—A weighed quantity of the halide was dissolved in "Kahlbaum" formic acid (which contained about 0.5% of water), and the solution made up to a definite volume at room temperature. Portions of 5 ml. were then enclosed in small sealed tubes, which were heated for known times in the thermostat (at 95.15° ± 0.01°), cooled in solid carbon dioxide-alcohol, and their halide-ion contents estimated electrometrically. Owing to the slight decomposition of the formic acid which causes pressure in the reaction tubes, it was not possible to proceed with the runs for more than about 15 hours (*ca.* 5—10% reaction); nevertheless, it was possible to measure the initial rates quite accurately. The observations are adequately summarised in Table I; the results of two typical experiments are recorded in detail in Table III, where k_1 is in sec.⁻¹.

TABLE III.

Illustrating Determination of First-order Rate Constants.([RBr] expressed in equivalent ml. of 0.01N-AgNO₃ per 5 ml. of reaction mixture.)

1. <i>n</i> -Propyl bromide.								
<i>t</i> (hrs.)	0	1	2	4	5	6	7	8
[RBr]	51.94	51.57	51.21	50.55	50.27	49.94	49.70	49.36
<i>k</i> ₁ × 10 ⁶	—	1.98	1.95	1.89	1.82	1.81	1.75	1.78
Mean <i>k</i> ₁ = 1.85 × 10 ⁻⁶ . A duplicate run gave <i>k</i> ₁ = 1.84 × 10 ⁻⁶ .								
2. neoPentyl bromide.								
<i>t</i> (hrs.)	0	1	3	6	9	13	17.5	
[RBr]	55.17	54.87	54.23	53.35	52.50	51.52	50.19	
<i>k</i> ₁ × 10 ⁶	—	1.47	1.60	1.56	1.53	1.46	1.51	
Mean <i>k</i> ₁ = 1.52 × 10 ⁻⁶ . A duplicate run gave <i>k</i> ₁ = 1.54 × 10 ⁻⁶ .								

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