48. *Mechanism of Substitution at a Saturated Carbon Atom. Part XXX. The Rôle of Steric Hindrance. (Section E) A Comparison of the Rates of Reaction of Methyl, Ethyl, n-Propyl, isoButyl, and neoPentyl Halides with Silver Nitrate in Aqueous Ethyl Alcohol.*

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A comparison has been made of the rates of reaction of the halides, named in the title, with silver nitrate in " 70% " aqueous ethyl alcohol. The rate sequence is found to be Me<Et>n-Pr>isoBu>neoPentyl, the relative rates (Et = 1) for the bromides at 64° being : Me 0·81, Et 1, n-Pr 0·51, isoBu 0·084, and neoPentyl 0·013. By comparison with the results for the bimolecular reaction with sodium ethoxide in dry ethyl alcohol (see Abstract on p. 157), and the solvolytic reaction with 50% aqueous ethyl alcohol (Abstract, p. 164), the sequence of rates for the methyl and ethyl halides is reversed, and the rate differences due to the progressive introduction of β-methyl substituents are, on the whole, smaller than before. The mechanism of the silver reaction is complex, but the available information concerning it is consistent with the conclusion that the effects are associated with an ionisation mechanism, which if fully developed throughout the series should lead to the inequality Me<Et, and might lead to the sequence Me<Et<n-Pr<isoBu<neoPentyl (cf. following paper). It seems clear that the ionisation process is a greater influence on the variation of rate in the series as a whole than was the case in the solvolytic reaction. Some special aspects of the results are discussed in Part XXXII (p. 173).

REACTIONS involving the elimination of halogen from organic halides are often carried out with the aid of silver salts in appropriate solvents. The results of investigations concerning the mechanism of these reactions have led to the conclusion that they are mainly heterogeneous, the removal of the halogen by the electrophilic silver ions being facilitated by adsorption of the reagents on the surface of the precipitated silver halide (Hughes, Ingold, *et al.*, J., 1937, 1236, 1243, 1252). The process then depends essentially on an assisted heterogeneous ionisation of the alkyl halide, which is generally succeeded, under the conditions usually employed, by the reaction of the carbon cation with a nucleophilic solvent or solute molecule (*e.g.*, H_2O, $\overline{NO_3}$). The general resemblance to the homogeneous unimolecular substitution mechanism (S_N1) is then reflected in certain similarities in the characteristic features of the two processes. The analogy of behaviour has been observed particularly in connection with the stereochemical consequences of the substitution processes, and the effects on the reaction rates of structural changes in the organic halide (Hughes, Ingold, *et al.*, *loc. cit.*).

With this impression of the reaction mechanism in mind, we decided to compare the rates of reaction between *neo*pentyl halides and silver nitrate in aqueous ethyl alcohol with the corresponding rates for the halides of the other alkyl groups named in the title. We considered that we could thus assess the comparative reactivities of these compounds towards a reaction which is in common use in organic chemistry, and which may be of such a mechanism as to give an indication of the relative rates under conditions more favourable to ionisation in the alkyl series as a whole than those obtaining in the work described in the preceding papers.

As already implied, the reaction is complex, but it often approximates to one of the second order (Chiminello, *Gazzetta*, 1895, **25**, ii, 410; v. Biron, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 667; Burke and Donnan, *J.*, 1904, **85**, 555; Senter, *J.*, 1911, **99**, 95). We found this to be the case in our work; for the same initial concentration of the silver salt, the second-order rate coefficients were nearly constant for the greater part of the reaction (cf. experimental section); thus they afford the best means of expressing the comparative reactivities of the halides. The main results of the investigation are summarised in Table I, where k_2 is in sec.$^{-1}$ g.-mol.$^{-1}$ l. The relative rates (Et = 1) for the alkyl bromides are given in Table II, where a comparison is made with the results for two other reactions previously studied (preceding papers).

TABLE I.

Summary of Second-order Rate Coefficients for the Reaction of Alkyl Halides in " 70% " * *Aqueous Ethyl Alcohol.*

Halide.	Initial [Halide].	Initial [AgNO$_3$].	Temp.	$k_2 \times 10^4$.	Halide.	Initial [Halide].	Initial [AgNO$_3$].	Temp.	$k_2 \times 10^4$.
MeBr	~0·10M	~0·14M	63·95°	62·5	CMe$_3$·CH$_2$Br ...	~0·10M	~0·14M	63·95°	1·01
EtBr	~0·10M	~0·14M	63·95°	76·9	n-PrCl	~0·20M	~0·50M	95·0	3·43
n-PrBr	~0·10M	~0·14M	63·95	42·0	isoBuCl	~0·20M	~0·50M	95·0	0·634
isoBuBr ...	~0·10M	~0·14M	63·95	6·44	CMe$_3$·CH$_2$Cl ...	~0·20M	~0·50M	95·0	0·159

* Cf. experimental section.

TABLE II.

Relative Rates (Et = 1) for the Reactions of Alkyl Bromides.

(1) = Bimolecular reaction with NaOEt in EtOH at 95°.   (2) = Solvolytic reaction in " 50% " H$_2$O–EtOH at 95°.   (3) = Reaction with AgNO$_3$ in " 70% " EtOH at 64.° †‡

Alkyl bromide.	(1).	(2).	(3).	Alkyl bromide.	(1).	(2).	(3).
Me	15	2·0	0·81	isoBu	0·41	0·080	0·084
Et	1	1	1	CMe$_3$·CH$_2$·	0·00001	0·0065	0·013
n-Pr	(0·28) *	0·57	0·55				

* Calculated on the assumption that the ratio $k_{\text{EtBr}}/k_{n-\text{PrBr}}$ is independent of temperature.

† The differences of rate between the three chlorides included in our investigation (Table I) are somewhat smaller (relative rates: n-Pr, 1; isoBu, 0·18; neoPentyl, 0·046) than those found for the corresponding bromides (relative rates: n-Pr, 1; isoBu, 0·16; neoPentyl, 0·025), but it should be noted that the experimental conditions were different in the two sets of experiments.

‡ A similar order of rates for part of the alkyl series (relative rates: Me, 0·43; Et, 1; n-Pr, 0·45; isoBu, 0·063) was observed by Burke and Donnan (*loc. cit.*) for the reaction of the alkyl iodides with silver nitrate in dry ethyl alcohol at 24·5°.

The most important feature of the results (see Table II) is that the main differences of behaviour which the solvolytic reaction (this vol., p. 164) exhibits, by comparison with the bimolecular reaction with sodium ethoxide (this vol., p. 157), are now emphasised. Thus, the retarding effect of β-alkyl substitution, which was reduced on passing from the bimolecular reaction to the solvolytic process, is, on the whole, further reduced in the silver reaction, so that the neopentyl halides, though still the slowest of the halides, are not notably unreactive towards silver nitrate.* Again, the effect of changing from the bimolecular to the solvolytic reaction on the relative reactivities of the methyl and ethyl halides is emphasised, so much so that the rate for methyl bromide is now reduced below that for ethyl bromide. The results are consistent with the hypothesis that, in the silver reaction, the effects which are expected to be associated with an ionisation mechanism are exerting a greater influence on the variation of rate in the series as a whole than is the case in the solvolytic reaction.

To attempt a detailed explanation of the rate relationship for the silver reaction would be unjustified in view of the complex nature of the reaction, but we suggest three reasons for the absence of the theoretical rate sequence to be expected for a simple ionisation process, namely, Me <Et <n-Pr <isoBu <neoPentyl. First, the inequality Me <Et is in fact observed, and the remaining inequalities, which should be much smaller because of the loss suffered by the inductive effect in transmission through an intervening carbon atom, may fail to appear because we work with energised molecules, not the static molecules contemplated by the simple theory which underlies a polar sequence. Secondly, owing to the heterogeneous catalysis by silver halide, there may be a facilitating effect which depends on the ease of adsorption of the halide and decreases in importance in the order Me >Et >n-Pr >isoBu >neoPentyl. Thirdly, the electrophilic catalysis by silver ions may be assisted by solvent molecules, or by nitrate ions, acting by virtue of their nucleophilic activity towards the α-carbon atom. Such an assistance would involve an adsorbed transition state of the type [H$_2$O . . . R . . . Br . . . Ag],$^+$ and its importance would again diminish in the order Me >Et >n-Pr >isoBu >neoPentyl. For the neopentyl halides, it may be safely assumed that any effect of this type would be quite negligible because of the resistance of the structure to the attack of a reagent on the α-carbon atom. The work of Whitmore, Wittle, and Popkin (*J. Amer. Chem. Soc.*, 1939, **61**, 1586) indirectly shows that the reaction involves rearrangement of the neopentyl group.

EXPERIMENTAL.

Materials.—neoPentyl chloride, prepared by chlorination of neopentane (Whitmore and Fleming, *J. Amer. Chem. Soc.*, 1932, **54**, 3460; 1933, **55**, 3803, 4161), was fractionated through a 15-plate column (this vol., p. 159); b. p. 85·0—85·1°/760 mm. neoPentyl bromide was prepared and purified as previously described. The other halides used were commercial samples which had been subjected to rigorous purification (cf. this vol., pp. 160, 163, and 165). Commercial absolute ethyl alcohol was dried (this vol., p. 160), refluxed with silver nitrate for several hours, and fractionated.

Rate Measurements.—For the experiments with the alkyl chlorides, the appropriate quantity of " AnalaR " silver nitrate was dissolved in 600 ml. of distilled water and the solution made up to 2 l., at room temperature, with purified ethyl alcohol. This reagent was used in all the comparative measurements involving the alkyl chlorides and the medium will be referred to as " 70% " EtOH (B). In the experiments with the bromides, silver nitrate was dissolved in the medium [" 70% " EtOH (A)] obtaining by mixing, at room temperature, 70 vols. of alcohol and 30 vols. of distilled water. In all cases, weighed quantities of the halides were made up to 100 ml. at 0° with the reagent solutions described above, and portions of 5 ml. were sealed up in tubes, which were wrapped in tin foil and immersed in the thermostat. Tubes

* This result was evident from the work of Whitmore and his co-workers (see this vol., p. 157).

were removed at intervals, and the silver nitrate content estimated either by electrometric titration with standard potassium chloride solution or by titration with ammonium thiocyanate, using ferric sulphate as indicator. The reaction is complex, but it approximates to one of the second order (cf. p. 169), and, for comparative purposes, the second-order rate coefficients were averaged. The average values obtained in all the experiments have already been recorded (Table I); these have been corrected for thermal expansion between the temperature at which the 5-ml. portions were measured and the temperature of the thermostat. The results of some typical experiments (uncorrected for expansion) are shown in Table III; k_2 is in sec.$^{-1}$ g.-mol.$^{-1}$ l.

TABLE III.

Illustrating Determination of Second-order Rate Coefficients.

I. *Alkyl bromides in " 70% " EtOH (A) at 63·95°.*

(i) *neo*Pentyl bromide. [RBr] and [AgNO$_3$] expressed in ml. of 0·03N-KCl per 5 ml. of solution.

t (hrs.) ...	0	1	3	5	10	11·3	18	21·5
[RBr] ...	15·74	15·05	13·59	12·60	10·50	9·98	8·21	7·43
]AgNO$_3$]	23·52	22·83	21·37	20·38	18·28	17·76	15·99	15·21
$k_2 \times 10^5$	—	9·72	10·23	9·53	9·16	9·31	8·86	8·84

(ii) *iso*Butyl bromide. [RBr] and [AgNO$_3$] expressed in ml. of 0·03N-KCl per 5 ml. of solution.

t (mins.)	0	9	18	30	42	57·5	72	81	99	120	135	156
[RBr] ...	15·68	15·07	14·35	13·57	12·95	12·18	11·37	11·05	10·42	9·71	9·19	8·71
[AgNO$_3$]	22·31	21·70	20·98	20·20	19·58	18·81	18·00	17·68	17·05	16·34	15·82	15·34
$k_2 \times 10^4$	—	5·59	6·34	6·32	6·06	5·99	6·23	6·09	5·93	5·87	5·93	5·78

(iii) Ethyl bromide. [RBr] and [AgNO$_3$] expressed in ml. of 0·0306M-ammonium thiocyanate per 5 ml. of reaction mixture.

t (mins.)	0	3	6	8·5	11	15	21	25	30	47	56
[RBr] ...	10·76	9·20	7·87	7·23	6·68	5·50	4·57	3·90	3·33	2·06	1·65
[AgNO$_3$]	19·56	18·00	16·67	16·03	15·48	14·30	13·37	12·70	12·13	10·86	10·45
$k_2 \times 10^3$	—	7·62	7·86	7·23	6·83	7·38	7·00	7·23	7·19	7·05	6·90

II. neo*Pentyl chloride in 70% EtOH (B) at 95·0°.*

[RBr] and [AgNO$_3$] expressed in ml. of 0·0734N-ammonium thiocyanate per 5 ml. of solution.

t (hrs.) ...	0	4	6	7	8	10	11·25	11·75	15	16	18	18·5
[RBr] ...	12·33	11·14	10·29	10·29	10·09	9·49	9·39	9·19	8·73	8·76	8·22	8·14
[AgNO$_3$]	33·64	32·45	31·60	31·60	31·40	30·80	30·70	30·50	30·04	30·07	29·53	29·45
$k_2 \times 10^5$	—	1·46	1·76	1·51	1·47	1·54	1·41	1·48	1·37	1·28	1·36	1·36

t (hrs.) ...	20	22	23
[RBr] ...	7·86	7·20	7·20
[AgNO$_5$]	29·17	28·50	28·50
$k_2 \times 10^5$	1·37	1·50	1·44

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