45. *Mechanism of Substitution at a Saturated Carbon Atom. Part XXVII. The Rôle of Steric Hindrance. (Section B) A Comparison of the Rates of Reaction of Ethyl and* neo*Pentyl Bromides with Inorganic Iodides in Acetone Solution.*

By I. Dostrovsky and E. D. Hughes.

A comparison of the rates of reaction of ethyl and *neo*pentyl bromides with inorganic iodides in acetone solution has been made. This reaction is again of the bimolecular type, and, when the results are compared with those obtained for the reaction with sodium ethoxide in alcohol (preceding paper), it is found that the *neo*pentyl structure is responsible for a similarly large decrease of rate in both cases. An analysis of the complications which may arise in the halogen-exchange reaction is given. The main results are discussed in Part XXXII.

In the preceding paper it was shown that *neo*pentyl bromide is, by comparison with other primary alkyl bromides, extremely unreactive in its bimolecular reaction with sodium ethoxide in ethyl alcohol [some relative rates at 55° were as follows: $(CH_3)_3C{\cdot}CH_2Br$, 1; $CH_3{\cdot}CH_2{\cdot}CH_2Br$, $6{\cdot}6 \times 10^4$; $CH_3{\cdot}CH_2Br$, $2{\cdot}4 \times 10^5$]. In order to ascertain if such behaviour is characteristic of bimolecular substitution generally, it is necessary to consider comparative data of a similar type relating to other reactions proceeding by this mechanism. After the completion of our work on the reaction with sodium ethoxide, Bartlett and Rosen published the results of an investigation of the rates of reaction of *neo*pentyl bromide, and of certain other alkyl bromides, with potassium iodide in acetone solution (*J. Amer. Chem. Soc.*, 1942, **64**, 543; cf. this vol., p. 157). This reaction is also of the bimolecular type, and is clearly suitable for comparison with the ethoxylation process.

Qualitatively, the work of Bartlett and Rosen shows that *neo*pentyl bromide exhibits a similarly inert behaviour towards potassium iodide; but the magnitude of the " *neo*pentyl effect " appears, from their results, to be much smaller than in the reaction with sodium ethoxide. These authors compared the reactions of *neo*pentyl bromide and *n*-butyl bromide at 25°. Since our alkyl series did not include *n*-butyl bromide, a rigorous comparison of their data and ours cannot be made; but, as the results of other investigations indicate that the rate differences between *n*-propyl bromide and *n*-butyl bromide are invariably small in bimolecular substitutions (Hughes and Ingold, J., 1935, 244; Hammett, " Physical Organic Chemistry," McGraw Hill Book Co., Inc., N.Y., 1940, p. 154; McKay, *J. Amer. Chem. Soc.*, 1943, **65**, 702), we may obtain a good indication of the position by comparing our ratio (1/66,000) for the ethoxide reactions of *neo*pentyl and *n*-propyl bromides with Bartlett and Rosen's ratio (1/470) for the iodide reactions of *neo*pentyl and *n*-butyl bromides. It would thus appear that the " *neo*pentyl effect " for the reaction with potassium iodide at 25° is smaller than that for the reaction with sodium ethoxide at 55° by a factor of the order of 10^2. Since the reactions involving *neo*pentyl bromide have higher activation energies than those of the other halides under discussion (see below, and the preceding paper), the difference would be even greater if the comparisons referred to the same temperature. An identical factor for the *neo*pentyl effect in two different reactions is not to be expected, even when these reactions proceed by the same mechanism, but we did not anticipate quite such a large difference between the two processes under consideration, and therefore decided to examine the reactions of ethyl bromide and *neo*pentyl bromide with metallic iodides in acetone solution. The results are recorded in this paper.

The reactions of alkyl chlorides and bromides with metallic iodides are, in principle, always reversible, $RBr(Cl) + MI \rightleftharpoons RI + MBr(Cl)$, but in acetone solution the solubilities of the chlorides and bromides of some of the metals usually employed are small (the iodides are generally much more soluble), and the formation of the organic iodide is thereby greatly favoured. The solubility factor is important when, for example, the iodides of sodium and potassium are used, but it is unimportant in the case of lithium, because the halides of lithium are comparatively soluble and the solution with this cation remains homogeneous throughout reaction.

With *neo*pentyl bromide and sodium iodide, fairly good second-order coefficients for the first 60% of reaction were obtained by using the ordinary second-order rate equation

$$k_2 = [1/(a - b)t] \log_e [b(a - x)/a(b - x)]$$

where a and b are the initial concentrations of the reactants, and x is the decrease in the concentration of either after time t. Similar results were obtained with potassium iodide. When allowance is made for small differences in the initial concentrations of the inorganic iodides (see experimental section), the rate coefficient found in both cases was approximately the same as that obtained from a study of the first third of the homogeneous, and therefore much more reversible, reaction with lithium iodide. As is usual for these reactions, the second-order coefficient decreases somewhat when the initial concentration of the inorganic iodide is increased (cf. Hughes, Juliusburger, Masterman, Topley, and Weiss, J., 1935, 1525; and the experimental section of this paper).

At a temperature for which a direct comparison with *neo*pentyl bromide could be made (64°), the reaction of ethyl bromide with sodium iodide was rapid and reversible, equilibrium being reached in about 20 minutes with the formation of approximately 85% of the theoretical yield of ethyl iodide. The results obtained were slightly erratic in that the second order rate coefficients calculated from the analysis of various reaction tubes occasionally showed considerable divergence, especially after about the first third of the reaction had been completed (see below). In order to minimise both this disturbance and the effect of reversibility, detailed measurements, from which the rate coefficients adopted in our discussion were deduced, were confined to the first 30% of reaction. Similar results were obtained with potassium iodide, but the mean value of the rate coefficient was somewhat lower (see Table I, below) than for the reaction with sodium iodide. The reaction of ethyl bromide with lithium iodide at 64° came to rapid equilibrium with the formation of about 10% of ethyl iodide, and it could not be accurately followed; but it was shown that the rate coefficient calculated from measurements of initial rates at two lower temperatures (0° and 20°) was comparable with the coefficients deduced for the reactions with sodium and potassium iodides (Table I).

The variation of rate in the measurements with sodium and potassium iodides is probably to be ascribed mainly to the heterogeneous nature of the reactions. The rate of formation of the organic iodide would be expected to be free from complications due to reversibility if the inorganic bromide was precipitated more or less completely and instantaneously. The salt formed has, however, an appreciable solubility, and, furthermore, the solution may at times become supersaturated, resulting in a non-reproducible apparent decrease of rate. The same difficulty does not arise to the same degree in the case of *neo*pentyl bromide, partly because the relative rates of the opposing processes are more favourable to the forward reaction, and partly because the reaction is slow enough greatly to reduce complication due to supersaturation.*

Another factor which arises from the heterogeneous nature of the reaction with sodium and potassium iodides has been detected, namely, that the separation of the inorganic bromides involves co-precipitation of inorganic iodide. Since we use the miniature sealed tube technique for the heterogeneous processes (cf. experimental section), this factor cannot vitiate our analytical procedure for estimating the total iodide ion concentration in aliquot portions of the reaction mixture (which was initially homogeneous); but it has some influence on the effective concentration of the inorganic iodide in solution, and therefore on the second-order rate coefficients calculated on the assumption that the whole of the iodide remains dissolved. In general, the disturbance is not serious, as is shown by the result that the rate coefficients for the reactions with sodium and potassium iodides are usually about the same as those obtained for the homogeneous reaction with lithium iodide (cf. Conant and Hussey, *J. Amer. Chem. Soc.*, 1925, **47**, 476; and also our results for *neo*pentyl bromide) The effect on the rate coefficients will, however, depend to some extent on the supersaturation factor, and on the nature of the precipitated salt and its state of aggregation during the period of reaction, so that somewhat variable results may be obtained in certain cases as already described.

The main results of the investigation are summarised in Table I, where the rate coefficients are in sec.$^{-1}$ g.-mol.$^{-1}$ l.

If we neglect small differences in the concentrations of the reagents employed in some of the experiments (cf. experimental section), the ratios for the rates of reaction of the bromides with the inorganic iodides specified are as shown in the last row of the table. Notwithstanding the complications referred to, and the lack of complete agreement between the results for the various iodides, the approximate value of the " *neo*pentyl effect " in this reaction cannot be in doubt. If we adopt the figure 2×10^4 as the average value for the ratio of the rates at 64°, we may conclude that it is smaller than the corresponding ratio for the rates of reaction of the same two bromides with sodium ethoxide at 55° by a factor of 12. For equal temperatures the factor would be smaller (cf. p. 161).

---

* A disturbance of this type will undoubtedly be dependent both on the rate of precipitation and on the rate of reaction; it will be of serious consequence if a considerable part of the reaction is completed before the formation of nuclei has occurred, and the conditions governing rapid precipitation have been reached.

TABLE I.

Comparison of the Rates of Reaction of Ethyl and neo*Pentyl Bromides* (RBr) *with Metallic Iodides* (MI) *in Acetone Solution at* 64°.

([RBr] and [MI] ~0·05M.)

Reaction.	(1) RBr + NaI.	(2) RBr + KI.	(3) RBr + LiI.
10^3k_{EtBr}	69	48	45 *
$10^3k_{\mathrm{C_5H_{11}Br}}$	0·0031	0·0027	0·0028
$k_{\mathrm{EtBr}}/k_{\mathrm{C_5H_{11}Br}}$	$2{\cdot}2 \times 10^4$	$1{\cdot}8 \times 10^4$	$1{\cdot}6 \times 10^4$

* Calculated from experiments at lower temperatures.

The Arrhenius activation energy of the reaction of *neo*pentyl bromide with sodium iodide is found to be approximately 25 kg.-cals., whereas that for ethyl bromide and lithium iodide is 19 kg.-cals. These figures are deduced from measurements at two temperatures only, and may be subject to considerable error; nevertheless, it may be safely concluded that the comparative inactivity of *neo*pentyl bromide in bimolecular halogen exchange is largely due to an increase in the activation energy of the reaction. A discussion of these facts is given in Part XXXII (this vol., p. 173). Further work on the halogen-exchange reactions of alkyl halides is in progress.

EXPERIMENTAL.

Materials.—Acetone was purified by the method of Conant and Kirner (*J. Amer. Chem. Soc.*, 1924, **46**, 245), and fractionated through a seven-plate column. The inorganic halides were dried in a vacuum at 140° in an Abderhalden apparatus. *neo*Pentyl bromide was obtained as described in the preceding paper. Ethyl bromide was obtained from a commercial sample, which was purified by fractionation through a 15-plate column; b. p. 37·9—38·1°/760 mm.

Kinetic Methods.—For the experiments with ethyl bromide and lithium iodide, a weighed quantity of the inorganic halide was dissolved in acetone in a graduated flask at 0° or 20°, about 0·5 ml. of the organic halide was added, and the solution was made up to 100 ml. with solvent which had attained the thermostat temperature. At suitable intervals aliquot portions of the reaction mixture were withdrawn and estimated by a modification (see below) of Lang's "iodine cyanide" method (*Z. anorg. Chem.*, 1922, **122**, 332; 1925, **142**, 229, 279; **144**, 75). In the experiments with sodium and potassium iodides, solutions of the organic and inorganic halides were made up separately at room temperature. Portions of 5 ml. of the ethyl bromide solutions were then introduced into small tubes which were cooled to *ca.* – 80°. Then 5 ml. of the solution of the inorganic iodide were added to each, and the tubes sealed and kept at *ca.* – 80° until required. For the rate measurements, the small sealed tubes were immersed in the thermostat for known times, and the contents estimated as in the experiments with lithium iodide. The initial concentration of ethyl bromide was determined in all cases by quantitative hydrolysis of aliquot portions of the reaction mixtures with alkali in small sealed tubes at 95°. For *neo*pentyl bromide, weighed quantities of the organic and the inorganic halides were used to make up

TABLE II.

Summary of Second-order Rate Coefficients for the Reaction of Ethyl and neo*Pentyl Bromides* (RBr) *with Metallic Iodides* (MI) *in Acetone Solution.*

(k_2 in sec.$^{-1}$ g.-mol.$^{-1}$ l.)

Reactants.		RBr.	MI.	Temp.	10^3k_2.	Reactants.		RBr.	MI.	Temp.	10^3k_2.
$C_5H_{11}Br$	NaI	0·07M	0·10M	95·2°	0·062	EtBr	NaI	0·04M	0·03M	64·05°	69
,,	,,	0·07M	0·05M	95·2	0·075	,,	KI	0·04M	0·03M	64·05	48
,,	,,	0·07M	0·05M	64·05	0·0031	,,	LiI	0·05M	0·07M	20·0	0·65
,,	KI	0·05M	0·07M	64·05	0·0027	,,	,,	0·05M	0·07M	0·0	0·061
,,	LiI	0·05M	0·07M	64·05	0·0028						

TABLE III.

Illustrating Determination of Second-order Rate Coefficients.

(k_2 in sec^{-1}. g.-mol.$^{-1}$ l.)

1. Reaction of *neo*Pentyl Bromide with Sodium Iodide. [RBr] and [NaI] expressed in ml. of 0·01665N-KIO_3 per 5·41 ml. sample.

(*a*) Temperature = 95·2°.

t (hrs.)	0	17·5	20·5	25·0	41·0	42·0	43·0	43·83	89·0	89·15
[RBr]	23·34	20·32	19·71	19·01	16·73	16·79	16·65	16·53	13·04	13·00
[NaI]	17·04	13·02	12·41	11·71	9·43	9·49	9·35	9·23	5·74	5·70
10^5k_2	—	6·27	6·41	6·32	6·54	6·30	6·34	6·39	6·44	6·49

(*b*) Temperature = 64·05°.

t (hrs.)	0	171	268	451	668	1492	1860
[RBr]	23·03	21·04	20·19	18·69	17·28	14·26	13·14
[NaI]	15·57	13·58	12·73	11·23	9·82	6·80	5·68
10^6k_2	—	3·00	2·96	3·06	3·08	2·80	2·89

2. Reaction of Ethyl Bromide with Sodium Iodide at 64·05°. [RBr] and [NaI] expressed in ml. of 0·01665N-KIO_3 per 10·00 ml. sample.

t (mins.)	0	0·5	0·75	1·00	1·00	1·5	11·5	2·0
[RBr]	24·10	22·56	22·10	21·48	21·52	20·46	20·56	19·51
[NaI]	18·34	16·80	16·34	15·72	15·76	14·70	14·80	13·75
10^2k_2	—	7·60	6·66	6·76	6·56	6·66	6·45	6·66

a standard mixture at 0°; 5 ml. portions were then sealed in small bulbs, and the reaction followed as described for ethyl bromide. Lang's method of estimation had to be slightly modified for our purpose in order to avoid interference due to the presence of acetone.* Our procedure was as follows: The sample was diluted with 100 ml. of ice-cold water, the aqueous solution was then acidified with 20 ml. of a cold aqueous mixture of sulphuric and hydrochloric acids (12N in H_2SO_4 and 3N in HCl), 5 ml. of 15% aqueous potassium cyanide were added, and the mixture titrated with standard potassium iodate solution, using starch as indicator. Initial or "zero" readings were obtained by the analysis of samples which had been kept in the thermostat for periods sufficient for them to attain the correct temperature.

The most important features of the results are illustrated in the tables on p. 163. The mean second-order coefficients recorded in Table II are corrected for thermal expansion between the temperature at which the samples were measured and that of the thermostat. The results for a few typical experiments shown in Table III have not been corrected for expansion, but this does not, of course, alter the relative values of the coefficients of any one experiment.

Sir William Ramsay and Ralph Forster Laboratories, University College, London, W.C.1.
University College of North Wales, Bangor.

[*Received, August 28th,* 1945.]