958. *Solvolysis and Rearrangement of n-Propyl Bromide under the Influence of Mercury Salts in Slightly Aqueous Formic Acid.*

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The solvolysis of n-propyl bromide catalysed by mercury salts in 90% formic acid at 25° is a fast reaction with complicated kinetics. The products of reaction include isopropyl derivatives and these are formed in constant proportion with a variety of catalyst concentrations. Direct rearrangement of a carbonium-ion intermediate with intramolecular hydrogen shift is discussed as a probable mechanism for the formation of rearranged products. An alternative possibility, involving the formation of propene and its subsequent hydration, is excluded by the experimental evidence.

The formation of rearranged products is a feature of many reactions in which carbonium ions are formed. Most of the examples [1,2] involving alkyl halides refer to non-solvolytic conditions, a notable exception being neopentyl bromide [3] which yields mainly tertiary pentyl derivatives as its substitution products (in addition to olefin).[3,4]

The present work was directed towards the problem whether a rearrangement involving only hydride transfer can be realised during the solvolysis of a primary alkyl halide in conditions favourable to the intermediate generation of carbonium ions. The compound chosen was an n-propyl halide, since this is the simplest system in which the occurrence of rearrangement can be observed without recourse to isotopic tracer methods. It is known that under the influence of Friedel–Crafts catalysts n-propyl derivatives rearrange to compounds of the isopropyl group.[2] This rearrangement is in the expected direction, since secondary carbonium ions are more stable than primary ones. The medium employed for our solvolysis experiments was formic acid containing 10% of water and mercury salts, prepared by dissolving pure mercuric oxide in 90% formic acid. These conditions were suggested by (i) the studies of earlier workers [5] who had shown that the uncatalysed solvolyses of primary halides may proceed, at least in part, by a carbonium-ion mechanism in slightly aqueous formic acid, and (ii) two sets of investigations [6,7] on the solvolyses of alkyl halides in the presence of mercury salts from which it was concluded that these salts

Table 1. *Catalysed solvolysis of n-propyl bromide.*

					Product composition	
Expt.	$10^3[\mathrm{Pr^nBr}]_0$	$10^3[\mathrm{HgO}]_0$	$10^6\left[\frac{\mathrm{d}[\mathrm{Br}^-]}{\mathrm{d}t}\right]_{\text{initial}}$ (mole l.$^{-1}$ sec.$^{-1}$)	10^3k_2* (l. mole^{-1} sec.$^{-1}$)	Reaction † (%)	$\mathrm{Pr^iOH}$ (%) in product
1	80·0	128	27	2·5	73·2	13·7
					50·7	12·5
2	80·0	80·0	$17{\cdot}_5$	2·7	68·8	12·3
					45·0	13·6
3	80·0	40·0	8	$2{\cdot}_5$	48·7	12·8
					33·1	13·7
4	40·0	39·0	4	$2{\cdot}_6$	51·3	12·2
					Mean	13·0

* $k_2 = (\mathrm{d}[\mathrm{Br}^-]/\mathrm{d}t)_{\text{initial}}/[\mathrm{HgO}]_0[\text{n-PrBr}]_0$.

† This value in this column indicates the stage of the reaction (expressed as $100[\mathrm{Br}^-]/[\mathrm{Pr^nBr}]_0$) to which the sample for measuring product composition refers.

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[1] McMahon and Hine, *J. Amer. Chem. Soc.*, 1949, **71**, 1896; J. D. Roberts, McMahon, and Hine, *J. Amer. Chem. Soc.*, 1950, **72**, 4237; Sixma and Hendriks, *Rec. Trav. chim.*, 1956, **75**, 169; R. M. Roberts and Panayides, *J. Org. Chem.*, 1958, **23**, 1080.

[2] Baddeley, *Quart. Rev.*, 1954, **8**, 355.

[3] Whitmore and Fleming, *J. Amer. Chem. Soc.*, 1933, **55**, 4161.

[4] Whitmore, Wittle, and Popkin, *J. Amer. Chem. Soc.*, 1939, **61**, 1586; Dostrovsky and Hughes, *J.*, 1946, 166.

[5] Bateman and Hughes, *J.*, 1940, 945; Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979; Dostrovsky and Hughes, *J.*, 1946, 171.

[6] Benfey, *J. Amer. Chem. Soc.*, 1948, **70**, 2165.

[7] Oae and VanderWerf, *J. Amer. Chem. Soc.*, 1953, **75**, 5037.

further favour the ionisation of alkyl halides. The results of our experiments are given in Table 1.

The precise nature of the catalyst is not known, owing to the probable importance of equilibria such as:

$$\mathrm{Hg^{2+} + H{\cdot}CO{\cdot}O^- \rightleftharpoons [H{\cdot}CO{\cdot}OHg]^+}$$
$$\mathrm{[H{\cdot}CO{\cdot}OHg]^+ + H{\cdot}CO{\cdot}O^- \rightleftharpoons (H{\cdot}CO{\cdot}O)_2Hg}$$

However, it is to be expected that the general effect of mercuric species would be an electrophilic catalysis of halide removal, according to a scheme similar in principle to the reactions:

$$\mathrm{Pr^nBr + Hg^{2+} \longrightarrow n\text{-}Pr^{\delta+} \ldots Br^{\delta-} \ldots Hg^{2+} \longrightarrow n\text{-}Pr^+ + HgBr^+}$$
$$\mathrm{HgBr^+ + H{\cdot}CO{\cdot}O^- \rightleftharpoons [H{\cdot}CO{\cdot}OHg]^+ + Br^-}$$

The values of k_2 in the Table represent the rate constants calculated from initial rates on the assumption that the catalytic activity of the medium in each case is proportional to the stoicheiometric concentration of mercuric oxide.

During the reaction, some reduction of mercuric to mercurous derivatives takes place and, in addition, difficulties arise in measuring accurately the gradients of reaction curves. The values given for k_2 must therefore by taken as representing only the order of magnitude of the initial rate constant.

The most significant result is that isopropyl derivatives are found in the reaction products. These isopropyl compounds might be formed by direct rearrangement of the n-propyl cation, followed by reaction with water or formic acid molecules. Alternatively, as olefin formation frequently accompanies substitution in solvolytic reactions, isopropyl derivatives could arise from the addition of water or formic acid to propene. The latter possibility is excluded in the present case by the following two results.

(1) When propene is dissolved in 90% formic acid the gas may be removed by bubbling air through the solution, and the propene carried over may be estimated by absorption in a solution of bromine in acetic acid. With a mixture of 90% formic acid and mercuric oxide as solvent (the conditions of the solvolysis experiments), propene is not removed by bubbling air through the mixture, but the product of interaction of propene and the mercury solution is not isopropyl alcohol or formate. This was shown by subjecting a solution of propene in 90% formic acid containing mercuric oxide to the analytical procedure used in the estimation of isopropyl derivatives in the solvolysis experiments. Many examples are known [8] of interactions (to form addition complexes) between olefins and mercury salts in solution, and it seems likely that any propene formed during the catalysed solvolysis of n-propyl bromide might be trapped in this way.

(2) When the solvolysis of n-propyl bromide is carried out in a tritiated medium (under conditions as for the experiments reported) the product alcohol contains no C–T bonds. It is to be expected that at least one C–T bond per molecule would be found if the isopropyl derivatives had been formed through propene as an intermediate. This result also shows that intermediates formed in the solvolysis reaction do not undergo hydrogen exchange with the medium. A similar conclusion was reached by Cannell and Taft [9] in their investigation of the deamination of isobutylamine in deuterated aqueous perchloric acid.

The two lines of evidence outlined show conclusively that the formation of propene and subsequent solvent-addition to propene cannot account for the formation of isopropyl derivatives in the catalysed solvolysis, and that the rearrangement must involve an intramolecular hydrogen shift.

It seems reasonable to suppose that the rearrangement occurs at the carbonium-ion stage for, in the absence of mercuric salts (when the reaction is much slower and the

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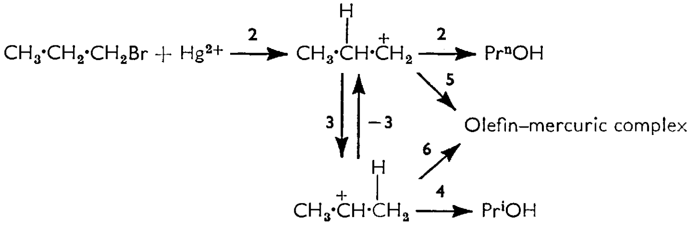
[8] Chatt, *Chem. Rev.*, 1951, **48**, 7.

[9] Cannell and Taft, *J. Amer. Chem. Soc.*, 1956, **78**, 5812.

proportion of the unimolecular mechanism is likely to be considerably reduced), the extent of rearrangement is much smaller.[10]

Stripped of details such as ion association and solvation, the reaction could then be represented by the scheme:



The absence of hydrogen exchange during the reaction accords with the conclusion reached previously [11] that, in the absence of a reaction *via* an olefin, carbonium ions do not undergo exchange with an acidic solvent.

A notable feature of the results in the Table is the constancy of the proportion of isopropyl derivatives formed in reactions of varying rates and with varying catalyst concentrations. It is conceivable that this constancy might be due to a constant ratio for the two paths (2 and 3) by which the intermediate ion can be destroyed, and negligible reversal (—3) of the isomerisation step. This hypothesis is not untenable but seems fairly unlikely when it is remembered that the addition of mercuric oxide is expected to alter the formate concentration and hence increase the nucleophilic activity of the solution. One would therefore expect to find the proportion of rearrangement (reaction 3) to decrease relatively to the nucleophilic attack in the n-propyl cation (2) as the concentration of mercuric salt in the system is raised. Alternatively, the figure of 13% might represent the proportion of isopropyl cations at equilibrium (*i.e.*, $100k_3/k_{-3}$), and therefore be constant, as long as the rate of solvent attack is low relative to the rate of rearrangement. On this basis the value 13% for the proportion of isopropyl derivatives in the reaction products would appear to be low in view of the expected relative stabilities of the n-propyl and isopropyl cations. However, proton elimination may be an important reaction of these ions (cf. deamination of n-propylamine [12]), competing with direct substitution. Benfey [6] has given evidence for the formation of olefin (*ca.* 63% of reaction products) in the solvolysis of isobutyl bromide in 70% aqueous dioxan with mercuric nitrate as catalyst. Smaller amounts of olefin were formed in the solvolysis of isopropyl bromide but the evidence was against olefin formation in the corresponding reaction of n-propyl bromide. We are unable to say how much elimination occurs under the conditions of our reactions, but it is possible that the isopropyl derivatives may constitute more than 13% of the total *substitution* products, and accordingly we defer the further consideration of this problem.

EXPERIMENTAL

Materials.—n-Propyl bromide (Hopkin and Williams) (containing small quantities of propan-1-ol and isopropyl bromide) was washed with sodium hydrogen carbonate solution and with water, dried ($CaCl_2$; P_2O_5) and fractionated; [13] it then had b. p. 71·5—71·6°/771 mm. The purified sample was shown by vapour-phase chromatography to be free from impurities. Propan-2-ol (" AnalaR " material) was refluxed with magnesium turnings and iodine and distilled, then having b. p. 82·2—82·4°/761 mm. Isopropyl formate, prepared by Vogel's method,[14] had b. p. 66·5—67·5°/747 mm. Formic acid was purified as described previously.[11]

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[10] Coe and Gold, unpublished work.

[11] Coe and Gold, *J.*, 1960, 4185.

[12] Meyer and Forster, *Ber.*, 1876, **9**, 535; Whitmore and Thorpe, *J. Amer. Chem. Soc.*, 1941, **63**, 1118; J. D. Roberts and Halmann, *ibid.*, 1953, **75**, 5759; Huisgen and Rüchardt, *Annalen*, 1956, **601**, 1.

[13] Cowley and Partington, *J.*, 1938, 977.

[14] Vogel, *J.*, 1948, 624.

Mercuric oxide was prepared by Kolthoff and Stenger's method.[15] Analysis of the sample by titration of its solution in nitric acid with ammonium thiocyanate gave the percentage purity as 100·8% HgO. The propene used was gas (propene 60%, propane 40%) from a cylinder kindly supplied by Petrochemicals Ltd. Analysis by bromine addition showed it to contain 58·5% of unsaturated constituents (calculated as propene).

Kinetic Measurements.—Stock solutions of n-propyl bromide and of mercuric oxide in 90% formic acid were prepared and brought to 25°. Reaction mixtures were made from 2 ml. of each freshly prepared stock solution. After various times at 25°, the contents of reaction vessels were washed into cooled flasks. A slight excess of 40% sodium hydroxide solution was then added to precipitate mercury compounds, and the mixture cooled and filtered after addition of activated charcoal. The presence of the latter prevented finely divided oxides of mercury from passing through the filter. The filtrate was then analysed for bromide ion by Volhard's method. In some cases this filtrate was also used for estimation of isopropyl derivatives and for radioactivity measurements (see below). The procedure for bromide analysis was tested by comparing the results of direct titration of a hydrobromic acid solution with those obtained by first mixing this acid with a solution of mercuric oxide in 90% formic acid. The method was thus shown to be accurate to about ±5%. In the later stages of the solvolysis reaction a pale yellow precipitate separated and qualitative tests showed that this was probably mercurous bromide. It was established that bromide ion could be liberated quantitatively from mercurous bromide by the treatment with 40% sodium hydroxide solution described above, and also that unchanged n-propyl bromide did not interfere. The evaluation of the initial rate is illustrated by the data in Table 2.

TABLE 2. *Specimen results for evaluation of initial rate (Expt. 1).*

Time, t (sec.)...	0	600	1200	1800	2700	3660	4800	6600	8400	10,800
$10^3[Br^-]$	0	14·0	24·8	30·6	43·2	47·1	51·5	58·5	60·5	67·5
$10^6[Br^-]/t$	—	23·3	20·6	17·0	16·0	12·9	11·7	8·9	7·2	6·3

Extrapolated $10^6[d[Br^-]/dt]_{initial} = 27$.

Estimation of Isopropyl Derivatives.—The method used was a modification of that described by Neish,[16] involving the oxidation of propan-2-ol (or isopropyl formate) to acetone by chromic acid and estimation of the acetone spectrophotometrically. For calibration, standard solutions of propan-2-ol and isopropyl formate were added to 10 ml. portions of oxidation mixture (45 g. of $Na_2Cr_2O_7,2H_2O$ in 500 ml. of approx. 50% sulphuric acid) contained in 100 ml. conical flasks. The total volume in each flask was made up to 20—25 ml. with water, and the flasks were attached to condensers mounted vertically, with delivery tubes under the surface of 20 ml. quantities of 40% aqueous sodium hydroxide contained in 50 ml. volumetric flasks. After 1 hr. at room temperature the flasks were heated, about 15 ml. of distillate collected, and the volumetric flasks stoppered; 10 ml. of 10% salicylaldehyde solution in ethyl alcohol were added to each flask in turn (at 10-min. intervals), and the volumes made up to 50 ml. with water. Each flask was heated at 50° ± 0·2° for 20 min. and stored at room temperature for 30 min. Optical densities were measured at 530 mμ against a " blank " (prepared as above with water in place of distillate), a Beckman DU spectrophotometer being used. The concentration of propan-2-ol or isopropyl formate was found to be proportional to the optical density at least up to a concentration of *ca.* 2·5 mg./l. of isopropanol in the solution used for optical density measurement.

No interference from n-propyl bromide was found in this method, and corrections were made when necessary for slight interference by propan-1-ol and propene. Bromide (or chloride) ion caused interference if present during the oxidation stage of the procedure. It was found, however, that propan-2-ol could be distilled quantitatively from an alkaline solution even in the presence of bromide or chloride, giving a distillate suitable for analysis. Samples for the estimation of propan-2-ol in reaction mixtures were obtained by distilling part of the filtrate used for bromide-ion analysis (see above). The accuracy and reproducibility of the distillation procedure are illustrated in Table 3.

Propene Analysis.—Propene was estimated by bubbling air through its solution and

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[15] Kolthoff and Stenger, " Volumetric Analysis," Vol. II, Interscience, Publ. Inc., New York, 1947.

[16] Neish, Nat. Res. Council Canada Report 46-8-3, 1952.

absorbing the gas in a standard solution of bromine in glacial acetic acid. The results from this method (when used with standard solutions prepared from the cylinder sample) agreed with those obtained by using known volumes of dry gas in the same apparatus. Neither hydrogen bromide nor formic acid caused interference.

TABLE 3. *Calibration experiments for estimation of propan-2-ol in formic acid (distillation method).*

(The results below were obtained by using six different standard solutions of propan-2-ol.)

Wt. of propan-2-ol (γ)		Measured optical density	Standard solution †	Wt. of propan-2-ol (γ)		Measured optical density	Standard solution †
Taken	Calc.*			Taken	Calc.*		
5·8	5·8	0·028	A	21·7	21·1	0·106	B
7·2	7·4	0·036	B	23·3	23·6	0·115	A
9·3	10·1 (av.)	0·046, 0·052	C, E	28·7	27·9 (av.)	0·132, 0·135, 0·140	C, D, E
11·7	12·1	0·059	A	29·1	29·8 (av.)	0·145, 0·143	B, F
14·5	15·8 (av.)	0·077, 0·072	B, F	37·0	35·9 (av.)	0·168, 0·175, 0·183	C, D, E
17·5	16·9	0·082	A	43·6	44·1	0·215	F
18·5	18·4 (av.)	0·087, 0·090, 0·093	C, D, E	58·2	54·3	0·265	F

* Calc. from the calibration relation: Wt. of propan-2-ol = 205 × optical density.

† Solution F contained additional n-propyl bromide.

Reaction of Propene with 90% *Formic Acid containing Mercuric Oxide.*—Two stock solutions were prepared: (*a*) propene in 90% formic acid, and (*b*) mercuric oxide (0·136M) and hydrogen bromide (0·025M) in 90% formic acid. Samples of (*a*) and also mixtures of equal amounts of (*a*) and (*b*) were sealed in glass tubes. After fixed periods the contents of the tubes were analysed for propene (with use of a device to ensure that propene could not escape on breaking the tubes) or for propan-2-ol (by the method used in the kinetic experiments).

Radioactivity Measurements.—Part of the filtrate used for the estimation of bromide ion and propan-2-ol was diluted with propan-2-ol and treated with 40% aqueous sodium hydroxide as described previously in the case of t-butyl alcohol.[11] The counting procedure was also as previously described.[11]

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