

819. *Solvolysis and Hydrogen Exchange of t-Butyl Chloride in Formic Acid.*

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The solvolysis of t-butyl chloride in tritiated 90% formic acid occurs without the formation of C-T bonds in the alcoholic product up to the time at which equilibrium is established. As carbonium ions are known to participate in this reaction, the results disprove the validity of a criterion for carbonium-ion formation proposed recently. The occurrence of tritium exchange can be detected after reaction times greatly in excess of the half-life of the solvolysis.

USING deuterium-enriched acids, Kursanov, Setkina, *et al.* have shown recently¹⁻⁴ that extensive exchange of α -hydrogen atoms occurs during the reaction of t-alkyl halides with concentrated hydrochloric acid, formic acid, or hydriodic acid. In acetic acid the extent of exchange was much smaller than in formic acid. No exchange was observed on treating isopropyl iodide or ethyl iodide with 56% hydriodic acid, or on treating n-butyl chloride with concentrated hydrochloric acid. The authors note that the observation of exchange appears to coincide with conditions favouring the intermediate formation of carbonium ions in the reaction. Accordingly, they suggest that carbonium ions undergo rapid hydrogen exchange with the media employed in their experiments, and that the occurrence of hydrogen isotope exchange may therefore be used as a criterion for the formation of carbonium ions during the course of a reaction. Conversely, Kursanov and Setkina² conclude from their observation of negligible hydrogen exchange between t-butyl alcohol and concentrated hydrochloric acid (except after long periods) that carbonium ions do not intervene in the reaction between these compounds.

The general validity of Kursanov and Setkina's suggestion is immediately questionable, for several reactions are known⁵⁻⁸ for which a carbonium-ion mechanism is accepted and in which hydrogen exchange does not occur, even when these processes involve hydrogen shifts. However, on existing experimental evidence it seemed difficult to dismiss these ideas in relation to aliphatic carbonium ions, particularly the t-butyl cation, concerning which Otvos *et al.*⁹ drew very similar conclusions (see also Stewart and Harman¹⁰). On

¹ Kursanov, Setkina, Parnes, and Bykova, *Trudy Vsesoyuz. Nauch.-Tekh. Konf. Primenen. Radioaktiv i Stabil. Izotopov i Izlucheni v Narod. Khoz. i Nauke. Izotopy i Izluchen. v Khim.*, 1957, 13. (*Chem. Abs.*, 1959, **53**, 19,538b.)

² Setkina and Kursanov, *Doklady Akad. Nauk S.S.S.R.*, 1958, **120**, 801.

³ Setkina, Kursanov, and Bykova, *Izvest. Akad. Nauk S.S.S.R.*, 1959, 758.

⁴ Kursanov, Bykova, and Setkina, *Izvest. Akad. Nauk S.S.S.R.*, 1959, 2007.

⁵ Prelog, *Experientia*, Suppl. VII, 1957, 261.

⁶ Collins, Rainey, Smith, and Kaye, *J. Amer. Chem. Soc.*, 1959, **81**, 460.

⁷ Smith, Bowman, and Kmet, *J. Amer. Chem. Soc.*, 1959, **81**, 997.

⁸ Cram and Tadanier, *J. Amer. Chem. Soc.*, 1959, **81**, 2737.

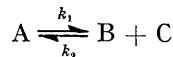
⁹ Otvos, Stevenson, Wagner, and Beeck, *J. Amer. Chem. Soc.*, 1951, **73**, 5741.

¹⁰ Stewart and Harman, *J. Amer. Chem. Soc.*, 1946, **68**, 1135.

the other hand, it has previously been pointed out¹¹ that there are theoretical difficulties in accepting the occurrence of rapid exchange in carbonium ions.

For these reasons we have now re-investigated the question whether hydrogen exchange between t-butyl cations and an acidic solvent is rapid. It seemed to us that Kursanov and Setkina's results concerning the occurrence of exchange during the solvolysis of t-alkyl halides in formic acid were open to the objections that the systems used were heterogeneous and that the contact times before isotope analysis were probably much longer than the time required for the attainment of solvolysis equilibrium.

Our results relate to reactions of t-butyl chloride in 90% formic acid, at 25°. Bateman and Hughes¹² had made a thorough study of the solvolysis under very similar conditions (at 15°) and it is well established that the mechanism involves the formation of t-butyl cations. The results of our brief experiments (Table 1) confirm that the reaction at 25° is of the type



and, in conjunction with those of Bateman and Hughes ($k_1 = 2.12 \times 10^{-2} \text{ min.}^{-1}$ at 15°), lead to a reasonable value for the activation energy of the ionisation step (cf. Ross and Labes¹³). [The values of k_1 were calculated from the integrated equation for the rate of a first-order reaction with second-order reversal, *i.e.*,

$$k_1 = \frac{x_\infty}{t(2a - x_\infty)} \ln \left\{ \frac{ax_\infty + x(a - x_\infty)}{a(x_\infty - x)} \right\}$$

where a is the initial concentration of t-butyl chloride and x and x_∞ are the concentrations after t min. and infinite time respectively.]

TABLE 1. *Solvolysis of t-butyl chloride in 90% formic acid at 25° ± 0.02°.*

Expt.	[t-BuCl] ₀	% Reaction at equilibrium	100k ₁ (min. ⁻¹)	Mean	E (kcal.)
1	0.157	85.4	8.23	} 8.20	24.2
2	0.160	85.3	8.17		

TABLE 2. *Hydrogen-exchange experiments.*

(Activity of medium in each case = 0.046 curie/g.-atom of exchangeable hydrogen.)

Expt.	Temp.	[t-BuCl] ₀	Samples taken for radioactivity estimation		
			time	% reaction	<i>n</i> *
3	25°	0.175	12 min.	60.6	0
			130 min.	85.2	0.06
			19 days	84.7	2.9
4	18—20	0.173	20 days	75.2 †	3.1
			39 days	84.2	3.8

* n = the number of C-H bonds involved in exchange per molecule of t-BuOH. As the unchanged t-butyl chloride in the mixture was not separated from the t-butyl alcohol before treatment with 40% sodium hydroxide (see Experimental section), values in this column were calculated on the assumptions that the molar radioactivities of the chloride and alcohol were equal and that the remaining t-butyl chloride would be hydrolysed during the treatment with sodium hydroxide.

† After 7 days, part of the mixture from experiment 4 was mixed with a known amount of t-butyl alcohol and stored for a further 13 days before estimation of the tritium content of the alcohol. The experimental value 75.2% gives the chloride-ion concentration in the new equilibrium mixture as a percentage of the initial t-butyl chloride concentration. The calculated value for this percentage (using a mean "equilibrium constant" calculated from the results given in Tables 1 and 2) is 73.3.

The results of Expt. 3 in Table 2 show that hydrogen exchange between reagents and medium does not occur during the solvolysis of t-butyl chloride, at least up to the time

¹¹ Gold and Satchell, *Quart. Rev.*, 1955, **9**, 51.

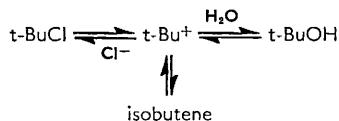
¹² Bateman and Hughes, *J.*, 1937, 1187; 1940, 935.

¹³ Ross and Labes, *J. Amer. Chem. Soc.*, 1957, **79**, 4155.

at which the equilibrium $t\text{-BuCl} + \text{H}_2\text{O} \rightleftharpoons t\text{-BuOH} + \text{HCl}$ is established. The result disproves the conclusion reached by Kursanov and Setkina. *t*-Butyl cations do not undergo rapid hydrogen exchange with the medium, and the presence or absence of hydrogen exchange cannot therefore be used as a mechanistic criterion in the sense suggested by these authors.

It is not impossible, on the evidence considered, that the slow exchange of C-H bonds which continues after chemical equilibrium is set up (Table 2) might be due to a slow exchange between *t*-butyl cations and the medium. Alternatively, the exchange might involve formation of olefin and re-addition of acid.

Although the presence of olefin was not detected by Bateman and Hughes⁶ during the solvolysis of *t*-butyl chloride in 90% formic acid, it seems possible that olefin may be formed in a very slow reaction, thus leading to equilibria of the type:



This would account for the slow accumulation of C-T bonds in the alcohol, and similar schemes might also explain the results of Kursanov and Setkina. By analogy with the case of *n*-propyl halides (where exchange is not found under conditions which favour the intermediate formation of carbonium ions but inhibit the addition to olefin¹⁴) the second alternative seems to be the more likely explanation of the exchange reaction. The direct interconversion of alkyl halide, alcohol, and olefin (without intermediate formation of a carbonium ion) may be unlikely in the present example, but would provide an additional route for the formation of C-T bonds in the alcohol. This exchange mechanism could clearly operate even in systems in which carbonium ions are not formed.

EXPERIMENTAL

Materials.—Formic acid (A.R., 98–100%) was fractionated through a heated column (50 × 2.5 cm.) packed with glass helices; it had b. p. 100.2–100.5°/771 mm., f. p. 8.2°. 90% Formic acid was prepared by diluting a quantity of water (or tritiated water) to ten times its volume with formic acid in a volumetric flask.

t-Butyl chloride (B.D.H. reagent) was dried (CaCl₂) and distilled; it had b. p. 50.2–50.5°/754 mm.

t-Butyl alcohol was stored over quicklime for several days and distilled; it had b. p. 82.5°/762 mm., f. p. 25.5°.

Tritiated water samples in sealed ampoules (0.200 curie/ml., from the Radiochemical Centre) were diluted as required.

Kinetic Measurements.—Samples of *t*-butyl chloride were sealed in thin-walled glass tubes and crushed under 90% formic acid at 25°. The reaction was followed by estimating the chloride ion concentration, Bateman and Hughes's method¹² being used.

Radioactivity Measurements.—In a typical experiment a 5-ml. sample of reaction mixture was diluted with 75 ml. of *t*-butyl alcohol and ca. 20 ml. of water. The mixture was shaken with a slight excess of solid sodium chloride, and the lower layer discarded. The upper (alcoholic) layer was then shaken successively with ten 100-ml. quantities of aqueous sodium hydroxide ("40%," *i.e.*, 40 g. NaOH in 100 ml. water).

In order to show that this procedure resulted in removal of all hydroxylic and carboxylic tritium, samples of the alcoholic layer, after the 9th and 10th extractions with 40% sodium hydroxide, were diluted with ethyl alcohol and the tritium content was estimated by the counting procedure described below. In each case no significant change in tritium content resulted from the 10th extraction. The alcoholic layer was then set aside over quicklime, refluxed, and distilled. In all cases the b. p. of the distillate was in the range 81.6–82.0°, and the f. p. above 23.6°. A weighed sample of the distillate was then diluted to a known volume with ethyl alcohol to give a solution of convenient activity for counting.

¹⁴ Coe and Gold, *J.*, in the press.

Counting Procedure.—Radioactivity measurements were made by using a liquid scintillation counter (Ekco N612) at -20° with a 0.3% solution of 2,5-diphenyloxazole in AnalaR toluene as scintillator. Stock solutions were prepared from equal volumes of scintillator solution and AnalaR ethyl alcohol together with either (a) inactive water, or (b) an equal volume of tritiated water. The activity of the active stock solution (b) was chosen to be comparable with that of the sample under investigation. Aliquot parts of the latter were mixed (in Pyrex cells) with equal amounts of stock solutions (a) and (b) respectively, and the counting rate recorded after 20 min. in the dark at -20° . After subtraction of the background count [obtained by using stock solution (a) alone] the ratio of values obtained ("count ratio") gives the factor by which the activity of the sample differs from that of stock solution (b). The reproducibility of this procedure was tested by using solutions of known activity derived from tritiated water and t-butyl, isopropyl, or ethyl alcohol.

		<i>Count ratio.</i>				
Found		0.513	0.509	0.473	0.504	2.63
Calc.		0.500				2.50
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