391. *The Reaction of* tert.*-Butyl Chloride with Formic Acid:* tert.*-Butyl Formate.*

By William Taylor.

The interpretation offered by Bateman and Hughes (this vol., p. 1187) for the constant rate of reaction of water, *tert.*-butyl chloride, and formic acid (solvent) to give *tert.*-butyl alcohol is shown to be inadequate, since they did not take into account the formation of *tert.*-butyl formate. An alternative explanation of their kinetic results is based on this fact, *viz.*, that *tert.*-butyl chloride reacts with the formic acid to give *tert.*-butyl formate.

The mechanism of hydrolysis of certain types of alkyl halides such as *tert.*-butyl halides was assumed by Hughes and Ingold (J., 1935, 244), on indirect evidence, to be unimolecular, with water playing the part of ionising medium; for others, such as methyl and ethyl halides, it was assumed to be bimolecular. The author (this vol., p. 344) on the other hand has assumed, also on indirect evidence, that for alkyl halides generally, the mechanism is the same and is bimolecular, with water acting as a direct reagent. Recently, Bateman and Hughes (this vol., p. 1187) presented what purports to be direct evidence in support of the ionisation mechanism, *viz.*, that the rate of reaction of *tert.*-butyl chloride with water in formic acid is of the first order, and independent of the (small) concentration of water. The kinetic results, obtained by measuring the rate of formation of hydrogen chloride by a modified Volhard method, apparently therefore show the mechanism of hydrolysis to be unimolecular, but only because they are based on the assumption that the primary reaction is between the *tert.*-butyl chloride and water. Seeing that these authors were unable to isolate *tert.*-butyl formate when using Kahlbaum's formic acid, and only *tert.*-butyl alcohol from the aqueous acid, this assumption was justified. However, it can no longer be maintained, since tert.*-butyl formate* has now been isolated from Kahlbaum's formic acid and *tert.*-butyl chloride at room temperature. The reaction (E) under these conditions being reversible, and the forward reaction normally taking place to the extent of only about 19% (Bateman and Hughes, *loc. cit.*), the equilibrium was pushed over to the right by having present an excess of powdered calcium formate. *tert.*-Butyl formate is hydrolysed almost instantaneously by aqueous alkali and extremely rapidly by hydrochloric acid even in a heterogeneous system. It is mainly to this ease of hydrolysis that Bateman and Hughes's failure to isolate the ester must be attributed, for in order to extract the end-products they added water to the reaction mixture before adding the organic solvent, ether or carbon tetrachloride.

From the foregoing, an alternative explanation of the kinetic results is possible, which briefly is that the primary reaction is bimolecular:

$$\mathrm{Bu^{\gamma}Cl + H{\cdot}CO_2H \rightleftharpoons H{\cdot}CO_2Bu^{\gamma} + HCl} \quad . \quad . \quad . \quad . \quad (E)$$

together with $\mathrm{Bu^{\gamma}Cl + H{\cdot}CO_2H \rightleftharpoons CMe_2{:}CH_2 + HCl + H{\cdot}CO_2H}$ to a small extent.

The forward reaction would be kinetically of the first order and, for reasons given below, the rate would be for all practical purposes independent of small concentrations of water. The principal obvious effect of water will be to alter the equilibrium position by ionising the hydrogen chloride, as pointed out by Bateman and Hughes, and by causing the partial hydrolysis of the formate. Probably some *tert.*-butyl alcohol is formed by the direct interaction of *tert.*-butyl chloride and water in formic acid containing small concentrations of water, but this will be a minor reaction, owing to the small concentration of water relative to formic acid, if its rate is either less than or approximately equal to that of the forward reaction in (E). That these two rates are comparable is probable, since the combined rate of alcoholysis and hydrolysis of *tert.*-butyl chloride at 15° in 50% aqueous ethyl alcohol is 1×10^{-4} sec.$^{-1}$ (approx.) (see Hughes, J., 1935, 255) whereas for the forward reaction in (E) the rate at 15° is $3{\cdot}7 \times 10^{-4}$ sec.$^{-1}$ (approx.) (Bateman and Hughes, *loc. cit.*). In other words, in this alternative explanation of the kinetic results of Bateman and Hughes, the view is taken that water and formic acid are approximately equally rapidly effective under these experimental conditions in reacting directly with *tert.*-butyl chloride to produce hydrogen chloride; hence small concentrations of water will not noticeably affect its rate of formation from *tert.*-butyl chloride in formic acid.

EXPERIMENTAL.

Isolation of tert.*-Butyl Formate.*—*tert.*-Butyl chloride (24 g.), Kahlbaum's formic acid (200 c.c.), and finely powdered calcium formate (70 g.) were kept at room temperature in a ground-glass stoppered bottle, with occasional shaking, for 3 days. Ether was then added, and the liquid washed with water till the washings were neutral to phenolphthalein, dried (sodium sulphate), and the ether distilled off; fractional distillation then gave three fractions: (1) b. p. 45—65° (14 g.), (2) b. p. 65—80° (4 g.), (3) b. p. 80—84° (6·5 g.). Redistillation of (2) gave 0·5 g. of b. p. 80—83·5°. Redistillation of this and (3) gave 6·5 g. of b. p. 82·5—83·5°/757 mm. (Found: C, 59·0; H, 9·7. $C_5H_{10}O_2$ requires C, 58·8; H, 9·8%).

Hydrolysis of tert.*-Butyl Formate.*—(*a*) 0·4528 G. of the ester, dropped into 50 c.c. of N/10-aqueous sodium hydroxide, disappeared in less than 1 min. at room temperature; after 5 minutes, back titration with N/10-acid gave *M*, 113·7 (Calc.: 114). (*b*) Hydrochloric acid (10 c.c., N.) hydrolysed the ester (0·5 g.) completely at room temperature during 10 mins.' shaking, as shown by the entire disappearance of the oily drops. (*c*) Water alone (5 c.c.) hydrolysed the ester (0·5 g.) completely at room temperature in 3 days, with occasional shaking.

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