**132.** *The Reaction of Hydrogen Chloride with Methyl Alcohol.*

By C. N. HINSHELWOOD.

SINCE in the formation of a carboxylic ester the hydroxyl group is detached from the acid (Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508), it must be the hydrogen atom and not the hydroxyl group which is detached from the alcohol. In the formation of an alkyl halide from the hydrogen halide and an alcohol, however, the hydroxyl must be

replaced by the halogen atom. Hence, there must be a rather important difference in mechanism between the two processes :

$$R \cdot CO|OH + RO|H = R \cdot CO_2R + H_2O \text{ and } H|Cl + R|OH = RCl + H_2O.$$
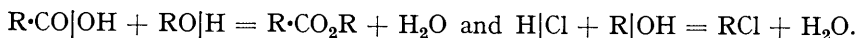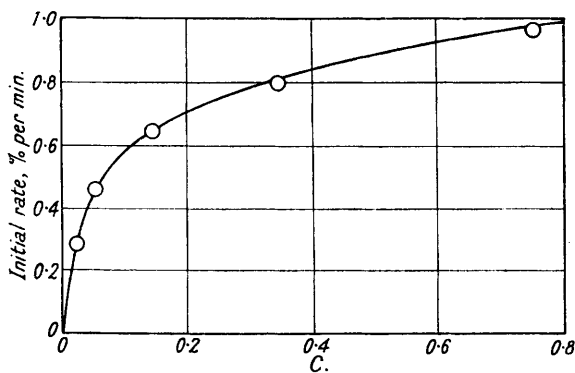
This difference is reflected in the different effects of substitution on the two types of reaction (Bennett and Reynolds, this vol., p. 131), tertiary alcohols reacting less rapidly than primary alcohols with acetic acid and more rapidly with hydrogen bromide.

It is the object of this paper to point out that kinetic observations also indicate a fundamental difference between the mechanisms concerned in the formation of alkyl halides and in that of carboxylic esters.

The interaction of hydrogen chloride with ethyl and with propyl alcohol was investigated by Kilpi (*Z. physikal. Chem.*, 1929, *A*, **141**, 424; 1933, *A*, **166**, 285), who found complex relations between the rate of reaction and the concentrations of reactants, water, and added electrolytes. He concluded that the results could be interpreted by assuming that the rate varied as the product of the activities of chlorine ions and hydrogen ions.

In the course of investigations of the formation of carboxylic esters under the influence of hydrogen chloride as a catalyst, measurements have been made of the rate of interaction of methyl alcohol and hydrogen chloride. The method of measurement was to seal up solutions of hydrogen chloride in anhydrous methyl alcohol (prepared by the method of Hartley and Raikes, J., 1925, **127**, 524), and analyse them after they had been kept for a known time in a thermostat.

The reaction is retarded by the water formed : to eliminate this complication as far as possible, initial rates of reaction were found by drawing tangents to curves of percentage change against time. The values of the initial rate, r, expressed as percentage change per minute at 80·0°, are given below and plotted in the figure. The concentration, c, is the total acidity determined by titration, and expressed as a normality.

c	0·754	0·345	0·144	0·0553	0·0216
r	0·97	0·80	0·645	0·47	0·285

If we assume the only species present, apart from solvent, to be chlorine ions, methoxonium ions, and ion-pairs $MeOH_2{}^+ \cdot Cl^-$, then we have

$$c_{\mathrm{MeOH_2^+Cl^-}} = c_{\mathrm{Cl^-}} c_{\mathrm{MeOH_2^+}} \quad f_{\mathrm{Cl^-}} f_{\mathrm{MeOH_2^+}} / f_{\mathrm{MeOH_2^+ \cdot Cl^-}}$$

The rate of reaction may depend upon the rate of dehydration of the methoxonium chloride ion-pairs. The degree of ionisation is considerable. Therefore, if the activity coefficients were constant, the reaction would be bimolecular with respect to the total hydrogen chloride, and the curve in the figure would be a straight line passing through the origin and inclined at an angle to the axes. But the activity product on the right will diminish with increasing total ionic concentration; hence the rate will increase less rapidly than corresponds to a second-order reaction, which is qualitatively in accordance with the behaviour shown in the figure.

The temperature coefficient was determined for 0·0991N-solutions.

Temp.	100·0°	84·2°	80·0°	68·4°	56·3°	40·0°
Initial rate, % per min.	2·77	0·80	0·57	0·146	0·037	0·00419

These values give an energy of activation of 26,000 cals. This result is not sensitive to the influence of water, since from the times required for 25% and 50% reaction respectively, the values of E found are 26,900 and 27,000.

Experiments were also made with 0·426N-solutions of hydrogen chloride in *tert.*-butyl alcohol, and led to the result $E = 26,800$ cals.

These values are to be compared with that just published by Bennett and Reynolds (*loc. cit.*) for methyl alcohol and hydrogen bromide, *viz.*, 26,600 cals.

These high activation energies for the formation of alkyl halides are to be contrasted with the much smaller values found for the formation of carboxylic esters, *e.g.*, 10,200 for the esterification of acetic acid by methyl alcohol under the influence of the hydrion, and 13,000 for the same reaction catalysed by the undissociated molecules of acetic acid itself.

The differences appear to be out of all proportion to the differences in the rates, and themselves indicate a fundamentally different mechanism for the two types of reaction.

The esterification of a carboxylic acid demands the presence of acid, alcohol, and acid catalyst, and if interpreted as a termolecular interaction of these compounds it can be shown to be very much slower than the possible rate of activation (Rolfe and Hinshelwood, *Trans. Faraday Soc.*, 1934, **30**, 935). It will now be of interest to examine the hypothesis that the formation of alkyl halides depends upon the dehydration of the alkoxonium chloride ion-pairs. If this is the mechanism, the observed activation energy must be corrected for the variation of ion-pairs with temperature. This depends upon the differences between much larger thermal quantities measuring the interaction of ions and solvent and may be positive or negative. In view of the closeness of the values of E for methyl and *tert.*-butyl alcohol, and for hydrogen chloride and hydrogen bromide, we will risk the assumption that the correction is not large, and that it certainly will not reduce the value 26,000—27,000 cals., characteristic of the halide formation, to anything like the value 10,000—15,000 characteristic of carboxylic ester formation.

We may reach certain qualitative, but interesting, conclusions about the molecular statistics of the reaction in the following way, using the results recorded above for the formation of methyl chloride. At 80·0° for $N/2$-solution, $-(100/c) \cdot dc/dt = 0·865$ min.$^{-1}$ $= 1·44 \times 10^{-2}$ sec.$^{-1}$, whence $(1/c) \cdot dc/dt = 1·44 \times 10^{-4}$. This would be the unimolecular velocity constant for the decomposition of the methoxonium chloride if all the hydrogen chloride present were in that form. Since only a fraction is actually present in the form of undissociated ion-pairs, we are safe in assuming that the unimolecular velocity constant for the actual decomposition of the ion-pairs is not less than this value. We conclude, then, that k is greater than 10^{-4} sec.$^{-1}$, and probably very considerably greater.

Activation of the ion-pairs presumably occurs by collision with solvent molecules. Applying the formula $k = (3\pi\sigma\eta/2m)e^{-E/RT}$ (see preceding paper), and adding to 26,000 the viscosity correction for methyl alcohol, *viz.*, 2500 cals., making $E = 28,500$ cals., we find for 80°, $k = 2 \times 10^{-5}$. Thus the observed value must be considerably greater than that given by the formula. That this formula can give more than the crudest idea of the rate of activation by collision with solvent molecules is improbable. But the fact worthy of attention is that the result is similar to that found by applying the same formula to the decomposition of iodonium, sulphonium, and ammonium salts (see preceding paper), where the introduction of internal degrees of freedom is necessary to account for the rate. Thus, whatever the limitations of the method of calculation, it serves to indicate the probable analogy between the decomposition of the alkoxonium salt and that of the other " onium " salts. Moreover, the formula is probably exact enough at least to show that the reactions in question are not " slow " reactions in the same way as the esterification of the carboxylic acids.

SUMMARY.

Kinetic considerations confirm the conclusions of organic chemical theory that the interaction of hydrogen halides and the simple alcohols differs in mechanism from the esterification of carboxylic acids. Experimental data for the reaction between methyl alcohol and hydrogen chloride are recorded.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL COLLEGE AND TRINITY COLLEGE, OXFORD.