The Gas-phase Hydrogen Bromide-catalysed Decomposition of Trimethylacetic Acid

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CARBOXYLATION of olefins is achieved with carbon monoxide at high pressure in the presence of strong acid catalysts, doubtless *via* the acylium ion, and, in view of the mechanisms suggested for the hydrogen halide-catalysed decompositions of alcohols[1] and ethers,[2] the reverse reaction in the gas phase has been sought. For trimethylacetic acid and hydrogen bromide reaction does occur at measurable rates at 343—462°C for 21—184 and 12—341 mm. initial pressures of the reactants, respectively. Isobutene, carbon monoxide, and water are produced quantitatively and hydrogen bromide is not lost.

$$Me_3C{\cdot}CO_2H + HBr \rightarrow$$
$$Me_2C{:}CH_2 + CO + H_2O + HBr$$

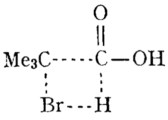
Individual runs followed the first-order rate law accurately to 50% reaction in general, and the first-order constants were proportional to the initial pressures of hydrogen bromide, *e.g.*, at 422° for variations of 9 and 12 times in the reactants' pressures. The rates fit well the Arrhenius equation

$$k_2(\text{sec.}^{-1}\ \text{c.c. mole}^{-1}) = 10^{12\cdot 28}\exp(-\ 31{,}700/\boldsymbol{R}T)$$

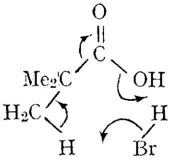
Addition of cyclohexene (7—13 cm.) to the reaction or increase in the surface: volume ratio of the vessel by 8 times did not affect the rate.

Preliminary measurements under comparable conditions indicate that the acid itself decomposes at above *ca.* 450°, probably by a radical mechanism, to a number of breakdown products including C_3-hydrocarbons; this reaction was not significant compared with the catalysed reaction.

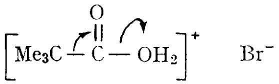
Formation of olefin *via* the alkyl halide (I) (*cf.* Case I, ref. 1) is not here kinetically reasonable. Concerted electron movements in a seven-membered ring (II), a type not usually favoured, is required for a ring transition state analogous to Case II of ref. 1. The extreme case of gas-phase heterolysis analogous to Case III, ref. 1, may be represented by (III), and this implies the reverse of the synthesis of the acid in solution; acid-catalysed loss of carbon monoxide is well known for tertiary acids in solution.[3]



(I)



(II)



(III)

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[1] A. Maccoll and V. R. Stimson, *J. Chem. Soc.*, 1960, 2836.

[2] V. R. Stimson and E. J. Watson, *Austral. J. Chem.*, 1966, **19**, 75.

[3] E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1949, 1950 and 1961.