The Effect of Isobutene on the Gas-phase Reaction of Acetic Acid with Hydrogen Bromide

By N. J. DALY* and M. F. GILLIGAN

(*Department of Chemistry, School of General Studies, Australian National University, Canberra A.C.T.* 2600, *Australia*)

Summary The addition of isobutene to the reaction mixture of acetic acid and hydrogen bromide lowers the rate of change of pressure observed over the temperature range 420—474°: this is explained in terms of a molecular reaction forming mesityl oxide.

IN THE gas-phase (412—492°), AcOH reacts with HBr by a molecular mechanism[1] to give MeBr, CO, and H_2O. We now find that when kinetic runs are carried out in the presence of isobutene the rate of change of pressure is lowered. Such an effect is classically associated with the inhibition of a free radical chain-mechanism. In this case however, it can be explained in terms of a competing reaction producing mesityl oxide.

The plots of the pressure-time data obtained for runs in a static system[2] with fixed initial pressures of AcOH and HBr, and variable pressures of isobutene are essentially linear over the initial period, and Δp at a given time measures the rate of change of pressure. The results (Figure) show that Δp decreases as the initial pressure of isobutene increases, but do not show a region of maximal inhibition. The major products of reaction are CO, MeBr, and water, together with smaller quantities of mesityl oxide and a mixture of the three isomers of methylbutene.

When initial pressures of AcOH and HBr were fixed, the amount of mesityl oxide formed in a given time increased steadily as the initial pressure of isobutene increased.

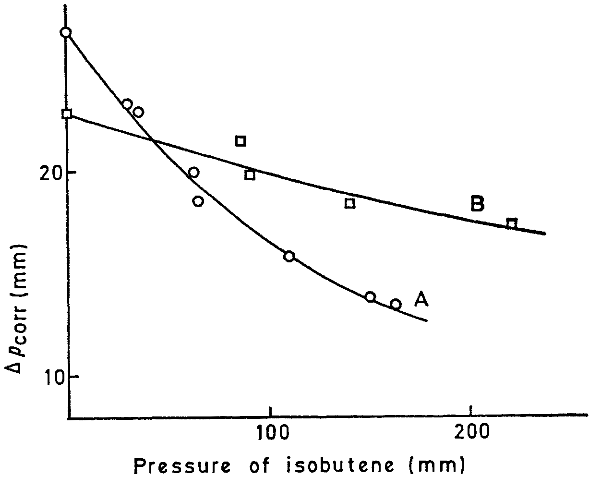

FIGURE. *Plot of* Δp versus *pressure of isobutene*: A. Δp *afte* 40 *min. at* 407°: B. Δp *after* 10 *min. at* 440·7°.

When initial pressures of all reagents were fixed mesityl oxide is formed steadily throughout the reaction. The reaction of acetic acid with hydrogen bromide has been discussed[1] in terms of the steps

$$CH_3CO_2H + HBr \rightarrow A^* \tag{1}$$

$$A^* \rightarrow CH_3Br + CO + H_2O \tag{2}$$

It is now suggested that mesityl oxide is formed according to the step

$$A^{*} + i\text{-}C_4H_8 \rightarrow (CH_3)_2C = CH{\cdot}COCH_3 + HBr + H_2O \qquad (3)$$

which provides an alternative route for removing the intermediate A*. Application of steady state treatment for initial conditions leads to the rate expression

$$\frac{d(CH_3Br)}{dt} = \frac{dp}{dt} = \frac{k_1[CH_3CO_2H][HBr]}{1 + \frac{k_3}{k_2}[i\text{-}C_4H_8]}$$

which describes the general shape of the curves in the Figure. The methylbutenes formed can be satisfactorily explained as arising from the thermal decomposition of mesityl oxide which proceeds according to the steps.

$$(CH_3)_2C{=}CH{\cdot}CO{\cdot}CH_3 \rightarrow \text{methylbutene} + CO \qquad (4)$$

$$(CH_3)_2C{=}CH{\cdot}COCH_3 \rightarrow i\text{-}C_4H_8 + CH_2{=}C{=}O \qquad (5)$$

for which the overall first-order rate constant† is given by the equation $(k_4 + k_5) = 10^{14.22}\ \exp(-63240/\boldsymbol{R}T)\ \sec^{-1}$. In the presence of hydrogen bromide mesityl oxide undergoes the additional reaction

$$(CH_3)_2C{=}CH{\cdot}COCH_3 + HBr \rightarrow i\text{-}C_4H_8 + CO + CH_3Br \qquad (6)$$

At each temperature, the rate constant for step (6), calculated as first order in each reagent, is *ca.* one-tenth of that observed for the reaction of acetic acid with hydrogen bromide. Steps (4), (5), and (6) are slow under initial conditions and become important only in the later stages of the reaction.

Formation of mesityl oxide by a free-radical mechanism could proceed by the addition of acetyl to isobutene. This is unlikely under the conditions used since above 160° acetyl decomposition is fast.[3] Runs at 441·6° with AcOH and HBr in the presence of NO in pressures ranging from 25 mm to 140 mm gave a mean $k_1 = 231$ ml mole^{-1} sec^{-1} identical with that observed for the reaction of AcOH with HBr alone which confirmed that reactions (1) and (2) are molecular, and supports a molecular process for (3). Increasing the surface-to-volume ratio of the reaction vessel from 0·8 to 8·0 cm^{-1} did not affect the rate of formation of mesityl oxide and the reaction is considered homogeneous. The similarity of this reaction to the hydrogen halide-catalysed decompositions of carboxylic acids studied by Stimson and his co-workers has been noted before.[1] The formation of mesityl oxide from isobutene can be explained in terms of a polar reaction which is similar to that of alcohols with the intermediate generated in the reactions of esters with HBr.[4] The lowering of the rate of change of pressure effected by isobutene is due to the stoicheiometry of reactions (1) and (3) rather than to inhibition of a free-radical chain mechanism.

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† These steps are inhibited by isobutene and first-order kinetics describe only the initial 20% of reaction.

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[2] A. Maccoll and V. R. Stimson, *J. Chem. Soc.*, 1960, 2836.
[3] M. H. J. Wijnen, *J. Chem. Phys.*, 1957, **27**, 710.
[4] J. T. D. Cross and V. R. Stimson, *Austral. J. Chem.*, 1968, **21**, 687 and previous papers in the series.