

THE GAS-PHASE REACTION OF ACETIC ACID WITH HYDROGEN BROMIDE. THE EFFECT OF METHANOL

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[Manuscript received October 28, 1970]

Introduction

The hydrogen bromide catalysed decarbonylations of carboxylic acids in the gas phase proceed through intermediates which are sufficiently long-lived to react with alcohols to form esters.¹ The reaction of acetic acid with hydrogen bromide seems to belong to the same class of reactions,² and has been shown to form an intermediate A* which acetylates isobutene to produce mesityl oxide.³ Accordingly, addition of an alcohol to those reactions which generate A* should result in some ester formation. The results of the study of the effect of methanol on the reactions of acetic acid with hydrogen bromide are now reported.

Experimental

Materials and Procedures

The static apparatus and general procedures have been described previously.² Methanol (May & Baker, A.R. grade) was twice fractionated, and the sample boiling at 63.9°/727.0 mm (lit. 64.6°/760 mm) was shown to have a purity of >99.8% (gas chromatography). Reactions were commenced by adding hydrogen bromide to known pressures of acetic acid and methanol. Progress of reactions was followed by measuring rate of pressure change.

Results and Discussion

Acetic acid, methanol, and hydrogen bromide were allowed to react at 412° and 487°. Initially the observed rates of pressure change were essentially zero, but, after a certain delay, pressure increased smoothly with time. Typical pressure-time curves are shown in Figure 1. Details of runs and observed delay times are listed in Table 1. Products were investigated both within, and after, the delay time.

Methanol (156.6 mm), acetic acid (102.5 mm), and hydrogen bromide (67.4 mm) were allowed to react for 9.0 min at 412° ($\Delta P = 0.5 \pm 2$ mm) and the reaction mixture was trapped at -80°. No permanent gases were formed. The mass spectrum is shown in Figure 2. The spectrum corresponds to that of a mixture containing

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¹ Cross, J. T. D., and Stimson, V. R., *Aust. J. Chem.*, 1968, **21**, 713 and earlier papers in the series.

² Daly, N. J., and Gilligan, M. F., *Aust. J. Chem.*, 1969, **22**, 713.

³ Daly, N. J., and Gilligan, M. F., *Chem. Commun.*, 1970, 525.

methyl acetate (m/e 74, 59, 43), acetic acid (m/e 60, 43), methanol (m/e 32), and water (m/e 18), together with their fragmentation patterns. Small quantities of methyl bromide (m/e 94, 96) were present, but the combined signals at m/e 94, 96 are less than 10% of that at m/e 74. The ratio of the peaks at m/e 74 and m/e 32 is $c. 1.6 : 1$, so that although no pressure change had occurred, much of the methanol had been converted into methyl acetate.

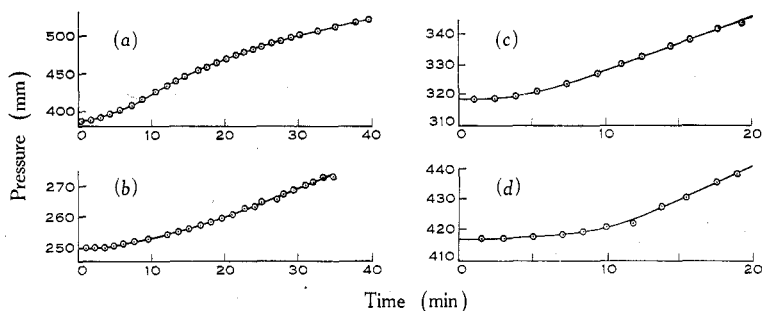


Fig. 1.—Pressure-time curves for runs in the presence of methanol.
 (a) 487°; $P_0(\text{MeOH})$ 175.9 mm, $P_0(\text{HBr})$ 84.6 mm, $P_0(\text{AcOH})$ 126.2 mm.
 (b) 487°; $P_0(\text{MeOH})$ 157.5 mm, $P_0(\text{HBr})$ 20.8 mm, $P_0(\text{AcOH})$ 77.1 mm.
 (c) 412°; $P_0(\text{MeOH})$ 14.7 mm, $P_0(\text{HBr})$ 165.4 mm, $P_0(\text{AcOH})$ 138.3 mm.
 (d) 412°; $P_0(\text{MeOH})$ 27.5 mm, $P_0(\text{HBr})$ 124.2 mm, $P_0(\text{AcOH})$ 160.0 mm.

TABLE 1

DELAY TIMES PRODUCED BY METHANOL

The delay time is calculated from the point at which the line produced along the initial flat region intersects the line produced from the region of changing pressure

Temp. (°C)	$P_0(\text{CH}_3\text{OH})$ (mm)	$P_0(\text{HBr})$ (mm)	$P_0(\text{AcOH})$ (mm)	Delay Time (min)
412	14.7	165.4	138.3	5
412	27.5	124.2	160.0	7
412	40.9	188.8	187.4	9
412	80.9	118.9	145.2	14
412	149.2	61.2	117.3	> 20
412	156.6	67.4	102.5	> 9
412	156.7	92.3	126.2	> 20
487	157.5	20.8	77.1	3
487	160.6	126.8	93.9	2
487	175.9	84.6	126.2	2
487	212.7	125.9	44.4	4

Methanol (27.5 mm), acetic acid (160.0 mm), and hydrogen bromide (124.2 mm) were allowed to react for 32 min at 412° ($\Delta P = 26.0$ mm) and the reaction mixture was trapped at -80° . Permanent gas was formed. The mass spectrum of the -80° condensables corresponds to the reaction mixture as before, but the relative intensities of peaks at m/e 94, 96 and m/e 74 is $c. 3 : 1$ which shows that methyl bromide becomes

a significant product after the delay time. Analyses of the products of a number of reactions confirmed these results.

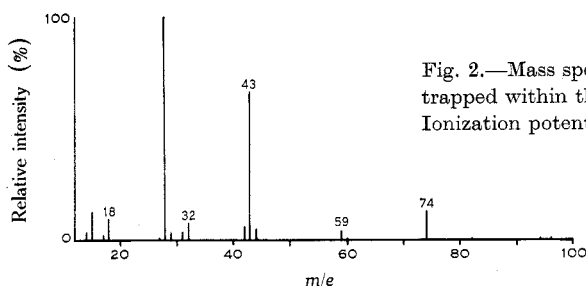


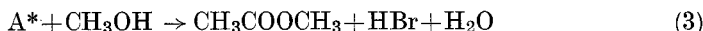
Fig. 2.—Mass spectrum of -80° condensables trapped within the delay time. Ionization potential 70 eV, ion current 50 μ A.

In a control experiment, acetic acid (73.1 mm) and methanol (78.7 mm) were allowed to react at 415° for 20 min ($\Delta P = 0 \pm 0.5$ mm). The mixture was trapped at -80° (no permanent gas was formed), and the mass spectrum was recorded. The spectrum corresponds to that of a mixture of acetic acid, methanol, with traces of water and methyl acetate. The relative intensities of the peaks at m/e 74 and 32 is *c.* 1 : 15 which establishes that very little methanol is converted into methyl acetate in the gas phase and in the analytical procedures. Thus hydrogen bromide has a role in the esterification.

The results establish that a substantial portion of the methanol is converted into methyl acetate during the delay time in a reaction with no resultant pressure change. The pressure change after the delay time results from the formation of methyl bromide by the established reactions²



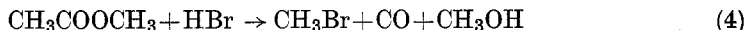
The reaction



explains the formation of methyl acetate and is formally analogous to that proposed for the pivalic acid, and methyl pivalate systems.¹

At 412° delay times are roughly proportional to the pressure of methanol and show that with moderate pressures of methanol the formation of methyl acetate effectively races the decomposition of the intermediate A^* . At 487° the decomposition becomes more effective, and the pressures of methanol need to be considerably higher than those of hydrogen bromide or acetic acid to enable the delay time to be observed.

Values observed for dp/dt after the delay time are close to initial rates calculated for the runs without methanol which indicates that methyl acetate decomposes in the presence of hydrogen bromide at a rate comparable with that of acetic acid. The reaction is under investigation and proceeds according to the equation



which is reversed by addition of methanol. It seems likely that a step involving reversal of (3) occurs in the mechanism.