Tetrahedron Letters No.19, pp. 2321-2323, 1968. Pergamon Press. Printed in Great Britain.

THE ACID-CATALYSED HYDROLYSIS OF 3-DIAZO-1-METHOXYCARBONYLOXY-1-PHENYL-ACETONE

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(Received in UK 5 January 1968; accepted for publication 8 February 1968)

McCauley and King (1) studied the acid-catalysed decomposition of diazoacetone (I, R = R' = H) and concluded that it proceeded via an A-2 mechanism. The effectiveness of halogens acids fell in order of decreasing nucleophilic power of the acid anion, i.e. HI > HBr > HCl, suggesting a rate controlling step involving halide ion.

Dahn and Gold (2) recently showed that the perchloric acid-catalysed hydrolysis of a number of diazoketones in aqueous dioxan involved specific hydrogen ion catalysis. They also concluded, however, that the subsequent rate-determining step was unimolecular (i.e. an A-1 mechanism).

We have attempted to resolve these apparently conflicting reports by a more detailed study of the acid-catalysed hydrolysis of 3-diazo-1-methoxycarbonyloxy-1-phenyl-acetone, (I, R = Ph, R' = $OCOOCH_3$), one of the compounds originally studied by Dahn and Gold (2).

Our value for the kinetic deuterium solvent effect ($k_1^{D_2O}/k_1^{H_2O}$ = 3.1 in 40% dioxan at 25°) is in reasonable accord with Dahn and Gold's value (2.5 in 60% dioxan at 70°) and confirms their finding of specific hydrogen ion catalysis.

The pH-rate dependence in perchloric acid gives rise to a linear correlation with the Hammett acidity function (3) H_0, the plot of log k_1 against $-H_0$ having a slope of 1.0. (c.f. 1.1 ref. (2)). Such a pseudo Hammett correlation could be given by a bimolecular reaction on which was superimposed a large positive salt effect. That this is indeed the case for 3-Diazo-1-methoxycarbonyloxy-1-phenyl-acetone is shown by the fact that, in mixtures of perchloric acid and sodium perchlorate at approximately constant perchlorate ion concentration (2.41 M), the rate is more nearly proportional to stoicheiometric acidity (Figure 1).

It is generally assumed that, in such mixtures, the ionic strength effect will be approximately independent of the nature of the cation. Grube and Schmid (4), however, showed that for the hydrolysis of cyanamide, smaller cations are more effective in catalysis. The slight positive deviation observed in the present case at high acid strength probably arises

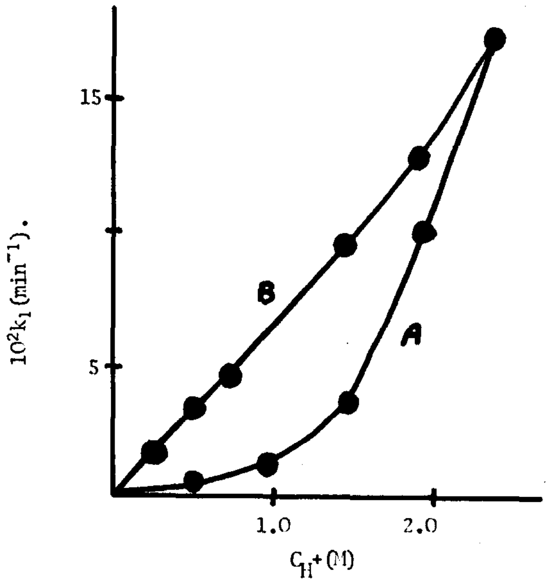


Figure 1

Acid-catalysed hydrolysis at 44° in 40% dioxan-water (v/v) A, $HClO_4$; B, $HClO_4$ + $LiClO_4$.

from this effect as lithium cations are gradually replaced by protons.

The use of the Zucker-Hammett hypothesis as the sole criterion of the mechanism of a particular reaction has been particularly criticised (5) and the correlation obtained here would appear to be one more example of the limitation of this criterion. Zwanenburg et. al. (6) have recently discussed the failure of such a correlation for the hydrolysis of the analogous diazosulphones.

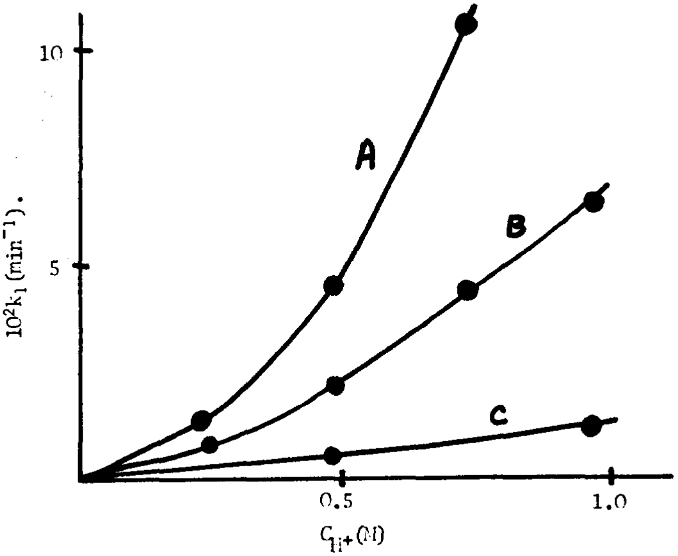
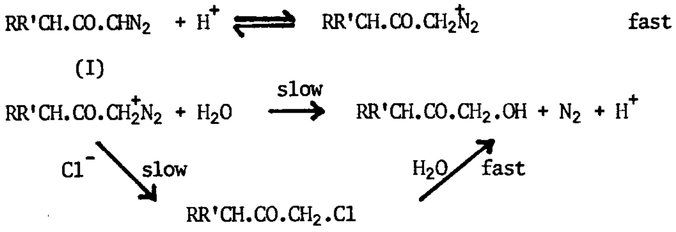


Figure 2

Acid-catalysed hydrolysis with A, HBr; B, HCl; C, $HClO_4$.

In Figure 2 are shown the effects of various acids on the rate of hydrolysis. As for the case of diazoacetone(1) the effect of halides is far too large to be ascribed to a simple salt effect and suggests that in the presence of halide ions an alternative pathway is available as shown in the reaction scheme below.



Another criterion of mechanism which can be used is the generalisation that for substrates of similar type the entropy of activation, $\Delta S^{\ddagger}$, for A-1 hydrolyses will be close to zero, but will be considerably more negative for A-2 hydrolyses (7). Our value ($\Delta S^{\ddagger} = -16.0$ e.u.) calculated from the rate constant in 1.00 Molar perchloric acid at 35° is in marked contrast to that obtained earlier by Dahn and Gold ($\Delta S^{\ddagger} = -6.0$ e.u.) from data in 2.50 Molar acid (2) and indicates that the entropy of activation varies very considerably with both the strength and nature of the acid used. (In HCl, $\Delta S^{\ddagger} = -5.6$ e.u.)

Whalley has previously pointed out (5) that whereas this criterion may in certain cases give fortuitously correct results, it is not reliable as an unambiguous criterion of mechanism. Thus the hydrolysis of ethylene oxide with $\Delta S^{\ddagger} = -6.1$ e.u. proceeds via an A-2 mechanism.

On balance therefore, the evidence at present available indicates that the hydrolysis of 3-Diazo-1-methoxycarbonyloxy-1-phenyl-acetone proceeds via an A-2 mechanism.

Further work is in progress to establish whether this is the general mode of hydrolysis of diazoketones.

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