Deuterium Isotope Effects on the Silver Ion-Promoted Hydrolyses of S,S-Diethylacetals of p-Substituted Benzaldehydes

Derek P. N. Satchell and Rosemary S. Satchell

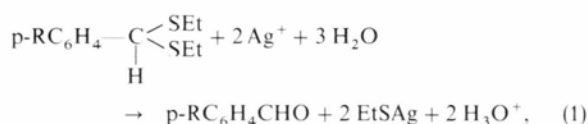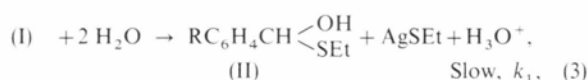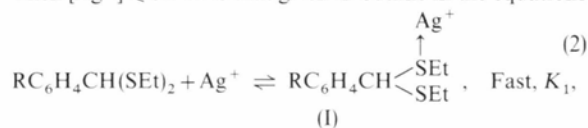*This paper is dedicated to Professor Jacob Bigeleisen on the occasion of his 70th birthday*

Solvent deuterium isotope effects support the view that the p-NO_2 and p-Me derivatives of benzaldehyde S,S-diethylacetal undergo silver ion-promoted hydrolysis in water by different mechanisms.

Introduction

Silver ions promote the hydrolysis of S-acetals in aqueous solution. The kinetic and mechanistic details depend upon the structure of the S-acetal [1, 2]. For the (open-chain) S,S-diethylacetals of substituted benzaldehydes,

$$p\text{-}RC_6H_4 - \underset{\underset{H}{|}}{C} \overset{SEt}{\underset{SEt}{<}} + 2\,Ag^+ + 3\,H_2O$$

$$\rightarrow\ p\text{-}RC_6H_4CHO + 2\,EtSAg + 2\,H_3O^+, \quad (1)$$

we have found [2] that the dominant path leading to hydrolysis when $[Ag^+] \gtrsim 0.1$ M is that given in outline in the equations

$$RC_6H_4CH(SEt)_2 + Ag^+ \rightleftharpoons RC_6H_4CH\overset{\overset{Ag^+}{\uparrow}}{\underset{SEt}{<}}SEt, \quad Fast,\ K_1, \quad (2)$$
$$(I)$$

$$(I)\ + 2\,H_2O\ \rightarrow\ RC_6H_4CH\overset{OH}{\underset{SEt}{<}} + AgSEt + H_3O^+,$$
$$(II) \qquad\qquad Slow,\ k_1, \quad (3)$$

$$(II)\ \xrightarrow{Ag^+/H_2O}\ RC_6H_4CHO + AgSEt + H_3O^+, \quad Fast. \quad (4)$$

In the presence of an excess of silver ions, the observed first-order rate constant for loss of acetal, k_{obs}, is given by

$$k_{obs} = k_1\,K_1\,[Ag^+]/(1 + K_1\,[Ag^+]). \quad (5)$$

Using solutions in 1% (v/v) dioxane-water we have shown [2] that plots of (5) lead to values of K_1 and k_1 for various S,S-diethylacetals. Comparisons of the k_1 values, and of the corresponding activation parameters, led us to suggest [2] that there occurs a change in the detailed mechanism of step (3) on passing from the S,S-acetals with R = p-MeO and p-Me to the p-NO_2 derivative: for the former acetals we postulated a unimolecular mechanism analogous to the A1

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scheme common [3] for O,O-acetals in the presence of H_3O^+ ions, while for the latter we suggested a bimolecular A2-type mechanism with one (or more) water molecules in the slow phase of step (3). The compound with R = H may be an intermediate case [1, 2].

Solvent deuterium isotope effects are sometimes helpful in distinguishing between reaction mechanisms in solution [4]. Relatively few studies, however, have examined such isotope effects in systems involving metal ion-promotion or catalysis. No general pattern of behaviour has been established in the way that it has for H_3O^+-catalysed processes [4]. We have now studied the effect of using D_2O in place of H_2O on some of the results for two of these S,S-acetals: the p-Me and p-NO_2 compounds.

Experimental

Deuterium oxide was the Goss product (99.8%). Our methods, concentration and other conditions were similar to those used [1, 2] for H_2O solutions, and the reproducibility of k_{obs} ($\pm 10\%$) was also similar to that obtained in H_2O. Our results are compared with those for H_2O in Figure 1. The derived K_1 and k_1 values were obtained via the slopes and intercepts of plots both of $1/k_{obs}$ against $1/[Ag^+]$, and of $[Ag^+]/k_{obs}$ against $[Ag^+]$. Good rectilinear behaviour was observed, in keeping with (5).

Discussion

It is evident from Fig. 1 that the change to D_2O has little effect on the reaction rate of the p-Me compound. At 25.0 °C the derived values of K_1 (dm³ mol⁻¹) and k_1 (s⁻¹) for the hydrolyses in H_2O and D_2O are $(K_1)_{H_2O} = 230 \pm 10$, $(K_1)_{D_2O} = 235 \pm 10$, $(k_1)_{H_2O} = 1.6 \pm 0.5$, $(k_1)_{D_2O} = 1.6 \pm 0.5$. The absence of a significant isotope effect on k_1 is compatible [4] with our suggestion [2] that water species are not involved in the slow phase of step (3) for the p-Me derivative. That the K_1 values are also so close is interesting: it could imply that the net effects on $\Delta G°$ of the enthalpy and entropy changes accompanying the return of one (possibly more) water molecule(s) from the silver ion solvation water to the bulk on forming the adduct (I) are, in this case, much the same for both H_2O and D_2O.

For the p-NO_2 derivative the change of solvent has a clearly detectable effect (Figure 1). At 44.2 °C the derived parameters are $(K_1)_{H_2O} = 9 \pm 1$, $(K_1)_{D_2O} = 18 \pm 2$, $(k_1)_{H_2O} = 7.0 \pm 0.8$, and $(k_1)_{D_2O} = 4.1 \pm 0.5$. The relative k_1 values appear compatible [4] with our suggestion that one or more water molecules are involved in a nucleophilic attack on the pro-carbonyl carbon atom in the slow phase of step (3) for the p-NO_2 compound and point to some change in mechanism compared with the p-Me derivative. For the p-NO_2 compound the K_1 values in the two solvents are also notably different. In previous work [2] we found that the thermodynamic quantities $\Delta H°$ and $\Delta S°$ corresponding to equilibrium (2) in H_2O have values (77 ± 5) kJ mol⁻¹ and (259 ± 10)
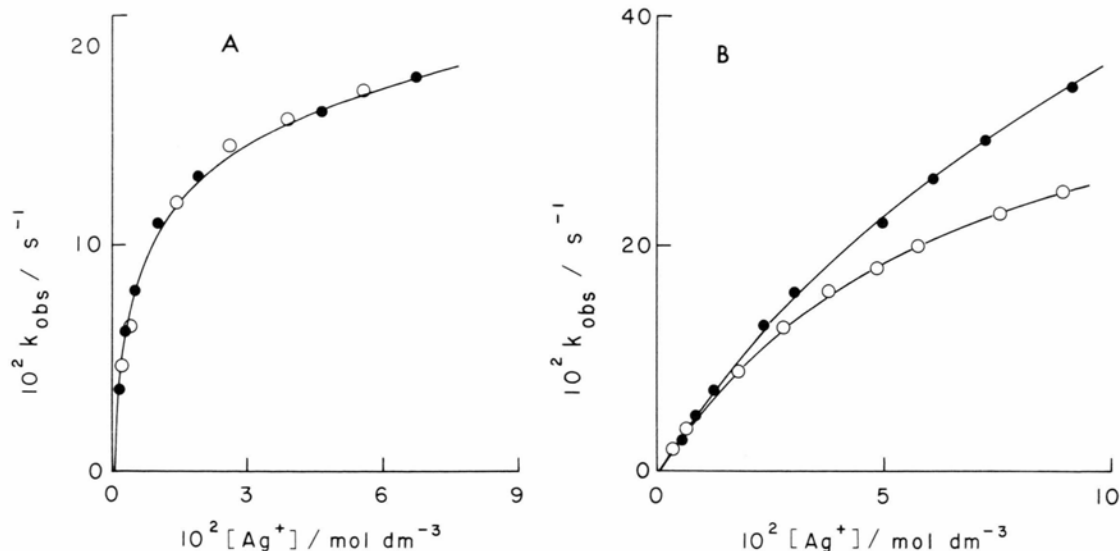
Fig. 1. Variation of k_{obs} with [Ag$^+$] in H$_2$O and in D$_2$O. **A:** p-methyl derivative at 25.0 °C; **B:** p-nitro derivative at 44.2 °C. [S,S-acetal]$_{initial} \cong 10^{-5}$ M, [H$_3$O$^+$]=0.05 M, and ionic strength=0.51 M in all runs; k_{obs} insensitivee to [H$_3$O$^+$], see [1]; D$_2$O ○, H$_2$O ●.

J K mole^{-1}, respectively, for the p-NO$_2$ derivative, whereas for the p-Me (and the p-MeO) compound both ΔH° and ΔS° are negative. We interpreted this difference in thermodynamic parameters in terms of a much greater degree of desolvation of the reactants (especially the Ag$^+$ ion) being required for formation of (I) with the p-NO$_2$ compound owing to the latter's relative weakness as an S-base. The isotope

effect now found seems to us possibly compatible with that picture, and certainly indicates some difference in the details of adduct formation for the p-NO$_2$ and p-Me compounds. In all, the isotope effects evidently support our view that the p-NO$_2$ and p-Me compounds react via mechanisms containing significant differences in detail.

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[4] P. M. Laughton and R. E. Robinson, in: Solute-Solvent Interactions (J. F. Coetzee and D. C. Ritchie, eds.), Marcel Dekker, New York 1969, Chapt. 7.