Acid-catalysed Cleavage of Diacetonylmercury

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Summary The $HClO_4$-catalysed cleavage of diacetonylmercury yields one mole of acetone and one mole of mercuriacetone ion; the kinetic rate law and solvent deuterium isotope effect are consistent with a mechanism in which protonation of the enol of acetone is rate determining.

THE recent work[1] by Byrd and Halpern on the mechanism of the $AcCH_2Hg^+$-catalysed hydrolysis of isopropenyl acetate prompts us to report our results on the closely related reaction, the cleavage of diacetonylmercury (I) induced by aqueous $HClO_4$. Acetone and mercuriacetone ion were shown to be products of the reaction by isolation and characterization as the known solid derivatives, $\mathrm{AcCH_2HgCl}$ (II)[2] and the 2,4-dinitrophenylhydrazine derivative of acetone. The stoicheiometry of equation (1) was established by u.v. spectral analysis, using $\mathrm{AcCH_2Hg^+}$ prepared *in situ* from (II) and $\mathrm{AgClO_4}$ for comparison, and by monitoring the increase of pH with time as a function of varying initial concentrations of (I) and $\mathrm{HClO_4}$. Independent experiments confirmed that subsequent hydrolysis of the $\mathrm{AcCH_2Hg^+}$ product was negligible under the conditions of the kinetics measurements [aqueous solutions at 25° containing 3% v/v tetrahydrofuran and $(2{\cdot}07–7{\cdot}94) \times 10^{-3}$ M-$\mathrm{HClO_4}$].

$$\underset{\textstyle(\mathrm{I})}{(\mathrm{AcCH_2})_2\mathrm{Hg}} + \mathrm{HClO_4} \xrightarrow{\mathrm{H_2O}} \mathrm{Me_2CO} + \mathrm{AcCH_2HgClO_4} \qquad (1)$$

Reaction rates were followed spectrophotometrically at 270 nm using solutions which were initially $(1{\cdot}14–4{\cdot}13) \times 10^{-4}$ M in (I) and which contained a 10-fold or greater molar excess of $\mathrm{HClO_4}$. The reaction obeyed no simple order and was inhibited by the build-up of $\mathrm{AcCH_2Hg^+}$. After rapid establishment of steady-state conditions, the rate law of equation (2) was followed with very good precision, giving for k_{T} a value of $1{\cdot}21 \times 10^{-2}$ $\mathrm{M^{-1}\,s^{-1}}$ at 25°.

$$-\,\mathrm{d}[(\mathrm{I})]/\mathrm{d}t = k_{\mathrm{T}}[(\mathrm{I})][\mathrm{H^+}]^2/[\mathrm{AcCH_2Hg^+}] \qquad (2)$$

These kinetics are analogous to those recently reported[3] for the hydrolysis of α-ethoxycarbonylbenzylmercuric chloride, simplified in the present case due to the absence of halide ion.

The results can be accommodated by the mechanism of equations (3)—(5), provided that $k_{-2}[\mathrm{AcCH_2Hg^+}] >> k_3[\mathrm{H^+}]$.

$$(\mathrm{I}) + \mathrm{H^+} \xrightleftharpoons{K_1} (\mathrm{IH^+}) \qquad \text{(Rapid equilibrium)} \qquad (3)$$

$$(\mathrm{IH^+}) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{AcCH_2Hg^+} + \mathrm{CH_2{=}C(OH)Me} \qquad (4)$$

$$\mathrm{CH_2{=}C(OH)Me} + \mathrm{H^+} \xrightarrow{k_3} \mathrm{Me_2CO} + \mathrm{H^+} \qquad (5)$$

That proton transfer to the enol form of acetone is rate determining is supported by the solvent deuterium isotope effect, $k(\mathrm{H_2O})/k(\mathrm{D_2O}) = 1{\cdot}49$. The isotope effect on step (5) is therefore probably of the order of 3—5 since that on step (3) can be predicted[4] to be in the range 0·3—0·5. This compares with the deuterium isotope effect for hydrogen ion transfer to ethyl vinyl ether which has been found[5] to be 2·95.

Further support for the suggested mechanism comes from the observation that one of the two pH-dependent steps, presumably the ketonization stage, is subject to general acid and general base catalysis in $\mathrm{HCO_2H{-}HCO_2^-}$ buffers as indicated by equation (6).

$$k_{\mathrm{obs}} = 1{\cdot}21 \times 10^{-2}[\mathrm{H^+}]^2 + 2 \times 10^{-3}[\mathrm{H^+}][\mathrm{HCO_2H}] + 5 \times 10^{-3}[\mathrm{H^+}][\mathrm{HCO_2^-}] \qquad (6)$$

Our results eliminate a plausible alternative mechanism for diacetonylmercury hydrolysis, namely one involving direct electrophilic attack[6] by $\mathrm{H_3O^+}$ on the methylene carbon of (I). We have provided indirect evidence for the ready addition of $\mathrm{AcCH_2Hg^+}$ to an activated alkene, thereby lending support to Byrd and Halpern's suggested mechanism.[1] Bach's account[7] of the methoxymercuration of cyclonona-1,2-diene with $\mathrm{EtHg^+}$ and $\mathrm{PhHg^+}$ provides the only other evidence for the addition of an $\mathrm{RHg^+}$ moiety to an olefinic linkage. The present work is also relevant to the nature of product formation in the $\mathrm{HgSO_4}$-catalysed hydration of alkynes in aqueous $\mathrm{H_2SO_4}$, inasmuch as intermediates of the type $\mathrm{RCOCH_2HgX}$ are probably involved.

This work was supported by the National Science Foundation.

(*Received, January* 11th, 1971; *Com.* 046.)

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