

Acid-catalysed Cleavage of Diacetylmercury

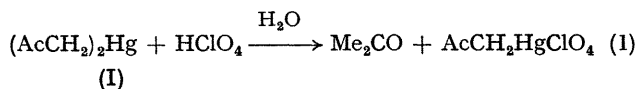
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Summary The HClO_4 -catalysed cleavage of diacetylmercury yields one mole of acetone and one mole of mercuriacetone ion; the kinetic rate law and solvent deuterium isotope effect are consistent with a mechanism in which protonation of the enol of acetone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

THE recent work¹ 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 diacetylmercury (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, AcCH_2HgCl (II)² and the 2,4-dinitrophenylhydrazine derivative of acetone. The stoichiometry of equation (1) was established by u.v. spectral analysis, using AcCH_2Hg^+ prepared *in situ* from (II) and AgClO_4 for comparison, and by monitoring the increase of pH with time as a function of varying initial concentrations of (I) and HClO_4 . Independent experiments confirmed that subsequent hydrolysis of the AcCH_2Hg^+ product was negligible under the conditions of the kinetics measurements [aqueous solutions at 25° containing 3% v/v tetrahydrofuran and (2.07—7.94) $\times 10^{-3}$ M- HClO_4].

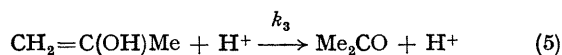
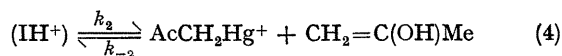
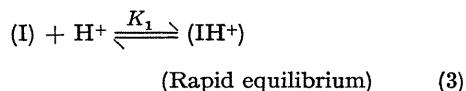


Reaction rates were followed spectrophotometrically at 270 nm using solutions which were initially (1.14—4.13) $\times 10^{-4}$ M in (I) and which contained a 10-fold or greater molar excess of HClO_4 . The reaction obeyed no simple order and was inhibited by the build-up of AcCH_2Hg^+ . After rapid establishment of steady-state conditions, the rate law of equation (2) was followed with very good precision, giving for k_r a value of 1.21×10^{-2} M⁻¹ s⁻¹ at 25°.

$$-d[(\text{I})]/dt = k_r[(\text{I})][\text{H}^+]^2/[\text{AcCH}_2\text{Hg}^+] \quad (2)$$

These kinetics are analogous to those recently reported³ 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 $k_{-2}[\text{AcCH}_2\text{Hg}^+] > k_3[\text{H}^+]$.



That proton transfer to the enol form of acetone is rate determining is supported by the solvent deuterium isotope effect, $k(\text{H}_2\text{O})/k(\text{D}_2\text{O}) = 1.49$. The isotope effect on step (5) is therefore probably of the order of 3—5 since that on step (3) can be predicted⁴ 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 found⁵ 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 $\text{HCO}_2\text{H}-\text{HCO}_2^-$ buffers as indicated by equation (6).

$$k_{\text{obs}} = 1.21 \times 10^{-2}[\text{H}^+]^2 + 2 \times 10^{-3}[\text{H}^+][\text{HCO}_2\text{H}] + 5 \times 10^{-3}[\text{H}^+][\text{HCO}_2^-] \quad (6)$$

Our results eliminate a plausible alternative mechanism for diacetylmercury hydrolysis, namely one involving direct electrophilic attack⁶ by H_3O^+ on the methylene carbon of (I). We have provided indirect evidence for the ready addition of AcCH_2Hg^+ to an activated alkene, thereby lending support to Byrd and Halpern's suggested mechanism.¹ Bach's account⁷ of the methoxymercuration of cyclonona-1,2-diene with EtHg^+ and PhHg^+ provides the only other evidence for the addition of an RHg^+ moiety to an olefinic linkage. The present work is also relevant to the nature of product formation in the HgSO_4 -catalysed hydration of alkynes in aqueous H_2SO_4 , inasmuch as intermediates of the type RCOCH_2HgX are probably involved.

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