Mercury(II)-catalysed Hydrolysis of Isopropenyl Acetate

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Summary The mercuriacetone ion and other mercurials catalyse the hydrolysis of isopropenyl acetate to acetone; the catalytic reaction is shown to proceed through an oxymercuration–deoxymercuration mechanism.

THE addition of an excess of isopropenyl acetate to a solution of $HgClO_4$ (*ca.* 10^{-3} M) in dilute aqueous $HClO_4$ (0·03—0·5 M) resulted in a rapid stoicheiometric reaction to form the mercuriacetone ion (I), according to equation (1), followed by hydrolysis of the excess of isopropenyl acetate to acetone according to equation (2). The hydrolysis reaction was catalysed by (I).

$$Hg^{2+} + H_2C:C(OAc)CH_3 + H_2O \rightarrow \underset{\text{(I)}}{HgCH_2COCH_3^+} + HOAc + H^+ \qquad (1)$$

$$H_2C:C(OAc)CH_3 + H_2O \rightarrow CH_3COCH_3 + HOAc \qquad (2)$$

The stoicheiometry of reaction (1) was established by spectral titration, by ^1H n.m.r. characterization of (I), and by isolation and characterization of (I) as the known[1] chloride $ClHgCH_2COCH_3$. Reaction (1) obeyed the second-order rate-law, $d[(I)]/dt = k_1[Hg^{2+}][H_2C:C(OAc)CH_3]$, with $k_1 = 2{\cdot}6 \times 10^4$ M^{-1} s^{-1} at 25°. The kinetics are similar to those of the oxymercuration of other olefinic compounds[2] and it seems likely that the reaction proceeds *via* oxymercuration of isopropenyl acetate to form $HgCH_2C(OH)(OAc)CH_3^+$, followed by elimination of HOAc to form (I). The direct mercuration of acetone[3] was found to be too slow for this route to contribute significantly to the formation of (I) under our conditions.

Investigation of the kinetics of reaction (2), catalysed by (I), yielded convincing evidence for the mechanism depicted by equations (3) and (4).

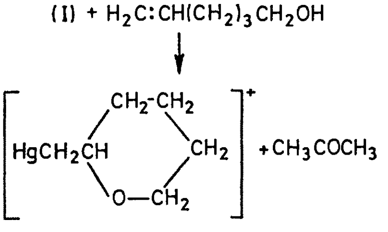
$$\text{(I)} + H_2O + H_2C\!:\!C(OAc)CH_3 \overset{K}{\rightleftharpoons} CH_3C(OH)(OAc)CH_2HgCH_2COCH_3 + H^+ \quad \text{(II)} \quad \text{(Rapid-equilibrium)} \qquad (3)$$

$$\text{(II)} + H^+ \xrightarrow{k_4} \text{(I)} + CH_3COCH_3 + HOAc \qquad (4)$$

When the concentration of $H_2C\!:\!C(OAc)CH_3$ is in substantial excess over that of (I), this mechanism yields the rate law described by equation (5) where $[(I)_0]$ is the total catalyst concentration, *i.e.*, $[(I)] + [(II)]$. Kinetic experiments [using ^{1}H n.m.r. to follow reaction (2)] spanning the concentration ranges $8{\cdot}3 \times 10^{-4}$ to $1{\cdot}7 \times 10^{-2}$ M $(I)_0$, 0·10 to 0·38 M-$H_2C\!:\!C(OAc)CH_3$, and 0·03 to 0·50 M-$HClO_4$, yielded results in excellent agreement with equation (5),† from which the following values were determined: $K = 1{\cdot}5$ and $k_4 = 2{\cdot}5\ \text{M}^{-1}\ \text{s}^{-1}$, both at 40° and an ionic strength of 1·5 M adjusted with $NaClO_4$. The pre-equilibrium (3) could also be examined spectrally at lower temperatures [to slow down reaction (4)] yielding a value of K in good accord with the kinetically determined value.

$$\frac{d[CH_3COCH_3]}{dt} = k_4[(II)][H^+] = \frac{k_4K[(I)]_0][H^+][H_2C\!:\!C(OAc)CH_3]}{[H^+] + K[H_2C\!:\!C(OAc)CH_3]} \qquad (5)$$

In view of the occurrence of reaction (3) it was to be expected that other olefinic compounds would also react with (I) to displace acetone. This was confirmed by demonstrating that hex-1-en-6-ol reacts quantitatively with (I) to displace acetone and form the very stable previously characterized[2] oxymercurial (III) in accord with equation (6). Furthermore, it was found that, as expected, (III) is also a catalyst for the hydrolysis of isopropenyl acetate, presumably through an oxymercuration–deoxymercuration mechanism analogous to that of the $HgCH_2COCH_3^+$-catalysed reaction.



(6)

(III)

The mechanism that we have demonstrated above for the mercury(II)-catalysed hydrolysis of isopropenyl acetate is analogous to, and provides support for, one of the alternative mechanisms previously suggested for the mercury-catalysed transetherefication and transesterification of vinyl ethers and esters, respectively.[4,5]

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† An appropriate correction was applied for the separately determined small contribution from the acid-catalysed hydrolysis path.

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