DECOMPOSITION OF PERACETIC ACID CATALYZED BY VANADIUM COMPLEXES

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The oxidation of hydrocarbons by peracetic acid catalyzed by transition-metal compounds has great importance in organic synthesis [1], and thus the selectivity of reactions involving this peracid has great practical significance. However, information on the stability of peracetic acid in the presence of transition-metal compounds is only limited.

In the present work, we studied the decomposition of peracetic acid (AcOOH) in acetic acid (AcOH) catalyzed by vanadium complexes.

EXPERIMENTAL

The reactions were carried out in a 60-ml Pyrex vessel equipped with a magnetic stirrer and thermometer. Samples were taken during the experiments, in which the AcOOH and H_2O_2 contents were determined according to Dean et al. [2]. The volume and composition of the gases released were analyzed on a VTI-2 gas analyzer. Methanol and acetic anhydride were analyzed by gas–liquid chromatography using a Tsvet chromatograph with a flame-ionization detector using a 1 m × 3 mm glass column packed with 10% DEGA on Chromosorb W (0.20-0.25 mm), 20 ml/min nitrogen gas carrier flow rate, 30 ml/min hydrogen flow rate, and 300 ml/min air flow rate, 110°C column temperature, and 250°C injector temperature. We used All-Union State Standard (GOST) 9336-60 ammonium metavanadate and cp grade GOST 61-75 acetic acid redistilled over CrO_3 taking the fraction with bp 117.9-118.1°C (760 mm). A sample of peracetic acid was obtained according to Swen [3]. The ESR spectra were taken on a Bruker ER-200D spectrometer at 9500 MHz.

RESULTS AND DISCUSSION

Peracetic acid decomposes in acetic acid solutions of vanadium compounds largely by the reaction

$$\mathrm{AcOOH} \rightarrow \mathrm{AcOH} + \mathrm{O_2} \tag{1}$$

In all the experiments, H_2O_2 which might form upon the hydrolysis of AcOOH, was not detected in amounts $\geqslant 10^{-3}$ M.

There is no induction period on the kinetic curves for the decomposition of AcOOH, and radical reaction inhibitors such as tri-tert-butylphenol and tetranitromethanes (10^{-3} M) do not affect the reaction rate, indicating the absence or negligibly small contribution of an induced free-radical decomposition of the peroxide. Support for this hypothesis is also found in the ESR spectra at 293 and 77°K, which do not show signals for paramagnetic species such as V^{4+}, $AcO^{\cdot}$, and $HO_2^{\cdot}$, which might be expected in the case of a radical chain reaction mechanism.

Change in the H^+ concentration dictated by possible solvolysis of V^{5+} complexes apparently does not affect reaction (1) since the addition of strong proton-donor acids such as $HClO_4$ and H_2SO_4 (10^{-2} M) does not have a significant effect on the rate of this reaction.

The rate of reaction (1) obeys first-order kinetics relative to the catalyst concentration in the range from 10^{-5} to $5 \cdot 10^{-4}$ M, while the dependence of the initial rate of AcOOH decomposition on its composition is given by a curve with saturation. The inverse values of the initial rates of AcOOH decomposition are approximated satisfactorily by a linear function of the inverse AcOOH concentrations (Fig. 1). The simplest scheme satisfying this kinetic

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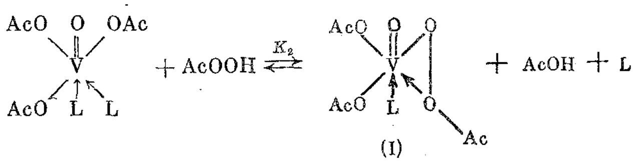
behavior involves the rapid and reversible formation of a complex of V^{5+} with AcOOH and a slow reaction of this complex followed by the appearance of the observed products.



(I) (2)

$$(I) \xrightarrow{k_3} \text{products} \qquad (3)$$

$L = AcOH, H_2O$.

According to this scheme [reactions (2) and (3)], the initial rate of reaction (1) should be given by the equation

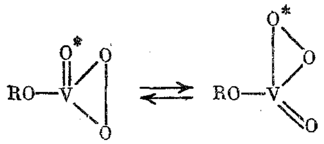
$$W_0 = \frac{k_3 K_2 [V]_0 [AcOOH]_0}{1 + K_2 [AcOOH]_0} \qquad (4)$$

or

$$\frac{1}{W_0} = \frac{1}{k_3 [V]_0} + \frac{1}{k_3 K_2 [V]_0 [AcOOH]_0} \qquad (5)$$

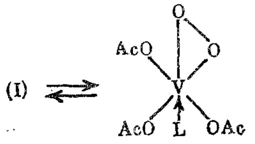
This relationship holds as demonstrated by the plot in Fig. 1. Analysis of this plot according to Eq. (5) gives $k_3 = 364\ \text{min}^{-1}$ and $K_2 = 18.7$ liters/mole at 30°C.

Taking account of the tendency of peroxy compounds to act as n-donor two-center ligands [4], we might have expected that the $AcOO^-$ anion would coordinate at the V^{5+} ion using both oxygen atoms of the peroxy group. In peroxo compounds of V^{5+}, the oxygen atoms of the peroxide and vanadyl groups exchange as a result of an intrasphere rearrangement [5]:



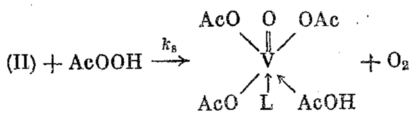
(6)

It is not excluded that the decomposition of AcOOH also proceeds through a similar step which would be rate-limiting.



(II) (7)

Peroxo complex (II) rapidly reacts with AcOOH [Eq. (8)] ($k_8 = 12.1 \cdot 10^{-3}$ liters/mole·min [6]) to release O_2 and regenerate the catalyst:



(8)

In the first step of this reaction AcOOH probably coordinates the V^{5+} ion of complex (II) to give a diperoxo complex, in which the stronger oxidizing agent AcOOH is coordinated in addition to O_2^{2-}. In contrast to the diperoxo complex VO_5^- which is relatively stable in solution [7], a two-electron transfer is possible in this complex from coordinated O_2^{2-} to coordinated AcOOH to form the reaction products [Eq. (8)].

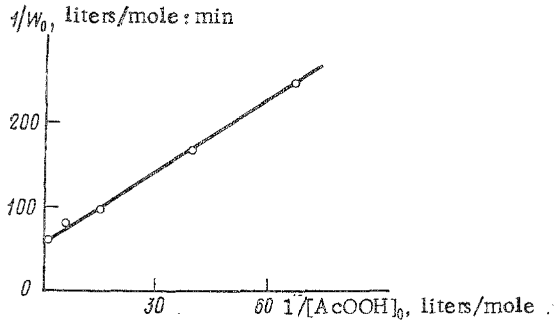


Fig. 1. Dependence of the initial rate of AcOOH decomposition on its initial concentration $[NH_4VO_3] = 5\cdot10^{-5}$ M, 30°C.

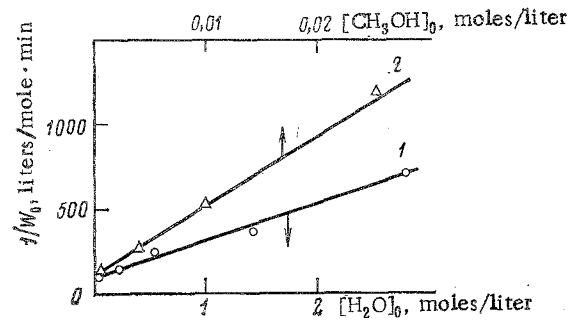


Fig. 2. Dependence of the initial rate of AcOOH decomposition on the concentration of H_2O (1) and MeOH (2). $[NH_4VO_3] = 5\cdot10^{-5}$ M, 30°C.

The addition of water or methanol strongly affects the rate of reaction (1). Molecules of these compounds may compete with AcOOH for a site in the coordination sphere of vanadium, leading to a decrease in the equilibrium concentration of complex (I) responsible for the observed reaction.

$$V^{5+}\cdot OOAc + H_2O \overset{K_9}{\rightleftarrows} V^{5+}\cdot OH + AcOOH \tag{9}$$

$$V^{5+}\cdot OOAc + CH_3OH \overset{K_{10}}{\rightleftarrows} V^{5+}\cdot OCH_3 + AcOOH \tag{10}$$

Taking account of reactions (9) and (10), Eq. (4) acquires the form

$$W_0 = \frac{k_3K_2[V]_0[AcOOH]_0}{1 + K_x[X] + K_2[AcOOH]_0}, \tag{11}$$

where $K_X = K_9$, K_{10} and $X = H_2O$ or MeOH, or

$$\frac{1}{W_0} = \frac{1}{k_3[V]_0} + \frac{1 + K_x[X]}{k_3K_2[V]_0[AcOOH]_0} \tag{12}$$

The inverse initial AcOOH decomposition rates are linearly dependent on the concentrations of H_2O and CH_3OH (Fig. 2) up to 3 and 0.03 M, respectively. Treatment of the experimental data using Eq. (12) with values $k_3 = 364\ min^{-1}$ and $K_2 = 18.7\ M^{-1}$ found at 30°C gives $K_9 = 11$ and $K_{10} = 900\ M^{-1}$.

The kinetic curves for AcOOH decomposition become sigmoid in shape with increasing methanol concentration. For 0.5 M MeOH, the segment of the curve characterizing reaction acceleration continues up to 85% AcOOH conversion. In solutions containing methanol, esterification of MeOH probably proceeds with the formation of methyl acetate which does not inhibit the reaction along with AcOOH decomposition. As a result of this esterification, the strong MeOH inhibitor is replaced by a weak inhibitor (H_2O).

At AcOOH concentrations up to 0.1 M and 30-60°C, the gas released contains 2-5% CO_2 in addition to O_2 and at 100-120°C for [AcOOH] = 1-4 M, the CO_2 content reaches 50 vol.%. In the liquid phase, up to 1 M MeOH and MeOAc are found in such experiments. The formation of these products as a result of the radical decomposition of AcOOH is unlikely since there are no ESR signals for V^{4+} or AcO' radicals. CO_2 is apparently formed as a result of intrasphere reactions proceeding in the vanadium peroxo complexes. The dependence of the CO_2 yield on the AcOOH concentration indicates that complexes, in which the V^{5+} ion is coordinated by more than one AcOOH molecule, are responsible for CO_2 formation. The electron-withdrawing ligands (O_2^{2-} and AcOOH) may impart strong Lewis acid properties to the vanadium ion which permits catalysis of AcOOH decomposition

$$\mathrm{AcOOH} \rightarrow \mathrm{MeOH} + \mathrm{CO_2} \qquad (13)$$

Further data are required in order to discuss the mechanism of this reaction.

Comparison of the volume and composition of the gases released with the amount of AcOOH consumed indicates that the decomposition of AcOOH is 20-30% greater than the yield of O_2 and CO_2 formed. This finding indicates the complexity of these reactions.

CONCLUSIONS

1. Peractic acid in acetic acid solutions of ammonium vanadate decomposes with the predominant formation of O_2 and small amounts of CO_2, the yield of which increases with increasing temperature and peracetic acid concentration.

2. Both these reactions proceed without the formation of free radicals in amounts detectable by ESR spectroscopy.

3. The rate of oxygen release under conditions in which the formation of CO_2 is insignificant obeys a kinetic equation indicating the intermediate formation of a complex between V^{5+} ions and peracetic acid and the slow conversion of this complex into the observed products.

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