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KINETICS AND MECHANISM OF THE PERMANGANATE OXIDATION OF ACETYLENEDICARBOXYLIC ACID

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To our knowledge, the kinetics of the permanganate oxidation of acetylene derivatives have not been studied so far although detailed kinetic information is available on the oxidation of alkenes in basic and neutral solutions [1]. We wish to report on the kinetics of acetylenedicarboxylic acid (H_2A) oxidation with acid permanganate. The results of direct titration indicate the following overall process

$$HO_2C-C\equiv C-CO_2H + 2MnO_4^- + 6H^+ \longrightarrow 4CO_2 + 4H_2O + 2Mn^{2+} \qquad (1)$$

Since the reaction is fast, the rate of MnO_4^- disappearance was followed spectrophotometrically on a stopped-flow system [2] equipped with a 4-jet mixer, permitting the measurement of half-lives above 15 msec. The kinetic curves were displayed on a Tektronix storage oscilloscope and photographed with a Polaroid camera.

The reaction was studied in aqueous solution at 14-30°C in the presence of a 10-20-fold excess of H_2A over MnO_4^-, in the pH range between 0.25 and 5.0 at an ionic strength of 1.5 M ($NaClO_4$). Buffer was added when necessary. The kinetic curves at 540 nm yielded excellent first order plots, the slopes at a fixed pH being proportional to the overall concentration of H_2A. Consequently the rate law is (no autocatalytic behaviour is observed)

$$-\frac{d[MnO_4]}{dt} = k_o[H_2A]_T[MnO_4^-] \qquad (2)$$

where $[H_2A]_T = [H_2A] + [HA^-] + [A^{2-}]$.

The stopped-flow traces at 250 nm reveal the accumulation and decay of an intermediate which, on the basis of the initial sign of the slope, has been identified as Mn(III) present as the oxalate or acetylenedicarboxylate complex. Since at 250 nm $\varepsilon_{Mn(VII)} \ll \varepsilon_{Mn(III)}$ [3], the disappearance of MnO_4^- brings about an increasing optical density while the reverse is true at 540 nm. The maximum optical density at 250 nm is reached after 2-3 half-lives of the pseudo first order disappearance of MnO_4^-. As shown by Drummond and Waters [5], manganese(III) may be an intermediate in the oxidation of some alkenes by acid permanganate. No other manganese intermediate was detected in the visible and UV spectral region. In an attempt to identify the product formed from H_2A at the Mn(III) stage, the reaction was run on a quenching device which ensured that after a fixed reaction time, Mn(III) was removed by precipitation with base. The predominant product at this stage is 1 mole of oxalic acid per mole of H_2A. Without quenching, the oxalic acid intermediate is partly oxidized by Mn(III) but the latter also attacks H_2A present in a large excess. In the pH range of interest, the reaction of Mn(III) with H_2A cannot be studied separately due to the instability of Mn(III) [6]. Rate law (2) and the subsequent results refer to the first stage, i.e.

$$H_2A + 2MnO_4^- + 5H^+ \longrightarrow MnC_2O_4^+ + 2CO_2 + 3H_2O + MnOH^{2+}$$

followed by rapid complex formation between $MnOH^{2+}$ and A^{2-}. The pH dependence of the observed rate constant at 25°C is shown in Fig. 1, indicating that the reactivity order of the three possible acetylenedicarboxylic species is $H_2A > HA^- > A^{2-}$. In order to resolve the observed pH profile, we have determined the acid dissociation constants K_1 and K_2 of H_2A at an ionic strength of 1.5 M (25°C) by potentiometric titration. At variance with earlier data [4], the following constants have been obtained

$$K_1 = 0.36\ M \quad \text{and} \quad K_2 = 0.041\ M.$$

Assuming that all three forms are reactive, the following expression can be derived for k_o

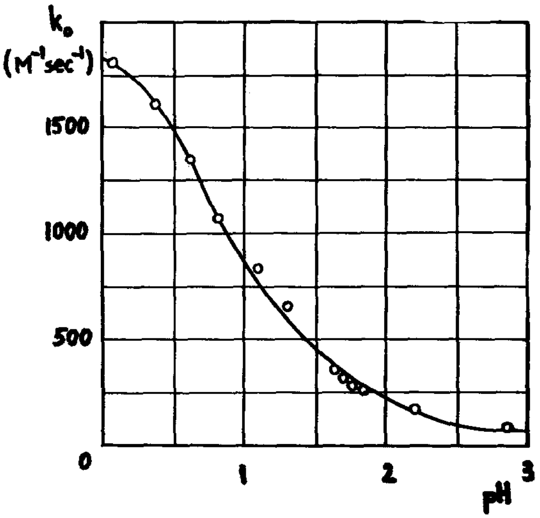


Fig.1

$$k_o = 2\,\frac{k_1 a_H^2 + k_2 K_1 a_H + k_3 K_1 K_2}{K_1 K_2 + K_1 a_H + a_H^2} \qquad (3)$$

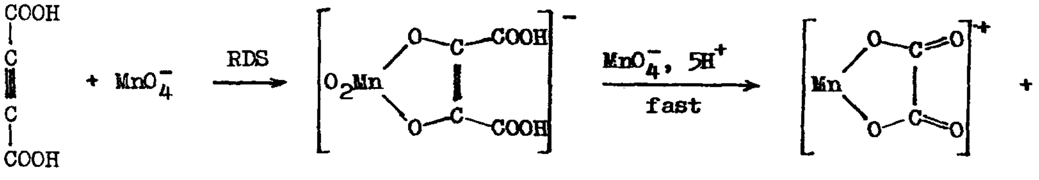
where a_H is the hydrogen ion activity and k_1, k_2 and k_3 are second order rate constants for the reaction of H_2A, HA^- and A^{2-}, respectively, with MnO_4^-. The value of k_3 was obtained from the limiting k_o at pH > 3, while k_1 and k_2 were determined from linear plots of Eq.(3). The resolved rate constants are (in $M^{-1}sec^{-1}$ units)

$k_3 = 35$; $k_2 = 520$ and $k_1 = 1230$.

The activation parameters were determined at the plateau observed at pH > 3, and thus are ascribed to k_3 since A^{2-} is the only reactant at these acidities. The result is

$$\Delta H^{\ddagger} = 6.1 \text{ kcal/mole} \qquad \Delta S^{\ddagger} = -32 \text{ e.u.}$$

The kinetic results are consistent with the following mechanism (written for H_2A) where the first step is rate-determining



$$+ \; 2CO_2 + 3H_2O + MnOH^{2+}$$

The resulting Mn(III)-oxalato complex decomposes according to the mechanism proposed by Taube [7] , but there is appreciable contribution from the reaction of Mn(III) with acetylenedicarboxylic acid to the disappearance of the Mn(III) intermediate. The cyclic activated complex receives support from the high negative $\Delta S^{\ddagger}$.

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