

The Kinetics of the Oxidation of Acetaldehyde by Acid Permanganate

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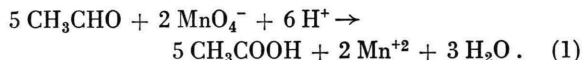
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The kinetics of the oxidation of acetaldehyde by acid permanganate has been studied. The reaction is of first order with respect to the aldehyde, the oxidant and hydrogen ion individually. The oxidation does not induce polymerisation of acrylonitrile and show a kinetic isotope effect ($k_H/k_D=6.1$). The activation parameters for the oxidation and enolisation reactions have been evaluated. The rate of enolisation, under similar conditions, is less than that of oxidation. A mechanism involving the transfer of a hydride ion from the aldehyde hydrate to the oxidant has been suggested.

The oxidation of aliphatic aldehydes by permanganate has not received much attention¹ except that of fluoral hydrate². Recently it has been shown that chromic acid oxidations of aliphatic ketones³ and aldehydes⁴ proceed via different mechanistic pathways. The acid permanganate oxidation of ketones is known to involve the enol intermediate⁵. There is a possibility that the aldehydes may also be oxidised via the enol form. The present investigation was taken up to determine the role of enol form in the oxidation.

Results

Product Analysis: Oxidation of acetaldehyde by acid permanganate produces mainly acetic acid, as detected by the characteristic spot test⁶. Estimation of the acid produced showed that reduction of one mole of permanganate by acetaldehyde produces 2.47 moles acetic acid. The overall reaction may be written as follows (eq. 1)



Rate Laws: When the concentration of acetaldehyde and hydrogen ions are in excess the rate of disappearance of permanganate follows first order rate laws. The reaction is also of first order with respect to the aldehyde (Table 1). Under the conditions of

constant ionic strength the rate varies linearly with the concentration of hydrogen ions (Table 2).

[MnO ₄ ⁻] 1×10 ⁻³ M [CH ₃ CHO] 1×10 ⁻² M		[NaF] 1×10 ⁻² M Ionic strength (μ) = 2.5 M					
[H ⁺] mol l ⁻¹	0.25	0.50	1.00	1.50	2.00	2.50	
10 ⁴ k ₁ (sec ⁻¹)	0.48	0.94	1.87	2.85	3.75	4.70	
10 ⁴ k ₁ /[H ⁺]	1.92	1.88	1.87	1.90	1.87	1.88	

Table 2. Acidity dependence of the reaction rate.

Induced Polymerisation of Acrylonitrile: The reaction was carried out in presence of acrylonitrile, under nitrogen. No polymerisation was observed. This strongly indicate that no free radical is formed in the reaction.

Kinetic Isotope Effect: The oxidation of acetaldehyde-d₁ (CH₃CDO) by acid permanganate is considerably slower than that of the ordinary compound (Table 3). The value of k_H/k_D at 25 °C is 6.1. The specific rate constant, k , is defined as $k = k_1/[\text{CH}_3\text{CHO}][\text{H}^+]$.

[H ⁺] = 1.0 M		
k _{CH₃CDO} l ² mole ⁻² sec ⁻¹	k _{CH₃CHO} l ² mole ⁻¹ sec ⁻¹	k _H /k _D
1.65 × 10 ⁻³	1.01 × 10 ⁻²	6.1

Table 3. The kinetic isotope effect.

Effect of Temperature: The rate of oxidation was measured at different temperatures (Table 4). The plot of log k against the inverse of temperature is a straight line. The Arrhenius equation is, there-

[MnO ₄ ⁻] 1×10 ⁻³ M	[H ⁺] 1.0 M					[NaF] 1×10 ⁻² M
10 ² [CH ₃ CHO] mol l ⁻¹	0.5	1.0	2.0	3.0	4.0	5.0
10 ⁴ k ₁ (sec ⁻¹)	0.5	1.01	2.00	3.10	4.10	5.05
10 ² k ₁ /[CH ₃ CHO]	1.0	1.01	1.0	1.03	1.02	1.01

Table 1. Substrate concentration dependence of the reaction rate.

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fore, valid for this reaction. The activation parameters were also evaluated.

Temperature [°K]	$k \times 10^2$ l ² mole ⁻² sec ⁻¹	$\Delta H^\ddagger$ kcal/mole	$\Delta S^\ddagger$ e. u.
298	1.01	10 ± 0.5	-20 ± 2
303	1.36		
308	1.82		
313	2.34		
321.5	3.57		

Table 4. Temperature dependence of the reaction rate.

Rate of Enolisation: The rate of enolisation was measured by the bromination method. The rate of bromination of acetaldehyde is of zero order to bromine and first order with respect to each the aldehyde and hydrogen ion. Table 5 records the rate of bromination (k_2) at different temperatures and the activation parameters. It is assumed that the rate of bromination equals the rate of enolisation.

Temperature [°K]	$10^4 k_2$ l ² mole ⁻² sec ⁻¹	$\Delta H^\ddagger$ kcal/mole	$\Delta S^\ddagger$ e. u.
293	1.08	15.3 ± 0.5	-25 ± 2
298	1.63		
303	2.50		
308	3.83		
313	6.20		

Table 5. Rate of enolisation at different temperatures.

Discussion

The linear increase in the rate of oxidation with the increase in acidity may well be due to protonation of permanganate anion to give permanganic acid, a more powerful oxidant (eq. 2).



This accords well with the suggestion of STEWART and MOCEK that in the oxidation of fluoral hydrate, in strong acid solution, the active species is permanganic acid². LITTER also suggested a protonation in the pre-equilibrium in the oxidation of cyclohexanol⁷.

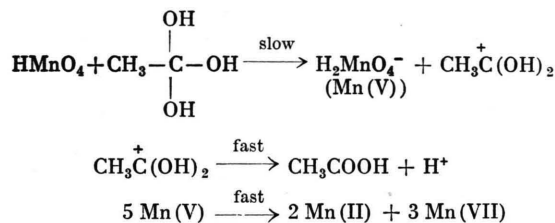
A comparison of data of Tables 4 and 5 shows that the oxidation is much faster than the enolisation. Moreover, the energy of activation is more in the enolisation than in the oxidation process. On both these grounds it is concluded that enolisation cannot be a step in the oxidation of acetaldehyde by permanganate.

The results obtained here are consistent with the following rate equation which is very similar to that previously derived for methanol and ethanol⁸.

$$-d[\text{Mn(VII)}]/dt = k[\text{CH}_3\text{CHO}][\text{MnO}_4^-][\text{H}^+].$$

It has been shown that in chromic acid oxidation, acetaldehyde is oxidised via its hydrate⁴. STEWART and MOCEK² also suggested similar intermediate in the oxidation of fluoral. Hence either acetaldehyde hydrate or its simple derivative is the most likely intermediate.

The primary isotope effect clearly indicate that a C—H bond is ruptured in the rate determining step. However, it is far less clear in what form hydrogen is removed. The absence of acrylonitrile polymerisation rules out the possibility of hydrogen abstraction, giving rise to free radicals. KURZ⁹ has shown, using STEWART and MOCEK's data, by a novel approach, that the oxidation of fluoral hydrate² by acid permanganate is best represented by a hydride transfer. Moreover, the aldehyde hydrate resembles alcohols so closely in both structure as well as in practically every facet of the oxidation that it is reasonable to expect a similarity in their mode of oxidation as well. It has been recently shown that acid permanganate oxidation of alcohols involves the transfer of a hydride ion from the carbon atom bearing the functional group to the oxidant^{8,10}. Thus it is very likely that the oxidation of acetaldehyde by acid permanganate involves a transfer of a hydride ion as follows:



The existence of manganese (V) as a reaction intermediate is well known.

Experimental

Materials: Acetaldehyde (B.D.H.) was purified by the usual methods. Acetaldehyde-d₁ (CH₃CDO) of 98% atomic purity was used. Perchloric acid (E. Merck) was used as a source of hydrogen ions. Ionic strength was kept constant by using sodium perchlorate. All other chemicals used were chemically pure and used as such.

Product Analysis: For quantitative estimation of acetic acid formed, the completely reduced reaction

mixture was shaken with ether and the amount of the acid present in ether solution was determined colourimetrically as ferric-hydroximate¹¹.

Kinetic Measurements: In permanganate oxidations, reactions of intermediate valency states of manganese introduce many complications. The oxidation was, therefore, carried out in the presence of large excess of fluoride ions. Fluoride ions are known to suppress the reactivities of Mn(III) and Mn(IV) by complexation.

The reaction was carried out at 25 °C ($\pm 0.05^\circ$) unless mentioned otherwise. The concentration of the aldehyde was always in excess to that of permanganate. The reactions were followed both spectrophotometrically and titrimetrically⁸. The rate constants reported are mean of duplicate runs and are correct to $\pm 3\%$.

The enolisation rates were measured by the method reported earlier⁴.

- ¹ Pertinent reviews on the subject are: R. STEWART, in: "Oxidation in Organic Chemistry", p. 30, Part A, K. B. WIBERG, Ed., Academic Press, New York 1965; J. ROCEK, in: "The chemistry of the Carbonyl Group", p. 478, S. PATAI, Ed., Interscience Publishers, New York 1966.
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Nematische Systeme, V¹

Nematische *p, p'*-disubstituierte Benzoessäurephenylester und niedrig schmelzende eutektische Gemische

Nematic *p, p'*-disubstituted Phenylbenzoates and Low Melting Eutectic Mixtures

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One unsymmetrically *p, p'*-disubstituted *trans*-stilben and more than 60 new phenylbenzoates are described (Tab. 1). These compounds show partly enantiotropic, partly monotropic nematic behaviour. Some low melting substances and especially eutectic mixtures of this class of compounds are useful as room-temperature nematic, colourless liquids for electro-optical applications.

Nematische flüssige Kristalle haben seit einigen Jahren besonderes Interesse erregt, weil sich mit ihrer Hilfe elektrische Signale ohne großen Energieverlust in optische Informationen umwandeln lassen². Man kann durch elektrische Gleich- oder Wechselfelder von wenigen Volt die Lichtreflexion oder die Transparenz von Vorrichtungen steuern, die zwischen zwei Leitgläsern eine dünne Schicht eines nematischen Dielektrikums enthalten. Es lassen sich so Buchstaben, Ziffern und andere Symbole wiedergeben.

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Für die praktische Anwendung dieses als „dynamic scattering“ bekannten Phänomens sind nematische Substanzen oder Substanzgemische Voraussetzung, die bereits bei oder unterhalb Zimmertemperatur im nematischen flüssig-kristallinen Zustand vorliegen und erst oberhalb der normalerweise vorkommenden Umgebungstemperaturen in die isotrope Phase übergehen.

Bei den bisher bekannten, bei Zimmertemperatur nematischen Flüssigkeiten handelt es sich vorwiegend um Substanzen aus den Stoffklassen der *p, p'*-disubstituierten Azoxybenzole¹ und der Benzylidenaniline^{3, 4}. Die Azoxybenzolderivate sind gelblich gefärbte Substanzen, die eine für die erwähnte An-