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Kinetics and Mechanism of the Oxidation of Aliphatic Alcohols by Acid Permanganate

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Barter and Littler[1] suggested, on the basis of similar rate laws, that the oxidation of alcohols by acid permanganate, bromine and other two-electron oxidants follow similar mechanisms. The oxidation of alcohols by bromine involves removal of hydride ion in the rate-determining step.[2] A similar mechanism also was suggested for the oxidation of benzyl alcohol by acid permanganate.[3] The chromic acid oxidation, another two-electron process, however, is proposed to involve a proton transfer.[4] No conclusive evidence is available in literature about the form of hydrogen removed from the alcohol in permanganate oxidation.

If α-C–H bond is ruptured in the rate-determining step, then an unequivocal evidence about the flow of electrons leading to the transition state can be obtained by studying the effect of polar substituents on the rate of the oxidation of a suitable alcohol.

This paper reports the kinetics of the oxidation of some primary alcohols and evaluates the reaction constant. The mechanistic conclusions are discussed.

Results

Product Analysis. The oxidation of ethanol by acid permanganate eventually gives acetic acid. An estimation of the carboxylic acid formed indicated the following stoichiometry:

$$4MnO_4^- + 12H^+ + 5CH_3CH_2OH \longrightarrow 5CH_3COOH + 4Mn^{+2} + 11H_2O$$

Rate Laws. The oxidation of alcohols by acid permanganate is autocatalytic and this may be due to the effect of Mn(III)/Mn(IV). Addition of sodium fluoride suppresses the autocatalysis, though it does not affect the initial rate. Therefore, an excess of sodium fluoride was added to each reaction mixture.

The reaction were followed under pseudo-first-order conditions by keeping a large excess of the alcohol over permanganate. The rate of disappearance of permanganate, under these conditions, is of first order. The order with respect to the alcohol is also one (Table 1). The rate varies linearly with acidity, at constant ionic strength.

TABLE 1. SUBSTRATE DEPENDENCE OF THE REACTION RATE

[KMnO$_4$] 1×10^{-4} M	[H$^+$] 1.0M	[NaF] 0.01M	Temp. 25 °C		
10^2 [EtOH]M	1.0	2.0	4.0	6.0	8.0
10^4 k_1(s^{-1})	9.55	19.0	37.5	57.0	76.8
10^2 k_1/[EtOH]	9.55	9.50	9.40	9.50	9.60

The rate constants for the oxidation of ethanol and α,α-dideuterioethanol at 30 °C are $10^2k=13.0$ and 5.0 l^2 mol^{-2} s^{-1} respectively. The kinetic isotope effect, $k_H/k_D=2.60$ at 30 °C.

The oxidation of ethanol, under nitrogen, failed to induce the polymerization of acrylonitrile. The formation of free radicals is, therefore, unlikely.

The rate constants for the oxidation of ethanol in deuterium oxide and in water at 30 °C are $10^2k=12.5$ and 13.0 l^2 mol^{-2} s^{-1} respectively. The solvent isotope effect, $k(H_2O)/k(D_2O)=1.04$.

The rate of the acid permanganate oxidation of ten primary aliphatic alcohols were obtained at different temperatures and the activation parameters evaluated (Tables 2 and 3).

TABLE 2. OXIDATION OF ALCOHOLS, RCH$_2$OH, BY ACID PERMANGANATE

R	10^4 k (l^2 mol^{-2} s^{-1})				
	25 °C	30 °C	35 °C	40 °C	45 °C
CH$_3$	955	1300	1740	2300	3100
C$_2$H$_5$	1410	1910	2500	3300	4360
n-C$_3$H$_7$	1730	2300	3000	4000	5100
i-C$_3$H$_7$	2340	3100	4000	5100	6500
t-C$_4$H$_9$	3850	4920	6200	7800	9800
C$_6$H$_{11}$(cyclohexyl)	1820	2400	3150	4070	2550
H	87.0	128	182	257	370
CH$_3$OCH$_2$	72.5	110	157	240	330
ClCH$_2$	6.90	10.7	16.6	25.0	38.0
BrCH$_2$	8.50	13.2	20.0	28.8	43.0

TABLE 3. ACTIVATION PARAMETERS FOR THE OXIDATION OF ALCOHOLS, RCH$_2$OH, BY ACID PERMANGANATE

R	CH$_3$	C$_2$H$_5$	n-C$_3$H$_7$	i-C$_3$H$_7$	t-C$_4$H$_9$
$\Delta H^{\neq}$ kcal/mol	11.0	10.5	10.2	9.6	8.8
$-\Delta S^{\neq}$ e.u.	26.4	27.9	28.5	29.9	31.6
R	C$_6$H$_{11}$	H	CH$_3$OCH$_2$	ClCH$_2$	BrCH$_2$
$\Delta H^{\neq}$ kcal/mol	10.0	13.5	14.0	16.0	15.8
$-\Delta S^{\neq}$ e.u.	29.1	23.3	22.0	20.0	20.2

Discussion

The linear dependence of the oxidation rate on acidity, may be attributed to the protonation of permanganate anion to give permanganic acid, a more

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powerful oxidant.[3,5]

The kinetic isotope effect shown in the oxidation of ethanol is very close to the value obtained by Littler[6] in the oxidation of cyclohexanol ($k_H/k_D=2.41$). It confirms that α-C–H bond is ruptured in the rate-determining step. There is no kinetic evidence that the alcohol and the oxidant are involved in any pre-equilibrium. The formation of a permanganate ester is unlikely in view of the almost equal ease of the oxidation of alcohol and ethers.[1]

No systematic study on the effect of structure in the permanganate oxidation of alcohols has been reported. Barter and Littler reported the rate data of the oxidation of methanol, ethanol and 2-methoxyethanol.[1] However, no reaction constant could be evaluated with those limited data. In the present investigation, the rate of the oxidation of the ten alcohols give a good correlation ($r=0.993$) in the Taft plot with a reaction constant $\rho^* = -2.02 \pm 0.08$ at 30 °C. The negative ρ^* points to an electron-deficient carbon centre in the transition state. The magnitude of the reaction constant decreases with temperature, as expected.

The activation entropies and enthalpies of the ten compounds are linearly related ($r=0.988$), the value of isokinetic temperature being 650 ± 40 K. Present views do not attach much significance to the value of isokinetic temperature,[7] though a linear correlation between $\Delta H^{\ne}$ and $\Delta S^{\ne}$ is usually a necessary condition for the validity of the Taft equation.[2]

The results reported in this paper supports the hydride transfer mechanism. The small magnitude of the solvent isotope effect suggests that the removal of the hydroxylic proton simultaneously with the hydride ion transfer is unlikely and is more so in view of the magnitude of the reaction constant. The polar requirement on the carbinol carbon of hydride release from C–H is opposite to that of proton release from O–H and in a fully concerted process, the reaction constant should be nearer zero.

Experimental

Materials. Methanol, ethanol, 1-propanol, 1-butanol, 2-chloroethanol, 2-methyl 1-propanol, and 2,2-dimethyl 1-propanol were commercial products and were purified by the usual methods. Cyclohexylmethanol,[8] 2-bromoethanol,[9] and 2-methoxyethanol[10] were prepared by the methods described in literature.

α,α-Dideuterioethanol (CH_3CD_2OH) was prepared by the method reported by Kaplan.[11] Perchloric acid (Baker) was used as a source of hydrogen ions. All reagents used were of analytical grade.

Product Analysis. Acetic acid produced in the oxidation of ethanol was estimated colorimetrically as ferric hydroximate.[12]

Kinetic Measurements. The reactions were followed by estimating permanganate spectrophotometrically at 532 nm. The rate constants reported are averages of multiple runs and are reproducible within ±4%.

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