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STUDIES OF REACTION KINETICS OF MONOHYDRIC ALCOHOLS
BY ACID PERMANGANATE

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The kinetics of the reaction of methanol and ethanol with acid perman-
ganate was studied. The reactions were found to be first order with respect to
permanganate ion concentration in both cases. The Arrhenius equation has
found to be valid in the temperature range of the experiments. The rate con-
stant increased with the increase of H^+ ion concentration. Mn (II) ions retarded
the rate of reaction. The thermodynamic parameters, i.e. ΔE, $\log_{10} PZ$ and $-\Delta S$
have been calculated. The mechanism proposed by Ardon[12] for the oxidation
of alcohol accounts for the kinetics of the oxidation of methanol and ethanol
by permanganate. It is suggested that the reacting species of manganese is Mn
(III) and the reactants pass through a transition state involving the alcohols
and Mn (III).

Oxidation of organic compounds were first investigated systematically in the Utrecht laboratory.
According to Imhof[1], the oxidation of an organic compound with permanganate proceeds more ra-
pidly in alkaline than in the acid. Nanji and Norman[2] showed that the alcohols can be oxidized
quantitatively by alkaline permanganate. Stamn[3] also developed a new method for the direct deter-
mination of methanol. In acid medium ethanol[4] was oxidized to the acetic acid stage.
Although the reduction of permanganate has been studied, its reduction has not been studied by
alcohols from stand point of kinetics. Therefore, the purpose of the present work is to study the ki-
netics of the oxidation of these two alcohols, e.g., methanol and ethanol by acid permanganate.
The reactions have been studied under various conditions. An attempt has also been made to discuss
the mechanism of the reactions.

Experimental

All the reagents were of extra pure quality and the solutions were made in freshly prepared
distilled water. The potassium permanganate used was of E. Merck's grade and the solution was es-
timated by the iodometric method. The alcohols used were of E. Merck's grade and contained some

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1) J. G. Imhof, Thesis Utrecht, (1932)
2) D. R. Nanji and A. G. Norman, J. Soc. Chem. Ind. (London), 45, 337 T (1926)
3) H. Stamn, Z. angew. Chem., 47, 791 (1934)
4) Kolthoff and Belcher, "Volumetric analysis", Vol. III, 525, Interscience Publishing Inc., New
York, (1957)

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aldehyde formed by the atmospheric oxidation. These were refluxed with KOH for some hours. After that, the mixture was treated with Al-foil and again refluxed for 2 hours. The products formed after distillation in a fractionating column were used for the reaction.

The stable manganic salt was prepared by the method suggested by Levesley and Waters[5]. Mn (II) sulphate (AnalaR) solution was mixed with the solution of sodium pyrophosphate (G. R.) grade. The pH of the solution was adjusted to 6. The resultant solution was then titrated electrometrically with $KMnO_4$ solution to the manganic end point, a Cambridge electrotitration apparatus being used. Larger batches of the Mn(III) solution were then prepared in calculated volume as required. The pH adjustments were made in dilute H_2SO_4 and all measurements were carried out by means of the photo volt pH-meter (Adair Dutt & Company) calibrated before use against standard buffers.

All measurements were carried out in diffused light in conical flasks of Pyrex glass of 250cc. capacity. The calculated amounts of permanganate solution was taken in the reaction vessel kept in the thermostat maintained at the temperature of the experiment. The flask containing the alcohol solution was also kept in the thermostat. The reaction was started by adding a calculated amount of alcohol solution into the reaction vessel. After measured time intervals, aliquot portions of the mixtures were added to KI solution and the liberated iodine was titrated by a standard thiosulphate solution. The ionic strength of each solutions was kept constant by the addition of potassium sulphate to the reaction mixture. There was a period of induction at the beginning of the reaction after which the reaction followed first order law with respect to permanganate ion concentration in both the cases of the oxidation of alcohols by acid permanganate.

Effect of pH on the rate constants

The effect of pH was studied at 20°C. In every experiment, the total volume, permanganate and substrate concentrations were kept constant and the reaction were studied in a wide range of pH values in both cases. The rate constants at different pH values have been recorded in Table 1. It has been found that log K exhibits a linear relation with pH.

Effect of oxidants on the rate

The values of the rate constants were calculated for different permanganate concentrations. In this case, the total volume, ionic strength, pH and the substrate concentrations were kept fixed. The only variable for each mixture was the permanganate ion concentration. It has been found that the rate constant tends to diminish as the concentration of the oxidant increases. Table 2 summarises the rate constants for different concentrations of the oxidants.

Influence of substrates on the rate

The reactions have also been studied at different substrate concentrations of the reaction mixtures. Here the concentration of permanganate ion as well as the total volume was kept fixed. It has been found that the rate tends to increase as the concentration of substrate increases. The values of the rate constants at different substrate concentration are shown in Table 3.

Influence of foreign salts on the reaction velocity

The reactions have also been studied for different ionic strengths of the reaction mixtures. The

5) P. Levesley and W.A. Waters, *J. Chem. Soc.*, 217 (1955)

ionic strengths were varied by the addition of either K_2SO_4 or $MnSO_4$. It has been found that neutral salt like K_2SO_4 has no effect on the reaction (Table 4) whereas $MnSO_4$ retards the rate of the reaction and the plot of $\sqrt{\mu}$ against log K exhibits a linear relation. The results are given in Table 5.

Influence of temperature on the rate constant

The velocity constants have been calculated at four different temperatures. All of the four experiments were performed under identical conditions of pH, ionic strength, substrate and permanganate concentrations. The results are given in Table 6.

Since, $K=\left(\dfrac{kT}{h}\right)\cdot e^{\Delta S/R}\cdot e^{-E/RT}$.

Table 1   Effect of pH on the rate constant

	[MeOH]$=3.974\times10^{-2}$M, [KMnO$_4$]$=12.3\times10^{-3}$M $\mu=0.132$, Temp.$=20°$C.				[EtOH]$=4.352\times10^{-3}$M, [KMnO$_4$] $=8.21\times10^{-3}$M, $\mu=0.108$, Temp.$=20°$C.		
No.	pH		$K\times10^2$(min^{-1})	No.	pH		$K\times10^3$(min^{-1})
1	1.22	——	2.990	1	1.42	——	5.934
2	1.63	——	2.763	2	1.98	——	5.501
3	2.12	——	2.073	3	2.88	——	3.915
4	2.50	——	1.842	4	3.82	——	3.684
5	2.95	——	1.382				

Table 2   Variation of oxidant on the rate constant

	[MeOH]$=2.208\times10^{-2}$M, pH$=2.52$, $\mu=0.136$, Temp.$=20°$C.				[EtOH]$=4.352\times10^{-3}$M, pH$=1.05$, $\mu=0.108$, Temp.$=20°$C.		
No.	KMnO$_4$]$\times10^3$ in molarity		$K\times10^2$ (min^{-1})	No.	[KMnO$_4$]$\times10^3$ in molarity		$K\times10^3$ (min^{-1})
1	12.31	——	1.802	1	8.210	——	9.212
2	24.62	——	1.382	2	10.05	——	5.757
3	30.75	——	1.151	3	14.35	——	4.606

Table 3   Influence of substrate concentration on the rate

	[KMnO$_4$]$=12.31\times10^{-3}$M, pH$=2.84$. Temp.$=20°$C			[KMnO$_4$]$=8.210\times10^{-3}$M, pH$=1.61$ Temp.$=20°$C	
No.	[MeOH]$\times10^2$ in molarity	$K\times10^2$ (min^{-1})	No.	[EtOH]$\times10^3$ in molarity	$K\times10^3$ (min^{-1})
1	2.650	1.612	1	8.704	4.606
2	3.093	1.824	2	9.245	6.909
3	3.532	2.072	3	10.78	8.060
4	3.971	2.763	4	—	—

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$$\therefore \quad \ln K = \ln \frac{kT}{h} + \Delta S/R - E/RT$$

where k=Boltzmann constant and h=Planck's constant.

In the following experiments T is varied from 288 to 304 in the case of the oxidation of methanol and 278 to 293 in the case of the oxidation of ethanol and hence $\ln\left(\frac{kT}{h}\right)$ and $\Delta S/R$ may be taken as constant. Therefore, a plot of ln k against $1/T$ will be linear. From the slopes, the activation energies have been caluclated. The activation energies in the cases of the oxidation of methanol and that of ethanol are found to be 9.2±0.5 and 11.5±0.7 kcals respectively. The values of $\log_{10} PZ$ and ΔS are recorded in Table 7.

Table 4   Influence of salt on the rate constant

[MeOH]= 2.208 × 10⁻²M, [KMnO₄]= 10.25 × 10⁻³M, pH = 2.95, Temp. = 20°C			[EtOH]= 8.704 × 10⁻³M, [KMnO₄]=8.210× ⁻³M, pH=1.72, Temp.= 20°C		
No.		$K \times 10^2$ (min⁻¹)	No.		$K \times 10^3$ (min⁻¹)
1	0.132 ——	1.382	1	0.120 ——	5.181
2	0.144 ——	//	2	0.132 ——	//
3	0.180 ——	//	3	0.144 ——	//
4	0.240 ——	//	4	0.156 ——	//
5	—	—	5	0.168 ——	//

Table 5   Effect of Mn⁺² ions on the rate constants

[MeOH]= 2208 × 10⁻²M, [KMnO₄]= 10.25 × 10⁻³M, pH = 2.52, Temp. = 20°C			[EtOH]= 8.704 × 10⁻³M, [KMnO₄]=8.210 × 10⁻³M, pH=1.72, Temp.= 20°C		
No.	μ	$K \times 10^2$ (min⁻¹)	No.	μ	$K \times 10^3$ (min⁻¹)
1	0.136 ——	1.151	1	0.124 ——	4.606
2	0.152 ——	0.6909	2	0.140 ——	4.030
3	0.168 ——	0.4606	3	0.156 ——	2.878
4	0.184 ——	0.2303	4	0.172 ——	2.303

Table 6   Influence of temperature on the reaction velocity

[MeOH]=3.974 × 10⁻²M, [KMnO₄]= 12.31 × 10⁻³M, pH = 1.22, μ=0.132			[EtOH]=4.352 × 10⁻³M [KMnO₄]= 2.121 × 10⁻³M, pH = 2.88, μ=0.108		
No.	Temp. in °C	$K \times 10^2$ (min⁻¹)	No.	Temp. in °C	$K \times 10^2$ (min⁻¹)
1	31 ——	6.448	1	20 ——	3.815
2	25 ——	5.824	2	15 ——	2.993
3	20 ——	2.994	3	10 ——	2.187
4	15 ——	2.303	4	5 ——	1.842

Table 7   Thermodynamic data of the oxidation process

| Thermodynamic parameters	Methanol	Ethanol
$\varDelta E$(kcals)	9.2 ± 0.5	11.5 ± 0.7
$\log_{10} PZ$(Sec^{-1})	4.45 ± 0.5	5.12 ± 0.6
$-\varDelta S$(e.u.)	$39.? \pm 2.0$	36.3 ± 2.5

Discussion

The products formed in the oxidation of methanol and ethanol were tested. Formaldehyde and acetaldehyde were found as their respective product of oxidation. On leaving the alcohols. however, overnight with large excess of oxidant, formic acid and acetic acid were also found respectively as their reaction products in addition to aldehydes. This was obviously due to the oxidation of the respective aldehydes which appeared to be a slow process. In our studies, we have traced upto aldehyde stage, i. e. the consumption of 0.4 moles of the oxidant per mole of the alcohols. Therefore, the reduction of permanganate can be represented stoichiometrically by the equation :

$$5R \cdot CHOH + 2MnO_4^- + 6H^+ \longrightarrow 5R \cdot CHO + 2Mn(II) + 8H_2O \qquad (1)$$

where $R = H$ or CH_3.

It is well known that the oxidation of organic compounds by potassium permanganate is usually the multistage process where the degradation of organic compounds by the rupture of discrete two electron bonds undergoing an overall 5 electron transition, MnO_4^-——$Mn(II)$ in acid solution or a 3 electron transition MnO_4^-——MnO_2 in neutral or alkaline solution. Other manganese ions of intermediate valence may also occur although very little is known about them and $Mn(III)$ is certainly involved in many of the rate determining processes. Moreover, Noyer et al.[6] suggested that permanganate remains in equilibrium with the oxygen in solution and $Mn(II)$ ions are produced by the dynamic equilibrium, and $Mn(II)$ ions are formed by the equation :

$$Mn(II) + MnO_4^- \Longleftrightarrow Mn(III) + MnO_4^-. \qquad (2)$$
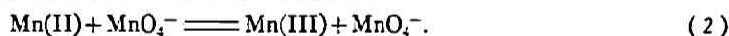
The hexavalent manganese produces more $Mn(III)$ by the successive fast steps, such as

$$Mn(VI) + Mn(II) \xrightarrow{fast} 2Mn(IV). \qquad (3)$$

$$Mn(IV) + Mn(II) \xrightarrow{fast} 2Mn(III). \qquad (4)$$
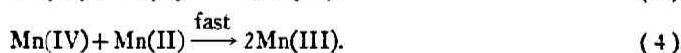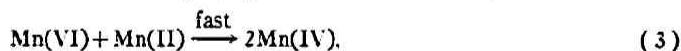
There would arise now, the question which one is the reacting species of manganese in solution during the oxidation of alcohols by acid permanganate ? As has been observed in the present case. the reduction of permanganate is preceded by a noticeable induction period but the later course of the reaction becomes obscured by the separation of fresh manganese dioxide through the Guyard reaction :
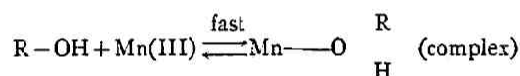
$$2MnO_4^- + 3Mn(III) + 2H_2O \longrightarrow 5MnO_2 + 4H_2O. \qquad (5)$$

Initial addition of $Mn(II)$ sulphate eliminates the induction period but hastens the formation of

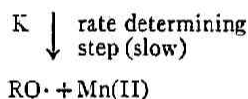6)   R. M. Noyes and S. J. Adler. *J. Amer. Chem. Soc.*, **77**, 2036 (1955)

MnO_2. Conversely, the addition of a fluoride ion greatly prolongs the disturbance period and completely prevents the separation of MnO_2. It can be concluded that in dilute acid MnO_4^- does not attack the alcohols. But, if Mn(III) ion is added initially, the acid permanganate oxidation of alcohols immediately commences. Presumably, Mn(III) ion first attacks the alcohol molecule.

Now the stages through which the reaction proceeds can be explained on the basis of free radical mechanism similar to the scheme suggested by the previous workers. The work of Bawn and White[7,8] on the oxidation of alcohol by Ce(IV) demonstrated the formation of free radical. Again, on the basis of his kinetic studies on the trivalent manganese-oxalate reaction[10], Duke suggested the theory of the oxidation of glycols and related compounds. He assumed that co-ordinated intermediates are first formed and a slow disproportionation of the complex occured. The oxidation of 2, 3 butane-diol by Ce(IV) ion was shown by Duke and Forist[11] to proceed through disproportionation of a mono glycollated complex. Later on, Arden[12] and Rao *et al.*[13] showed that both ethanol and methanol are oxidized by Ce(IV) ion in the similar way. On these bases, the reactions of methanol and ethanol may be represented in the following way :

(i) It is suggested that co-ordinated intermediates arcs first formed through rapidly established equilibrium between the Mn(III) ion and the alcohols. The complex then disproportionates to give the alkoxy radical :
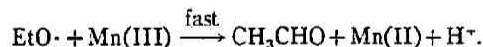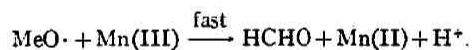
$$R-OH + Mn(III) \underset{}{\overset{fast}{\rightleftharpoons}} Mn-\!\!-\!\!O \begin{matrix} R \\ \\ H \end{matrix} \quad (complex)$$

where, $R=CH_3$ or C_2H_5 $K \downarrow$ rate determining step (slow)

$$RO\cdot + Mn(II)$$

here $RO\cdot$ being an alkoxy radical.

(ii) Further, the free radicals take up Mn(III) and by fast steps form the rest of the products as follows :

$$MeO\cdot + Mn(III) \xrightarrow{fast} HCHO + Mn(II) + H^+.$$

$$EtO\cdot + Mn(III) \xrightarrow{fast} CH_3CHO + Mn(II) + H^+.$$

It has already been mentioned that there is a period of disturbance at the beginning of the reaction. The reason for this is that the formation of di, tri and tetravalent manganese ions formed slowly followed by a final period in which the compounds of intermediate valence react rapidly to give the stable Mn(III), which then reacts with the alcohols.

The effect of the absence of indifferent salt like K_2SO_4 on the rate suggests that the reaction pas-

7) C. E. H. Bawn and A.C White, *J. Chem. Soc.*, 323, 331 (1951)

8) C. E. H. Bawn and A. C. White, *Discussion Farad. Soc.*, 14, 181 (1953)

9) G. Mino, S. Kaizerman and E. Rusmussen, *J. Amer. Chem. Soc.*, 81, 1494 (1959)

10) F. R. Duke, *J. Amer. Chem. Soc.*, 69, 2855 (1947), *ibid*, 70, 419, (1948)

11) F. R. Duke and A. Forist, *ibid*, 71, 2790, (1949), *ibid*, 73, 3179, (1951)

12) M. Ardon, *J. Chem. Soc.*, 1811, (1957)

13) A. Muhammed and K.V. Rao, *Bull. Chem. Soc. Japan*, 36, 943, (1963)

ses through a free radical or else the rate would have been affected by the change in ionic strength.

It should be pointed out that some unimolecular reactions have high velocities[14], the frequency factors are of the order of 10^{10} sec^{-1} or less.

This is sometimes due to the fact that activated complex has a more rigid structure than the initial state and hence ΔS is negative. The calculated values of $\log_{10} PZ$ and negative entropy values justifies the proposed mechanism.

The decrease of the reaction rate with the increase of oxidant may be attributed to the formation of stronger complexes in the presence of excess of oxidant, whereas, reverse is the case when the substrate is in excess, where the rate constant is much greater.

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14) S. Glasstone, "Text book of physical chemistry", p. 1110. Macmillan & Co. Ltd., London, 2nd. Ed., (1960)