Oxidations with permanganate in a strong alkaline medium: Calculation of deprotonation constant

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The process $2MnO_4^- + substrate \rightarrow 2MnO_4^{2-} + product$, has been studied employing the substrates methanol, ethanol, n-butanol and formaldehyde in aqueous solutions of [alkali] in the region of 0.1-2.0 mol dm^{-3}. The reactive species is the alkoxy anion and the deprotonation constant (K_B) of these substrates can be calculated from the kinetic data, which are in good agreement with literature data obtained by other methods. The procedure seems to be applicable for the determination of the deprotonation constant of other organic substrates containing a hydroxyl group. A mechanism based on electron abstraction from the alkoxy anion and simultaneous nucleophilic attack by OH^- has been proposed.

It has been known[1-4] tor a long time that permanganate ion in alkaline medium oxidises numerous organic compounds, which are not or only very slowly oxidised by this compound in acidic or neutral media. If $[OH] \geq 1$ mol dm^{-3}, pemanganate is reduced only to manganate in the majority of cases, and this undergoes further reaction at a much slower rate, owing to its considerably lower reactivity[3-6].

Thus the process, $Mn(VII) \rightarrow Mn(IV)$, consisting of several steps can be divided into partial steps and each can individually be studied. Manganese dioxide appears almost at the end when permanganate has been totally consumed in the reaction and, hence, the reaction can be followed spectrophotometrically. Nevertheless, the mechanisms of the reactions are not yet clear, and in some cases the doubt persists whether direct oxidation or oxidation induced by hydroxyl radical takes place. Permanganate is, mainly, reduced spontaneously to manganate in alkaline medium with the evolution of O_2, and as the first step of the complex mechanism, hydroxyl radical is formed[7] (see Eq. 1).

$$MnO_4^- + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MnO_4^{2-} + HO^{\cdot} \qquad \dots(1)$$
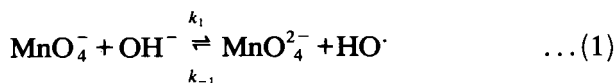
which undergoes further reaction represented by Eq. (2),

$$RH + {\cdot}OH \xrightarrow{k_2} R^{\cdot} + H_2O \qquad \dots(2)$$

This mechanism is supported by experiments carried out with labelled ^{18}O and the results indicate that the oxygen atom is always generated from water and

O_2 evolution observed in the absence of substrate is suppressed when substrate is present, and racemic products are always obtained[7-10]. Symons found that reaction (1) was the rate-determining step and he could estimate the value of k_1 as 3×10^{-3} $mol^{-1}dm^{-3}s^{-1}$ at $[OH^-] = 1.0$ mol dm^{-3}. The earlier assumption of Wiberg[11] that the oxidation of substituted benzene derivatives also occurs by this mechanism does not appear to be logical because the rate constants measured by him were greater by several orders of magnitude. At the same time, it is likely that the $C-H$ bond of the tertiary carbon atom is oxidized by this radical pathway[12,13], even the primary carbon atom is oxidised in this way but this oxidation is slower by two orders of magnitude than that found by Zielinski in the case of acetic acid[14]. These facts lead to the conclusion that the oxidation of alcohols and carbonyl compounds cannot take place by the intervention of hydroxyl radical due to the high reaction rate, and only a direct oxidation can be assumed. Nevertheless, since the process,

$$MnO_4^- + MnO_4^{3-} \rightarrow 2MnO_4^{2-} \qquad \dots(3)$$
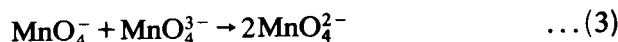
is very fast[2,5,6], it is difficult to decide if permanganate is reduced in one-electron steps (Scheme 1),

$$Mn(VII) + S \xrightarrow{k_1} Mn(VI) + S^{\cdot}$$

$$Mn(VII) + \overline{S^{\cdot}} \xrightarrow{k_2} Mn(VI) + Product$$
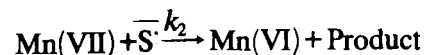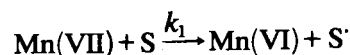
$$k_2 \gg k_1$$

Scheme 1

or hypomanganate is formed previously in a two-electron step, followed by a fast reaction (3) (Scheme 2).

$$Mn(VII) + S \xrightarrow{k_1} Mn(V) + Product$$

$$Mn(VII) + Mn(V) \xrightarrow{k_2} 2Mn(VI)$$
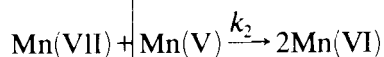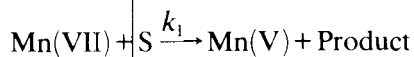
$$k_2 \gg k_1$$

Scheme 2

Permanganate oxidation of primary alcohols also proceeds in acid medium[16-21], but this reaction is not as fast as in alkaline medium[15]. The reaction rate in alkaline medium increases with increase in [OH⁻], indicating considerably higher reactivity of the alcoholate anion than that of the undissociated alcohol molecule. A mechanism based on hydride (H⁻) ion abstraction was proposed by Stewart[22,23] in the case of substituted benzhydrols and by Freemann[24] in the case of mandelic acid based on extremely high kinetic isotope effect and on the observation that according to the investigations carried out with ^{18}O, no oxygen atom is transferred into the product. At the same time, they admitted that the above observations are not in harmony with the very little substituent effect; therefore, the one-electron oxidation mechanism with H⁺ abstraction or with H atom elimination can not be excluded either.

In the case of aldehydes, a few investigations were carried out mainly in acidic medium[25-27], in alkaline medium, a mechanism based on H⁻ abstraction from the hydrate form, similar to that for alcohols was proposed in the oxidation of fluoral[28] and furfural[29].

Concerning the substrates studied by us in the present paper, methanol is quantitatively oxidized to carbon dioxide[1] while ethanol yields 10-20 mol% oxalic acid[1,30,31] also. As for the kinetics, in alkaline medium rate constants higher by three orders of magnitude have been measured[32] at [OH⁻]= 0.2 mol dm⁻³ compared to those in neutral and acidic media[17,18,21]. It has been known for a long time that formaldehyde, being almost completely hydrated[33], behaves as a geminal glycol rather than as a carbonyl compound. The hydration of acetaldehyde and n-butyraldehyde is not complete, presumably due to enolization. Therefore, the substrate choice is restricted and such substrates have not been pictured within present investigation. Formic acid is a typical example of how complicated the oxidation of such a simple substrate leading to a consistent end-product can be, because in spite of

numerous thorough investigations, several mechanisms are assumed[34-38].

Materials and Methods

The reagents $KMnO_4$, $NaClO_4$ and $NaOH$ were of AR (Merck) grade. The substrates were extra pure reagent from Fluka.

Stoichiometry

Substrate (2.0×10^{-4} mol) was added to permanganate (6.0×10^{-4}-16.0×10^{-4} mol) after previous adjustment of appropriate [alkali] in both solutions. After the reaction time, solid KI was added, followed by 10% H_2SO_4. Excess permanganate at the end of the reaction was titrated against thiosulfate solution. If the reaction time exceeded 15 min, the oxidation equivalent did not change at any [alkali].

Products

After adjustment of appropriate [alkali], permanganate solution exceeding the determined stoichiometric ratio was added to ethanol or acetaldehyde (1.0×10^{-3} mol). After a reaction period of 15 min, the excess permanganate and manganate were reduced by hydrazine hydrate solution to manganese dioxide. After filtration, the solution was neutralized, acidified with acetic acid and finally calcium oxalate was precipitated by a standard method. Oxalic acid was qualitatively identified by the diphenylamine test, and determined quantitatively by weight measurement. The reaction was carried out as described above and after filtering the MnO_2 formed, phosphoric acid (50 ml, 85%) was added to the solution which was distilled till no more distillate was obtained. After the addition of water (2×50 ml) distillation was continued. The acetic acid content of the distillate was determined by titration with alkali.

Kinetics

Kinetic measurements were performed on a Shimadzu recording spectrophotometer (model UV 300) equipped with a rapid mixing attachment (model RMA-1A) and on a Hewlett-Packard (8452A) spectrophotometer connected to a rapid kinetics accessory (HI-TECH-SFA-11). Each k_{obs} and k_0 value represents a mean value of 3 to 5 individual measurements. For the calculation of initial slopes and for curve fittings a Hewlett-Packard 9000-300 type computer, directly coupled to the spectrophotometer, was used.

Results

Stoichiometry

The oxidation equivalents required for the oxida-

tion of substrates to end products were determined by iodometric titration of the excess of permanganate at the end of reaction. The oxidation equivalent values per mole obtained at each [alkali] were: 6.0 ± 0.2 for methanol; 4.0 ± 0.2 for formaldehyde, ethanol and *n*-butanol; and 2.0 ± 0.1 for formic acid.

Products

Excess permanganate was added to ethanol. After the oxidation was over, the unreacted permanganate and manganate were removed as manganese dioxide. No calcium oxalate could be precipitated from the reaction mixture but, after acidifying by conc. phosphoric acid, 100 ± 4 mol % acetic acid could be distilled. When the same experiment was carrried out with previously basified acetaldehyde, the reaction mixture contained only about 70 mol % acetic acid; oxalic acid was also present.

Kinetic measurements

Kinetic measurements were carried out under pseudo-first order conditions (at least 10-fold excess of substrate). Decay of permanganate was followed spectrophotometrically at 524 nm. The [OH$^-$] was adjusted by adding NaOH while the ionic strength was maintained constant by adding NaClO$_4$. The temperature was uniformly maintained at 25°C. During reaction, colour of the reaction mixture changed from violet to blue and finally to green. The spectrum of the green solution was identical to that of MnO$_4^{2-}$. The spectrophotometer could record the total spectrum every 0.5 second. This enabled us to observe that the blue colour originated from violet of permanganate and the green from manganate, excluding the accumulation of hypomanganate.

The log (A − A$_\infty$) versus time plots (A = the absorbance measured at 524 nm), except for methanol, were good linear at least up to 75% consumption of permanganate, indicating first order in [permanganate]. The k_{obs} values calculated from the

slopes of the linear plots are listed in Table 1. For methanol, the k value calculated from the slope extrapolated to zero by numerical method was taken as k_{obs} value. The value obtained did not change by decreasing the initial [permanganate] to its half value, indicating that the first order in [permanganate] is valid for methanol as well. At the same time, k_{obs} versus [S]$_0$ plots were linear passing through the origin in all cases, verifying that the reaction is first order in [substrate] at a given [OH$^-$] leading to the rate law (4).

$$-\frac{d[\text{MnO}_4^-]}{dt} = k_{obs}[\text{MnO}_4^-] = k_0[\text{S}]_0[\text{MnO}_4^-] \quad \ldots (4)$$

The k_0 values measured at diverse [OH$^-$] are listed in Table 2, together with k_0 values measured at pH 4.6 and, in the case of formic acid at [H$^+$] = 1.0 mol dm^{-3}. For assessing the role of manganate some measurements were performed also with manganate ion. The aim was to determine the inaccuracy caused by the consumption of manganate in the value of A$_\infty$. The k_0 values obtained in the presence of manganate by the method of initial fitting (these are also listed in Table 2) are by orders of magnitude smaller than those of permanganate, thus the interference due to manganate can be neglected.

The kinetic stoichiometric factor of the reactions relates to the number of fast steps following the rate determining step. For the determination of this, the following relatively sensitive method was applied. The reagents were reacted with each other in the ratio of the assumed [MnO$_4^-$]$_0$ = ν[S]$_0$ initial concentration ratio, and if this ratio was correct, then the integrated kinetic Eq. (5) must hold.

$$\frac{1}{[\text{MnO}_4^-]} - \frac{1}{[\text{MnO}_4^-]_0} = kt \quad \ldots (5)$$

The 1/[MnO$_4^-$] versus time plot were linear at initial concentrations ν = 4 for ethanol and butanol

Table 1 — Pseudo-first order rate constants at varying [substrate]

[MnO$_4^-$] = 1.0 × 10^{-3} mol dm^{-3}; [NaOH] = 0.50 mol dm^{-3}; I = 2.0 mol dm^{-3}; temp. = 25°C

10^2 × [Substrate]$_0$ (mol dm^{-3})	10^2 × k_{obs}(s^{-1})				
	Methanol	Formaldehyde hydrate	Formic acid	Ethanol	*n*-Butanol
1.0	0.82	121	9.3	3.27	7.39
2.0	1.58	249	17.7	6.62	14.3
3.0	2.46	353	28.4	9.71	21.7
4.0	3.24	491	38.0	13.2	30.1
5.0	4.18	602	45.9	16.1	37.3

Table 2—Dependence of rate constants $(k_0, dm^3mol^{-1}s^{-1})$ on $[OH^-]$

$[Substrate]_0 = 1.00 \times 10^{-2} mol\ dm^{-3}; [MnO_4^-]_0 = 1.0 \times 10^{-3}\ mol\ dm^{-3}; (or\ [MnO_4^{2-}]_0 = 1.0 \times 10^{-3})^d;$
$I = 2.0\ mol\ dm^{-3}; temp. = 25°C.$

$[OH^-]$ (mol dm^{-3})	Methanol	Formaldehyde hydrate	Formic acid	Ethanol	n-Butanol
0.10	0.18	47.4	9.1	0.66	1.49
0.25	0.43	79.3	9.4	1.65	3.72
0.50	0.82	121	9.3	3.27	7.39
0.75	1.17	160	9.2	4.85	11.04
1.00	1.48	196	9.5	6.41	14.6
1.50	2.03	264	9.2	9.35	21.5
2.00	2.49	327	9.4	12.3	28.5
0.10[a]	0.079	24.2	5.1	0.34	0.92
pH 4.6[b]	~0	9×10^{-2}	—	~0	~0
$[H^+] = 1.0$[c]	—	—	1.5×10^{-3}	—	—
0.25[d]	4.3×10^{-3}	13.5	59×10^{-3}	6.9×10^{-3}	14.2×10^{-3}
2.00[d]	14.0×10^{-3}	5.6	62×10^{-3}	26.8×10^{-3}	37.4×10^{-3}

[a]Ionic strength = 0.10 mol dm^{-3}

[b]Adjusted by adding succinic acid buffer

[c]$[HClO_4] = 1.0$ mol dm^{-3}

[d]Oxidation by manganate (MnO_4^{2-})

and at $v = 2$ for formaldehyde and formic acid. The k values obtained from the slopes were identical to those obtained under pseudo-first order conditions. Thus, the consumption ratio $\Delta[MnO_4^-]/\Delta[S]$ in the process measured kinetically is 4 and 2, respectively. For methanol, no consistent v value could be obtained.

Discussion

It should be noted that the problem has been partially treated in an earlier publication[15] (at an ionic strength of 1.5 mol dm^{-3}), but the kinetic data have not been used there for the determination of K_B value. On the other hand, earlier we had considered other assumptions concerning the mechanism as well.

The results of stoichiometric measurements indicate that the oxidation equivalents consumed decrease by two in the series: methanol-formaldehyde-formic acid, suggesting that these substrates are transformed into each other in the same sequence, each of them being oxidized finally to carbon dioxide. Ethanol and butanol are converted, via the corresponding aldehydes, into acetic acid and butyric acid, respectively, although their oxidation is very slow; therefore, their consumption need not be taken into account. Oxidation of ethanol yielded acetic acid quantitatively. The oxidation must proceed via acetaldehyde in spite of the fact that in the oxidation of acetaldehyde some oxalic acid is also

formed, which could not be found in the case of oxidation of ethanol. This is presumably due to the formation of geminal glycol in the direct oxidation step; its enolization followed by elimination of water is slower than its direct oxidation. Oxidation studies on acetaldehyde and butyraldehyde indicate that both these aldehydes react with at least 150 times higher rate constant in the whole [alkali] range than the corresponding alcohol. Thus the oxidation of aldehydes can be considered with a factor of two, which is supported by the measured $v = 4$ value. Oxidation kinetics of formaldehyde, estimated from the calculations of Benson[39], is not disturbed by formic acid reacting slower. In the case of methanol, the situation is somewhat different. The intermediate product, formaldehyde, always reacts at a rate more than 130 times higher than methanol. This can be taken into account theoretically by a factor of two, while formic acid formed from formaldehyde reacts further at a rate of only 4-55 times higher than methanol. Consequently, the k_0 values for methanol had to be determined by numerical extrapolation to zero in which no intermediate products are yet present.

The value of k_0, except for formic acid, increases with increase in $[OH^-]$, indicating that the alcoholate anion is the reactive form.

Assuming

$$AOH + OH^- \overset{K_B}{\rightleftharpoons} AO^- + H_2O \qquad \ldots(6)$$
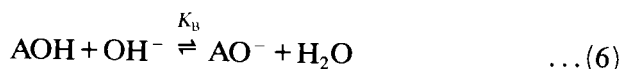
we get,

$$K_B = \frac{[AO^-]}{[AOH][OH^-]} \qquad \ldots(7)$$

(Owing to the ionic strength of 2.0 mol dm^{-3}, K_B is of course not a thermodynamic constant.)

Considering that

$$[S]_0 = [AOH] + [AO^-] \qquad \ldots(8)$$

we get,

$$[AO^-] = \frac{K_B[OH]}{1 + K_B[OH^-]}[S]_0 \qquad \ldots(9)$$

At pH 4.6 only the undissociated form can be present and, according to the k_0 values measured here, this form reacts at a rate constant several orders of magnitude smaller than the deprotonated form. This indicates that the permanganate consumption of the undissociated form is within the limits of error of the measurement; thus its role can be neglected in the kinetic equation.

Consequently, the rate law assumes the form (10)

$$-\frac{d[MnO_4^-]}{dt} = k' \frac{K_B[OH^-]}{1 + K_B[OH^-]}[S]_0[MnO_4^-] \quad \ldots(10)$$

Equations (10) and (4) lead to:

$$k_0 = k' \frac{K_B[OH^-]}{1 + K_B[OH^-]} \qquad \ldots(11)$$

The value of k_0 varies parallel to the ionic strength, indicating again that two reactants with equal charge, i.e., negatively charged MnO_4^- and negatively charged species, react in the rate determining step.

In the case of formic acid, the dissociation is suppressed only at high acidity ($pK_a = 3.75$) and the low rate constant measured at $[H^+] = 1.0$ mol dm^{-3} indicates considerably lower reactivity of the undeprotonated species. In the measuring region $[OH^-] = 0.10-2.0$ mol dm^{-3}, already the anion is present, and consequently k_0 does not change.

Equation (11) can be linearized by reciprocal formation and the plots $1/k_0$ versus $1/[OH^-]$ were linear except for formaldehyde. The k' and K_B values obtained from the slopes and intercepts of these linear plots, as well as those by direct simulation of Eq. (11) are listed in Table 3. In our opinion it is just the form of $k_0 \sim [OH^-]$ function following the deprotonation curve that verifies completely the participation of alkoxy anion in the oxidation.

The kinetic results obtained for formaldehyde could not be fitted by Eq. (11). It had to be assumed that the deprotonation of other hydroxyl groups of formaldehyde hydrate also occurs simultaneously. The corresponding four-parameter fitting according to Eq. (12)

$$k_0 = \frac{k_1' K_{B1}[OH^-] + k_2' K_{B1} K_{B2}[OH^-]^2}{1 + K_{B1}[OH^-] + K_{B1} K_{B2}[OH^-]^2} \qquad \ldots(12)$$

was already found satisfactory. (In Eq. (12) k_1' denotes the rate constant of formaldehyde monoanion

Table 3—Kinetically determined equilibrium and rate constants at 25°C
(Ionic strength = 2.0 mol dm^{-3})

	Methanol	Formaldehyde hydrate	Formic acid	Ethanol	n-Butanol
K_B (dm^{3}mol^{-1})	0.234 ± 0.01	19 ± 2 (0.080 ± 0.03)[a]	—	$4.3(\pm 0.2) \times 10^{-2}$	$2.6(\pm 0.1) \times 10^{-2}$
k' (dm^{3}mol^{-1}s^{-1})	7.8 ± 0.4	56 ± 6 (2070 ± 800)[a]	9.4 ± 0.4	157 ± 7	570 ± 60
ν	2	2	2	4	4
k (dm^{3}mol^{-1}s^{-1})	3.9	28 (1035)[a]	4.7	39.2	142
pK_a	14.63	12.72 (15.1)[a]	—	15.37	15.58
pK_a[b]	15.5[40]	13.27[44]	3.75	15.9[40]	—
	15.09[41]			15.93[41]	16.1[41]
	15.07[42]			15.83[42]	15.87[42]
	—			15.14[43]	

[a]For dianion
[b]Literature data

while k'_2 that of the dianion.) Owing to the relatively narrow range of [OH$^-$] of the measurements, the rate constants of formaldehyde could be calculated within broad limits of error. Consequently, these constants are informative only.

The constants k relating to the rate determining step are listed in Table 3 as well. The reaction proceeds either by Scheme 1 or by Scheme 2; the quick second reaction involves the appearance of a factor of 2. If the intermediate product reacts more than 150 times faster, this requires another multiplying factor of two. Thus, $k = k'/v$. Table 3 also contains literature pK values which are in accord with the values measured by us presently with the observation that acidity decreases in the sequence methanol-ethanol-butanol. Compared to the thermodynamic values, we have measured pK_a values lower by about half a unit, but it can be explained by the high ionic strength.
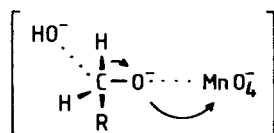
Now coming to the mechanism, we do not accept the assumptions based on H$^-$ or H abstraction. The C$-$H bond does not seem more loosened in the alcoholate anion than in the neutral molecule. Therefore, the abstraction of either H$^-$ or H atom from the non-dissociated species might just as well or even more readily take place. Electron abstraction from the oxygen atom of the anion and simultaneous proton elimination seem more probable. This is the two-electron step corresponding to that shown in Scheme 2. The positively polarized C-atom is *ab ovo* surrounded by OH$^-$ ions in the concentrated alkaline solution, and the nucleophilic attack of OH$^-$ on the carbon atom can take place simultaneously with the electron abstraction. The transition state in such a mechanism can be represented by structure (I).

The reactivity sequence in terms of constants k is in harmony with the inductive effect in the case of alcohols. By the increasing length of the electron donating alkyl chain, the electron can more easily be abstracted from the alkoxy O-atom of ethanol and butanol than from methanol. Likewise, in the case of formaldehyde the C$-$H bond in the dianion is hardly more fragile than in the monoanion. Therefore, the difference of about one and a half order of magnitude between k_1 and k_2 supports the mechanism based on electron abstraction as well; the elec-

tron abstraction from the dianion with higher electron density is more favoured.

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$$\left[\begin{array}{c} HO^- \quad H \\ \ddots \; | \curvearrowleft \\ H \diagup \overset{|}{\underset{R}{C}} - O^- \cdots Mn\,O_4^- \\ \end{array} \right]$$

I

R = H, CH$_3$, C$_3$H$_7$