Permanganate Oxidation of Unsaturated Alcohols in Alkaline Media

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ABSTRACT: A study was made on permanganate oxidation of olefinic and acetylenic alcohols in aqueous alkali media. Deprotonation constants of alcohols can be calculated from the kinetic data. The rate constant of alkoxide group oxidation exceeded that of the unsaturated bond. For oxidation of the alcoholic group a mechanism based on hydride ion transfer is proposed. © 2002 Wiley Periodicals, Inc. Int J Chem Kinet 34: 561–567, 2002

INTRODUCTION

As is known, permanganate ion is very reactive to unsaturated bonds both in aqueous acidic and alkaline media, and these reactions are considered to be some of the fastest reactions in organic chemistry. This can be stated in spite of the fact that the vast majority of rate constants measured for double bonds vary in a rather wide range, between the values 250 and 3000 dm³ mol⁻¹ s⁻¹ [1–9]. For the acetylene bond somewhat lower values were measured [10–12].

In the oxidation of aliphatic alcohols in alkaline medium, alcoholate (alkoxide) anions are the reactive species, which may be oxidized by permanganate by means of direct electron [13–16] or hydride ion (H^-) abstraction [17–25]. The dissociation constant of alcohols can be calculated from the kinetic results [13–16].

In this paper we study the oxidation of olefinic and acetylenic alcohols (and halides) with aqueous alkaline permanganate. In this case two processes, i.e. the oxidation of unsaturated bonds and that of alkoxide anions, proceed simultaneously. According to experience so far, the rate constants of alkoxide anions were found to be much lower than those of unsaturated bonds (for methanol, ethanol, and *n*-butanol values of 3.9, 39.2, and 142 dm³ mol⁻¹ s⁻¹ were measured [13]). Based on the analysis of kinetic results obtained in this work, however, a surprising conclusion may be drawn: in some cases the oxidation rates of alkoxide anions considerably exceed those of unsaturated bonds.

Measurements were performed in the range of $0.1 \le [OH^-] \le 2.0 \text{ mol dm}^{-3}$. Under these conditions permanganate is in the first step reduced only to manganate, which then further reacts at a much lower rate. In spite of the apparent one-electron reduction of permanganate, instead of a radical mechanism, two-electron oxidation steps are generally assumed in the literature [20,26]. Namely the manganate (V) species produced could not accumulate in detectable amount owing to its very fast reaction with permanganate [20,27–29].

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EXPERIMENTAL

Materials

The reagents KMnO₄, NaClO₄, NaOH, and HClO₄ were of analytical grade (Merck). The substrates were also of analytical grade (Fluka), further purified by fractional distillation and dried on 4A molecular sieves or by recrystallization in the case of solids as recommended in the literature [30].

Kinetics

Kinetic measurements were carried out with at least tenfold excess of substrates under pseudofirst-order conditions. Ionic strength was maintained with NaClO₄. Alkali concentration was adjusted with NaOH. In some supplementary measurements hydrogen ion concentration was adjusted with HClO₄, and pyrophosphate ions were applied in fivefold excess related to permanganate in order to avoid disproportionation and fast reactions of the Mn³⁺ ions formed.

Permanganate consumption was monitored with the use of a Hewlett-Packard spectrophotometer (type 8452A) coupled to a stopped-flow device (developed in our laboratory). The lg($A - A_{\infty}$) vs. time plots (Ais the absorbance at 524 nm) showed a slight curvature owing to consecutive reactions of the intermediates. Therefore, the rate constants were computed from the initial slopes of the plots determined by means of a Hewlett-Packard computer (type 9000-300) directly coupled to the spectrophotometer. Each value represents the average of 5–9 individual measurements. Estimated accuracy was $\pm 3\%$.

The orders related to the reagents were determined in 0.25 mol dm⁻³ base concentration by varying substrate concentration between 1.0×10^{-2} and 10.0×10^{-2} mol dm⁻³, or permanganate concentration in the range of 1.0×10^{-3} – 5.0×10^{-3} mol dm⁻³. The k_{obs} values were strictly proportional to both [Substrate]₀ and [MnO₄]₀.

If the rate-determining step is followed by very fast reactions, where further MnO_4^- molecules are consumed, these reactions act as multipliers in the rate constant of the first reaction. In order to determine this kinetic factor (ν) we applied the relatively sensitive method of reacting reagents in the initial concentration ratio of the presumed ν value. If this ratio is correct, then the integrated kinetic equation $1/[MnO_4^-] - 1/[MnO_4^-]_0 = kt$ must be valid, and the *k* value gained from the slope must be equivalent to the *k* value obtained under pseudo-first-order conditions. Measurements were performed in acidic medium, where only unsaturated bonds are oxidized,

and therefore the k values measured could be related to k_1 (see Eq. (2)). Although the $1/[MnO_4^-]$ vs. time plots always showed a slight curvature, the k values determined from the initial section of the plots verified the validity of $\nu = 2$ for olefinic and $\nu = 4$ for acetylenic alcohols.

Products

For determination of the products, we applied a reaction mixture containing the substrate in 1.0×10^{-3} mol dm⁻³, and permanganate in 2×10^{-3} (for allyl alcohol (1)) or in 4×10^{-3} mol dm⁻³ (for propargyl alcohol (7)) initial concentration. After quenching with hydrazine hydrate and filtering the MnO₂, the products were determined by means of the HPLC method (ISCO instrument, model 2350, detector V4) as described in detail in our earlier papers [16,31]. In order to evaluate the quantity of products, we compared the HPLC peakareas with the peaks given by standards in 1×10^{-3} mol dm⁻³ concentration under the same conditions.

RESULTS AND DISCUSSION

The reactions were found to obey first-order with respect to both permanganate and the substrate:

$$-\frac{d[MnO_4^{-}]}{dt} = k_0[AOH]_T[MnO_4^{-}]$$
(1)

where AOH stands for substrate alcohol.

The k_0 values measured (Table I) increase with the concentration of hydroxide ions, which may be attributed to alcoholate dissociation [13–16].

Let us denote the individual rate constants as follows:

$$\begin{array}{ll} R-CH=CH-CH_{2}OH + MnO_{4}^{-} \xrightarrow{k_{1}} Intermediate \\ (R-C=C-CH_{2}OH) & (2) \\ R-CH=CH-CH_{2}O^{-} + MnO_{4}^{-} \xrightarrow{k_{1}'} Intermediate \\ (R-C=C-CH_{2}O^{-}) & (3) \\ R-CH=CH-CH_{2}O^{-} + MnO_{4}^{-} \\ (R-C=C-CH_{2}O^{-}) & \overset{k_{2}}{\longrightarrow} R-CH=CH-CHO(R-C=C-CHO) \\ & + MnO_{4}^{3-} + H^{-} & (4) \end{array}$$

The term *Intermediate* indicates the well-known shortlived cyclic hypomanganate diester, which is assumed to hydrolyze fast, resulting in MnO₄^{3–} and further organic intermediates and products.

		$k_0 \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ at different [OH ⁻] (mol dm ⁻³)							
		0.10	0.25	0.50	0.75	1.00	1.50	2.00	0.10 ^a
1	2-Propen-1-ol (allyl alcohol) CH ₂ =CH-CH ₂ OH	354	376	397	431	451	509	552	258
2	1-Propene, 3-bromo (allyl bromide) CH2=CH-CH2Br	179	182	180		174			178
3	1-Propene, 3-chloro (allyl chloride) CH2=CH-CH2Cl	175	173	176		181			177
4	2-Propen-1-ol, 2-methyl (methallyl alcohol) CH ₂ =C(CH ₃)-CH ₂ OH	336	374	443	513	583	714	835	254
5	2-Buten-1-ol (crotyl alcohol) CH3-CH=CH-CH2OH	743	786	831	938	1019	1153	1295	534
6	2-Butene-1,4-diol HOCH ₂ —CH=CH–CH ₂ OH	534	598	657	709	735	770	800	379
7	2-Propyn-1-ol (propargyl alcohol) CH≡C−CH ₂ OH	135	192	233	253	265	277	282	94
8	1-Propyne, 3-bromo (propargyl bromide) CH≡C−CH2Br	48	47	49		48			48
9	1-Propyne, 3-chloro (propargyl chloride) CH≡C−CH ₂ Cl	46	47	46		49			45
10	2-Butyne-1,4-diol HOCH2−C≡C−CH2OH	218	254	275	277	283	285	287	151

Table I Apparent Second-Order Rate Constants (k_0 , dm³ mol⁻¹ s⁻¹) as a Function of NaOH Concentration

 $[\text{Substrate}]_0 = 1.00 \times 10^{-2} \text{ mol dm}^{-3}; [\text{MnO}_4]_0 = 1.0 \times 10^{-3} \text{ mol dm}^{-3}; I = 2.0 \text{ mol dm}^{-3}; T = 25^{\circ}\text{C}.$ ^{*a*} Ionic strength 0.10 mol dm⁻³.

The oxidation rate of nondissociated hydroxyl groups can be neglected on the basis of available data [13–16].

All three processes were followed by the fast reaction:

$$MnO_4{}^{3-} + MnO_4{}^{-} \xrightarrow{k_4} 2MnO_4{}^{2-}$$
(5)

where $k_1, k'_1, k_2 \ll k_4$.

Let us define the equilibrium

$$AOH + OH^{-} \stackrel{K_{B}}{\rightleftharpoons} AO^{-} + H_{2}O$$
 (6)

From this, based on the consideration that $[AOH]_T = [AOH] + [AO^-]$, we obtain

$$[AO^{-}] = \frac{K_{\rm B} \lfloor OH^{-} \rfloor}{1 + K_{\rm B} [OH^{-}]} [AOH]_{\rm T}$$

With the use of this equation we attain the kinetic equation

$$-\frac{d[MnO_4^{-}]}{dt} = 2\frac{k_1 + k_1'K_B[OH^{-}] + k_2K_B[OH^{-}]}{1 + K_B[OH^{-}]} \times [AOH]_T[MnO_4^{-}]$$
(7)

Factor 2 appears as a result of the fast reaction (5). By comparison of Eqs. (1) and (7), we obtain

$$k_{0} = \frac{2k_{1} + (2k'_{1} + 2k_{2})K_{B}[OH^{-}]}{1 + K_{B}[OH^{-}]}$$
$$\equiv \frac{2k_{1} + kK_{B}[OH^{-}]}{1 + K_{B}[OH^{-}]}$$
(8)

In the case of acetylenic compounds, reactions (2) and (3) are followed by a fast attack of another permanganate molecule, since the remaining double bond of the short-lived intermediate, or that of its hydrolytic product, i.e. unsaturated glycol, is very reactive [10–12,32]. This is also supported by the observation that in these cases $\nu = 4$. Therefore, for acetylenic alcohols Eq. (8) changes as follows:

$$k_{0} = \frac{4k_{1} + (4k'_{1} + 2k_{2})K_{B}[OH^{-}]}{1 + K_{B}[OH^{-}]}$$
$$\equiv \frac{4k_{1} + kK_{B}[OH^{-}]}{1 + K_{B}[OH^{-}]}$$
(9)

Considering the k_1 values to be equal to the rate constants measured in acidic media may be a good approximation, since the short-lived intermediates i.e. the cyclic hypomanganate diesters, are identical in both media. This assumption is also supported by the fact that identical rate constants were measured for unsaturated alkylhalides in acidic and alkaline media $[k = 2k_1$ for allyl (**2**, **3**) and $k = 4k_1$ for propargyl (**8**, **9**) halides (see Table II)].

After accomplishing the two-parameter fitting of Eqs. (8) and (9), respectively, we obtain the values k and $K_{\rm B}$ shown in Table II.

It must be admitted that the $K_{\rm B}$ and $pK_{\rm a}$ ($pK_{\rm a}$ = 14 – lg $K_{\rm B}$) values measured cannot be regarded as thermodynamic constants owing to 2.0 mol dm⁻³ ionic strength. The $pK_{\rm a}$ values gained are somewhat lower

than the literature data [33–36], which is in accordance with the trend expected due to high ionic strength.

Rate constants k'_1 and k_2 cannot be separated by kinetic methods, since both are comprised in k. An estimation, however, can be made: k'_1 cannot be higher than k_1 . There are data available only for unsaturated carboxylic acids, where the anions with negative charge are less reactive than their neutral nondissociated forms [3,4,8,9]. This phenomenon may be due to electrostatic effects. We think that no significant error is made by the assumption of $k'_1 \approx k_1$. Based on this consideration k_2 values could be calculated (Table II). As can be seen, the rate constants of alkoxide anions (k_2) are significantly higher than those of the unsaturated bond (k_1) for substrates studied in this article. Moreover, these k_2 values exceed most rate constants known for permanganate oxidation of the unsaturated bond.

The k_2/k_1 ratios measured were also supported by product analysis carried out for allyl (1) and propargyl (7) alcohols. HPLC investigations justified that glycerin and acrylic acid, or glycollic and propyolic acids were formed. (Other products or intermediates did not accumulate in measurable amount.) The unsaturated carboxylic acids were the products of alkoxide group oxidation, while oxidation of the unsaturated bond yielded glycerin or chain rupture products (see Scheme 1).

		k_1	k	KB	pK_a (Literature)	$\sim k_2$
1	2-Propen-1-ol	171	1934	0.076	$15.120(15.52^a; 15.48^b)$	796
	(allyl alcohol)					
2	1-Propene, 3-bromo	87	179			
	(allyl bromide)					
3	1-Propene, 3-chloro	86	176			
	(allyl chloride)					
4	2-Propen-1-ol, 2-methyl	154	9620	0.030	15.52	4656
	(methallyl alcohol)					
5	2-Buten-1-ol	356	8769	0.039	$15.41(15.80^b)$	4028
	(crotyl alcohol)					
6	2-Butene-1,4-diol	240^{c}	910	1.45	$13.84(14.0^d)$	215
7	2-Propyn-1-ol	10^e	304	5.62	$13.25(13.55^a; 13.57^b)$	132
	(propargyl alcohol)					
8	1-Propyne, 3-bromo	11.5^{e}	48			
	(propargyl bromide)					
9	1-Propyne, 3-chloro	11.5^{e}	47			
	(propargyl chloride)					
10	2-Butyne-1,4-diol	12.5 ^e	292	22.91	$12.64(12.94^{f})$	121

Table II The Measured Dissociation and Rate Constants

^a Ref. 33;

^d Ref. 35;

e Ref. 10;

^f Ref. 36.

^b Ref. 34;

^c Ref. 5;



In the case of both substrates P_1 stands for the products of unsaturated bond oxidation and P_2 designates those of the alkoxide group.

Measured and calculated product ratios are given in Table III. For calculations made with the use of Eq. (10) the assumption $k_1 = k'_1$ was accepted.

$$\frac{[P_2]}{[P_1]} = \frac{k_2}{k_1} \frac{K_B[OH^-]}{1 + K_B[OH^-]}$$
(10)

Validity of this assumption is also verified by the relatively good agreement between measured and calculated values. This can be stated in spite of the fact that P_2 always appeared in lower amount than expected, which

Table III Amounts of Products of Unsaturated Bond Oxidation (P_1) and Those of Alkoxide Group Oxidation (P_2) as a Function of Hydroxide Ion Concentration^{*a*}

			$[OH^{-}] (mol dm^{-3})$				
		0.10	0.25	0.50	1.0		
1	Allyl alcohol						
	P_1	0.92	0.82	0.71	0.59		
	P ₂	0.018	0.057	0.11	0.17		
	P_2/P_1	0.020	0.070	0.155	0.290		
	(P_2/P_1)	(0.033)	(0.086)	(0.170)	(0.330)		
7	Propargyl alcohol						
	P_1	0.14	0.10	0.082	0.073		
	P ₂	0.62	0.73	0.77	0.80		
	P_2/P_1	4.4	7.3	9.4	11.0		
	(P_2/P_1)	(4.75)	(7.71)	(9.74)	(11.2)		

^{*a*} The amounts represent HPLC peak areas related to those of standard solutions of 1.0×10^{-3} mol dm⁻³. The ratios calculated by Eq. (10) are given in parentheses.

may be due to the fact that in the case of aldehyde intermediates the oxidation rate of the unsaturated bond related to the aldehyde group is not negligible.

In summary, the following conclusions may be drawn:

On the basis of the $K_{\rm B}$ values measured the following is the order of acidity: methallyl alcohol (4) < crotyl alcohol (5) < allyl alcohol (1) < 2-butene-1,4-diol (6) < propargyl alcohol (7) < 2-butyne-1,4diol (10), which agrees with the acidity scale expected according to literature data. Owing to positive inductive effect the alkyl group reduces the acidity of alcohols (decreasing $K_{\rm B}$ and increasing $pK_{\rm a}$). On the other hand, because of conjugation the unsaturated bond acts as an electron-withdrawing group and accordingly, increases acidity. This effect is enhanced in the case of the acetylenic bond.

In this article we do not intend to deal with the mechanism of reactions (2) and (3) as it has been discussed in detail in the literature [7-9,37-40]. We wish to make some remarks, however, on the oxidation mechanism of alkoxide anion (Eq. (4)).

For the oxidation rate constants of alkoxide anions an opposite order was found: k_2 increases with decreasing acidity. This order is in accordance with the fact that in the presence of an electron-withdrawing group, electron or H⁻ abstraction is hindered. The Taft σ^* values for crotyl (5), allyl (1), and propargyl (7) alcohols are available (0.36, 0.56, and 1.7 [34]). Although the lg k_2 vs. σ^* plot is not a straight line, the declining trend of the plot ($\rho^* < 0$) points to an electron-deficient carbon center in the transition state.

A mechanism based on hydride transfer was generally suggested for the permanganate oxidation of alcohols both in acidic and alkali media [17–25]. The same mechanism was proposed for some other oxidants as well [41–47]. The main argument for H⁻ abstraction is the substantial kinetic isotope effect observed in each case, which points to the important role of C–H bond cleavage in the rate-determining step. Banerji considers the H-atom abstraction less probable, as in this case a higher kinetic isotope effect would be expected than had been measured [23,24]. According to Lee et al. [48] there is a possibility of MnO_4^- addition to the C–H bond, giving an organometallic intermediate. Homolytic cleavage of the C–Mn bond would then result in the formation of free radicals.

Most recently, further possibilities have been raised based on quantum mechanical computation. According to the approach of Lee et al. [49], the reaction could be initiated by HOMO–LUMO interaction. In the opinion of Strassner et al. [50], concerted 3+2 cycloaddition is capable of activating the C–H bond. Ab initio calculations of Wiberg and Freeman [51] showed that energetically all four variations (H⁻, H, e⁻, 2e⁻ abstraction) are possible. Considering the above, this problem does not seem to be fully resolved yet.

In our previous papers we argued against the mechanism based on H⁻ or H transfer and for direct electron abstraction from the alkoxide anion [13–16]. Although the C–H bond in the negatively charged alkoxide anion does not seem to be more loosened than in the neutral molecule, alcohols are oxidized by orders of magnitude faster in alkali than in acidic media. Our assumption was that the interaction between permanganate and the alcoholic O-atom enhances polarization on the C-atom, which facilitates the simultaneous nucleophilic attack of the hydroxide ion. Transition state was suggested to be



Decomposition of the activated complex may take place with proton elimination. It should be noted that proton elimination and two-electron transfer to the oxidant manifest themselves as hydride transfer.

In support of this assumption the following facts were brought up:

1. Mesoxalic acid hydrate cannot be oxidized via H^- or H abstraction, as there is no C–H bond. In spite of this, the rate constant is commensurable to that of tartronic, lactic, and D,L-tartaric acids [15,16,52]. (The somewhat lower value can rather be ascribed to steric hindrance.)

- 2. The oxidation of ethylene glycol proceeds with twice as high rate constant in D_2O as in H_2O . As is known, DO^- is more nucleophilic than HO^- ; therefore the higher rate constant is in accordance with the activated complex proposed [14].
- 3. Meso-tartaric acid was oxidized almost 10 times as fast as D,L-tartaric acid. In the expected antiparallel open position both hydroxyl groups of the D,L-form are close to each other, which may hinder the reaction. This may account for the lower rate constant. At the same time, the Hatoms are more accessible than in the meso-form; therefore H⁻ abstraction would be more favorable for the D,L-form, which is in contradiction with experience [16].

In spite of the above considerations, our previous assumption on the mechanism must be revised. In some cases, for example in the case of mesoxalic acid hydrate, only pure electron abstraction is possible. The fact that the rate constants of alkoxide anions of unsaturated alcohols are considerably higher than those of saturated alcohols, however, cannot be explained by this mechanism, since exactly the opposite could be expected owing to the negative inductive effect [compare the values of 87 and 137 $dm^3 mol^{-1} s^{-1}$ for propanol [this work] and n-butanol [13] with the values of 796 and 4028 dm³ mol⁻¹ s⁻¹ for allyl alcohol (1) and crotyl alcohol (5)]. The following explanation seems plausible. Delocalization of the negative charge in the mesomer system, comprising the unsaturated bond and electron pairs of the alkoxide O-atom, promotes hydride ion abstraction. In the case of methallyl alcohol this effect is enhanced by the hyperconjugation of the methyl H-atoms. The mesomer system for acetylenes does not seem to be symmetrical. Delocalization of the negative charge is shifted towards the triple bond, which is less favorable for hydride abstraction. This might explain the relatively low k_2 values of the acetylenic compounds.

Accepting the suggestion made by Lee [49], we propose the following activated complex:



The lone pairs of electrons of the alcoholic O-atom might occupy the lowest unoccupied molecular orbital of the Mn-atom. This initial interaction may be followed by rate-limiting hydride transfer through internal cyclic electron transfer. It should be noted that this assumption also explains the higher rate constant of meso-tartaric acid than that observed for D,L-tartaric acid.

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