Kinetics and mechanisms of oxidation of 1-octene and heptanal by crown ether-solubilized potassium permanganate in non-aqueous solvents

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Abstract

The kinetics of oxidation of 1-octene and heptanal by 18-crown-6-ether-solubilized $KMnO_4$ in benzene and CH_2Cl_2 have been investigated. In benzene, the oxidation of 1-octene is first order with respect to the oxidant and zero order with respect to the substrate, whereas in CH_2Cl_2 the reaction is first order with respect to both substrate and oxidant. The reaction of heptanal followed different kinetics being first order with respect to both substrate and oxidant, regardless of whether benzene or CH_2Cl_2 was employed as the solvent. The values of activation energy E_a, standard enthalpy ΔH^*, standard entropy change ΔS^*, and standard free energy ΔG^*, for the reaction, are reported. Mechanistic pathways for the studied reactions are also proposed.

Introduction

Despite the ability of permanganate ion to oxidize different organic compounds such as alkenes [1, 2], alcohols [3–9] and aldehydes [10–12], the usefulness of this ion is limited to reactions in aqueous solutions. To overcome this difficulty, quaternary ammonium salts [13], diethyl polyethylene glycol [14] and phosphinium salts [15] were used to solubilize potassium permanganate in organic solvents. Crown ethers have also been proposed to accomplish this purpose [16–18]. When potassium permanganate is brought into contact with a solution of 18-crown-6-ether, the cation (K^+) is complexed by the crown ether and thus the counter ion (MnO_4^-) will dissolve in the organic solvent [3, 19–23]. The technique of crown-ether solubilization has been employed in several industrially valuable processes such as saponification [19], alcohol reduction by $NaBH_4$ [16], nucleophilic substitution [16], α-elimination [24], the Darzen reaction [24], rearrangements [4, 29], the Wittig reaction [30], and the Michael addition [31]. In this paper, the kinetics and mechanisms of the oxidation of 1-octene and heptanal by 18-crown-6-ether-solubilized potassium permanganate are reported, employing benzene and methylene chloride as solvents.

Experimental

The substrates, 1-octene and heptanal, were purchased from Merck Co. Ltd. in the purest form and were used as received. 18-Crown-6-ether (1,4,7,10,13,16-hexaoxa-cyclooctadecane) and $KMnO_4$ were purchased from Fluka. C_6H_6 and CH_2Cl_2 solvents were purified and dried according to standard procedures [29].

The visible spectra were measured on a SP 8-100 and/or UV2 Pye-Unicam u.v.–vis. double beam spectrometer. Thermostated 1.0-cm^3 glass cells were used to measure the solution spectra of the samples. The i.r. spectra were measured on a FT-IR Shimadzu 8201 spectrophotometer, as liquid thin films between NaCl discs.

Preparation of the 18-crown-6-ether-solubilized $KMnO_4$ was carried out following literature methods [32, 33].

In a typical oxidation experiment, a known vol of the solution of the substrate (1-octene or the heptanal) in C_6H_6 (or CH_2Cl_2) was mixed with another known vol of the solution of 18-crown-6-ether/$KMnO_4$ in C_6H_6 (or CH_2Cl_2) at room temperature. Care was taken to keep the total vol the same throughout each reaction run. As soon as the two solutions were mixed, the reaction time monitor (stopwatch) was switched on. The reaction mixture was then shaken for 15 s and transferred to the thermostated spectrophotometer cell. The absorbance at 546 nm, characteristic for the $KMnO_4$ ion, was measured at appropriate time intervals, as early as 30 s after mixing. The course of the reaction was thus followed by monitoring the disappearance of the $KMnO_4$ ion with time.

For each substrate studied, qualitative analysis was conducted at least once in order to check the resulting product. For confirmation purposes, the reaction was allowed to proceed for enough time until it ceased, *ca.* 48 h, and the reaction mixture was then separated by fractionation. Each fraction was analyzed using FT-IR spectrophotometry. The reaction product(s) resulting from each substrate are listed in the results section, *vide infra.*

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Results and discussion

Oxidation of 1-octene

When added to the reaction mixture, 18-crown-6-ether-solubilized permanganate ion in benzene or methylene chloride, 1-octene was oxidized to the heptanoate anion, which appeared as a water hydrolysis product. The rate of appearance of the reaction product was equivalent to the rate of disappearance of 1-octene. The reaction stoichiometry, measured in methylene chloride, showed that for each mole of reacted permanganate ion 2 mol of 1-octene were consumed. In benzene, however, 3 mol of the solubilized permanganate ion were needed to oxidize 1 mol of 1-octene. These findings are consistent with other reports [3]. In either solvent, the kinetics of the reaction were followed spectrophotometrically by monitoring the rate of disappearance of the permanganate ion. The effects of different parameters, such as the concentration of the 1-octene and the solubilized permanganate, together with the effects of the temperature and the solvent type, on the rate of the reaction were investigated.

Effect of reactant concentrations on the rate of 1-octene oxidation

The oxidation of 1-octene was conducted using different initial concentrations of solubilized permanganate ion, keeping other reaction conditions constant. Measured at 30 °C, in both benzene and methylene chloride solvents, the reaction half-life $(t_{1/2})$ was constant and independent of the permanganate ion concentration (Table 1). This indicates a first order dependence with respect to the solubilized permanganate ion in both solvents.

The effect of the concentration of 1-octene on the reaction rate was studied under a large excess (10-fold) of octene over permanganate ion concentration; thus it was assumed that the concentration of 1-octene does not change very much during the reaction. In benzene, a zero order dependence of the reaction with respect to [1-octene] was again exhibited from plots of $\log(t_{1/2})$ versus $\log[1\text{-octene}]$, viz. the $(t_{1/2})$ value was independent of [1-octene] (Table 1). In methylene chloride, however, a different behavior was observed. Plots of $\log(t_{1/2})$ versus $\log[1\text{-octene}]$ showed, approximately, a negative unity slope indicating a first order process with respect to the octene (Table 1).

From these data, the rate laws for the 1-octene oxidation in the two different solvents were found to be:

$$\text{Rate} = k_{\text{obs}}[\text{MnO}_4^-] \quad \text{(in benzene)} \tag{1}$$

$$\text{Rate} = k_{\text{obs}}[\text{MnO}_4^-][1\text{-octene}]$$
$$\text{(in methylene chloride)} \tag{2}$$

The difference in the kinetic behavior of the oxidation of 1-octene (Equations 1 and 2) indicates that the solvent is, though not directly, involved in the reaction mechanism. A possible pathway for 18-crown-6-ether-oxidized
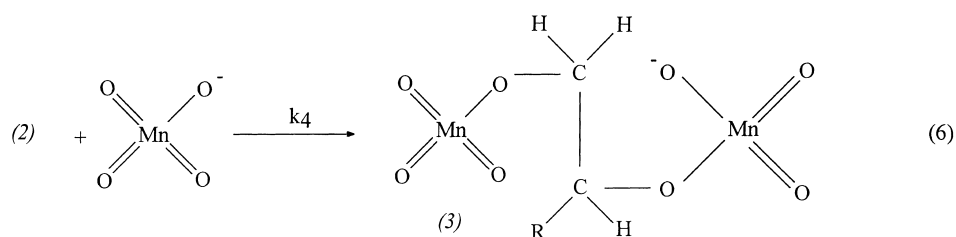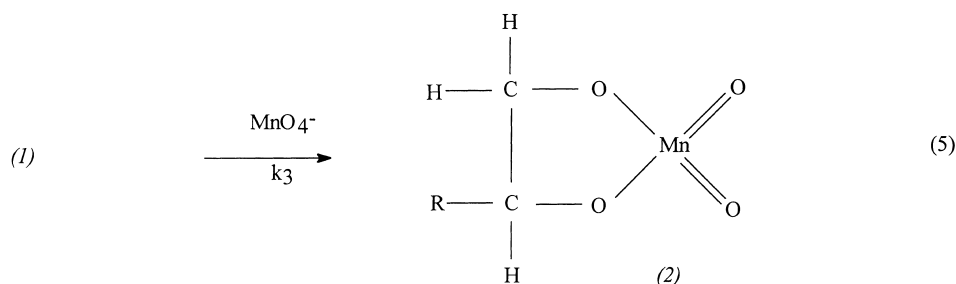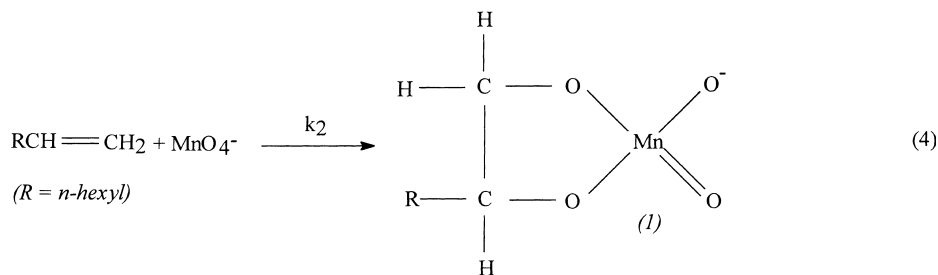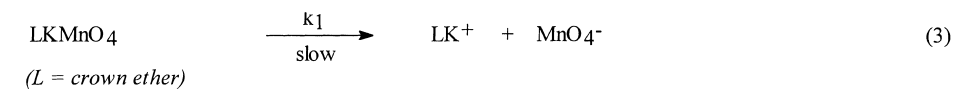
Table 1. Effect of reactant initial concentrations on time $t_{1/2}$ of oxidation of 1-octene at 30 °C using a constant molar ratio for [18-crown-6]:[KMnO$_4$] = 1.1:1

10^4 [KMnO$_4$] (M)	10^3 [1-octene] (M)	$\log t_{1/2}$ [a]
In benzene		
10.0	8.0	1.716
5.2	8.0	1.703
3.8	8.0	1.707
3.0	8.0	1.699
2.1	8.0	1.699
1.6	8.0	1.712
5.2	4.0	1.699
5.2	6.0	1.703
5.2	10.0	1.699
5.2	16.0	1.699
5.2	24.0	1.699
In CH$_2$Cl$_2$		
12.8	10.0	0.707
10.7	10.0	0.699
8.0	10.0	0.699
6.6	10.0	0.699
5.0	10.0	0.707
12.0	6.0	1.16
12.0	8.0	0.97
12.0	16.0	0.66
12.0	20.0	0.53
12.0	24.0	0.42
12.0	30.0	0.30

[a] $t_{1/2}$ (min).

1-octene in benzene is presented in Scheme 1. In this mechanism, the dissociation of the complex ion pair (LKMnO$_4$) to give the complex cation (LK$^+$) and the free anion (MnO$_4^-$) is assumed to occur in a slow step (Equation 3). This has been assumed to be due to the non-polar nature of benzene. In the next step, the permanganate ion couples to the 1-octene to yield the cyclic five-membered manganate(V) diester, *(1)*. Similar behavior has already been proposed for the permanganate ion [3]. *(1)* is then oxidized by another free permanganate ion, *via* a charge-transfer process, to yield the electrically neutral species *(2)*. A third free permanganate ion will then couple with *(2)* to yield the acyclic intermediate *(3)*, as shown in Equation (6). *(3)* will in turn yield the heptanoate upon hydrolysis by water, *via* Equation (7). This mechanism accounts for the fact that 3 mol of permanganate ion are needed to oxidize 1 mol of 1-octene. Furthermore, the mechanism explains why, in benzene, the reaction is first order with respect to permanganate and zero order in the octene.

In methylene chloride, a different pathway is presented in Scheme 2, in which 1 mol of the permanganate ion oxidizes 2 mol of octene. Equation (8) involves coupling of the olefin to the permanganate ion to yield intermediate *(1)* and is assumed to be the rate-controlling step. This step is followed by a fast step, Equation (9), resulting in the formation of the non-polar intermediate *(4)*. The mechanism thus presented for the oxidation of 1-octene in CH$_2$Cl$_2$ accounts for the observed stoichiometry and kinetics.

$$\text{LKMnO}_4 \xrightarrow[\text{slow}]{k_1} \text{LK}^+ + \text{MnO}_4^- \tag{3}$$

(L = crown ether)

$$\text{RCH}=\text{CH}_2 + \text{MnO}_4^- \xrightarrow{k_2} \quad (1) \tag{4}$$

(R = n-hexyl)

$$(1) \xrightarrow[k_3]{\text{MnO}_4^-} \quad (2) \tag{5}$$

$$(2) + \text{Mn} \xrightarrow{k_4} \quad (3) \tag{6}$$

$$(3) \xrightarrow{\text{H}_2\text{O}} \text{Products} \tag{7}$$

Scheme 1.

By measuring initial rates of reactions conducted at different temperatures, the k_{obs} values were calculated. The values of different activation parameters, such as activation energy (E_{act}), standard enthalpy of the reaction (ΔH^*), the standard entropy change (ΔS^*) and the standard free energy (ΔG^*) in the two solvents were also calculated, as shown in Table 2.
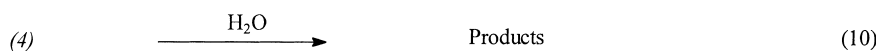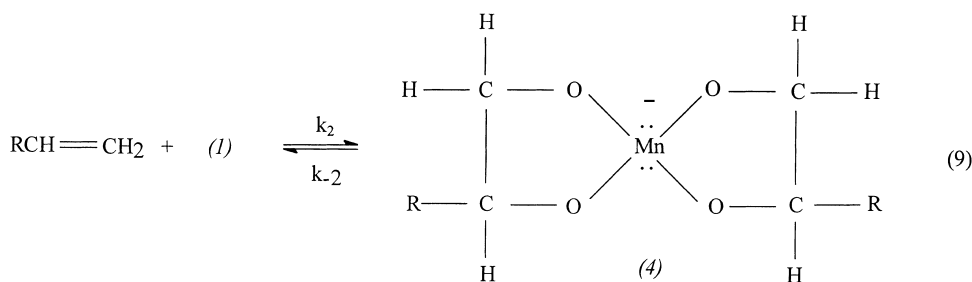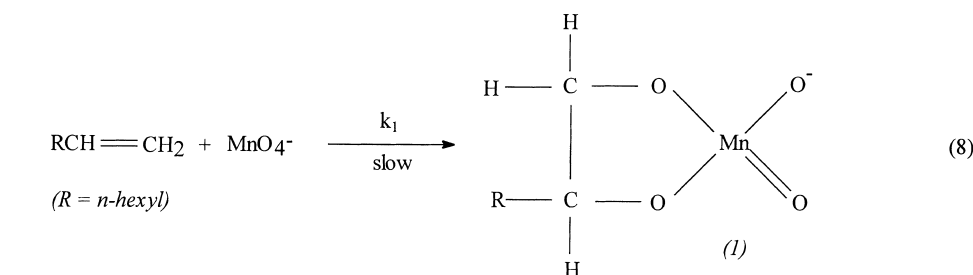
Oxidation of heptanal

Heptanal reacted with 18-crown-6-ether-solubilized permanganate ion to yield the heptanoate ion, exclusively. This result was confirmed by i.r. analysis of the fractions of the mixture after cessation of the reaction. The strong carboxylate ion stretching band at 1556 cm^{-1} and the weaker stretching band at 1415.7 cm^{-1} were observed. In both benzene and methylene chloride, 1 mol of the permanganate ion oxidized 2 mol of the aldehyde. This indicates that the reaction follows somewhat similar mechanistic pathways in both solvents.

Effect of the reactant concentrations on the rate of heptanal oxidation

In either benzene or methylene chloride, the measured $(t_{1/2})$ was independent of the initial solubilized permanganate ion used (Table 3). This result was apparent from plots of $\log(t_{1/2})$ *versus* log[permanganate] measured at 30 °C, which indicates that the heptanal oixdation is first order with respect to the permanganate concentration.

$$RCH{=}CH_2 \;+\; MnO_4^- \quad \xrightarrow[\text{slow}]{k_1} \quad (1) \qquad (8)$$

(R = n-hexyl)

$$RCH{=}CH_2 \;+\; (1) \quad \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \quad (4) \qquad (9)$$

$$(4) \quad \xrightarrow{H_2O} \quad \text{Products} \qquad (10)$$

Scheme 2.

Table 2. Values of different activation parameters for the 1-octene oxidation solubilized permanganate ion in different solvents[a]

Solvent	ΔE_{act} (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})	ΔG^* (kJ mol^{-1})
Benzene	23.49	21.31	−188.09	77.28
CH$_2$Cl$_2$	53.78	51.34	−80.25	75.14

[a] Reactions were conducted using 1-octene (10×10^{-3} M) and solubilized MnO$_4^-$ (1.3×10^{-3} M, with 18-crown-6-ether:MnO$_4^-$ mole ratio 1.1:1.0).

On the other hand, plots of $\log(t_{1/2})$ *versus* log[heptanal] indicate a first order reaction with respect to the heptanal, in both benzene and methylene chloride (Table 3). The measured rate law for the oxidation of heptanal in both benzene and methylene chloride is thus:

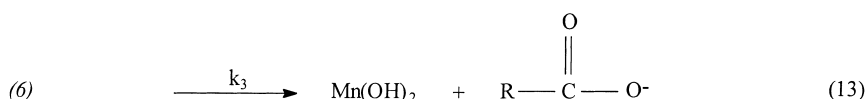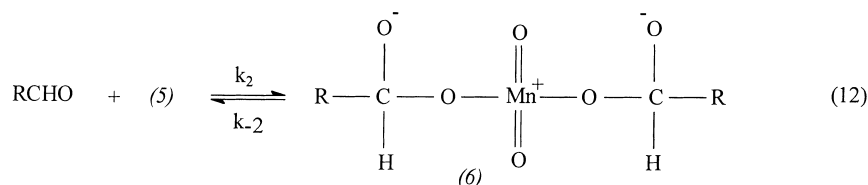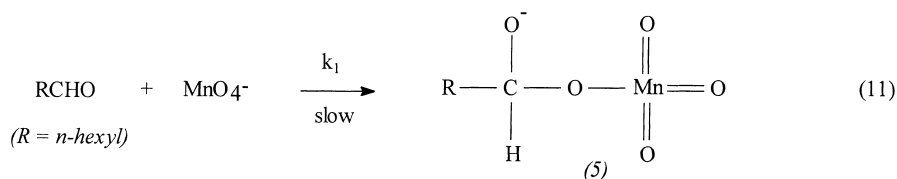$$\text{Rate} = k_{obs}[\text{permanganate}][\text{heptanal}]$$

The mechanism that best explains the kinetics is presented in Scheme 3. The permanganate ion adds to 1-heptanal in a slow step, Equation (11), yielding the permanganate ester *(5)*. Intermediate *(5)* then reacts with another 1-heptanal molecule to yield the diester *(6)*, as shown in Equation (12). Upon hydrolysis, *(6)* gives the heptanoate anion as the final product.

Thus, the proposed mechanism is consistent with the experimentally measured law and explains the consump-

Table 3. Effect of reactant initial concentrations on time $t_{1/2}$ of oxidation of heptanal at 30 °C using a constant molar ratio of [18-crown-6]:[KMnO$_4$] = 1.1:1

10^4 [KMnO$_4$] (M)	10^3 [heptanal] (M)	$\log t_{1/2}$[a]
In benzene		
4.8	8.0	0.39
3.8	8.0	0.39
3.4	8.0	0.39
2.4	8.0	0.36
1.5	8.0	0.39
5.2	6.0	0.53
5.2	5.0	0.64
5.2	4.0	0.71
5.2	3.0	0.84
5.2	2.0	1.00
In CH$_2$Cl$_2$		
5.0	8.0	1.07
6.2	8.0	1.09
8.8	8.0	1.09
11.0	8.0	1.10
13.5	8.0	1.10
10	6.0	1.41
10	8.0	1.31
10	10.0	1.16
10	16.0	0.96
10	20.0	0.83
10	24.0	0.78

[a] $t_{1/2}$ (min).

$$RCHO \quad + \quad MnO_4^- \quad \xrightarrow[\text{slow}]{k_1} \quad R\text{—}\overset{\displaystyle O^-}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}\text{—}O\text{—}Mn\text{=}O \qquad (11)$$

$(R = n\text{-hexyl})$

(5)

$$RCHO \quad + \quad (5) \quad \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \quad R\text{—}C\text{—}O\text{—}Mn^+\text{—}O\text{—}C\text{—}R \qquad (12)$$

(6)

$$(6) \quad \xrightarrow{k_3} \quad Mn(OH)_2 \quad + \quad R\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O^- \qquad (13)$$

Scheme 3.

Table 4. Values of different activation parameters for the heptanal oxidation reaction with solubilized permanganate ion in different solvents[a]

Solvent	ΔE_{act} (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})	ΔG^* (kJ mol^{-1})
Benzene	66.72	64.21	14.94	60.06
CH$_2$Cl$_2$	40.29	37.82	−121.22	73.92

[a] Reactions were conducted using 1-octene (10×10^{-3} M) and solubilized MnO$_4^-$ (1.3×10^{-3} M, with 18-crown-6-ether:MnO$_4^-$ mole ratio 1.1:1).

tion of 2 mol of the aldehyde per 1 mol of the permanganate ion.

The heptanal oxidation reaction was conducted at different temperatures. The different activation parameters have been calculated, and are listed in Table 4. The negative value for ΔS^* in methylene chloride indicates that the transition state in this solvent is more ordered than in benzene. In benzene, ΔS^* assumed a positive value.

Work is underway here to give an insight into the mechanisms of crown-ether-solubilized permanganate-induced oxidation of other organic systems.

Acknowledgment

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