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KINETICS AND MECHANISM OF THE PERMANGANATE OXIDATION OF DIETHYL MALEATE AND DIETHYL FUMARATE

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The permanganate oxidation of diethyl maleate and diethyl fumarate in aqueous ethanol has been studied by the stopped-flow technique. The reaction is first order with respect to both MnO_4^- and the esters. The rate constant is independent of the pH. The trans species is about 50 times more reactive than its cis counterpart, which is due predominantly to steric reasons.

Перманганатное окисление диэтиловых эфиров малеиновой и фумаровой кислот в водном этаноле было исследовано с помощью техники остановленной струи. Реакция имеет второй порядок как по отношению MnO_4^-, так и по отношению к эфирам. Константа скорости не зависит от pH. Транс-изомеры почти в 50 раз более реакционны, чем соответствующие цис-изомеры, что является следствием различных стерических затруднений.

INTRODUCTION

Compounds containing olefinic double bonds are known to react rapidly with permanganate in acidic solutions. The application of the stopped-flow technique has provided insight into the mechanistic details of these multi-step processes. In a study of the permanganate oxidation of maleic and fumaric acid as well as their methyl-substituted derivatives, it has been found that the trans-diacids are much more reactive than their cis counterparts and these differences become less pronounced upon going to the mono- and dianions /1-3/. This behaviour was interpreted in terms of steric hindrance against the cis-attack of MnO_4^- on the double bond, involving increased repulsion between the cis-substituents in the transition state. In order to establish whether intramolecular hydrogen bonding in the above diacids and anions exerts an influence on the relative reactivities of cis and trans isomers, we have investigated the behaviour of diethyl maleate (DEM) and diethyl fumarate (DEF), in which hydrogen bonding is not possible.

EXPERIMENTAL

The kinetic measurements were performed by the stopped-flow technique in 25 % aqueous ethanol to enhance solubility of the esters. The disappearance of MnO_4^- was followed at 540 nm. The kinetic curves were displayed on a Tektronix 564 storage oscilloscope and photographed with a Polaroid camera. A 10-fold excess of pyrophosphate was used to prevent manganese(III) from disproportionation, because the appearance of manganese(II) during the kinetic runs would lead to competition by the Guyard reaction and thus distort the results. The search for short-lived intermediates was performed by the stopped-flow technique, as described earlier in detail /4/. The same method was applied for recording the spectrum of the transient species observed. The glyoxylic acid formed was detected by the 2,7-dihydroxynaphthalene test /5/. Diethyl maleate and fumarate were Fluka chemicals.

RESULTS

A typical stopped-flow trace corresponding to the reaction of MnO_4^- with the esters is shown in Fig. 1 (trace 2). Upon the addition of a 10-fold excess of pyrophosphate, the transmission minimum disappears and trace 1 is observed. This behaviour is readily interpreted in terms of the formation and decay of manganese(III) and soluble manganese(IV) as short-lived intermediates. At the acidity used, manganese(III) is known to disproportionate rapidly into manganese (II) and manganese(IV), the latter being precipitated as MnO_2 within short times. However, the pyrophosphatomanganese(III) complex does not undergo disproportionation. Accordingly, the fate of manganese during the oxidation of DEM and DEF can be described by the sequence

$$MnO_4^- \longrightarrow Mn(III) \qquad (1)$$

$$Mn(III) \longrightarrow 1/2\ Mn(IV) + 1/2\ Mn(II) \qquad (2)$$

$$Mn(IV) + \text{organic intermediates} \longrightarrow Mn(II) + \text{products} \qquad (3)$$

The transmission maximum in Fig. 1 (trace 2) corresponds to manganese(III), which is subsequently converted to soluble manganese(IV) represented by the

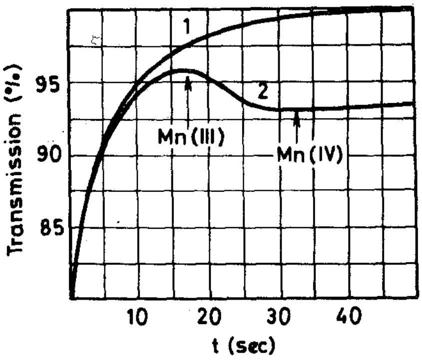

Fig. 1. Stopped-flow traces (540 nm) for the permanganate oxidation of DEM in the presence (1) and absence (2) of pyrophosphate.
$[MnO_4^-]_0 = 5 \times 10^{-4}M$, $[DEM] = 1 \times 10^{-3}M$, 0.1 M $HClO_4$,
T = 25°C, 25 vol.% aqueous EtOH.
For curve 1, [pyrophosphate] = 10 $[MnO_4^-]_0$

transmission minimum on the same trace. Manganese(IV) is finally consumed in a slower process according to eq. (3), only its initial stage being shown in Fig. 1. In the presence of pyrophosphate, reactions (2) and (3) are suppressed, therefore, only reaction (1) occurs as shown by trace 1 in Fig. 1. Clearly, the second intermediate is formed from manganese(III) as its precursor, consequently it should be a soluble form of manganese(IV), possibly H_2MnO_3. This is supported also by the facts that

(i) The spectrum of the intermediate constructed from the transmission minima at various wavelengths (Fig. 2) agrees well with the spectrum of soluble manganese(IV) described earlier,

(ii) The spectrum of the product solution containing pyrophosphate is identical with the known spectrum of the pyrophosphatomanganese(III) complex.

The product solution containing pyrophosphate shows a strongly positive test for glyoxylic acid. The spectrophotometric titration of DEM and DEF with permanganate in the presence of pyrophosphate reveals that the reactants are consumed in a 1:1 mole ratio.

According to these findings, the first reaction in the overall process can be given for both esters as

$$\text{EtOOC-CH=CH-COOEt} + MnO_4^- + 4\,H^+ + 3\,\text{pyr}^{2-} \longrightarrow$$

$$\longrightarrow 2\,\text{CHO-CO}_2\text{H} + \text{Mn(pyr)}_3^{3-} + 2\,\text{EtOH} \qquad (4)$$

As concerns manganese, this reaction is the same as that given by eq. (1).

The kinetic investigations reported in this paper refer to reaction (4), i. e. all subsequent transformations of manganese(III) at the time scale of the experiments were prevented by pyrophosphate acting as scavenger.

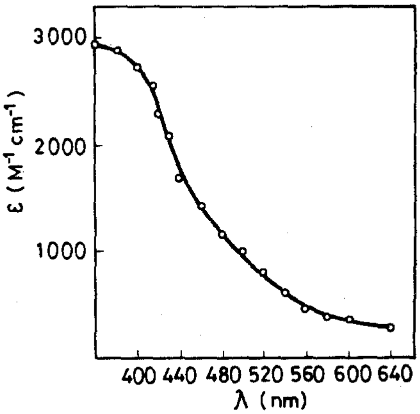

Fig. 2. Spectrum of the short-lived manganese(IV) intermediate

The rate of disappearance of MnO_4^- was found to be first order with respect to both permanganate and the substrate

$$-\frac{d\ MnO_4^-}{dt} = k\,[MnO_4^-]\ [S] \qquad (5)$$

where S stands for either DEM or DEF. The validity of rate equation (5) has been demonstrated under a variety of conditions using its integrated forms, i. e. eqs. (6) and (7). At equal reactant concentrations, i. e. $\underline{m} = [S]_0/[MnO_4^-]_0 = 1$, if the consumption ratio $\underline{r} = \Delta[MnO_4^-]/\Delta[S] = 1$, eq. (5) integrates to

$$\frac{1}{[MnO_4^-]} \quad \frac{1}{[MnO_4^-]_0} = kt \qquad (6)$$

On the other hand, if m > 1, the result of integration is

$$\lg \frac{B + [MnO_4^-]}{[MnO_4^-]} = \frac{B\,k\,t}{2.303\,r} + \lg \frac{[MnO_4^-]}{B + [MnO_4^-]_o} \qquad (7)$$

where $B = (mr - 1)[MnO_4^-]_o$. If the stopped-flow traces at 540 nm were plotted according to eqs. (6) or (7), assuming that r = 1, excellent straight lines were obtained throughout the concentration range studied for both DEM and DEF. The values of rate constant k under various conditions are listed in Tables 1 and 2.

The activation parameters determined in the temperature range of 10-40°C are collected in Table 3.

Table 1

Second-order rate constants for the oxidation of DEM*
(25 % EtOH in water, T = 25°C, 0.1 M $HClO_4$, 10-fold excess of pyrophosphate)

[DEM] x 10^3 (mol/l)	$[MnO_4^-]$ x 10^3 (mol/l)	k (mol/l sec)
0.50	0.25	304
1.00	0.25	316
0.50	0.50	326
1.00	0.50	270
1.50	0.50	230
2.00	0.50	242
1.00	0.50	279 **
	Average:	280 ± 28

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* Each value is the average result of 3 runs

** At pH = 2.9

Table 2

Second-order rate constants for the oxidation of DEF[*]
(25 % EtOH in water, T = 25 °C, 0.1 M $HClO_4$, 10-fold excess of pyrophosphate)

$[DEF] \times 10^3$ (mol/l)	$[MnO_4^-] \times 10^3$ (mol/l)	k (mol/l sec)
0.50	0.25	13200
0.75	0.50	13300
1.00	0.25	12700
0.50	0.50	15000
1.00	0.50	10700
1.50	0.50	14300
2.00	0.50	12800
1.00	0.50	14100[**]
	Average:	13300 ± 900

[*] Each value is the average result of 3 runs

[**] pH = 2.8

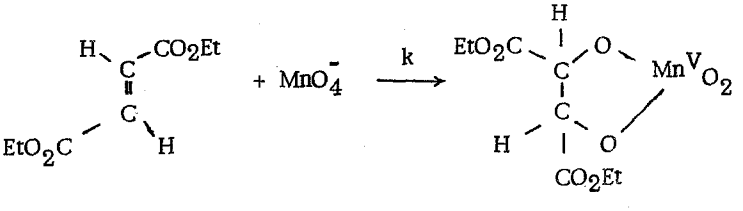
Table 3

Activation parameters for the oxidation of DEM and DEF

	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/mol K)
DEM	12	-147
DEF	11	-133

DISCUSSION

The observed kinetic behaviour is consistent with a reaction mechanism involving a bimolecular rate-determining step in which MnO_4^- attacks the double bond:



(8)

(I)

This is followed by the fast decomposition of the cyclic hypomanganate ester I

$$\mathrm{I} \xrightarrow[+4H^+,\ +3pyr^{2-}]{\text{fast}} Mn(pyr)_3^{3-} + 2\ CHO\text{-}CO_2H + 2\ EtOH \qquad (9)$$

The above mechanism is analogous to that proposed previously for maleic and fumaric acid, their methyl-substituted derivatives and the corresponding mono- and dianions /2, 3/. The rate constants obtained clearly show that the higher reactivity of the trans isomer is retained also if no hydrogen-bonding is possible in the cis species, consequently, this effect is purely steric in nature as suggested earlier. It is of interest that while fumaric acid is 15 times more reactive than maleic acid /2/, the ratio of the rate constants $\underline{k}$ is nearly 50 for the diethyl esters, the value of $\underline{k}$ being about the same for fumaric acid and DEF. The increased ratio is a result of a 3-fold drop in reactivity upon going from maleic acid to DEM. Apparently, in DEM the bulky CO_2Et substituents force one another out of the plane and this poses an obstacle to the approach of MnO_4^- from the most favourable perpendicular direction, whereas in maleic acid this is less important as hydrogen-bonding holds the substituents in a planar arrangement. The lack of significant differences between the reactivities of fumaric acid and DEF supports this concept.

Similarly to the substrates studied previously, the permanganate oxidation of DEM and DEF requires practically no energy of activation. The large negative entropies of activation point to a high degree of ordering in the transition state, which is consistent with the formation of a short-lived, cyclic intermediate containing manganese(V). This seems to be a general feature of the permanganate oxidation of olefinic and acetylenic substrates /4, 6-10/.

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