

# Oxidation of Aliphatic Aldehydes in Dichloromethane by Solubilized Permanganate†

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The oxidation kinetics of C<sub>4</sub>–C<sub>10</sub> aliphatic aldehydes by quaternary ammonium permanganates, R<sub>4</sub>NMnO<sub>4</sub> (R = ethyl, butyl and octyl), in dichloromethane is reported with special regard to the colloidal manganese(IV) intermediate.

The oxidations of various substrates with permanganate have been extensively studied in the past.<sup>1</sup> The reactions were carried out in aqueous as well as in organic solvents. In order to facilitate the oxidations in various solvents with low polarity the permanganate ion is combined with organophilic cations, mostly quaternary ammonium and phosphonium ions. The resulting salts are well soluble in dichloromethane, a solvent which has been used previously used.<sup>2–4</sup> The interpretation of earlier experiments dealing with the permanganate oxidations assume the existence of the manganate(V) diester as an intermediate.<sup>5</sup> However, it has been shown that the product was actually a form of manganese(IV).<sup>6</sup> Later Freeman and Kappos proved that this product had a colloidal nature.<sup>7</sup> The experimental results described in earlier papers demonstrate the existence of colloidal manganese(IV) as an intermediate of the permanganate oxidations of various substrates in water as well as in organic solvents.<sup>8</sup>

In the present work we centred our attention on this intermediate formed in the course of the oxidation of aldehydes in dichloromethane.

## Results and Discussion

The absorption spectrum of a reaction system shows typical dependence on time. The curves pass through an isosbestic point at 485 nm. The absorbance at shorter wavelengths increases while the absorption peak of permanganate at 526 nm diminishes. In the course of the reactions the absorbance changed from its initial value, being in most cases 0.9, to its final value of 0.2. At the end of the reaction, when the absorption bands of the permanganate disappear, a brown-yellow solution remains. The oxidation state of manganese in this solution found iodometrically using a method described was 4.<sup>9</sup> It is evident that this product is the colloidal MnO<sub>2</sub> intermediate which absorbs only a little at 526 nm and considerably at shorter wavelengths.<sup>8</sup> The rate constants *k* of permanganate reduction have been evaluated from the change of the absorbance. The Guggenheim equation for first-order reactions was found to be valid:

$$\ln \Delta A = -kt + \text{constant} \quad (1)$$

where  $\Delta A$  is the absorbance difference at times *t* and *t'*, where *t* – *t'* is a constant time interval greater than the reaction half-life. The number of data points taken per kinetic run was 30–40. The rate constants of the oxidation of investigated aldehydes by tetraethyl, tetrabutyl and tetraoctyl ammonium permanganate at 25 °C in dichloromethane are given in Table 1. The reported values of the rate constants are the means of 3–5 independent measurements.

**Table 1** Rate constants for the oxidation of aldehydes by quaternary ammonium permanganates in dichloromethane at 298.15 K; [aldehyde] = 1.5 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [permanganate] = 1.5 × 10<sup>-4</sup> mol dm<sup>-3</sup>

Aldehyde	10 <sup>4</sup> k/s <sup>-1</sup>		
	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NMnO <sub>4</sub>	(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NMnO <sub>4</sub>	(C <sub>8</sub> H <sub>17</sub> ) <sub>4</sub> NMnO <sub>4</sub>
Butanal	9.59 ± 0.39	9.62 ± 0.14	9.78 ± 0.36
Pentanal	15.4 ± 0.83	11.4 ± 0.24	11.0 ± 0.52
Hexanal	20.5 ± 1.11	8.89 ± 0.46	10.3 ± 0.20
Heptanal	14.9 ± 0.73	9.19 ± 0.48	6.83 ± 0.34
Octanal	11.6 ± 0.51	7.37 ± 0.36	7.51 ± 0.27
Nonanal	8.71 ± 0.38	5.74 ± 0.10	6.48 ± 0.41
Decanal	14.6 ± 1.00	7.50 ± 0.47	5.44 ± 0.11

Table 1 shows that the rate of the oxidation of aldehydes depends on the length of the alkyl chain of the measured aldehyde as well as on the tetraalkylammonium permanganate used. The highest values of the rate constants belong to the oxidation of hexanal by tetraethylammonium permanganate, and to the oxidation of pentanal also by the other two oxidants used.

The absorption spectrum recorded at the end of the reactions (after complete permanganate consumption) showed a uniform increase of the absorbance with decreasing wavelength, which is consistent with the Rayleigh law for light scattering.<sup>10</sup> According to the relationship:

$$A = C\lambda^{-4} \quad (2)$$

(where *C* is a constant including the polarizability, mass and the concentration of the colloidal particles) the plot of log *A* vs. log  $\lambda$  should be linear. The experimental plots gave straight lines with the slopes approaching the theoretical value. Dynamic light scattering measurements have shown that colloidal particles were present from the beginning of the reactions, their dimensions being around 250 nm and having differing polydispersity, which was largest for the reaction mixture with tetraethylammonium permanganate. The stability of the systems was directly proportional to the alkyl chain length of the tetraalkylammonium permanganate used.

Additional evidence for the colloidal nature of the brown-yellow intermediate of the permanganate reduction can be obtained from simultaneous monitoring of the reacting solution at two wavelengths, 418 and 526 nm. Permanganate exhibits its highest absorbance peak at 526 nm, whereas it is almost transparent at 418 nm. As a result it has been shown that the relationship (3) is valid:<sup>7,11,12</sup>

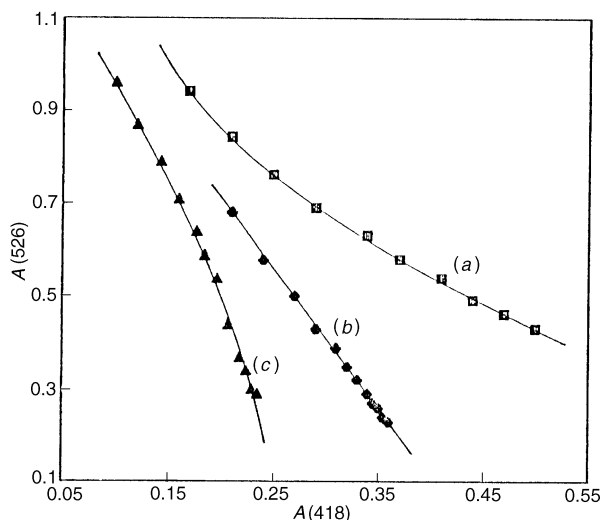
$$A(526) = \varepsilon_R^{526} p c_0 - [(\varepsilon_R^{526} - \varepsilon_P^{526})/\varepsilon_P^{418}] A(418) \quad (3)$$

where *p* is the optical pathlength, *c*<sub>0</sub> is the initial permanganate concentration,  $\varepsilon_R$  and  $\varepsilon_P$  are the extinction coefficients of the reactant (permanganate) and the product (colloidal MnO<sub>2</sub>) respectively.

The *A*(526) vs. *A*(418) plots based on eqn. (3) are very useful in kinetic experiments when colloidal MnO<sub>2</sub> is

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**Fig. 1**  $A(526)$  vs.  $A(418)$  plots according to eqn. (3) for the oxidation of (a) butanal by tetraoctylammonium permanganate; (b) heptanal by tetraethylammonium permanganate; (c) nonanal by tetraethylammonium permanganate, temperature 25 °C

(i) behaving as a stable species, (ii) being reduced to  $Mn^{II}$ , (iii) coagulating (*cf.* ref. 8). In the case (i), eqn. (3) leads to a linear relationship between  $A(526)$  and  $A(418)$ , in the case (ii) it provides a plot showing concave-downward curvature and in the case (iii) the  $A(526)$  vs.  $A(418)$  relationship leads to a plot showing a concave-upward curvature.

The stability and/or coagulation of the colloidal intermediate formed in the oxidation of aldehydes depends mainly on the quaternary ammonium permanganate used. The plots of the data for the reactions with tetraoctylammonium permanganate according to eqn. (3) show concave-upward curvature indicating that the coagulation of  $MnO_2$  takes place (Fig. 1a). The same plots are shown for the oxidation of  $C_6$ – $C_{10}$  aldehydes with tetrabutylammonium permanganate. However, the plot for the oxidation of  $C_9$  aldehyde by tetraethylammonium permanganate shows concave-downward curvature corresponding to the reduction of  $Mn^{IV}$  to lower oxidation states (Fig. 1c). A linear dependence according to eqn. (3) was observed only for the oxidation of heptaldehyde by tetraethylammonium permanganate (Fig. 1b).

## Experimental

Aldehydes (Merck, Darmstadt) were checked by elemental analysis. The oxidation agents were prepared by precipitation of aqueous solutions of the corresponding quaternary ammonium bromide with a saturated solution of potassium permanganate. The precipitates were washed with cold water and then dried for several hours in a desiccator. A weighed amount of the salt was dissolved in dichloromethane and homogenized by vigorous stirring. Then the appropriate volume of the aldehyde was added and the reaction mixture was immediately transferred into a thermostated cell of the spectrophotometer (SPECORD UV-VIS or SPEKOL 11, both C. Zeiss, Jena). The reactions were monitored by measuring the absorbance at 526 nm, where permanganate exhibits a maximum which diminishes in the whole course of the reaction. Dynamic light scattering measurements of colloidal  $MnO_2$  particles were carried out with Brookhaven Instruments light scattering goniometer BI-200 SM equipped with an argon ion laser operating at 514 nm. The intensity autocorrelation function at 90° was determined using a BI-2030AT 136 channel correlator. The experimental data were treated by the cumulant method.<sup>13</sup> All solutions were purified prior to measurements by filtration using dense glass filters.

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