

INSTABILITY OF SOLUTIONS OF QUATERNARY AMMONIUM PERMANGANATES IN DICHLOROMETHANE

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The paper deals with instability of solutions of quaternary ammonium permanganates, $QMnO_4$ ($Q =$ tetraethyl-, tetra-1-propyl-, tetra-1-butyl-, tetra-1-pentyl-, tetra-1-octyl-, and cetyltrimethylammonium), in dichloromethane and presents the rate constants and activation parameters of the reduction of permanganate. Attention was paid to the properties of colloidal Mn(IV) intermediate. The stability of the solutions depends markedly on the quaternary ammonium salt used.

Key words: Solubilized permanganate; Mn(IV) colloidal intermediate; Light scattering.

Oxidations of various reductants with permanganate were extensively studied in the past¹. In order to facilitate the oxidation-reduction reactions in various organic solvents, the permanganate ion is combined with organophilic cations, mostly quaternary ammonium and phosphonium ions². Such solutions of solubilized permanganate are unstable due to the reactivity of the permanganate which attacks practically all organic solvents³. The reduction product of permanganate was mistakenly described as a cyclic manganese(V) diester^{1,4}. However, Simándy and Jáky pointed out that the product actually was a form of manganese(IV) (ref.⁵). Later some evidence was given that this form is of colloidal nature^{6,7}. An exhaustive study on the occurrence and properties of the colloidal form of manganese dioxide in both aqueous and organic media has been reported recently⁸. Dichloromethane is frequently used as a solvent in the investigation of oxidation reactions with solubilized permanganate. In the solvent, permanganate is slowly reduced to yield first a yellow transparent solution and finally a brown precipitate of MnO_2 .

The aim of the present work was to investigate the reduction of various quaternary ammonium permanganates in dichloromethane. Attention was focused on the colloidal intermediate of Mn(IV) formed in the course of the reaction studied.

EXPERIMENTAL

All the chemicals used were of reagent grade (Merck). The quaternary ammonium permanganates were obtained by precipitating aqueous solutions of corresponding quaternary ammonium bromides

with the saturated solution of potassium permanganate as described in ref.⁹. The solutions of the salts in dichloromethane were checked spectrophotometrically by measuring the absorbance at 526 nm where the permanganate band exhibits the molar absorption coefficient of $2\,630\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ (see ref.¹⁰), this value being independent of the cation used. The absorption spectra were measured with the use of a Specord UV-VIS spectrophotometer, and the reactions were carried out in the measuring cell of a Spekol 11 spectrophotometer (both Zeiss, Jena) equipped with a thermostatted cell holder. In a typical experiment, a 50 ml volumetric flask containing dichloromethane was kept in a thermostat at the required temperature ($\pm 0.1\text{ }^\circ\text{C}$) for about 10 min. Then quaternary ammonium permanganate was added and the solution was stirred by means of ultrasound for about 10 s. An appropriate amount of the solution was immediately transferred into a thermostated cell of the spectrophotometer.

RESULTS AND DISCUSSION

A typical time dependence of absorption spectrum of the reacting system is shown in Fig. 1. The absorption peaks of permanganate diminish, whereas the absorbance increases at shorter wavelengths. The spectra exhibit an isosbestic point at 485 nm. The oxidation state of manganese in the yellow solution (in the absence of permanganate absorption bands) found iodometrically according to ref.¹¹ was 4.1 ± 0.3 . The rate constant k of permanganate reduction can be evaluated from the spectral changes measured. The Guggenheim equation (1) for first-order reactions was found to be valid.

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

ΔA is the absorbance difference at time t and t' where $t - t'$ is a constant time interval greater than the reaction half-life. The temperature dependence of the rate constants in the temperature interval from 20 to $37\text{ }^\circ\text{C}$ was used for calculation of the activation

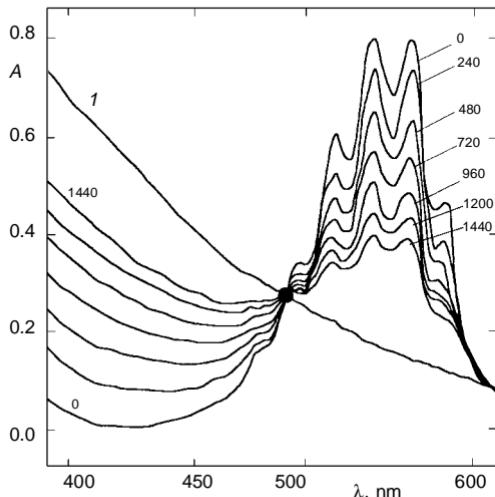


FIG. 1
Absorption spectrum of solubilized permanganate in dichloromethane; $1.5 \cdot 10^{-4}\text{ mol dm}^{-3}$ $(\text{C}_8\text{H}_{17})_4\text{NMnO}_4$, 2 cm cell path, the numbers at curves denote reaction time in seconds, curve 1 75 h from the start of reaction, temperature $25\text{ }^\circ\text{C}$

enthalpies and entropies which are given in Table I along with the rate constants at 25 °C. The rate constant values presented are mean values of 3–5 measurements. The values given show that the rates of reaction investigated depend on the length of alkyl chain in the quaternary ammonium cation. Like with some other physico-chemical properties of quaternary ammonium salts¹², the dependence shown is not monotonous. Negative values of the activation entropies indicate that the activated complex is more highly organized than the initial state. The formation of a complex with increased coordination number of manganese, theoretically calculated¹³, agrees with experiment.

The absorption spectrum recorded at the end of the reaction, *i.e.* after complete consumption of permanganate, showed a uniform absorbance increase with decreasing wavelength (Fig. 1, curve 1), which is consistent with the Rayleigh law for light scattering. The relationship¹⁴ between absorbance A in a system with small colloidal particles and the wavelength λ :

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

where C is a constant including the polarizability, mass and concentration of the colloidal particles, means that the plot of $\log A$ vs $\log \lambda$ should be linear. All the experimental plots obtained gave straight lines with correlation coefficients of 0.999 in most cases, however, their slopes were somewhat lower than the theoretical value of -4 in all the freshly prepared solutions. With progression of time after completion of the reduction of permanganate, the $\log A$ vs $\log \lambda$ plots were linear with slopes approaching the theoretical value (Table II). Similar behaviour was observed also in other oxidation-reduction systems with permanganate, which is interpreted by further reduction of the colloidal manganese(IV) species in dichloromethane solutions⁸. The presence of the colloidal particles in the solutions of permanganate with solubilizing higher aliphatic alcohols has recently been proved¹⁵ by the dynamic light-scattering measurements. The

TABLE I

Rate constants at 25 °C, activation enthalpies ΔH^\ddagger , and activation entropies ΔS^\ddagger for reduction of quaternary ammonium permanganates (R_4N)MnO₄ in dichloromethane

R	$k \cdot 10^3, \text{min}^{-1}$	$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$\Delta S^\ddagger, \text{J K}^{-1} \text{mol}^{-1}$
Ethyl	15.0 ± 0.2	50.7 ± 2.0	-107 ± 7
1-Propyl	7.22 ± 0.13	44.1 ± 1.0	-139 ± 4
1-Butyl	11.7 ± 0.4	58.8 ± 4.4	-29 ± 14
1-Pentyl	6.40 ± 0.19	39.3 ± 1.3	-156 ± 5
1-Octyl	9.82 ± 0.30	60.8 ± 1.8	-85 ± 6
Cetyltrimethyl	14.2 ± 0.1	41.7 ± 1.9	-141 ± 7

colloidal manganese(IV) produced during the reduction of permanganate solubilized in dichloromethane was investigated by the same method¹⁶.

Additional evidence for the colloidal nature of the brown-yellow intermediate of the permanganate reduction was obtained from simultaneous monitoring of the absorbances of quaternary ammonium permanganate solutions with the initial concentrations c_0 at 418 and 526 nm. The two absorbances, A_{418} at 418 nm and A_{526} at 526 nm, are interrelated as follows^{6,7}:

$$A_{526} = c_0 \epsilon_{526}^{(1)} + [(\epsilon_{526}^{(1)} - \epsilon_{526}^{(2)})/\epsilon_{418}^{(2)}]A_{418}, \quad (3)$$

where $\epsilon^{(1)}$ and $\epsilon^{(2)}$ are the molar absorption coefficients of permanganate ion and manganese(IV) dioxide, respectively, at the wavelengths indicated. According to Eq. (3) a linear dependence should exist between A_{526} and A_{418} . The linear dependence was observed in a reaction system containing tetraoctylammonium permanganate (Fig. 2,

TABLE II

Slopes of the straight lines according to Eq. (2) for the reaction intermediate of reduction of permanganate at various times t after completion of the first reaction step; temperature 25 °C

t , h	Slope
90	-4.54 ± 0.13
160	-4.43 ± 0.06
200	-4.20 ± 0.07
240	-4.12 ± 0.05
300	-3.99 ± 0.08

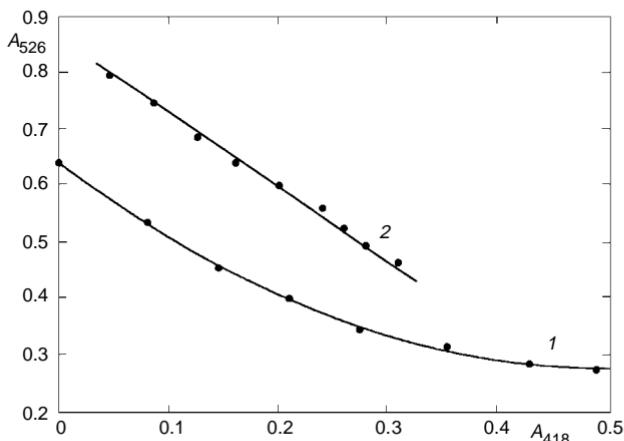


FIG. 2
 A_{418} vs A_{526} plot according to Eq. (2);
 1 $1.2 \cdot 10^{-4}$ mol dm⁻³ $(C_2H_5)_4NMnO_4$;
 2 $1.6 \cdot 10^{-4}$ mol dm⁻³ $(C_8H_{17})_4NMnO_4$;
 2 cm cell path; temperature 25 °C

curve 1). On the other hand, when tetraethylammonium permanganate was used as the oxidant, a concave curve was obtained instead of a straight line (Fig. 2, curve 2). Such behaviour of the A_{418} vs A_{526} plot is generally interpreted in terms of the stability and/or coagulation of the colloidal MnO_2 intermediate^{7,8}. Its instability in our systems is also demonstrated in Fig. 3 showing the successive scans of the spectrum of the solution of tetraethylammonium permanganate. It can be seen that the isosbestic point at 485 nm is less sharply defined than that in the solution of tetraoctylammonium permanganate where the rate of permanganate reduction was high compared to that of flocculation of the colloid. The difference observed between tetraethyl- and tetraoctylammonium permanganates is evidently due to the different abilities of these species to be adsorbed on the surface of the colloidal MnO_2 particles, the adsorption being responsible for the stability of the colloid. The presence of MnO_2 precipitate observed in the solutions of tetraethyl- and tetraoctylammonium permanganates is consistent with this interpretation. In the first case the precipitation of manganese dioxide occurs within a day, whereas the solutions with tetraoctylammonium permanganate are stable and no precipitation was observed at room temperature even after several weeks.

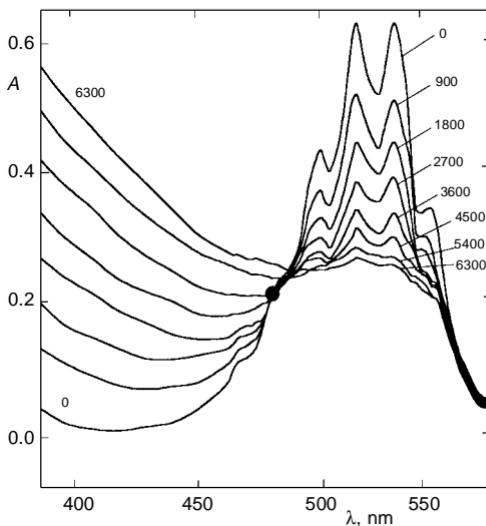


FIG. 3

Absorption spectrum of solubilized permanganate in dichloromethane; $1.2 \cdot 10^{-4}$ mol dm^{-3} $(\text{C}_2\text{H}_5)_4\text{NMnO}_4$, 2 cm cell path, the numbers at curves denote reaction time in seconds, temperature 25 °C

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REFERENCES

1. Steward R.: *Oxidations in Organic Chemistry* (K. B. Wiberg, Ed.), Part A, p. 1. Academic Press, New York 1965.
2. Karaman H., Barton R. J., Robertson B. E., Lee D. G.: *J. Org. Chem.* **49**, 4509 (1984).

3. Starks C. M., Liotta C.: *Phase Transfer Catalysis*, p. 298. Academic Press, New York 1978.
4. Lee D. G., Brownridge J. R.: *J. Am. Chem. Soc.* **96**, 5517 (1974).
5. Simandi L. I., Jaky M.: *J. Am. Chem. Soc.* **98**, 1995 (1976).
6. Freeman F., Kappos J. C.: *J. Am. Chem. Soc.* **107**, 6628 (1985).
7. Perez-Benito J. F., Lee D. G.: *Can. J. Chem.* **63**, 3545 (1985).
8. Perez-Benito J. F., Arias C.: *J. Colloid Interface Sci.* **152**, 70 (1992).
9. Sumichrast R., Holba V.: *Collect. Czech. Chem. Commun.* **58**, 1777 (1993).
10. Perez-Benito J. F., Lee D. G.: *J. Org. Chem.* **52**, 3239 (1987).
11. Perez-Benito J. F., Brillas E., Arias C.: *Can. J. Chem.* **68**, 79 (1990).
12. Wen W. Y.: *Water and Aqueous Solutions* (R. A. Horne, Ed.), p. 613. Wiley-Interscience, New York 1972.
13. Rappe A. G., Goddard III W. A.: *J. Am. Chem. Soc.* **104**, 3287 (1982).
14. Barrow G. M.: *Physical Chemistry*, p. 803. McGraw-Hill, New York 1966.
15. Sumichrast R., Lath D., Holba V.: *J. Chem. Res.* **1994**, 236.
16. Lath D.: Unpublished results.