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# Oxidation of Higher Alcanols by Tetra-1-butylammonium Permanganate

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**Summary.** Oxidations of hexan-1-ol, hexan-2-ol, hexan-3-ol, heptan-1-ol, heptan-2-ol, octan-1-ol, and octan-2-ol with tetra-1-butylammonium permanganate, dissolved in the same alcohols, proceed partly autocatalytically. The rate constants of both catalytic and non-catalytic reactions have been evaluated. Colloidal manganese dioxide, one of the reaction products, has been identified as the catalyst.

**Keywords.** Autocatalysis; Kinetic parameters; Colloidal $MnO_2$.

### Oxidation höherer Alkanole mit Tetra-1-butylammoniumpermanganat

**Zusammenfassung.** Die Oxidation von 1-Hexanol, 2-Hexanol, 3-Hexanol, 1-Heptanol, 2-Heptanol, 1-Octanol und 2-Octanol durch Tetra-1-butylammoniumpermanganat, gelöst in diesen Alkoholen, verläuft teilweise autokatalytisch. Die Geschwindigkeitskonstanten von katalytischen und nichtkatalytischen Teilreaktionen wurden bestimmt. Das kolloidale Mangandioxid, eines der Reaktionsprodukte, konnte als Katalysator identifiziert werden.

## Introduction

Quaternary ammonium permanganates have been used in the past as oxidants of organic substrates in nonaqueous solvents, mostly methylene chloride [1–4], or in two-phase systems under the conditions of ion-pair extraction techniques [5]. However, it is difficult to find a solvent that is not attacked by permanganate, and appropriate corrections on the rate of oxidation of the solvent are needed. To avoid these difficulties, we used the same method as in our previous investigations [6, 7], *i.e.* we dissolved the permanganate salt directly in the oxidized alcohols before starting the reactions.

It is well known that many permanganate reactions in aqueous as well as in nonaqueous media are at least partly autocatalytic. It is supposed that two of the reaction products – the colloidal $MnO_2$ or the soluble Mn(II)-can act as catalysts [3]. In the present work we studied the oxidations of higher alcanols by solubilized permanganate with special regard to the autocatalytic character of the investigated reactions.

## Results and Discussion

Gas chromatographic analyses showed that the oxidation of hexan-2-ol, hexan-3-ol, heptan-2-ol, and octan-2-ol yields hexan-2-one, hexan-3-one, heptan-2-one, and octan-2-one, respectively; the oxidation products of hexan-1-ol, heptan-1-ol, and octan-1-ol are the corresponding acids.

A typical dependence of the absorption spectrum of the reaction system on time is shown in Fig. 1. The absorption peaks of permanganate ions diminish, whereas at shorter wavelengths the absorbance increases. The sequential scans depicted in Fig. 1 exhibit an isosbestic point at 486 nm. However, in some cases the isosbestic point disappears near the end of the reaction (oxidation of hexan-1-ol, heptan-1-ol, octan-1-ol). The absorbance recorded after the completion of the reactions increases uniformly with decreasing wavelength (curve *a*). This dependence obeys *Rayleigh*'s law for the scattering of light (Eqn. 1) [9].

$$\log A = \log K' - 4 \log \lambda \qquad 1$$

The absorbance $A$ depends linearly on the wavelength $\lambda$ and thus demonstrates the occurrence of a colloid in the investigated systems. The colloidal intermediate is not equally stable in all examined alcohols. It is most labile in branched alcohols (heptan-3-ol, heptan-4-ol, and octan-3-ol). Oxidation of these compounds cannot be followed spectrophotometrically; the formation of an insoluble precipitate from the beginning of the reaction makes the measurements impossible. On the other hand, the oxidation of hexan-2-ol, hexan-3-ol, heptan-2-ol, and octan-2-ol could be followed for at least two half-times of the reactions. The insoluble precipitate appeared in these systems only after the completion of the reactions. The colloidal intermediate as one of the reaction products in the non-branched alcohols (hexan-1-ol, heptan-1-ol, and octan-1-ol) was stable for several weeks in dry solutions. The brown insoluble precipitate was excluded from these solutions only after vigorous stirring with water. Iodometric determination indicates that the apparent oxidation state of manganese after the completion of reactions is

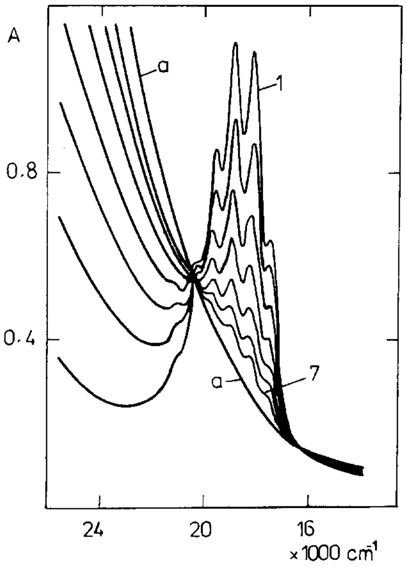

**Fig. 1.** Absorption spectrum of permanganate ion ($4.5 \times 10^{-4}$ mol·dm$^{-3}$ $(C_4H_9)_4NMnO_4$ in heptan-2-ol, 1 cm, time interval between curves 1–7: 240 s; curve *a*: 33 min after the beginning of the reaction; temperature 25 °C)

3.20 ± 0.05. It has been shown recently that in aqueous solutions of manganese oxides, Mn(III) in the form of MnO(OH) is formed during the reduction of colloidal $MnO_2$, and that this species is also capable to form stable suspensions [10]. With regard to the results of the iodometric measurements it was necessary to ascertain whether Mn(III) is produced in the course of the reduction of permanganate or not. The X-ray diffraction measurements showed that the isolated precipitate is practically amorphous. The same was found for $MnO_2$ in Ref. [10]. The comparison of the infrared spectra of $\gamma$-MnO(OH), synthesized $MnO_2$, and those of the precipitate isolated from the reaction mixtures showed that one of the products of the reduction of permanganate is $MnO_2$. The results of measurements of the oxidation state of manganese at the end of the reactions indicate that the product of the reduction of permanganate is most probably a mixture of colloidal $MnO_2$ and of soluble Mn(II), similar to the results of some oxidations with permanganate in methylene chloride solution [3]. Both $MnO_2$ and Mn(III) can act as catalysts and therefore create the autocatalytic character of the investigated reactions. This feature of the studied reactions is evidenced by the dependence of the reaction rate on time which exhibits a typical bell-shaped profile (Fig. 2, curve 1). The role of $MnO_2$ as a catalyst has been confirmed by the experiment in which the fresh permanganate was added to the solution at the end of the reaction. The initial rate increased and the reaction rate *vs.* time plot lost the bell-shaped form (Fig. 2, curve 2). The kinetic parameters of the studied reactions were evaluated from the measurements of absorbance changes with time at 526 nm. For the calculation of concentrations of permanganate, an extinction coefficient of 2530 $dm^3\,mol^{-1}\cdot cm^{-1}$ was used. With respect to a considerable excess of one of the reactants, the rate law for the total process, *i.e.* the non-catalytic and catalytic portion of the reaction, can be written as

$$-\mathrm{d}c/\mathrm{d}t = k_1 c + k_2 c\cdot(c_0 - c) \tag{2}$$

where $c$ and $c_0$ are the permanganate concentrations at time $t$ and at the beginning of the reaction and $k_1$ and $k_2$ are the rate constants corresponding to the

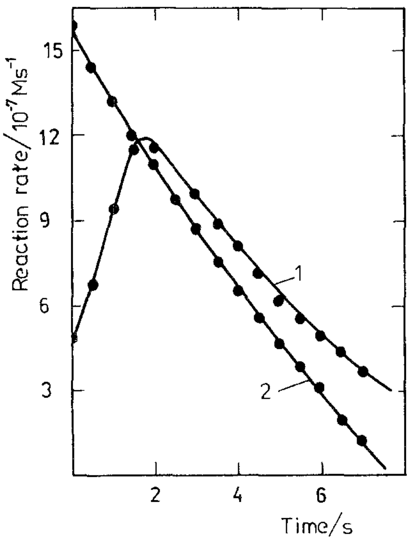

**Fig. 2.** Reaction rate *vs.* time plot for the oxidation of heptan-1-ol with $4.5\times10^{-4}$ mol·dm$^{-3}$ tetra-1-butylammonium permanganate at 30 °C; 1: in the absence of manganese products (beginning of the reaction); 2: in the presence of products

non-catalytic and catalytic mechanisms, respectively. Integration of Eqn. 2 gives the integral rate law (Eqn. 3, see Ref. [11]).

$$\ln[(k_1 + k_2c_0 - k_2c)/c] = \ln(k_1/c_0) + (k_1 + k_2c_0)t \qquad 3$$

The rate constants $k_1$ and $k_2$ have been evaluated by a computerized iterative procedure described in Ref. [7] and are reported in Table 1. The activation parameters of the studied reactions are presented in Table 2. It follows from Table 1 that the rate constants $k_1$ for the non-branched alcanols are substantially larger than those for the branched isomers. The data for $k_2$ show a similar but less pronounced tendency. The fact that the activation enthalpy, evaluated from the temperature dependence of $k_2$, is larger than the corresponding quantity for the non-catalyzed portions of the reactions indicates that from the temperature dependence of both $k_1$ and $k_2$ only apparent values of $\Delta H^{\#}$ can be obtained (Table 2). The large negative values of the activation entropy for the non-catalyzed path of all investigated alcanols is consistent with a reaction mechanism involving a highly organized activated complex. Some theoretical studies indicate that the reactions between permanganate and organic compounds involve the formation of complexes with an increased coordination number of manganese [12, 3]. This

**Table 1.** Rate constants for the non-catalyzed ($k_1$) and catalyzed ($k_2$) parts of the oxidation of higher alcanols with tetra-1-butylammonium permanganate at 25 °C

| Alcanol | $k_1$ ($s^{-1}$) | $k_2$ ($dm^3 \cdot mol^{-1} \cdot s^{-1}$) |
|---|---|---|
| Hexan-1-ol | $(7.94 \pm 0.20) \times 10^{-3}$ | $7.27 \pm 0.70$ |
| Hexan-2-ol | $(7.18 \pm 0.17) \times 10^{-4}$ | $2.31 \pm 0.12$ |
| Hexan-3-ol | $(8.16 \pm 0.67) \times 10^{-4}$ | $1.44 \pm 0.11$ |
| Heptan-1-ol | $(2.13 \pm 0.18) \times 10^{-3}$ | $8.42 \pm 0.45$ |
| Heptan-2-ol | $(6.23 \pm 0.23) \times 10^{-4}$ | $2.70 \pm 0.25$ |
| Octan-1-ol | $(1.50 \pm 0.14) \times 10^{-3}$ | $4.62 \pm 0.12$ |
| Octan-2-ol | $(1.73 \pm 0.05) \times 10^{-4}$ | $7.05 \pm 0.15$ |

**Table 2.** Thermodynamic activation parameters for non-catalyzed (index 1) and catalyzed (index 2) part of the oxidation of higher alcanols with tetra-1-butylammonium permanganate

| Alcanol | $\Delta H^{\#}_1$ | $\Delta H^{\#}_2$ | $\Delta S^{\#}_1$ | $\Delta S^{\#}_2$ |
|---|---|---|---|---|
| | ($kJ \cdot mol^{-1}$) | | ($J \cdot K^{-1} \cdot mol^{-1}$) | |
| Hexan-1-ol | $42.7 \pm 0.7$ | $96.9 \pm 5.3$ | $-142 \pm 3$ | $96 \pm 18$ |
| Hexan-2-ol | $38.3 \pm 2.6$ | $90.8 \pm 4.6$ | $-176 \pm 9$ | $66 \pm 15$ |
| Hexan-3-ol | $33.9 \pm 0.4$ | $86.9 \pm 2.7$ | $-190 \pm 2$ | $50 \pm 9$ |
| Heptan-1-ol | $25.5 \pm 0.4$ | $64.7 \pm 6$ | $-210 \pm 2$ | $-9 \pm 20$ |
| Heptan-2-ol | $33.3 \pm 1.2$ | $82.0 \pm 1.6$ | $-194 \pm 4$ | $38 \pm 5$ |
| Octan-1-ol | $21.0 \pm 1.1$ | $92.6 \pm 4.9$ | $-228 \pm 4$ | $77 \pm 11$ |
| Octan-2-ol | $36.6 \pm 3.7$ | $66.0 \pm 3.8$ | $-193 \pm 12$ | $8 \pm 13$ |

mechanism is in accordance with the observed negative activation entropies of the non-catalyzed portion of the reactions. The oxidation of primary alcohols can be described by equation 4, the oxidation of secondary alcohols by equation 5.

$$3RCH_2OH + 4(C_4H_9)_4NMnO_4 \rightarrow 3RCOOH + 4(C_4H_9)_4NOH + + 4MnO_2 + H_2O \qquad 4$$

$$3RCHOHCH_3 + 2(C_4H_9)_4NMnO_4 \rightarrow 3RCOCH_3 + 2(C_4H_9)_4NOH + + 2MnO_2 + 2H_2O \qquad 5$$

The larger amount of water liberated in the oxidation of secondary alcohols can account for less stability of the colloidal $MnO_2$ in these systems which is strongly affected by the presence of water.

For the catalyzed portion of the reaction, connected with $MnO_2$ developing in the course of the reduction of permanganate, the colloidal form of the intermediate seems to be most important [13]. According to Ref. [3], the permanganate is activated by adsorption on the surface of $MnO_2$ particles. The *Langmuir* isotherm has been used in the interpretation of the experiments [1, 3]. It follows from the isotherm that the reciprocal rate of the studied reaction should be linearly dependent on the reciprocal concentration of quaternary ammonium permanganate in solution. This linear dependence has indeed been observed in several investigations; this is in accordance with the proposed interpretation. The non-uniformity of colloidal particles as well as the dependence of their dimensions on time in the course of the reaction may considerably complicate the derivation of the corresponding rate equation. However, measurements of the scattering of light by colloidal $MnO_2$ seem to jusify the above mentioned mechanism [14]. The stability of colloidal $MnO_2$ which strongly depends on the nature of oxidized alcanols may also be connected with their different ability to adsorb on the surface of colloidal particles of manganese dioxide.

## Experimental

All used chemicals were of reagent grade. Alcohols (Merck, Darmstadt) were distilled prior to use. Tetra-1-butylammonium permanganate was prepared by precipitation from an aqueous solution of tetra-1-butylammonium bromide with a concentrated aqueous solution of potassium permanganate. The precipitate was washed with cold water and then dried for several hours under vacuum. Because of its instability, it was stored in the dark at low temperature and was used for a week at maximum. The measurement procedure was the same as described in Ref. [7]. The oxidation state of manganese at the end of the reaction was determined by means of an iodometric technique according to Ref. [3]. The oxidation products of alcohols were identified by gas chromatography. $\gamma$-MnO(OH) was synthesized according to Ref. [8]. Its infrared spectra (nujol mull) were recorded on a Specord M8 spectrophotometer (Zeiss, Jena). The powder diffraction patterns were registered on a Philips PW 1050 diffractometer using $CuK_\alpha$ radiation.

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