KINETIC STUDY OF THE OXIDATION OF ALCOHOLS WITH QUATERNARY AMMONIUM PERMANGANATES

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Kinetics of the oxidation of 2-propanol, 1-butanol, 2-butanol, and 1-pentanol with tetraalkylammonium permanganates have been investigated as function of temperature. The studied reactions are partly autocatalytic, colloidal manganese dioxide as one of the reaction products has been identified as the autocatalyst. A computerized iterative procedure has been used in order to obtain the rate constants of both non-catalytic and catalytic reaction steps together with the thermodynamic activation parameters.

The oxidation of both inorganic and organic substrates with permanganate have been extensively studied in the past and the mechanisms of many of these reactions are well understood[1]. The kinetics of the permanganate oxidations in aqueous media have been widely reported but only little information regarding the corresponding reactions in nonaqueous solvents is available[2]. The reason is the reactivity of the permanganate which attacks practically all organic solvents[3,4]. It was found that the permanganate anion, when combined with an organophilic cation, becomes a very effective reagent for the oxidation of organic compounds in nonaqueous solvents[5 – 7]. An interesting feature of several reactions involving permanganate ion is their autocatalytic course[2,8].

In the present work we investigated the oxidation of 2-propanol, 1-butanol, 2-butanol, and 1-pentanol with quaternary ammonium permanganates, $R_4N^+MnO_4^-$ (R = CH_3, C_2H_5, 1-C_3H_7, 1-C_4H_9). To avoid side reactions with the solvent the oxidizing agent was dissolved directly in the oxidated alcohols. Our aim was to contribute to the elucidation of the autocatalytic mechanisms of the investigated reactions.

EXPERIMENTAL

All used chemicals were of reagent grade, alcohols were distilled just prior to use. The oxidizing agents were obtained by precipitation of an aqueous solution of corresponding quaternary ammonium bromides by the concentrated solution of potassium permanganate. The precipitate was washed with cold water, and then dried several hours under vacuum. The weighed amount of the salt was dissolved in the investigated alcohol, homogenized by vigorous stirring, and immediately transferred into a thermostatted cell of the spectrophotometer (Specord UV-VIS, or Spekol 11, both Zeiss, Jena).

The reactions were followed by the measurements of the absorbance of MnO_4^- ion at 526 nm, which diminishes in the whole course of all investigated reactions. The extinction coefficient of permanganate ion was practically the same in all investigated alcohols, the value of 2 530 $dm^3\ mol^{-1}\ cm^{-1}$ being used in the calculations of permanganate concentrations. All measurements were performed at 20, 25, 30 and 40 °C.

RESULTS AND DISCUSSION

The products of the investigated reactions, originated from alcohols, have been identified by gas chromatography. Oxidation of 2-propanol and 2-butanol yields acetone and 2-butanone, respectively, the products of the oxidation of 1-butanol and 1-pentanol are the corresponding acids. A typical dependence of the absorption spectrum of permanganate on time is shown in Fig. 1. There is a continuous decrease of absorbance belonging to the absorption maxima of MnO_4^- ion, whereas at shorter wavelengths the absorbance increases. Numerous experiments with the permanganate oxidations in organic phase lead to the conclusion that MnO_2 is formed as one of the reaction product[3]. It is known that manganese dioxide forms a soluble colloid[8 – 11]. The existence of the isosbestic points on the time-dependent absorption spectra of studied reactions indicates that within the measured time interval only two absorbing species are present, namely MnO_4^- and MnO_2. The spectrum recorded at the end of the reactions shows that the absorbance increases uniformly with decreasing wavelength, which is in agreement with Rayleigh law for scattering of light (curve *a* in Fig. 1). For the absorbance *A* of the light in a system with small colloidal particles a relationship (*1*) can be derived[12]

$$\log A = \log k' - 4 \log \lambda, \qquad (1)$$

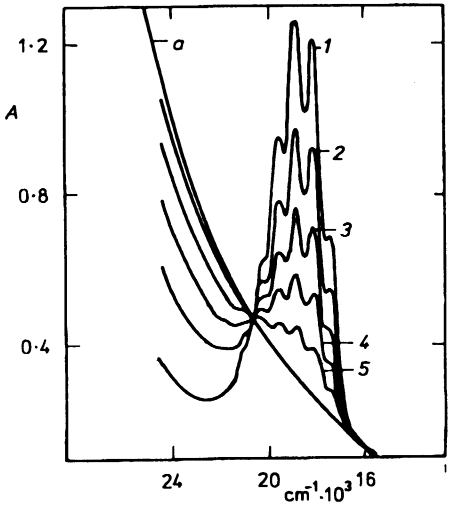

FIG. 1

Absorption spectrum of permanganate ion; 2.5 . 10^{-4} mol dm^{-3} $(C_4H_9)_4NMnO_4$ in 1-pentanol, 2 cm cell path, time interval between curves *1* – *5* 360 s; curve *a* 27 min since the beginning of the reaction, temperature 25 °C

k' includes the number of scattering particles in a volume unit, their polarizability, cell path as well as the numerical constants, λ is the wavelength of scattered light.

According to relation (*1*) the dependence of $\log A$ on $\log \lambda$ was linear with the correlation coefficient 0.999 in all investigated alcohols with the same slope of the value -5.553 ± 0.175. The difference between the theoretical value of the slope and the experimental one has been observed also in other systems and is ascribed to the properties of manganese dioxide[10]. The autocatalytic character of the studied reactions is evidenced by the dependence of reaction rate on time which exhibits a typical bell-shaped profile (Fig. 2, curve *1*). The role of MnO_2 as autocatalyst has been confirmed by the experiment in which the fresh permanganate was added to the solution at the end of the reaction. A marked increase of the initial rate was observed and, at the same time, the reaction rate vs time plot lost the bell-shaped feature (Fig. 2, curve *2*). With respect to a considerable excess of one of the reactants for the total process, i.e. the noncatalytic initial formation of the product, and the oxidation accelerated by it, the differential rate law (*2*), satisfying the experimental data, can be written

$$-\mathrm{d}c/\mathrm{d}t = k_1c + k_2c\,(c_0 - c)\,, \tag{2}$$

c and c_0 are the permanganate concentrations at time t and at the beginning of the reaction, k_1 and k_2 are the rate constants corresponding to the noncatalytic and catalytic mechanisms, respectively. Integration of Eq. (*2*) leads to the integral rate law[13]

$$\ln\left[(k_1 + k_2c_0 - k_2c)/c\right] = \ln(k_1/c_0) + (k_1 + k_2c_0)t\,. \tag{3}$$

For the concentration c of permanganate at the time t we have

$$c = (k_1 + k_2c_0)/[k_2 + (k_1/c_0)\exp(k_1 + k_2c_0)t\,] \tag{4}$$

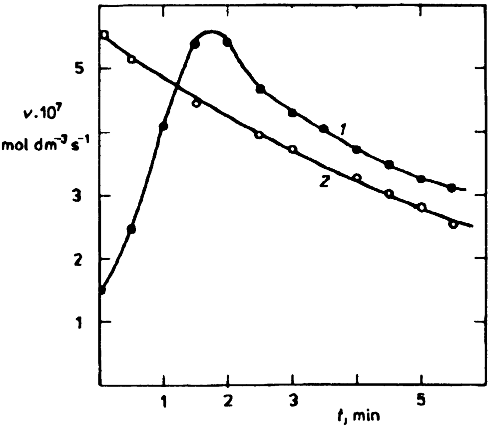

FIG. 2
Reaction rate v vs time plot for the oxidation of 1-pentanol with tetra-(1-butyl)-ammonium permanganate ($2 \cdot 10^{-4}$ mol dm^{-3}) at 40 °C; *1* in the absence of manganese products at the beginning of the reaction, *2* in the presence of products

and the absorbance at time t, A_t, is for 1 cm cell path given as

$$A_t = c\,(\varepsilon_1 - \varepsilon_2) + \varepsilon_2 c_0 , \tag{5}$$

ε_1 is the extinction coefficient of MnO_4^- ion, ε_2 that of the colloidal MnO_2. Combination of Eqs (*4*) and (*5*) gives after rearrangement for A_t

$$A_t = (\varepsilon_1' - \varepsilon_2')/[1 - (k_1/\beta)\,(1 - \exp(\beta t))] + \varepsilon_2' , \tag{6}$$

where $\varepsilon_1' = \varepsilon_1 c_0$, $\varepsilon_2' = \varepsilon_2 c_0$, $\beta = k_1 + k_2 c_0$. In order to apply the Eq. (*6*), modified[14] "brute force" iterative procedure has been used , ε_1, ε_2, k_1, and β are parameters to be fitted. From the temperature dependence of both rate constants k_1 and k_2, the corresponding activation parameters $\Delta H_1^{\neq}$, $\Delta H_2^{\neq}$, $\Delta S_1^{\neq}$, and $\Delta S_2^{\neq}$ were evaluated. The rate constants at 25 °C together with the activation parameters are reported in Table I. The reactions were followed at least two half-times, then the reaction mixture began to be cloudy, and

TABLE I
Rate constants k_1 (s^{-1}), k_2 ($dm^3\ mol^{-1}\ s^{-1}$) at 25 °C, activation enthalpies $\Delta H_1^{\neq}$ and $\Delta H_2^{\neq}$ (kJ mol^{-1}), and activation entropies $\Delta S_1^{\neq}$ and $\Delta S_2^{\neq}$ (J $K^{-1}\ mol^{-1}$) for uncatalyzed (index 1) and catalyzed (index 2) part of the oxidation of alcohols with tetraalkylammonium permanganates, R_4NMnO_4

R	$k_1 \cdot 10^3$	k_2	$\Delta H_1^{\neq}$	$\Delta H_2^{\neq}$	$\Delta S_1^{\neq}$	$\Delta S_2^{\neq}$
			2-Propanol			
CH_3[a]	0.55 ± 0.05	10.0 ± 0.8	30 ± 3	65 ± 6	−205 ± 8	−6 ± 21
C_2H_5	0.63 ± 0.06	2.8 ± 0.2	57.5 ± 5	65 ± 8	−115 ± 16	−19 ± 26
C_3H_7	0.44 ± 0.03	1.12 ± 0.05	41 ± 3	70 ± 7	−172 ± 10	10 ± 20
C_4H_9[a]	0.79 ± 0.05	6.3 ± 0.6	39 ± 4	82 ± 4	−175 ± 13	46 ± 14
			1-Butanol			
C_3H_7	1.02 ± 0.04	0.56 ± 0.05	27 ± 5	110 ± 20	−182 ± 14	121 ± 98
C_4H_9	0.75 ± 0.04	1.43 ± 0.5	52.2 ± 2	136 ± 28	−129 ± 6	213 ± 93
			2-Butanol			
C_3H_7	0.62 ± 0.02	0.31 ± 0.02	51 ± 4	69 ± 8	−135 ± 14	90 ± 20
C_4H_9[a]	0.48 ± 0.03	2.31 ± 0.07	42 ± 2	100 ± 2	−168 ± 6	97 ± 5
			1-Pentanol			
C_3H_7	0.73 ± 0.06	3.64 ± 0.30	47 ± 5	59 ± 5	−148 ± 8	−36 ± 16
C_4H_9	0.72 ± 0.07	3.63 ± 0.39	28 ± 5	90 ± 6	−210 ± 16	69 ± 20

[a] Initial concentration of permanganate 2.1 . 10^{-4} mol dm^{-3}, in all other cases 4.8 . 10^{-4} mol dm^{-3}.

finally the macroscopic precipitate of MnO_2 was formed except of systems with 1-pentanol in which the soluble colloidal manganese dioxide was stable for several days. In the oxidation of t-butyl alcohol the precipitate of MnO_2 appeared just at the beginning of the reaction, so it cannot be measured spectrophotometrically. The enthalpies of activation, reported in Table I, must be considered as complex quantities which involve the temperature dependence of adsorption equilibria of the reactants on the surface of colloidal MnO_2 particles which act as a heterogeneous catalyst[8,15]. According to ref.[8] the function of catalyst consist in the activation of the reactants by the adsorption and the rate of the catalytic portion of the reaction is proportional to the concentration of the adsorbed permanganate. It follows from this interpretation there should be a linear dependence of the reciprocal of reaction rate, $1/v$, versus $1/[QMnO_4]$. This conclusion has been verified in the present work by measurements of the oxidation of 1-pentanol in the presence of colloidal MnO_2. The dependence $1/v = f(1/[QMnO_4])$ was in this case indeed linear with the correlation coefficient 0.9999. However, the detailed mechanism of the activation of permanganate through the adsorption is evidently more complicated due to the non-uniformity of colloidal particles, their dimensions being moreover time dependent. The experimental values of the entropies of activation, which are almost negative, indicate that the reactions proceed through a highly organized activated complex. The formation of the complexes with an increased coordination number of the manganese, theoretically calculated[16], is in accord with the experimental entropies of activation.

REFERENCES

1. Steward R.: *Oxidations in Organic Chemistry* (K. B. Wiberg, Ed.), Part A, p. 1. Academic Press, New York 1965.
2. Lee D. G., Perez-Benito J. F.: Can. J. Chem. *63*, 1275 (1985).
3. Starks C. M., Liotta C.: *Phase Transfer Catalysis*, p. 298. Academic Press, New York 1978.
4. Holba V., Muchová J.: React. Kinet. Catal. Lett. *32*, 365 (1986).
5. Sala T., Sargent M. V.: J. Chem. Soc., Chem. Commun. *1978*, 253.
6. Karaman H., Barton R. J., Robertson B. E., Lee D. G.: J. Org. Chem. *49*, 4509 (1984).
7. Rathore R., Chandrasekaran S.: J. Chem. Res., Synop. *1986*, 458.
8. Lee D. G., Perez-Benito J. F.: J. Org. Chem. *53*, 5725 (1988).
9. Simándi L. I., Jáky M., Savage C. R., Schelly Z. A.: J. Am. Chem. Soc. *107*, 4220 (1985).
10. Freeman F., Kappos J.: J. Am. Chem. Soc. *107*, 6628 (1985).
11. Perez-Benito J. F, Arias C.: Int. J. Chem. Kinet. *23*, 717 (1991).
12. Oster G. in: *Physical Methods of Organic Chemistry* (A. Weissberger, Ed.), Part III, p. 2107. Interscience Publishers, New York 1960.
13. Mata-Perez M., Perez-Benito J. F.: J. Chem. Educ. *64*, 925 (1987).
14. Král D., Neogrády P.: Unpublished results.
15. Mata F., Perez-Benito J., Arranz A.: Z. Phys. Chem., N. F. *135*, 141 (1983).
16. Rappe A. K., Goddard W. A. III : J. Am. Chem. Soc. *104*, 3287 (1982).

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