KINETICS OF AUTOCATALYTIC OXIDATION OF Mn(II) IONS BY PERIODATE IN RELATION TO MANGANESE OSCILLATIONS

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Received March 28, 1991
Accepted October 7, 1991

Dedicated to Professor Antonín Tockstein on the occasion of his 65th birthday.

The kinetics of the autocatalytic oxidation of Mn(II) ions by periodate was investigated in unbuffered phosphoric acid solutions and in buffered solutions; the process was studied in a batch reactor in relation to the chemical oscillations in a continuously flow stirred tank reactor (CSTR), which are based on the chemistry of manganese. The rate constants k_1 and k_2' corresponding to the noncatalyzed and catalyzed reaction course were determined by the Schwartz method. While MnO_4^- ions are the reaction product in the unbuffered phosphoric acid medium, in a CH_3COOH–NaOH buffer the Mn^{2+} ions are only oxidized to Mn(IV). For this case, a reaction pathway is discussed where the key step encompasses dimerization of $MnO(OH)^+$ ions followed by the formation of $(MnO_2)_{col}$ colloids, stabilized by adsorption of $H_2PO_4^-$ ions on their surface. This reaction pathway is also of importance with respect to the new manganese oscillator which is based on the autocatalytic oxidation of Mn(II) ions by periodate in a CSTR.

Oxidation of Mn^{2+} ions by periodate in acid and neutral solutions is usually an autocatalytic process. Since autocatalysis as a positive feedback frequently gives rise to nonlinear dynamic phenomena such as kinetic bistability, hysteresis, and oscillatory behaviour of the chemical system in nonequilibrium conditions, autocatalytic redox reactions are generally suitable candidates when seeking for new chemical oscillators[1]. Recently we described a new chemical oscillator which is based on the oxidation of Mn^{2+} ions by sodium periodate in a continuously flow stirred tank reactor[2] (CSTR); therefore we decided to examine this reaction from the kinetic aspect.

Oxidation of Mn^{2+} ions by periodate in strongly acid solutions proceeds[3,4] autocatalytically giving MnO_2 and MnO_4^- ions. The oxidation to the latter is quantitative only if the reaction mixture is heated to boil, which is made use of in the quantitation of Mn(II). The kinetics and mechanism of oxidation of Mn^{2+} ions by periodate in neutral solutions have been studied by Tiginjanu and coworkers[5],

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according to whom the final products are Mn(IV) ions while MnO_4^- ions are only formed if periodate is present in an excess. The authors account for the autocatalytic nature of the reaction by means of a reaction scheme where dismutation of Mn(III) ions plays the key role. This is borne out by the fact that oxidation of Mn^{2+} ions by periodate in a medium containing diphosphates proceeds without autocatalysis[3].

With regard to the fact that all the invented permanganate oscillators[7-12] as well as the manganese oscillator based on the oxidation of Mn^{2+} ions by periodate[2] only operate in the presence of phosphoric acid, or $H_2PO_4^-$ ions, the objective of the present work was investigation of the autocatalytic oxidation of Mn^{2+} ions by periodate with regard to the specific effect of phosphate ions.

EXPERIMENTAL

Stock solutions were prepared from commercial reagent grade chemicals; these included $NaIO_4$ (Reanal, Budapest), $MnSO_4$, KH_2PO_4, CH_3COOH and NaOH (Lachema, Brno). The pH values of buffer solutions were determined potentiometrically with a glass electrode always before adding reactants, the concentration of CH_3COOH and NaOH in stock solutions was checked titrimetrically. All solutions were prepared from redistilled water. Stock solution of $NaIO_4$ was stored in a dark bottle in a refrigerator.

The kinetics of oxidation of Mn^{2+} ions by periodate in weakly acid unbuffered and buffered solutions was examined spectrophotometrically with a SPECORD M 40 instrument (Carl Zeiss, Jena), by recording the time dependence of the absorption spectrum in the visible region or of absorbance at a chosen wavelength (the absorbance at 528 nm is linearly dependent on the concentration of MnO_4^- ions in unbuffered solution of phosphoric acid, and the absorbance at 345 nm is linearly dependent on the concentration of Mn(IV) — see below). The quartz cell 10 cm optical pathlength was accommodated in a thermostatted block interfaced to an U 10 ultrathermostat (Medingen, Germany).

RESULTS

If the oxidation of Mn^{2+} ions by sodium periodate is conducted in an unbuffered solution of phosphoric acid, the time dependence of absorbance at 526 nm, corresponding to the absorption by MnO_4^- ions, has a sigmoid shape. In a solution of H_3PO_4 (2·5 mmol dm^{-3}) and $NaClO_4$ (10 mmol dm^{-3}) we examined the dependence of absorbance at 526 nm on the concentration of the reaction product of oxidation of Mn^{2+} ions by sodium periodate in excess, over the $MnSO_4$ concentration region of 10 to 63 μmol dm^{-3}. The dependence was linear, as is consistent with the Lambert–Beer law.

Since the sigmoid curves are symmetrical, the inflection times can be determined sufficiently accurately, and the rate constants of the noncatalyzed reaction k_1 and of the catalyzed reaction k_2 can be evaluated by using the Schwartz method[13]. The pseudo-first order of the reaction (which is a precondition for the applicability of this approach) can be explained so that periodate enters the reaction in the form of IO_4^- ions also in acid solutions, and Mn^{2+} ions are then present in an excess.

Fig. 1 demonstrates that the inflection time increases with increasing concentration of H_3O^+ ions. While the rate constant of the noncatalyzed reaction k_1 virtually does not vary with increasing concentration of H_3O^+ ions, the rate constant of the catalyzed reaction k'_2 decreases (Table I). Logarithmic analysis gave a reaction order of $n_{H_3O^+} = -0{\cdot}77$. Also, the rate constant k'_2 decreases with increasing temperature (Table II). Evaluation of the Eyring equation gave apparent activation parameter values of $\Delta H^{\neq} = -7{\cdot}8$ kJ mol^{-1} and $\Delta S^{\neq} = -229$ J mol^{-1} K^{-1}.

In the buffer solution of CH_3COOH + NaOH (pH 4·2 to 4·8) the oxidation of Mn^{2+} ions by sodium periodate has also an autocatalytic character. At the wavelength of 345 nm, corresponding to the absorption by Mn(IV) ions, the time dependence of absorbance also has a sigmoid shape. We verified the linear shape of the dependence of absorbance on the concentration of the reaction product of oxidation of Mn^{2+} ions by sodium periodate in excess, over the $MnSO_4$ concentration region of 0 to 16 μmol dm^{-3} in the above buffer solution at pH 4·6 and at a temperature of 20°C. In this case, also, the dependence was linear.

By analyzing the sigmoid curves by the Schwartz method[13] we examined the dependence of the rate constant k'_2 on the concentration of H_3O^+ ions (Table III). Logarithmic analysis gave the partial reaction order of $n_{H_3O^+} = -1{\cdot}77$. In that medium we also investigated the dependence of the rate constant k'_2 on the concentration of periodate (Table III) and, by logarithmic analysis, determined the partial reaction order $n_{IO_4^-} = +1{\cdot}8$.

Since phosphoric acid, or phosphate ions, play a key role in permanganate oscillators[7-12] as well as in the new manganese oscillator[2], we examined in detail the effect of phosphate on the rate constant k'_2 in the given medium at a constant ionic strength and at a constant acidity of pH 5·8. This rate constant decreased as the

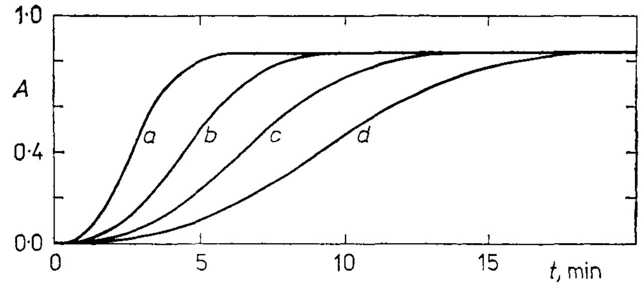


FIG. 1

Dependence of the sigmoid shape of the course of the autocatalytic oxidation of Mn^{2+} ions by periodate on the concentration of H_3O^+ ions. Reaction mixture composition: $MnSO_4$ (0·042 mmol dm^{-3}), $NaIO_4$ (48 mmol dm^{-3}), H_3PO_4 (2·5 mmol dm^{-3}); $c(NaClO_4)$, $c(HClO_4)$ (mmol dm^{-3}): *a* 10, 0; *b* 7·5, 2·5; *c* 5·0, 5·0; *d* 0, 10. Temperature 10°C

TABLE I

Dependence of the rate constant k'_2 of the catalyzed reaction on the concentration of H_3O^+ ions; $k_1 = 4{\cdot}4 \,.\, 10^{-4}$ s. Reaction system composition: $MnSO_4$ (0·042 mmol dm^{-3}), $NaIO_4$ (48 mmol dm^{-3}), H_3PO_4 (2·5 mmol dm^{-3}); $c(HClO_4) + c(NaClO_4) =$ const., $t = 10$°C

$c(H_3O^+)$ mmol dm^{-3}	k'_2 dm^3 s^{-1} mol^{-1}	$c(H_3O^+)$ mmol dm^{-3}	k'_2 dm^3 s^{-1} mol^{-1}
2·5	489·8	12·5	144·0
5·0	294·8	17·5	112·2
7·5	212·9	22·5	89·4

TABLE II

Temperature dependence of the rate constant k'_2. Reaction system composition: $MnSO_4$ (0·042 mmol dm^{-3}), $NaIO_4$ (48 mmol dm^{-3}), H_3PO_4 (2·5 mmol dm^{-3}), $HClO_4$ (5 mmol . . dm^{-3}), $NaClO_4$ (5 mmol dm^{-3})

T, K	k dm^3 s^{-1} mol^{-1}	T, K	k'_2 dm^3 s^{-1} mol^{-1}
278	240·1	303	162·3
283	214·3	313	144·5
293	188·8	—	—

TABLE III

Dependence of the rate constant k'_2 on the concentration of H_3O^+ ions[a] and of periodate[b]

$c(H_3O^+)$ µmol dm^{-3}	k'_2 dm^3 s^{-1} mol^{-1}	$c(NaIO_4)$ µmol dm^{-3}	k'_2 dm^3 s^{-1} mol^{-1}
16	8 980·3	0·6	551·4
25	4 416·0	1·05	1 628·3
40	2 052·6	1·3	2 369·2
—	—	1·6	3 299·0
—	—	1·8	4 294·0
—	—	2·1	5 490·8

Reaction mixture composition: [a] $MnSO_4$ (10·5 µmol dm^{-3}), $NaIO_4$ (210 µmol dm^{-3}), CH_3. .COOH + NaOH buffer solution, $t = 20$°C; [b] $MnSO_4$ (10·5 µmol dm^{-3}), CH_3COOH + NaOH buffer solution, pH 5·8, $t = 20$°C concentration of KH_2PO_4 was increased across the region of 0·5 to 1·5 mmol dm^{-3} (Table IV). The partial reaction order $n_{H_2PO_4^-} = -0{\cdot}5$ was obtained by logarithmic analysis. The experimental rate constant of the catalyzed reaction k'_2 in acetate buffer obeyed the relation

$$k'_2 = k'(c_{IO_4^-}/c_{H_3O^+})^{1{\cdot}8}/(c_{H_2PO_4^-})^{0{\cdot}5} \tag{1}$$

For gaining a better insight into the inhibiting effect of the $H_2PO_4^-$ ions on the oxidation of Mn^{2+} ions by periodate, we investigated the effect of temperature on the rate constant k'_2 at two different concentrations of KH_2PO_4 (Table V). Based on these data, we obtained the following activation parameters from the Eyring equation: $\Delta H^{\neq} = 14{\cdot}4$ and 16·3 kJ mol^{-1} and $\Delta S^{\neq} = -123$ and -127 J mol^{-1} . . K^{-1} at $c_{KH_2PO_4} = 0{\cdot}5$ and 5 mmol dm^{-3}, respectively.

The inhibiting effect of phosphate ions consists in an increase in the activation enthalpy of 1·9 kJ mol^{-1} if their concentration is increased one order of magnitude.

TABLE IV

Dependence of the rate constant k'_2 on the concentration of KH_2PO_4. Reaction mixture composition: $MnSO_4$ (10·5 μmol dm^{-3}), $NaIO_4$ (42 μmol dm^{-3}), buffer solution $CH_3COOH + NaOH$, t = 20°C

$c(KH_2PO_4)$ mmol dm^{-3}	k'_2 dm^3 s^{-1} mol^{-1}	$c(KH_2PO_4)$ mmol dm^{-3}	k'_2 dm^3 s^{-1} mol^{-1}
0·5	7 714·7	3·0	2 994·6
1·0	5 800·5	4·0	2 596·5
1·5	4 556·2	5·0	2 540·9
2·0	3 737·1	—	—

TABLE V

Temperature dependence of the rate constant k'_2 at $c(KH_2PO_4)$ = 0·5 mmol dm^{-3} (a) and 5 mmol dm^{-3} (b), pH 5·8

T, K	k'_2, dm^{3}s^{-1} mol^{-1}	
	a	b
283	4 957·5	1 377·1
293	6 337·3	1 801·3
303	7 966·4	2 330·3

DISCUSSION

The sigmoid shape of the time dependence of absorbance at 526 nm, corresponding to MnO_4^- ions, as well as of absorbance at 345 nm, corresponding to Mn(IV), gives evidence of the autocatalytic nature of oxidation of Mn^{2+} ions by periodate in the two media. However, while in the unbuffered acid solution of phosphoric acid the oxidation of Mn^{2+} ions goes as far as MnO_4^- ions, in the acetate buffer at pH 5·8 it only goes to Mn(IV). The conditions are favourable for the oscillatory behaviour of the system in a CSTR, as described previously[2], and therefore we concentrated on the elucidation of the reaction mechanism.

The direct, noncatalyzed oxidation of Mn^{2+} ions by periodate proceeds rather slowly with a rate constant k_1:

$$Mn^{2+} + IO_4^- + H_2O \xrightarrow{k_1} MnO(OH)^+ + IO_3^- + H^+ \qquad (A)$$

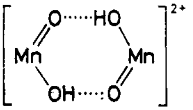
It involves the transfer of two electrons, which is accomplished either simultaneously or in two consecutive single-electron steps.

The solvated Mn(IV) in the form of $MnO(OH)^+$ in weakly acid solution probably dimerizes and forms colloids, stabilized by the $H_2PO_4^-$ ions[14]:

$$2\,MnO(OH)^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{dimer} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (MnO_2)_{col} \xrightarrow{k_4} (MnO_2)_{pt} \qquad (B)$$

where the subscripts col and pt refer to colloids and precipitate, respectively.

The observed absorbance can be primarily attributed to the intermediary dimer



The solvated Mn(IV) in the form of $MnO(OH)^{2+}$ ions reacts with Mn^{2+} ions in a parallel step,

$$MnO(OH)^+ + Mn^{2+} + H^+ \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} 2\,Mn(OH)^{2+} \qquad (C)$$

thereafter the $Mn(OH)^{2+}$ ions are oxidized in two consecutive steps, viz.

$$Mn(OH)^{2+} + IO_4^- \xrightarrow{k_6} MnO(OH)^+ + R^\bullet \qquad (D)$$

$$Mn(OH)^{2+} + R^\bullet \xrightarrow{k_7} MnO(OH)^+ + IO_3^- \qquad (E)$$

where $R^\bullet$ is an intermediary radical. The $MnO(OH)^+$ ions are taken up in two parallel steps, (*B*) and (*C*). The rate constant k_2' determined by the Schwartz method corresponds to the catalyzed reaction course, i.e. to the sequence of elementary steps (*C*), (*D*), (*E*) and (*B*). Since its determination relies on the time increase in the absorbance of the dimer – Mn(IV), the formula

$$k'_2 = \text{const}\,(c_{\text{IO}_4^-}/c_{\text{H}^+})^{1.8}$$

which is obeyed at a constant concentration of $H_2PO_4^-$ ions, can be qualitatively explained by means of the scheme suggested. The production of the Mn(IV) dimer requires two IO_4^- ions, so that the corresponding partial reaction order approaches +2, as follows from the scheme suggested. And since periodate at pH 4·2 to 4·8 occurs predominantly in the form of nondissociated HIO_4 molecules, the corresponding partial reaction order with respect to the concentration of H_3O^+ ions approaches −2.

The inhibiting effect of $H_2PO_4^-$ ions (Table IV) is apparently related with their stabilizing effect on the colloids, $(MnO_2)_{col}$, which has been explained by their adsorption on the surface of the colloid particles[14,15]. As far as our pathway is concerned, increased concentration of $H_2PO_4^-$ ions is presumably accompanied by a decrease in the rate constant k_4 corresponding to precipitation, and at the same time the rate of the reverse reactions with the rate constants k_{-3} and k_{-2} increases. This brings about a decrease in the rate of the overall step (*C*). The inhibiting effect is then manifested in an increase in the experimental activation enthalpy. The corresponding partial reaction order $n_{H_2PO_4^-} = -0.5$ suggests a microheterogeneous character of this inhibiting effect.

The overall reaction step (*B*) comprising dimerization of $MnO(OH)^+$ ions with a subsequent formation of stabilized colloids $(MnO_2)_{col}$ plays a key role in the kinetics of oxidation of Mn^{2+} ions by periodate in a batch reactor, as well as in the new oscillator which is based on this reaction in a CSTR[2].

The negative value of the apparent activation enthalpy $\Delta H^{\neq} = -7.8$ kJ mol^{-1} in unbuffered medium probably involves the reaction heat corresponding to the pre-equilibrium $HIO_4 = H^+ + IO_4^-$.

Mathematical simulation of the autocatalytic course of the reaction and of the dependence of the inflection time on the concentration of $H_2PO_4^-$ ions will be the subject of a forthcoming paper, in relation to the modelling of the new oscillator[2] in the sense of the reaction pathway suggested.

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Translated by P. Adámek.