Kinetics of the oxidation of iodine by hydrogen peroxide catalyzed by MoO_4^{2-} ions

Milan Meličerčík [1], Anna Olexová, Ludovít Treindl *

Department of Physical Chemistry, Comenius University, 842 15 Bratislava, Slovak Republic

Abstract

The kinetics of the oxidation of iodine by hydrogen peroxide catalyzed by MoO_4^{2-} ions with a 'clock' behaviour is described and the corresponding reaction scheme is proposed. The 'clock' behaviour is explained by the assumption that the oxidation of iodine cannot proceed until the iodide concentration drops to a certain treshold, since this reaction can only through the HOI species proceed. The noncatalyzed, direct oxidation of iodine by H_2O_2 is too slow to become one of the main two processes of the Bray–Liebhafsky oscillatory reaction. © 1997 Elsevier Science B.V.

Keywords: Iodine oxidation by hydrogen peroxide; Catalysis by molybdates; 'Clock' behaviour
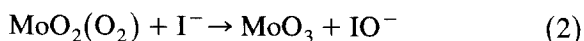
1. Introduction

The oxidation of iodine by hydrogen peroxide plays a crucial role as a component process of the Bray–Liebhafsky (BL) oscillatory reaction [1–3]. During the BL reaction oscillations result from alternating dominance of processes I and II. Process I is the oxidation of H_2O_2 to O_2 by IO_3^- while the oxidant is reduced to I_2. Process II is the oxidation of I_2 by H_2O_2 while the reductant is oxidized to IO_3^-. Treindl and Noyes [2] have proposed that real oxidant is O_2 and that H_2O_2 itself can oxidize no iodine-con-

taining species except iodide ion, I^-, even though H_2O_2 is the only oxidant in the overall stoichiometry for process II.
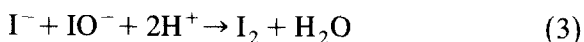
Only recently the molybdenum(VI) catalyzed oxidation of iodide ions by H_2O_2 has been reinterpreted [4]. The authors conclude that dioxoperoxomolybdenum(VI) is formed:
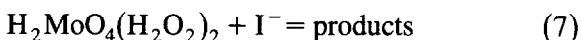
$$MoO_3 + H_2O_2 \rightarrow MoO_2(O_2) + H_2O \qquad (1)$$
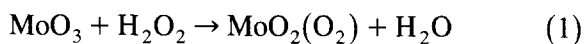
which attacks I^- ion

$$MoO_2(O_2) + I^- \rightarrow MoO_3 + IO^- \qquad (2)$$

and then

$$I^- + IO^- + 2H^+ \rightarrow I_2 + H_2O \qquad (3)$$

According to Smith and Kilford [5] the kinetics of the oxidation of iodide by H_2O_2 cat-

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alyzed by acidic molybdate can be interpreted in terms of the mechanism

$$H_2MoO_4 + H_2O_2 = H_2MoO_4(H_2O_2) \quad (4)$$

$$H_2MoO_4(H_2O_2) + H_2O_2$$
$$= H_2MoO_4(H_2O_2)_2 \quad (5)$$

$$H_2MoO_4 + I^- = H_2MoO_2I^- \quad (6)$$

$$H_2MoO_4(H_2O_2)_2 + I^- = \text{products} \quad (7)$$
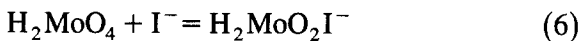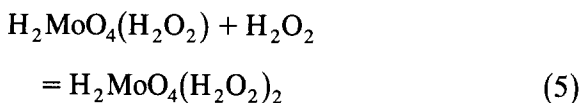
The oxidation of iodide ions to iodine in the presence of molecular oxygen is catalytically accelerated by traces of copper(II) ions in 10^{-7}–10^{-5} M concentrations [6]. The authors proposed a chain mechanism to account for the obtained results.

The aim of this work is to study:

(1) whether H_2O_2 can react with iodine directly with a rate which could be compatible with the above mentioned process II of the Bray–Liebhafsky oscillatory reaction, and

(2) the catalytic activity of molybdate ions on the oxidation of iodine by H_2O_2 that has not been described so far.

2. Experimental

Stock solutions of the components were prepared from commercially available hydrogen peroxide 30%, (Selectipur, E. Merck AB, Stockholm), I (iodum resublimatum), NaI, Na_2MoO_4, Na_2CrO_4, $NaVO_3$, $(NH_4)_2Fe(SO_4)_2$ and $HClO_4$ (p.a. Lachema, Brno, former Czechoslovakia). Dilutions were made with bidistilled water. The stock solution of iodine was prepared by the procedure of [9].

The reaction has been followed by measuring the absorbance-time curves by means of a thermostated oven 1 cm, 3 cm or 5 cm quartz cuvette, placed in a spectrophotometer Specord UV-VIS (Zeiss, Jena, Germany), at a wavelength of 465 or 487 nm, characteristic for the absorbance of iodine.

3. Results and discussion

If we follow the absorbance of iodine, as product of the oxidation of I^- ions by H_2O_2 catalyzed by molybdates with time (Fig. 1), we can see that after an induction period even iodine itself is oxidized by H_2O_2 under a catalytic influence of MoO_4^{2-} ions. The same effect can be observed, if we use the solution of iodine instead of sodium iodide. A similar but less pronounced catalytic influence can be observed with Na_2CrO_4, $NaVO_3$ or $(NH_4)_2Fe(SO_4)_2$. We can proclaim that this reaction has a 'clock' behaviour, especially at the higher temperatures. The decrease of the iodine absorbance with time corresponds to the first order kinetics. With an increasing concentration of MoO_4^{2-} ions the value of the rate constant increases tending to the limiting value and the value of the induction period decreases nonlinearly (Fig. 2a and b). If we plot the reciprocal value of inflection time against the concentration of molybdates, we get a straight line. It is interesting that the value of the rate constant k_{exp} decreases slightly with an increasing concentration of H_2O_2, but it increases with I^- ions concentration (Table 1). The value of the induction period also decreases with an increasing concentration of H_2O_2 (Table 2). At the concentration of H_3O^+ ions less than 1.7×10^{-2} M, the reaction looses its 'clock' charac-
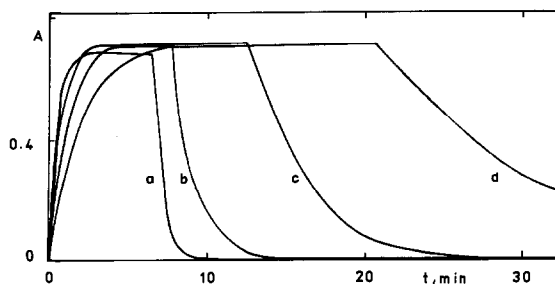

Fig. 1. Optical density trace at $\lambda = 487$ nm for the production of iodine in the iodide-hydrogen peroxide reaction, at different temperatures. $[NaI]_0 = 1.6 \times 10^{-3}$ M, $[H_2O_2]_0 = 10^{-2}$ M, $[HClO_4] = 10^{-1}$ M, $[MoO_4^{2-}] = 10^{-5}$ M, temperature of 50°C (a), 40°C (b), 30°C (c), 20°C (d).
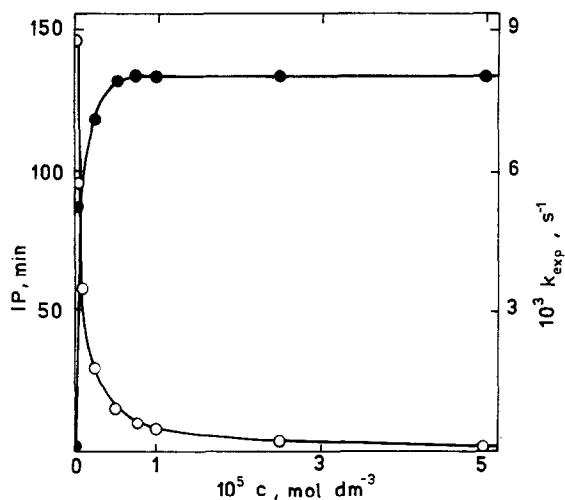
Fig. 2. The k_{exp}–[MoO_4^{2-}]$_o$ (●) and induction period–[MoO_4^{2-}]$_o$ (○) curves. [$HClO_4$]$_o$ = 10^{-1} M, [NaI]$_o$ = 1.6×10^{-3} M, [H_2O_2]$_o$ = 10^{-2} M, temperature of 30°C.
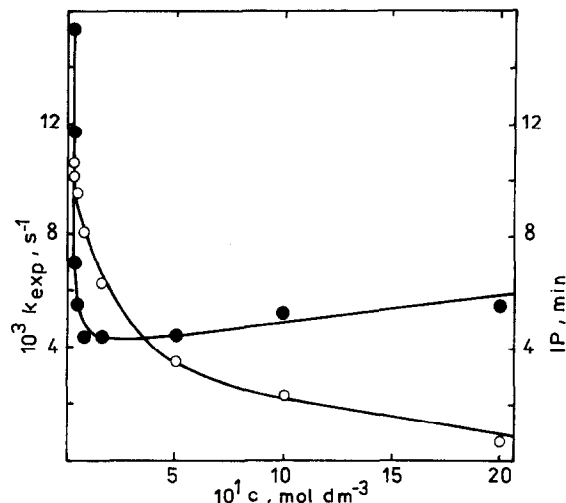
Fig. 3. The k_{exp}–[H_3O^+] (●) and induction period–[H_3O^+] (○) curves. [NaI]$_o$ = 1.6×10^{-3} M, [H_2O_2]$_o$ = 10^{-2} M, [MoO_4^{2-}]$_o$ = 10^{-5} M, Ionic strength I ($NaClO_4$) = 2.0 M, temperature of 30°C.

Table 1
The dependence of the rate constant k_{exp} on the concentration of H_2O_2 and I^- ions. [$HClO_4$]$_o$ = 10^{-1} M, [MoO_4]$^{2-}$ = 10^{-5} M, temperature 30°C

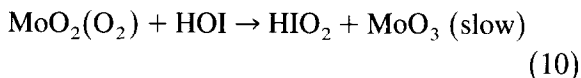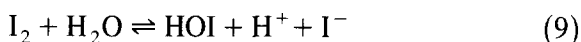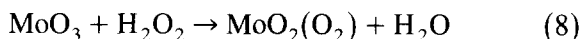| $k_{exp} \times 10^3$, s^{-1}	[H_2O_2]$_o \times 10^3$, M	[I^-]$_o \times 10^3$, M
8.3	5	1.6
8.05	10	1.6
5.04	50	1.6
3.10	100	1.6,
1.67	200	1.6
10.9	10	3.2
9.1	10	2.4
8.1	10	1.6
7.16	10	0.8
6.66	10	0.4

Table 2
The dependence of induction period on the concentration of H_2O_2. [$HClO_4$]$_o$ = 10^{-1} M, [NaI]$_o$ = 1.6×10^{-3} [MoO_4^{2-}]$_o$ = 10^{-5} M, temperature 30°C

Induction period, min	c (H_2O_2)$\times 10^3$ M
7.8	5
7.4	10
6.8	50
6.3	100
6.0	200

ter. The value of the rate constant k_{exp} decreases with an increasing concentration of H_3O^+ ion with the partial order of -0.5, and induction period first decreases, attains minimum and then increases slightly (Fig. 3).

Based on the experimental results described above, we can assume that besides the molybdate catalyzed oxidation of the I^- ions by H_2O_2 also that of iodine can proceed. As far as we know, it is the first report about the molybdate catalyzed oxidation of iodine by H_2O_2 so far. We can suggest the reaction scheme which is consistent with most of the experimental results

$$MoO_3 + H_2O_2 \rightarrow MoO_2(O_2) + H_2O \qquad (8)$$

$$I_2 + H_2O \rightleftharpoons HOI + H^+ + I^- \qquad (9)$$

$$MoO_2(O_2) + HOI \rightarrow HIO_2 + MoO_3 \text{ (slow)} \qquad (10)$$

$$2HIO_2 \rightleftharpoons HIO_3 + HOI \qquad (11)$$

$$HIO_2 + I^- + H^+ \rightleftharpoons 2HOI \qquad (12)$$

The sum of $5 \times$ Eq. (8), Eq. (9), $5 \times$ Eq. (10), $2 \times$ Eq. (11) and Eq. (12) corresponds to the stoichiometric process

$$I_2 + 5H_2O_2 \rightleftharpoons 2HIO_3 + 4H_2O \qquad (13)$$
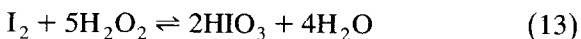
The formation of an intermediate between MoO_3 and H_2O_2 corresponding to the absorption band with $\lambda_{max} = 330$ nm can be followed spectrophotometrically. In the absence of the catalyst the reaction of Eq. (13) proceeds so slowly that it can hardly be responsible for the process II of the BL reaction. The explanation based on the iodine oxidation by oxygen [2] seems to be therefore more reasonable. The oxidation of iodine by hydrogen peroxide itself (without a catalyst) must await further progress in mechanistic studies [7,8].

The molybdate catalyzed oxidation of iodine by H_2O_2 is analogue in some extent to the complex bromate-iodine reaction which is known as 'clock' reaction [9]. Bromate ions are known to oxidize iodide ions to molecular iodine in acidic solution and in the presence of excess bromate the iodine is further oxidized to iodate [10]. In our case the two reactions also occur in tandem, the iodide–H_2O_2 reaction going to completion before the iodine–H_2O_2 reaction, catalyzed by MoO_4^{2-} ions, comences. The second reaction is preceded by an induction period and based on its temperature effect the value of the apparent activation energy $E = 33.5$ kJ mol^{-1} was determined. This stepwise oxidation of iodide to iodate makes also this reaction very interesting. The induction period increases, if some amount of iodide is added to the solution just before 'clock' reaction should occur. We can revive absorbance-time curve of this 'clock' reaction few times, if we add iodide to the solution just after 'clock' reaction has been finished (Fig. 4).

So we can see that I^- ions are responsible for the induction period, similarly as in the case of the bromate-iodide reaction [9]. As long as I^- ions are present above a certain treshold value, no oxidation of iodine can start to proceed. It means that the oxidation of iodine must pass in the step of Eq. (10) through the HOI molecules, (which are precursors to the oxidation of iodine), and the steady state concentration of the HOI molecules is diminished by addition of iodide due to the reverse reaction
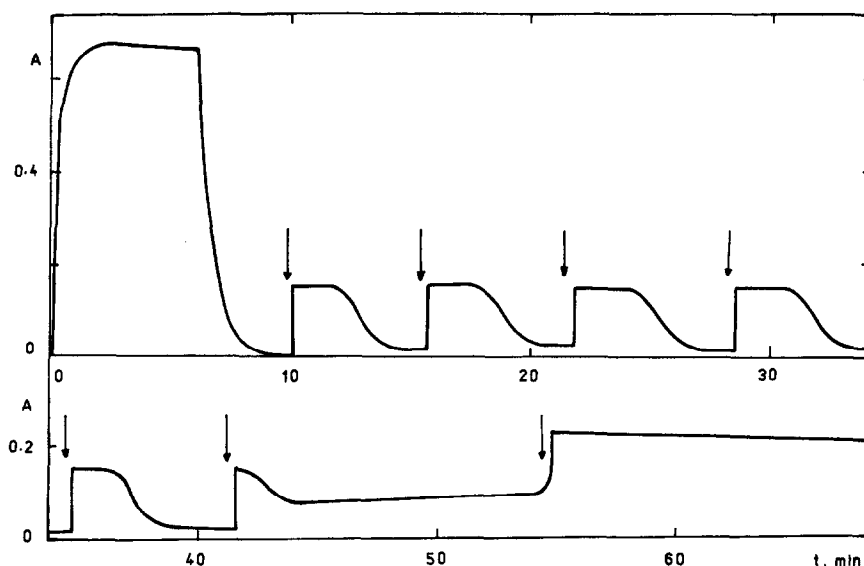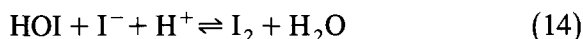
$$HOI + I^- + H^+ \rightleftharpoons I_2 + H_2O \qquad (14)$$

Fig. 4. The effect of the addition of I^- ions on the production of iodine in the iodide-hydrogen peroxide reaction. $[HClO_4]_o = 0.1$ M, $[NaI]_o = 1.6 \times 10^{-3}$ M, $[H_2O_2]_o = 10^{-2}$ M, $[MoO_4^{2-}]_o = 10^{-5}$ M, temperature of 50°C, at arrows always the addition of 0.2 ml 10^{-2} M NaI to the volume of 8 ml.

Similarly, we can explain the effect of $[H_3O^+]$ on the value of the rate constant k_{exp} (Fig. 3). Iodine catalysis, observed in the chlorite-iodide reaction [11], is also inhibited by I^- ions. In the presence of excess chlorite, the exponential rise of the iodine concentration toward the end of the reaction is terminated in an abrupt fall to zero as the iodine is further rapidly oxidized to iodate.

A detailed reaction mechanism together with its mathematical simulations will be the next project of our laboratory.

4. Conclusions

The oxidation of iodine by hydrogen peroxide in acidic solutions is catalysed by molybdates. According to the proposed reaction scheme, the oxidation of HOI by $MoO_2(O_2)$ intermediate is slow and rate-determining step.

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