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Influence of the MoO_4^{2-} Ions on the Bray−Liebhafsky Oscillatory Reaction

Janka Genigová, Milan Melicherčík,[†] Anna Olexová, and L'udovít Treindl*

Department of Physical Chemistry, Comenius University, 842 15 Bratislava, Slovakia

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The influence of the MoO_4^{2-} ions on the Bray−Liebhafsky (BL) oscillatory reaction is described. The MoO_4^{2-} ions affect the values of the parameters of the BL reaction; first of all, they decrease the induction period and the duration of oscillations, but they increase the average frequency of oscillations. A qualitative explanation of this influence is based on the Treindl−Noyes skeleton mechanism of the BL oscillatory reaction. The production of singlet oxygen ($^1O_2$) by the disproportionation of hydrogen peroxide catalyzed by molybdate ions, which is obviously quenched physically and/or chemically, may play a role too.

1. Introduction

The Bray−Liebhafsky (BL) reaction is based on the disproportionation of an aqueous solution of hydrogen peroxide catalyzed by iodates. After an induction period, oscillations in iodine and/or iodide concentration can be observed and hydrogen peroxide is periodically consumed.[1−8] Although more than 60 papers have been published about this reaction, its mechanism has not been definitively established. Kolar-Anic and Schmitz[5] presented detailed computations which are asserted to explain their reaction mechanism. Treindl and Noyes have also proposed a skeleton mechanism, which appears to explain most features of the observed behavoir.[6] Mathematical simulations performed on a model based on this mechanism, and consisting of only two concentration variables $[I_2]$ and $[O_2]$ and three composition parameters, led to the oscillations of $[O_2]$ and $[I_2]$ around the unstable steady state but not to oscillations involving a true limit cycle.[8] Thus, since a complete elucidation of the overall reaction has not been developed so far, its study seems to be still very actual. Kolar-Anic et al.[9,10] try to show that the calculated instability condition can be used as one criterion for the models selection and consider the decisive role of nonradical processes in the appearance of oscillations. Ševčík et al.[11−13] studying effects of a gas bubbling and stirring suggest the rate of transport of volatile iodine from the BL system to the gas phase may be a significant component of the reaction mechanism. Buchholtz et al.[14] studying the BL oscillations in a CSTR conclude that the principal reason for them is chemical and that the interaction with an overlying gas phase is not essential for the existence of oscillations. One of us et al.[15] describe the kinetics of the autoxidation of iodine with regard to the BL reaction and propose the reaction scheme which seems to be consistent with the Treindl−Noyes skeleton mechanism. Vilcu et al.[21] study the BL reaction over a wide range of temperatures and try to explain the described behavoir by means of the Kolar-Anic and Schmitz mechanism.[5] Stanisavljev et al.[22,23] monitor behavior of water during the oscillatory part of the BL reaction and stress the subtle role of water in its mechanism.

Recently, we have discovered the oxidation of iodine by hydrogen peroxide to be catalyzed by MoO_4^{2-} ions.[16] Therefore, we devote attention to the influence of MoO_4^{2-} ions upon the BL oscillations which is the topic of the present paper.

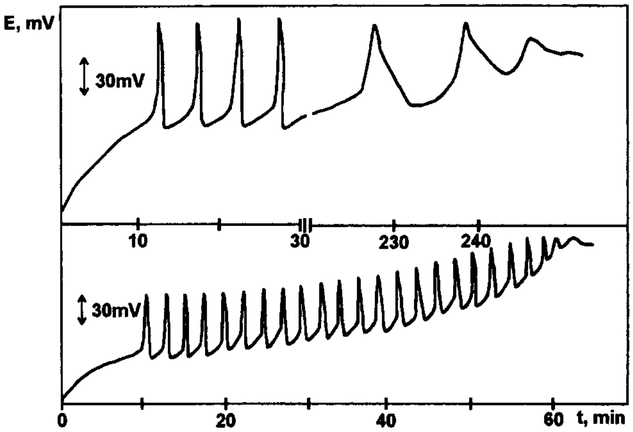

Figure 1. Potentiometric recording of the iodide concentration both in the absence and in the presence of the MoO_4^{2-}: $[H_2SO_4]_0 = 4.85 \times 10^{-2}$ M; $[H_2O_2]_0 = 7.6 \times 10^{-2}$ M; $[KIO_3]_0 = 2 \times 10^{-1}$ M; $T = 60$ °C; (upper trace) without molybdate; (lower trace) $[MoO_4^{2-}]_0 = 5 \times 10^{-4}$ M.

2. Experimental Section

A. Materials. Stock solutions of the components were prepared from commercially available hydrogen peroxide 30% (Selectipur, E. Merck AB, Stockholm), KIO_3, Na_2MoO_4, and H_2SO_4 (p.a. Lachema, Brno, former Czechoslovakia). Dilutions were made with bidistilled water.

B. Procedures. The oscillations of iodine in dependence on the MoO_4^{2-} ion concentration have been followed either spectrophotometrically by means of a spectrophotometer SPECORD M 40 (Carl Zeiss, Jena) as the absorbance−time curves at the wavelength of 445 nm or potentiometrically by means of a polarograph RADELKIS OH-105 (Hungary), (which is suitable for voltamperometric as well as for potentiometric measurements), as the redox potential−time curves. The quartz cuvette in the first case and the galvanic cell in the second one were put in a bath thermostated by means of thermostat U 3 (Medingen). During the measurements, the solution was kept in a relatively dark room and stirred magnetically to prevent development of gradients in composition. For the potentiometric

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[†] The present address: Faculty of Natural Sciences, Matej Bel University, 97401 Banska Bystrica, Slovakia.

* Corresponding author. E-mail: treindl@fns.uniba.sk.

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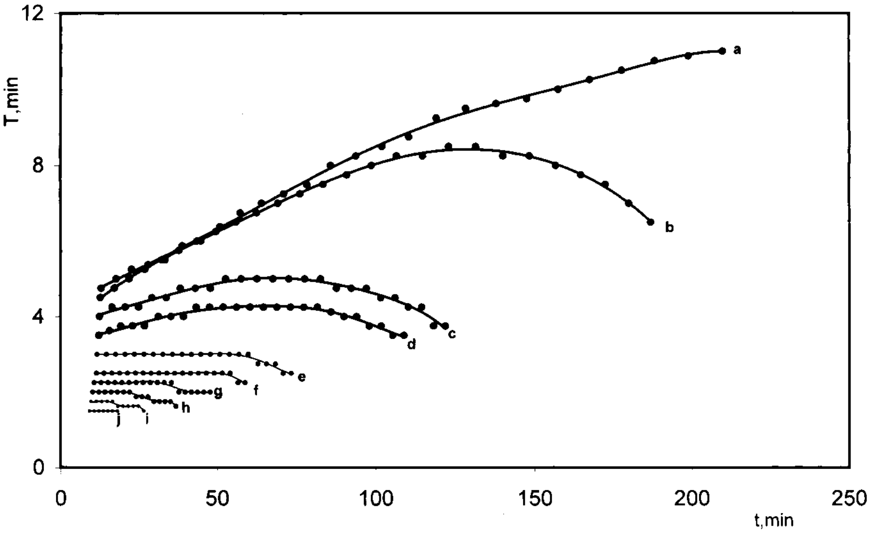

Figure 2. Temporal dependence of the period of oscillation on the concentration of the MoO_4^{2-} ions: $[H_2SO_4]_0 = 4.85 \times 10^{-2}$ M; $[H_2O_2]_0 = 7.6 \times 10^{-2}$ M; $[KIO_3]_0 = 2 \times 10^{-1}$ M; $T = 60$ °C; $10^4 \times [MoO_4^{2-}]_0 = 0$ (a), 1 (b), 2 (c), 3 (d), 4 (e), 5 (f), 6 (g), 7 (h), 8 (i), 9 (j).

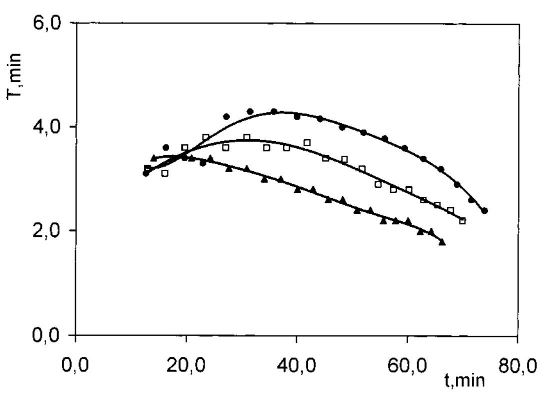

Figure 3. Interaction of the BL system with an overlying gas phase. The composition of the solution is the same as in Figure 1, $T = 60$ °C: (●) the cuvette is open and solution is stirred; (□) the cuvette is open and solution is not stirred; (▲) the cuvette is open partly and solution is not stirred.

TABLE 1: Dependence of Parameters of the BL Reaction upon the MoO_4^{2-} Ions Concentration[a]

$10^4 \times C$, M	IP-induction period, min	T_{3-4}, min[b]	number of oscillations	duration of oscillations, min
0	13.0	5.3	27	209.6
1	12.8	5.0	27	186.8
2	12.5	4.3	26	122.0
3	12.3	3.8	26	108.9
4	11.8	3.0	23	73.3
5	11.5	2.5	21	58.8
6	10.8	2.3	19	47.8
7	10.3	2.0	16	36.9
8	9.8	1.8	12	26.6
9	9.3	1.5	8	18.3

[a] $[H_2SO_4]_0 = 4.85 \times 10^{-2}$ M; $[H_2O_2]_0 = 7.6 \times 10^{-2}$ M, $[KIO_3]_0 = 2 \times 10^{-1}$ M; $T = 60$ °C. [b] T_{3-4} is the period between the third and the fourth oscillation.

measurements, a platinum electrode with an area of 1 cm^2 was used as an indicative electrode and a mercurosulfate elecrode as a reference electrode. These solutions also were lightly stirred. Almost all measurements were made at 60 °C.

3. Results and Discussion

The Bray−Liebhafsky (BL) oscillatory system consisting of 4.85×10^{-2} M H_2SO_4, 2×10^{-1} M KIO_3, and 7.6×10^{-2} M H_2O_2 is influenced by the presence of MoO_4^{2-} ions in their 10^{-4} M concentration so that the values of induction period and of duration of oscillations, respectively, diminish and the average frequency of oscillations increases. The catalytic influence of the MoO_4^{2-} ions upon the BL oscillations can be seen the best, if the induction period, IP, and the period of oscillation, T, are plot in dependence on the time, at increasing values of the MoO_4^{2-} ions (Figures 1and 2). As we can see in Figure 2, the oscillation period, T, increaeses with time, if no molybdate is present. In the presence of MoO_4^{2-} ions, it increases with time, attains a maximum, and then decreases. The duration of oscillations decreases with increasing initial concentration of molybdate. The $T = f(t)$ curve depends also on whether the cuvette is open and stirred, open and nonstirred, and finally partly open and nonstirred (Figure 3). These curves have the same character, irrespective of the method used, potentiometry or spectrophotometry. The main features of the influence of the MoO_4^{2-} ions on the BL oscillations can be characterized by the values of induction period, IP, period of oscillation, T, number of oscillations, NO, and the duration of oscillations, DO, respectively (Table 1).

The MoO_4^{2-} ions effect upon the BL oscillations described above can be explained from the point of view of the oxidation of iodine by hydrogen peroxide catalyzed by molybdate as described by us,[16] as well as from the point of view of the hydrogen peroxide disproportionation catalyzed by molybdate.[17−20] The oxidation of iodine by hydrogen peroxide

$$I_2 + 5H_2O_2 \rightarrow 2IO_3^- + 2H^+ + 4H_2O \qquad (1)$$

is one of the main stoichiometric processes of the BL reaction, but in general it proceeds too slowly to correspond to real interactions of the involved species during the BL reaction. Treindl and Noyes[6] proposed the reaction mechanism involving 10 individual steps, the seventh of which is the interaction of I radicals with O_2 produced by the reduction of iodate by hydrogen peroxide

$$2IO_3^- + 5H_2O_2 + 2H^+ \rightarrow I_2 + 5O_2(aq) + 4H_2O \qquad (2)$$

According to them,[6] oxygen is not only one of the products of the BL reaction but also an intermediate.

In the presence of molybdate, the oxidation of iodine by hydrogen peroxide is catalyzed by MoO_4^{2-} ions in the sense of the suggested reaction scheme[16]

$$MoO_3 + H_2O_2 \rightarrow MoO_2(O_2) + H_2O_2 \tag{3}$$

$$I_2 + H_2O = HOI + H^+ + I^- \tag{4}$$

$$MoO_2(O_2) + HOI \rightarrow HIO_2 + MoO_3 \text{ (slow)} \tag{5}$$

$$2HIO_2 = HIO_3 + HOI \tag{6}$$

$$HIO_2 + I^- + H^+ = 2HOI \tag{7}$$

The sum of 5 × eq 3, eq 4, 5 × eq 5, 2 × eq 6, and eq 7 corresponds to the stoichiometric process 1. Based on that study, we can proclaim that the noncatalyzed (direct) oxidation of iodine by hydrogen peroxide is too slow to become one of the two main processes of the BL oscillatory reaction. In the presence of molybdate, during the BL reaction the oxidation of iodine by hydrogen peroxide can proceed not only as suggested by Treindl and Noyes[6] but also as by MoO_4^{2-} ion catalyzed oxidation of hydrogen peroxide.[16] On the other side, we have to take into consideration the work of refs 17−20 too, according to which, during the disproportionation of hydrogen peroxide catalyzed by molybdate, the singlet oxygen is produced,

$$2H_2O_2 \xrightarrow{MoO_4^{2-}} 2H_2O + {}^1O_2 \tag{2}$$

Singlet oxygen produced by the disproportionation of hydrogen peroxide is quenched partly physically and/or chemically.[20] In any case, the total actual concentration of oxygen that can interact then with I atoms increases, in the sense of the mentioned reaction mechanism,[5] and finally, the rate of the process 1 can increase. Thus, we can explain (at least qualitatively) the effects of molybdate on the parameters of the BL reaction.

Although the geometry of a cuvette and the rate of the mild stirring have an influence on the parameters of the BL reaction (Figure 3), these factors are not essential for the occurrence of the oscillations. The interaction of the BL system with an overlying gas phase seems to contribute to changes only in the location of bifurcation points but not to the existence of oscillations.

Finally, we conclude that both kinds of MoO_4^{2-} ion catalytic activity upon the BL reaction, resulting in the increased average frequency and in the shortenning of induction period and of the duration of oscillations, are very probable.

Noyes and co-workers[8] used the Treindl−Noyes skeleton mechanism[6] to develop a model of the BL system based on only two concentration variables, $[O_2]$ and $[I_2]$, and three composition parameters. The changes of parameter values which cause the steady state to be stable or oscillatory are consistent with the experimental effects of changing acidity or stirring rate. However, while these oscillations can be quite long-lived, they take place around a stable or unstable focus and do not involve a true limit cycle.[6] Therefore, we continue in efforts of cited authors,[6] in experiments which should either support or discredit the proposed new mechanism. We believe that this work together with our published papers[15,16] do support it, at least qualitatively. We realize that a quantitative treatment and simulations of the phenomena described above, how the various component processes control the oscillations/frequency, are needed. Although we are not able to accomplish them at the present time, anyway, we believe that our present work is a worthwhile contribution to the efforts of several authors to develop a complete elucidation of the mechanism of the BL reaction. A detailed analysis of the importance of various proposed processes described above and their consistency with the mentioned mechanism[6] will be the subject of subsequent work.

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