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The Bray-Liebhafsky Oscillatory Reaction. Kinetic Investigations in Reduction and Oxidation Pathways Based on Hydrogen Peroxide Concentration Monitoring

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Abstract: *By direct monitoring of the hydrogen peroxide concentration during its catalytic decomposition into water and oxygen in the presence of potassium iodate and sulfuric acid, that is in the Bray-Liebhafsky system, the pseudo-rate constants of overall reduction and oxidation pathways were determined. The dependence of the obtained rate constants on acidity was evaluated. It was found that the pseudo-rate constant of the overall reduction process increases with increasing acidity, whereas the pseudo-rate constant of the overall oxidation process decreases with increasing acidity. The corresponding activation energies were also calculated using values of this constant at two temperatures.*

Keywords: *Chemical Kinetics; Nonlinear Dynamics; Bray-Liebhafsky Reaction; Rate Constants; Activation Energy.*

Резюме: *Исследованием концентрации перекиси водорода в процессе его каталитического разложения на воду и кислород в присутствии йодата калия и серной кислоты, т.е. в системе Bray-Liebhafsky, проведен анализ постоянных скорости восстановительного и окислительного путей в качестве постоянных скоростей псевдопервого ряда. Определены их зависимости от кислотности. С увеличением кислотности псевдопостоянная скорости восстановительного процесса увеличивается, в то время как псевдопостоянная скорости окислительного процесса с увеличением кислотности – уменьшается. Использованием их значений при двух температурах рассчитаны соответствующие энергии активации.*

Ключевые слова: *Химическая кинетика; динамика нелинейных систем; реакция Bray-Liebhafsky; постоянные скорости; энергия активации.*

Садржај: *Директним праћењем концентрације водоник-пероксида у току његовог каталитичког разлагања на воду и кисеоник у присуству калијум-јодата и сумпорне киселине, односно у Bray-Liebhafsky систему, анализиране су константе брзина*

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целокупног редукционог и оксидационог пута као константе брзина псеудо-првог реда. Изведене су њихове зависности од киселости. Нађено је да псеудо-константа брзине целокупног редукционог процеса расте са порастом киселости, док псеудо-константа брзине целокупног оксидационог процеса опада са порастом киселости. Коришћењем њихових вредности на две температуре израчунате су одговарајуће енергије активација.

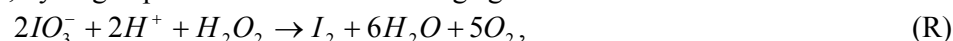
Кључне речи: Хемијска кинетика; нелинерна динамика; реакција *Bray-Liebhafsky*; константе брзине; енергија активације.

Introduction

It is well known that hydrogen peroxide decomposition into water and oxygen in the presence of hydrogen and iodate ions, viz.



is a complex reaction which takes place through two also complex reactions; in the first one, hydrogen peroxide acts as a reducing agent:



and, in the second one, hydrogen peroxide acts as an oxidizing agent:



It is also known that direct analysis of its kinetics with respect to hydrogen peroxide by its monitoring, besides monitoring other intermediate species, is of crucial importance in understanding the overall process [1-21].

Moreover, it is well known that a method of determining the hydrogen peroxide concentration exists based on the spectrophotometric measurements of the complex formed between titanium oxalate and hydrogen peroxide [11, 22]. However, although illustrations [11, 23] of hydrogen peroxide decomposition exists based on these measurements, no kinetic results were obtained on the ground of them. Naturally, we should ask ourselves why this is so? The answer is simple.

There are two serious difficulties related to the mentioned measurements of hydrogen peroxide concentrations in the system considered. The first is caused by periodic perturbations of the system as successive aliquots are taken from it during the reaction, that is while the system considered is in one of its steady states far from thermodynamic equilibrium; particularly, if it is in an oscillatory state.

The second difficulty is related to spectrophotometric measurements of hydrogen peroxide concentration by titanium oxalate in the presence of iodine species (in the presence of iodine species, the concentration of hydrogen peroxide cannot be monitored by the standard iodometric titration method [24]). More precisely, although this has not been noted in literature, we could observe that the absorbance obtained by the measurements mentioned, in some regions of parameters, is distinctly higher than expected for the hydrogen peroxide concentration in this system under the conditions considered.

This paper deals with hydrogen peroxide concentration monitoring during its decomposition into water and oxygen in the presence of potassium iodate and sulphuric acid (the Bray-Liebhafsky reaction), and, on the basis of these results, with

analyzing the corresponding kinetics based on the calculated pseudo-rate constants for the overall processes (R) and (O).

Experimental

The experiments were carried out in the manner similar to the ones described in our previous papers [25-26], where the same system was investigated under isothermal conditions. The hydrogen peroxide decomposition in the presence of potassium iodate and sulphuric acid was analyzed in a well stirred vessel (magnetic stirrer of 900 rpm) at constant temperatures $T_1 = 333.2 \pm 0.2$ K (60°C) and $T_2 = 328.2 \pm 0.2$ K (55°C). The introduction of 1 ml of hydrogen peroxide solution to the standardized mixture of 25 ml of potassium iodate and 25 ml of sulfuric acid solutions was taken as the initial moment for the reaction. The initial concentrations of hydrogen peroxide, potassium iodate and sulfuric acid are given in Tabs. I and II. The initial concentration of hydrogen peroxide was controlled by the standard iodometric titration method [24].

Tab. I The values of initial concentrations of sulfuric acid and potassium iodate and the calculated values for hydrogen and iodate ion concentrations in the reaction system at temperatures of $T = 333$ K (60°C) and $T = 328$ K (55°C).

T (K(°C))	$[\text{H}_2\text{SO}_4]_0$ (mol/dm ³)	$[\text{KIO}_3]_0$ (mol/dm ³)	$[\text{H}^+]$ (mol/dm ³)	$[\text{IO}_3^-]$ (mol/dm ³)
333 (60)	2.45×10^{-2}	6.62×10^{-2}	3.14×10^{-2}	5.74×10^{-2}
333 (60)	3.37×10^{-2}	6.88×10^{-2}	4.19×10^{-2}	5.74×10^{-2}
333 (60)	4.90×10^{-2}	7.38×10^{-2}	5.59×10^{-2}	5.74×10^{-2}
333 (60)	8.00×10^{-2}	8.23×10^{-2}	8.55×10^{-2}	5.74×10^{-2}
328 (55)	2.45×10^{-2}	6.62×10^{-2}	3.13×10^{-2}	5.74×10^{-2}
328 (55)	8.00×10^{-2}	8.23×10^{-2}	8.53×10^{-2}	5.74×10^{-2}

The mixture of sulfuric acid and potassium iodate solution was purified with nitrogen for 40 min. in order to maintain a mixture free of any dissolved oxygen before hydrogen peroxide was added.

The measurements were carried out in several independent series of experiments performed at different temperatures and for different acidities. In every series, that is at any fixed acidity and temperature, the initial concentrations of hydrogen peroxide had the values given in Tab. II.

Tab. II The four values of initial hydrogen peroxide concentrations, all four applied to every combination of the parameters given in Tab. I.

T (K (°C))	$[\text{H}_2\text{O}_2]_0$ (mol/dm ³)			
333 (60)	3.94×10^{-3}	9.85×10^{-3}	1.58×10^{-2}	1.98×10^{-2}
328 (55)	4.00×10^{-3}	1.00×10^{-2}	1.60×10^{-2}	2.00×10^{-2}

The initial concentrations of potassium iodate and sulphuric acid were varied but in such a way that the concentration of iodate in the system was kept constant at $5.74 \times 10^{-2} \text{ mol/dm}^3$ [27]. For this purpose the dissociation constant K_a at 60°C was taken from [28]. The initial combinations of sulphuric acid and potassium iodate, together with corresponding concentrations of iodate and hydrogen ions in the reaction mixture, are presented in Tab. I.

All measurements were carried out in two parallel independent series with the same initial concentrations of all species. In one of them, the time evolution of the system undergoing concentration oscillations of intermediates was followed potentiometrically, by means of iodide ion sensitive electrode connected to the Ag/AgCl reference electrode, with the aim to monitor the iodide ion as one of the intermediates in the system. In another one, the time evolution of the system was followed by two methods, potentiometric and spectrophotometric, at $\lambda = 405 \text{ nm}$, in parallel. The spectrophotometric method was used to monitor the hydrogen peroxide concentration as a reactant undergoing cascade decomposition. For hydrogen peroxide measurements, aliquots of 0.3 ml have been taken from the solution periodically.

Results

Examinations of disturbances of the system influenced by taking aliquots

The analyzed system belongs to the class of homogeneous oscillatory chemical reactions. In other words, in some of its dynamic states far from equilibrium, the concentration oscillations of intermediate species participating in it may set in. Generally, such processes are very sensitive to any perturbations [29] and, unfortunately, we had to take aliquots from our system to measure the hydrogen peroxide concentration by spectrophotometric method.

In order to investigate the influence of the permanent disturbance of the system introduced by taking aliquots during the reaction, we had to carry out two parallel, equivalent and independent experiments with one of them monitored without taking aliquots. As iodide is one of the most important intermediate species in the system, the corresponding potentiometric measurements were performed. One of the oscillograms obtained without taking aliquots is presented in Fig. 1a, whereas the one where aliquots are taken, for the same parameters of the system, is presented in Fig. 1b. Aliquots were taken at the moments denoted by arrows. The reproducibility of results is fascinating, especially if one bears in mind that reproducibility of the oscillatory evolution is very difficult to achieve, even in two equivalent successive unperturbed experiments. The average time intervals between starts of reactions and terminations of their oscillatory phases, τ_{end} , in the two experiments with the same parameters, except in two examples only, differed by less than 9 %.

Spectrophotometric measurements

The dependence of absorbance (proportional to the hydrogen peroxide concentration) on time is presented in Figs. 1c and 2.

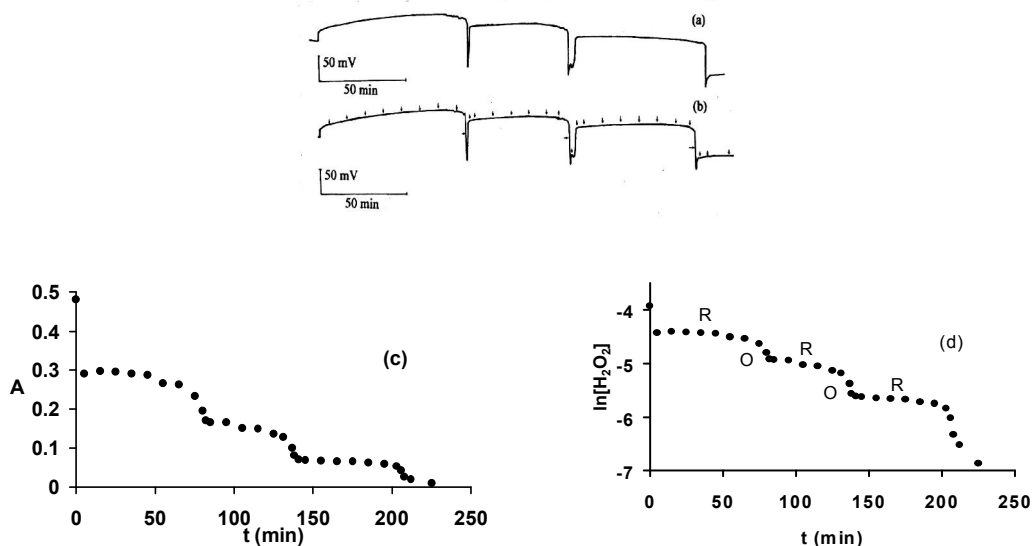
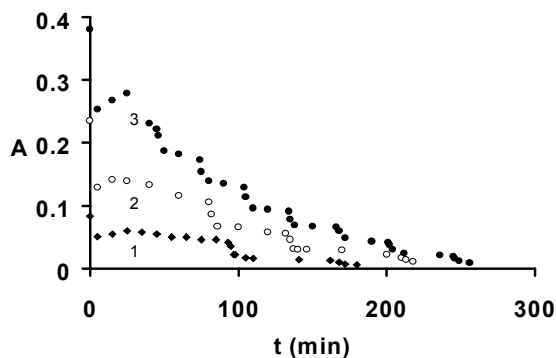


Fig. 1 The time evolution of the Bray-Liebafsky system for two independent experiments with the same initial conditions are considered; the first one is presented in (a) and the second one in (b), (c) and (d). Potentiometric traces of the iodide ion sensitive electrode (a) without taking aliquots, and (b) with taking aliquots from the system. The arrows denote the moments of taking aliquots. (c) The absorbance of aliquots versus time, obtained at 405 nm, during hydrogen peroxide decomposition. (d) Cascade curves presenting hydrogen peroxide decomposition given in the form $\ln[\text{H}_2\text{O}_2]$ versus time; $T = 333 \text{ K}$, $[\text{H}_2\text{SO}_4]_0 = 2.45 \times 10^{-2} \text{ mol/dm}^3$, $[\text{KIO}_3]_0 = 6.62 \times 10^{-2} \text{ mol/dm}^3$ ($[\text{H}^+]_0 = 3.14 \times 10^{-2} \text{ mol/dm}^3$, $[\text{IO}_3^-]_0 = 5.74 \times 10^{-2} \text{ mol/dm}^3$), $[\text{H}_2\text{O}_2]_0 = 1.98 \times 10^{-2} \text{ mol/dm}^3$.

In Fig. 2. one can notice an important increase of absorbance during the preoscillatory period, contrary to the case in Fig. 1c. This effect appeared only in experiments where the steady state concentration of iodine was high, as it is in the



examples presented in Fig. 2.

Fig. 2 The absorbance of aliquots versus time, obtained at 405 nm, during hydrogen peroxide decomposition in the BL system; $T = 333 \text{ K}$, $[\text{H}_2\text{SO}_4]_0 = 3.37 \times 10^{-2} \text{ mol/dm}^3$, $[\text{KIO}_3]_0 = 6.88 \times 10^{-2} \text{ mol/dm}^3$ ($[\text{H}^+]_0 = 4.19 \times 10^{-2} \text{ mol/dm}^3$, $[\text{IO}_3^-]_0 = 5.74 \times 10^{-2} \text{ mol/dm}^3$). The cascade curves denoted by 1, 2 and 3 are obtained with $[\text{H}_2\text{O}_2]_0 = 3.94 \times 10^{-3}$, 9.85×10^{-3} and

1.58×10^{-2} mol/dm³, respectively. For the acidity considered, $[H^+]_0 = 4.19 \times 10^{-2}$ mol/dm³, the influence of iodine on the overall absorbance of the Bray-Liebhafsky reaction is the highest.

If absorbance was a measure of the hydrogen peroxide concentration only, we could have conclude that its concentration might have rises in the period shortly following the beginning of the process. However, before reaching such a conclusion, we had to see the influence off the iodine species on absorbance. Therefore, water solutions of titanium oxalate and hydrogen peroxide, titanium oxalate and iodine and titanium oxalate and iodate were investigated separately. Other iodine species have very low concentrations in the Bray-Liebhafsky system.

Analyses of the absorbance of the solutions mentioned, have shown that titanium oxalate forms complexes with hydrogen peroxide and iodine only [30]. Therefore, the absorbance of the mixed hydrogen peroxide and iodine solutions with titanium oxalate was analyzed separately. The evaluated results were used for corrections of our cascade curves denoting absorbance versus time during hydrogen peroxide decomposition.

As the iodine concentration in the Bray-Liebhafsky reaction also depends on acidity [11], we found that corrections in absorbance due to iodine were necessary only in the preoscillatory period of some oscillograms. Hence, we could proceed to kinetic considerations of the cascade curves presenting hydrogen peroxide concentrations as functions of time, either by analyzing the overall curves with corrected preoscillatory periods or, simply, by analyzing the same curves omitting preoscillatory periods in order to avoid any possible errors due to correction. The results obtained by both procedures appeared to be independent of the method applied.

Kinetic results

The process of hydrogen peroxide decomposition, under considered conditions, has the characteristic cascade form with two obviously different rates. From the potentiometric measurements, we knew that, under the conditions considered, the overall hydrogen peroxide decomposition (D) obeys the first order kinetic law [3, 8, 31]. In other words that

$$\frac{d[H_2O_2]}{dt} = -k_D [H_2O_2] \quad (1)$$

and

$$k_D = -\frac{d(\ln[H_2O_2])}{dt} \quad (2)$$

Having this in mind, we presented here in one figure all four $\ln[H_2O_2]$ -time cascade curves obtained, under the same conditions, for four different initial concentrations of hydrogen peroxide (one example of the $\ln[H_2O_2]$ -time cascade curve is presented in Fig. 1d). We could note that linear dependence of $\ln[H_2O_2]$ on time is approximately satisfied in all (R) periods during oscillatory evolution of the system and that these slopes are, in a first approximation, parallel to one another .

Moreover, from the potentiometric measurements performed earlier at 25°C and 39°C, we know that the rate constant k_O is a complex function of hydrogen peroxide [32-33], but under considered conditions and $T = 60^\circ\text{C}$, the experimentally determined constant, noted as k_O , is apparently independent of the hydrogen peroxide

concentration and oxidation process can be also considered as a pseudo-first order one*. Therefore, as well as the fact that the activation energy calculated using rate constants obtained in the previous measurements by the method where the pseudo-first order kinetics is postulated and found [31] had a value characteristic for oxidation process [17], for periods (O), we also accept a linear and parallel dependence of $\ln[\text{H}_2\text{O}_2]$ on time.

From these two different linear and parallel slopes, the pseudo-first order rate constants of the overall processes of reduction (R) and oxidation (O) are determined. The rate constant with a lower value, due to process (R) [8, 12, 17-18], has been determined directly, since we always had several points in every such region. During domination of process (O) [8, 12, 17-18], where the rate constant has a higher value, but where we do not have a sufficient number of points in one oxidation period, we had to take into account the duration of an oxidation process, as obtained by potentiometric measurements. The change from slow to rapid hydrogen peroxide decomposition that corresponds to sudden decrease of iodide concentration (or sudden increase of potential), has been selected as the beginning of the domination of process (O). Similarly, the change from rapid to low hydrogen peroxide decomposition, that corresponds to the inflection point during the increase of the iodide concentration, is taken as the end of the same process [11, 23, 32]. The average values of the results obtained for the rate constants of processes (R) and (O) are listed in Tab. III. The rate constant of process (R), at the highest acidity considered, when $[\text{H}^+] = 8.5 \times 10^{-2} \text{ mol/dm}^3$, could not be determined, as the "oscillogram" did not have any standard form in that case. The time evolution consists here of a preoscillatory period with some characteristics of reduction, and a sudden shift to oxidation. A very regular oxidation pathway permits evaluation of the rate constant of oxidation under these conditions.

Tab. III Average pseudo-first order rate constants of processes (R) and (O).

T (K(°C))	$[\text{H}^+]_0$ (mol/dm ³)	$[\text{IO}_3^-]_0$ (mol/dm ³)	k_R (min ⁻¹)	k_O (min ⁻¹)
333 (60)	3.14×10^{-2}	5.74×10^{-2}	$(1.62 \pm 0.03) \times 10^{-3}$	0.54 ± 0.06
333 (60)	4.19×10^{-2}	5.74×10^{-2}	$(2.57 \pm 0.33) \times 10^{-3}$	0.16 ± 0.04
333 (60)	5.59×10^{-2}	5.74×10^{-2}	$(3.57 \pm 0.43) \times 10^{-3}$	0.09 ± 0.03
333 (60)	8.55×10^{-2}	5.74×10^{-2}	/	$(1.36 \pm 0.22) \times 10^{-2}$
328 (55)	3.13×10^{-2}	5.74×10^{-2}	$(1.34 \pm 0.22) \times 10^{-3}$	0.27 ± 0.05
328 (55)	8.53×10^{-2}	5.74×10^{-2}	/	$(8.90 \pm 0.70) \times 10^{-3}$

Discussion

The rate constants k_R and k_O are, obviously, functions of acidity. Their dependence on acidity is presented in Fig. 3. Under the conditions considered, the rate

* The temperature difference between these two series of experiments can be of essential importance for any generalisation. A decrease of temperatures produces a similar effect as an increase of acidity [34-35]. Under such conditions kinetics of the overall reaction can be changed.

constant k_R increases with acidity, while the rate constant k_O decreases with acidity. From linear dependences of the curves presenting $\log k_R$ and $\log k_O$ versus $\log [H^+]$, the coefficients n and m in the following equations:

$$k_R = k'_R [H^+]^n, \quad (3)$$

and

$$k_O = k'_O / [H^+]^m, \quad (4)$$

have been determined.

The values obtained are: $n = 1.4$ and $m = 3.6$. Ordinates at the point $\log [H^+] = 0$, yield the values for k'_R and k'_O . They are $k'_R = 1.8 \times 10^{-1} (\text{mol/dm}^3)^{-1.4} \text{min}^{-1}$ and $k'_O = 2.4 \times 10^{-6} (\text{mol/dm}^3)^{3.6} \text{min}^{-1}$ (the dimensions of k_R and k_O are given in min^{-1}).

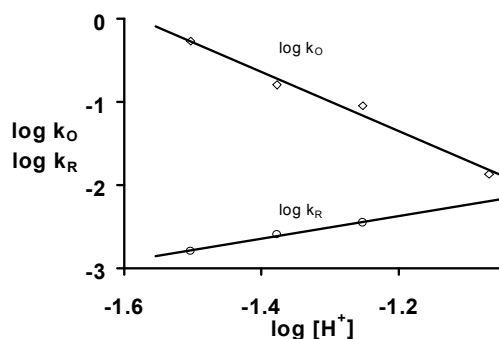


Fig. 3 The dependence of pseudo-rate constants of overall reduction and oxidation pathways, k_R and k_O , on acidity given in the form $\log k_R$ and $\log k_O$ versus $\log [H^+]$.

Using these rate constants at two temperatures (Tab. III), we calculated the corresponding activation energies. At the lowest acidity considered, (i.e. $[H^+] = 3.1 \times 10^{-2} \text{mol/dm}^3$), the activation energy obtained with the aid of k_R is $E(R) = 34 \text{kJ/mol}$, and the one obtained with the aid of k_O is $E(O) = 126 \text{kJ/mol}$. At the highest acidity considered ($[H^+] = 8.5 \times 10^{-2} \text{mol/dm}^3$), where only k_O can be obtained, the corresponding activation energy is $E(O) = 77 \text{kJ/mol}$.

The calculated values for the activation energies in reduction and oxidation pathways are in excellent agreement with the ones obtained previously by other methods. Thus, at low acidity, the activation energy of the overall process, that can be ascribed to the oxidation pathway [17], is found to be $120 \pm 20 \text{kJ/mol}$ [33]. In reference [17], where the activation energies at slightly higher acidities are calculated by several methods, the obtained activation energies of the reduction pathway were found to be between 31 and 35 kJ/mol, and those of the oxidation one between 75 and 78 kJ/mol. Also, the activation energy of the oxidation pathway, as determined in [34] at higher acidities and by a totally different experimental and calculating procedure, amounted to 80 kJ/mol.

Conclusion

Direct monitoring of hydrogen peroxide concentration during its decomposition into water and oxygen in the presence of potassium iodate and sulfuric acid, that is in the Bray-Liebafsky system, was carried out by the spectrophotometric method with

titanium oxalate. For this purpose, two problems were considered: a) eventual perturbations of the system due to taking aliquots, and b) the influence of iodine on hydrogen peroxide measurements.

By this direct monitoring of hydrogen peroxide decomposition in the Bray-Liebhafsky system, the rate constants of overall reduction and oxidation pathways, k_R and k_O , were analysed as pseudo-first order ones. The dependence of the obtained rate constants on acidity was evaluated. It was found that the rate constant of the overall process of reduction increases with increasing acidity, according to the relation given by eq. (3), whereas the rate constant of the overall process of oxidation decreases with increasing acidity as given by eq. (4).

Using values of the rate constants k_R and k_O at two temperatures, the corresponding activation energies were calculated. The obtained values of 34 kJ/mol for the reducing pathway and 126 kJ/mol for the oxidizing one at low acidity, and of 77 kJ/mol for the oxidizing one at higher acidity, are all in excellent agreement with the corresponding values obtained by other experimental and calculating procedures. Thus, the previously determined values of the two activation energies, i.e. the ones during domination of the oxidation process at lower and higher acidities corresponding to different oxidation pathways, are confirmed.

All kinetic results are evaluated for a constant initial concentration of iodate ions in the reaction mixture by adjusting the initial concentrations of sulfuric acid and potassium iodate. These are the first kinetic results obtained for the Bray-Liebhafsky reaction under the conditions mentioned.

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