Study of the Bray−Liebhafsky Reaction by On-Line Mass Spectrometry

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The experimental study of iodate-catalyzed disproportionation of aqueous hydrogen peroxide, called the Bray−Liebhafsky oscillating reaction (BLR), was performed by using membrane introduction mass spectrometry (MIMS). The sequence of species O_2, HIO_2, HIO, and I_2, which appear during the oscillation, was observed for the first time. The influence of ambient atmosphere, stirring rate, and temperature on the BLR was investigated. The contribution of gained results to the published models is discussed.

Introduction

A dual role of hydrogen peroxide as an oxidizing and as a reducing agent was investigated and reported by W. C. Bray in 1921[1] as the first periodic inorganic oscillating reaction in homogeneous solution. The reaction studied was the decomposition of hydrogen peroxide in acidic media in the presence of iodate. It can be written formally as a two complex processes:

$$5H_2O_2 + 2IO_3^- + 2H^+ = I_2 + 5O_2 + 6H_2O \qquad (1)$$

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

Both reactions involve the iodic acid-iodine oxidation−reduction couple. The net result of reactions 1 and 2 is the catalytic decomposition of hydrogen peroxide:

$$2H_2O_2 = O_2 + H_2O \qquad (3)$$

Bray[1] has found that reaction 1 is a markedly autocatalytic process which proceeds rapidly in solutions containing iodate and a moderately high concentration of acid. Anic and coworkers[2] have reported the activation energy to be between 31 and 35 kJ mol^{-1} for reaction 2 and activation energy between 75 and 78 kJ mol^{-1} for reaction 1. A thorough survey of the investigations of this reaction in the literature can be found in the paper of Treindl and Noyes,[3] who summarized known experimental behavior of BLR and analyzed its selected characteristics: chemical species which may be present, chemical processes which may occur, and characteristics of selected steady states. They performed also the comprehensive set of experiments to establish the conditions for oscillations. They examined the effect of stirring, and they found out that the dissolved oxygen could play an important role in the process. They finally proposed a new skeleton mechanism for the explanation of oscillations. Despite many investigations of the BLR, the mechanism of the BLR is not yet fully understood because both reactions 1 and 2 are complex. The difficulty is namely due to insufficient knowledge of the chemistry of reactive iodine intermediates. The Dushman reaction ($IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$) was recently reexamined by Schmitz,[4] who has found that the reduction of iodate by iodide to iodine in acid solution and low iodide concentration is first and second order in iodide.

Also the not fully known role of the transport of dissolved oxygen into an ambient atmosphere was recently investigated.[5] Treindl and Noyes[3] have proposed for BLR following skeleton mechanism:

$$IO_3^- + I^- + 2H^+ \rightarrow HIO_2 + HOI \qquad (4)$$

$$HIO_2 + I^- + H^+ \rightarrow 2HOI \qquad (5)$$

$$HOI + I^- + H^+ \leftrightarrow I_2 + H_2O \qquad (6)$$

$$HOI + H_2O_2 \rightarrow I^- + H^+ + O_2(aq) + H_2O \qquad (7)$$

$$I^- + H^+ + H_2O_2 \rightarrow HOI + H_2O \qquad (8)$$

$$I_2 \leftrightarrow 2\ I^\bullet \qquad (9)$$

$$I^\bullet + O_2(aq) \leftrightarrow IOO^\bullet \qquad (10)$$

$$IOO^\bullet \leftrightarrow IO_2^\bullet \qquad (11)$$

$$2IO_2^\bullet + H_2O \rightarrow IO_3^- + H^+ + HIO_2 \qquad (12)$$

$$O_2(aq) \leftrightarrow O_2(g) \qquad (13)$$

The new reaction which was taken into account in Treindl and Noyes[3] skeleton mechanism of BLR was the reaction of the transport of dissolved oxygen (O_2(aq)) into the atmosphere (O_2(g)), eq 13.

Kolar-Anic et al.[6] have presented a model which is a variation of that proposed by Schmitz in ref 7, which included the first

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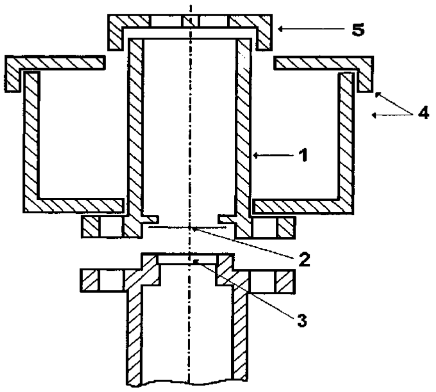


Figure 1. Scheme of the membrane introduction interface to the mass spectrometer. 1, Teflon closed stirred reactor; 2, Teflon foil; 3, steel frit; 4, thermostat; 5, Teflon lid.

six of following reactions:

$$IO_3^- + I^- + 2\,H^+ \leftrightarrow HIO + HIO_2 \qquad (14)$$

$$HIO_2 + I^- + H^+ \rightarrow I_2O + H_2O \qquad (15)$$

$$I_2O + H_2O \leftrightarrow 2HIO \qquad (16)$$

$$HIO + I^- + H^+ \leftrightarrow I_2 + H_2O \qquad (17)$$

$$HIO + H_2O_2 \rightarrow I^- + H^+ + O_2 + H_2O \qquad (18)$$

$$I_2O + H_2O_2 \rightarrow HIO + HIO_2 \qquad (19)$$

$$HIO_2 + H_2O_2 \rightarrow IO_3^- + H^+ + H_2O \qquad (20)$$

$$IO_3^- + H^+ + H_2O_2 \rightarrow HIO_2 + O_2 + H_2O \qquad (21)$$

The improved model of Schmitz[6] was successfully analyzed mathematically, finding the conditions for pseudo-steady-state and critical conditions for setting of oscillations. Recently, Vukojevic et al.[8] have investigated the dynamic behavior of BLR, and they have observed different types of bifurcation leading to simple periodic orbits, supercritical and subcritical Hopf bifurcations, saddle node infinite period bifurcation (SNIPER), saddle loop infinite period bifurcation, and jug handle bifurcation.

The aim of this paper is to contribute experimentally to the solution of the mechanism of BLR by using mass spectrometric techniques and to bring deeper insight to the BLR at molecular level.

Experimental Section

Materials and Procedures. The species H_2SO_4 and KIO_3 were reagent grade chemicals of Lachema a.s. Brno. Solutions of H_2O_2 were made from 30% aqueous material without stabilizer of Chemo a.s. Rájec Jestřebí.

The temperature was stabilized by a U-2 thermostat (Mechanik Prüfgeräte Medlingen, FRG) within the limit ±0.02 °C. Membrane introduction mass spectrometry (MIMS) was used for the kinetic study of BLR. The method consists of the use of a membrane as the separator in the input of mass spectrometer (Figure 1), and it is described in detail in ref 9. Polytetrafluoroethylene membranes (GoreTex, No. S10570 with pores 0.02 μm, thickness 75 μm, porosity 50%) supported by the steel frit Siperm R14 (Tridelta Siperm GmbH, Dortmund, SRN) were used for the experiments.

It was proved in our previous work[9] that the water does not penetrate through the membrane (a vacuum in mass spectrometer is reached) and the nonpolar, noncharged molecules (benzene, naphthalene, acetyl acid ethyl ester, and gases) penetrate through the membrane proportionally to their actual concentration with delay less than 1 s. The volume of the solution in the cell made from polytetrafluorethylene (closed stirred reactor, CSR) was 10 mL. The detection limit in this arrangement was determined[9] to be for benzene 2.7×10^{-5} mol dm^{-3} and for naphthalene 6.0×10^{-6} mol dm^{-3} in water solution. The BLR was studied experimentally in the mentioned reaction cell with a 1 cm^2 cross-section mechanical stirrer and analyzed by a mass spectrometer TRIO 1000 with SIM and mass range m/z (2−1000; Finnigan MAT, Fisions Instrument, San José, California, USA) with software MASSLAB for data collection and analysis.

Results

For this study, we have chosen initial concentrations of reactants in the region of oscillatory behavior according to the results published by Treindl and Noyes:[3] acidity [H^+] between 0.04 and 0.06 M, iodate concentration [IO_3^-] equal to 0.094 M, and hydrogen peroxide concentration [H_2O_2] equal to 0.19 M. These conditions enable us to clarify the influence of various physical and chemical factors (acidity, temperature, ambient atmosphere, and stirring rate) to the oscillatory behavior of BLR.

At first, the experiment was performed at an acid concentration of [H^+] = 0.05 M and temperature of (50 ± 0.02) °C in air. A solution of KIO_3 was bubbled with argon for 30 min. At the beginning of the experiment, H_2O_2 and H_2SO_4 were added so that the mentioned concentrations were reached. The mass spectra were recorded in selected ion monitoring (SIM) mode for which mass peaks were selected on the basis of the full-scan spectra, taken preliminary in separate a experiment. The solution was continuously stirred during the whole experiment. The results are shown in Figure 2a. (All experiments were repeated at least twice.) As expected, the molecules without charge (HIO, HIO_2, and I_2) and the gas (O_2) have penetrated through the membrane and have been detected by the mass spectrometer, after ionization in the ion source of the mass spectrometer. Oscillations exhibit rounded maximum in concentrations of all recorded species.

The change in concentration of acid to [H^+] = 0.04 M (with other parameters unchanged) causes the change of oscillation peaks to a more sharp form with only a little shorter oscillation period (Figure 2b).

New information is gained by mass spectrometry in comparison with previous studies: the direct evidence of present species and order of their appearance in solution could be read from the record. Two features, which appear in all experiments, without exception, could be emphasized: (1) the evolution of oxygen (O_2) precedes the increase of the concentration of iodine (I_2) and (2) the increase of the concentration of HIO and HIO_2 species proceeds at the same time (in the range of measuring error of time) and occurs between the evolution of oxygen and iodine.

This is a challenge for the modeling of oscillation process, which should respect the found oscillation sequence.

With respect to a new skeleton mechanism proposed by Treindl and Noyes,[3] the influence of ambient atmosphere on the oscillatory behavior of the BLR was studied. The reaction was started with the same condition as in Figure 2a, but the only difference was that pure argon (4N, Messer Technogas

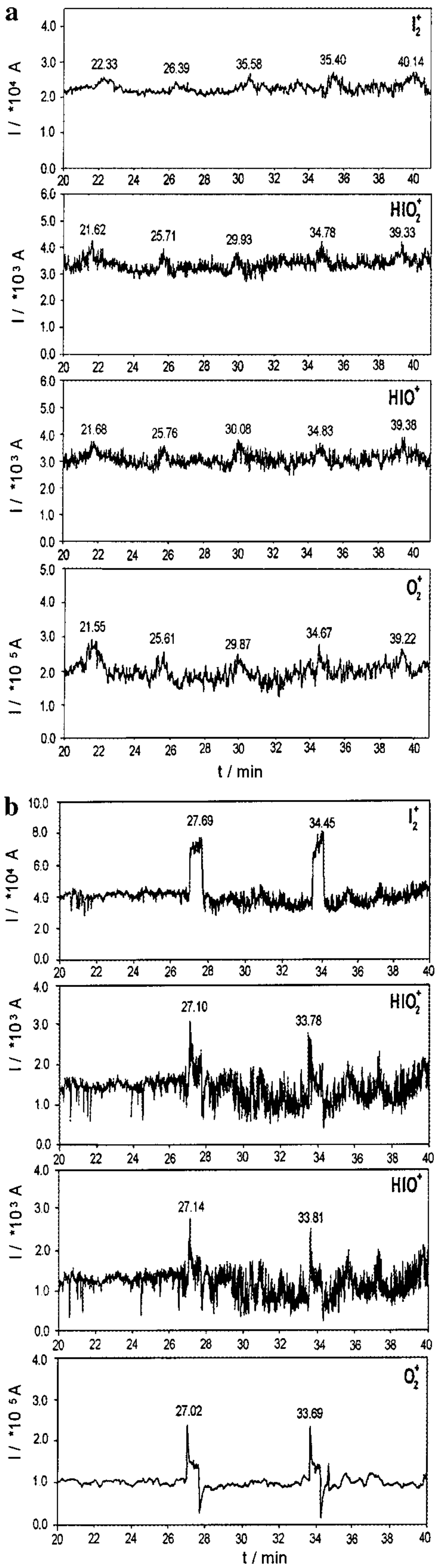


Figure 2. (a) Time dependence of mass spectral lines recorded for masses 32 (O_2^+), 144 (HIO^+), 160 (HIO_2^+), and 254 (I_2^+) at 50 °C in air as the ambient atmosphere. (Concentrations were $c_{H2O2} = 0.19$ M, $c_{KIO3} = 0.094$ M, and $c_{H2SO4} = 0.05$ M. The stirring rate was 2200 min^{-1}.) (b) Time dependence of mass spectral lines recorded for masses 32 (O_2^+), 144 (HIO^+), 160 (HIO_2^+), and 254 (I_2^+) at 50 °C in air as the ambient atmosphere. (Concentrations were $c_{H2O2} = 0.19$ M, $c_{KIO3} = 0.094$ M, and $c_{H2SO4} = 0.04$ M. The stirring rate was 2200 min^{-1}.)

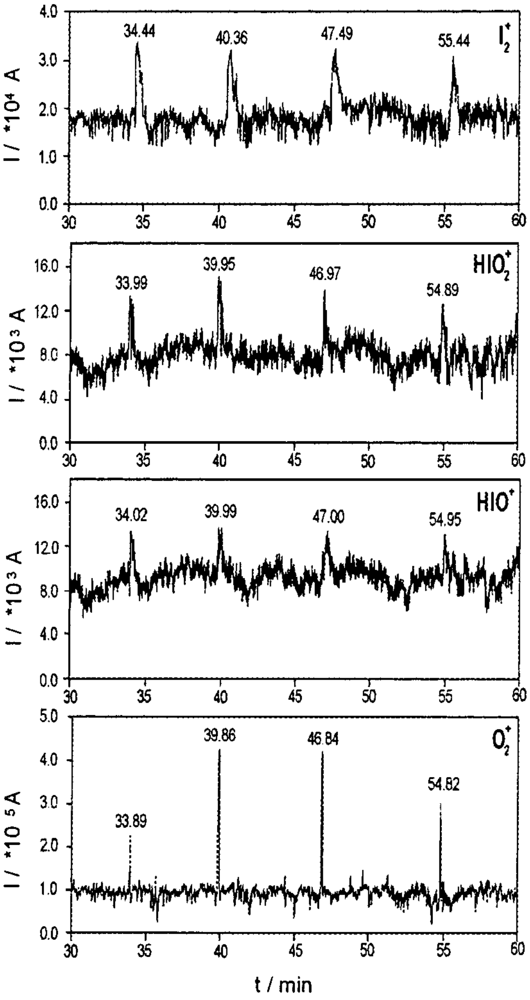


Figure 3. Time dependence of mass spectral lines recorded for masses 32 (O_2^+), 144 (HIO^+), 160 (HIO_2^+), and 254 (I_2^+) at 50 °C in argon as the ambient atmosphere. (Concentrations were $c_{H2O2} = 0.19$ M, $c_{KIO3} = 0.094$ M, and $c_{H2SO4} = 0.05$ M. The stirring rate was 2200 min^{-1}.)

TABLE 1: Dependence of the Time of the Oscillating Period and of the Preoscillating Period on the Temperature

atmos.	temp, K	oscillating period, min	activation energy, kJ.mol^{-1}	preoscillating period, min	activation energy, kJ.mol^{-1}
Ar	313.15	3.3		48.4	
Ar	323.15	7.05	80.4	33.9	32.3
Ar	333.15	21.05		23.0	

Ltd.) was used as an ambient atmosphere. The results are given in Figure 3. Very sharp peaks of oxygen and also others species demonstrate the higher speed of outflow of oxygen from the reaction vessel.

To compare our results with those of Anic et al.,[2] we have performed further experiments in an argon atmosphere at otherwise the same conditions at temperatures 40 and 60 °C. A longer oscillatory period was recorded at 60 °C than at 50 °C, and the shortest period was at 40 °C. The activation energy for the complex process, calculated from the value of the tangent of the dependence of $\ln(1/f) = F(1/T)$, where f is the oscillatory frequence (in argone), yields the value 80.4 kJ mol^{-1} (see Table 1). Anic et al.[2] have found 31 kJ mol^{-1} by the same method in a closed well stirred reactor (in air). From the time of the preoscillatory period, we have found the value 32.3 kJ mol^{-1}, which agrees well with the value of Anic et al.[2] of 34 kJ mol^{-1}.

The quantitative evaluation of the height of peaks by internal standard calibration yielded the value $\sim 1.5 \times 10^{-4}$ M for the

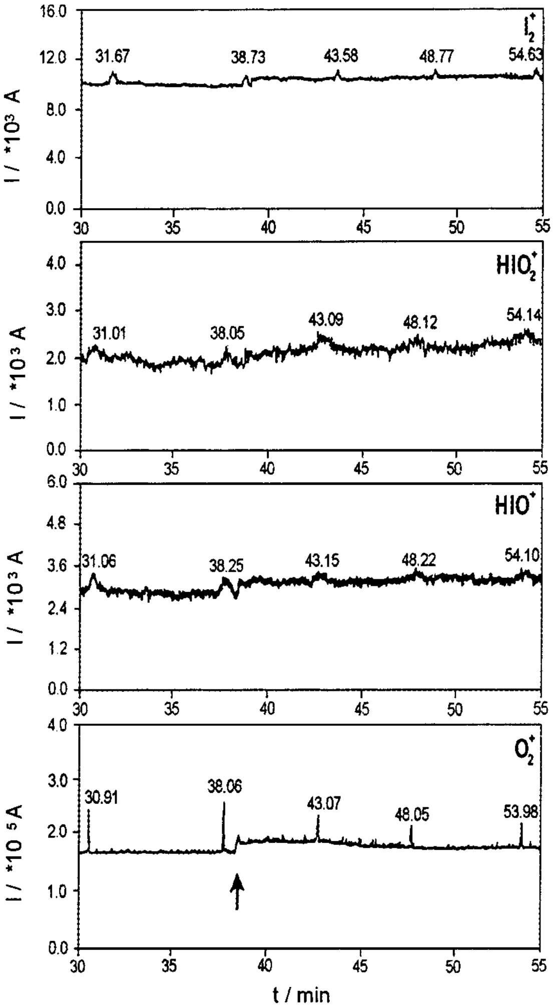


Figure 4. Time dependence of mass spectral lines recorded for masses 32 (O_2^+), 144 (HIO^+), 160 (HIO_2^+), and 254 (I_2^+) at 50 °C in argon as the ambient atmosphere. (Concentrations were $c_{H2O2} = 0.19$ M, $c_{KIO3} = 0.094$ M, and $c_{H2SO4} = 0.05$ M. The stirring rate was 2200 min^{-1}.) The stirring rate was 4500 min^{-1} from the arrow.

maximum concentration of O_2 and the value ∼1 × 10^{-5} M for the maximum concentration of I_2. The influence of the stirring rate was investigated separately. All experiments were done at moderate stirring, which amounts to 2200 min^{-1} with a 1 cm^2 cross-section mechanical stirrer. Higher stirring rates (4500 min^{-1} and 6800 min^{-1}) were used for the comparison with the results, published in ref 3. Complete agreement with the results published in ref 3 was reached (Figure 4).

Discussion

The mass spectrometric study of the BLR confirmed the complexity of the studied process by which iodine-containing species were detected in the sequence in which they appear in the reactor. The relative thermodynamic stability of the series of compounds, in which one element has a different oxidation number, is the Latimer diagram.[10] The new form of the Latimer diagram for iodine-containing species has been published by Stanisavljev,[11] containing new estimated values of standard reduction potentials of iodine species $IO^•$, HIO_2, and $IO_2^•$ in acidic media. The Latimer diagram, improved by Stanisavljev,[11] is presented in Scheme 1.

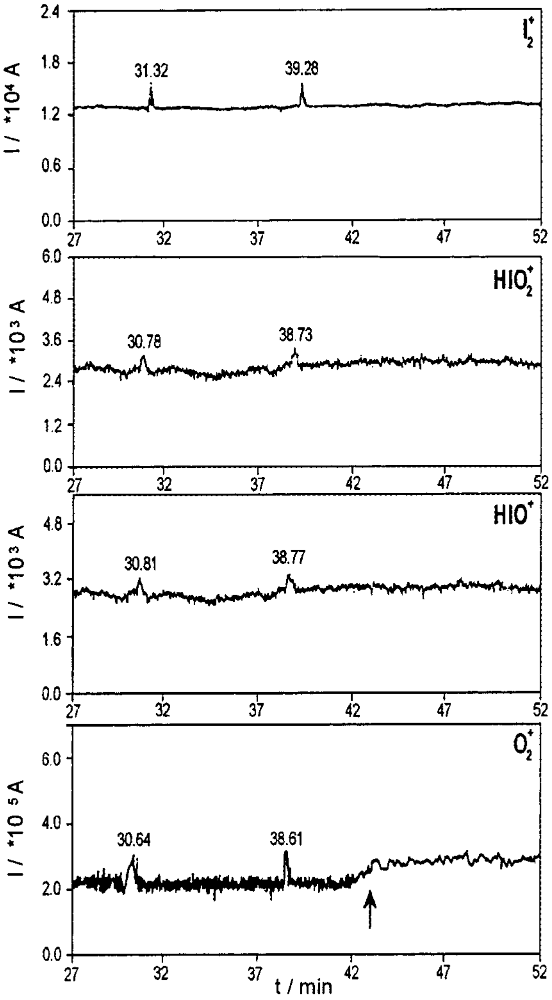
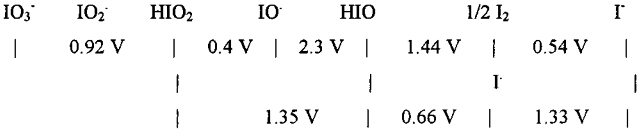


Figure 5. Time dependence of mass spectral lines recorded for masses 32 (O_2^+), 144 (HIO^+), 160 (HIO_2^+), and 254 (I_2^+) at 50 °C in air. Oxygen as the ambient atmosphere is from arrow. (Concentrations were $c_{H2O2} = 0.19$ M, $c_{KIO3} = 0.094$ M, and $c_{H2SO4} = 0.05$ M. The stirring rate was 2200 min^{-1}.)

SCHEME 1



It is evident that the direct reduction of HIO_2 to HIO is energetically advantageous in comparison with the reduction via $IO^•$ and that the reduction of HIO to I^- via I_2 is equivalent to the reduction via $I^•$. The measured reaction product sequence is in principle agreement with this scheme. Neutral molecules HIO_2, HIO, and I_2 appear in the sequence, which corresponds to existing model ideas[3,6] and which are expressed by eqs 4−13 and 14−21, respectively. Be reminded that the species HIO_2 and HIO appear in the mass spectrometric record in the same time in the range of the experimental errors of time measurements. This may be regarded as a proof of equilibrium between them. Oscillations of iodine in an argone ambient atmosphere are similar to potentiometrically recorded oscillations of iodide as described, e.g., in ref 2 (Figure 3). However, peaks of the iodine concentration are substantially broader than those of oxygen, and they are similar to known saw-shaped peaks in air (Figure 2a). It can be caused by equilibria of iodine in solution as was recently proposed, e.g., by Ševčík et al.[12] and by Schmitz.[5] The influence of argon as an ambient atmosphere supports the idea of Treindl and Noyes[3] about the importance of the process (13), i.e., about the importance of the escaping of dissolved oxygen from the solution. Under the use of argon as an ambient atmosphere, all pulses are very pronounced and short. This effect is connected with the larger difference between oxygen pressure in solution and in atmosphere, representing a higher driving force for the escaping of oxygen from solution, which shortens the oxygen pulses. On the other hand, the use of pure oxygen as ambient atmosphere results in the stopping of oscillations at all, when oxygen saturation in solution is reached (Figure 5).

The small concentration changes in acidity (within the limit of 0.04−0.06 M) have only little influence on oscillations (Figure 2 parts a and b).

Measurements at three temperatures at otherwise equal conditions make it possible to calculate the phenomenological activation energy of the process responsible for the preoscillation period and the activation energy of the process responsible for the oscillation periods. As it is shown in Table 1, the respective activation energies are 32.3 and 80.4 kJ mol^{-1}.

Conclusion

This first mass spectrometric study of the BLR using a membrane introduction interface to the mass spectrometer has brought new information. Direct proof of the sequence of neutral species in CSR was given as O_2, HIO_2, HIO, and I_2. Peaks of evolution of oxygen and iodine containing species were more pronounced and sharper when argon was used as an ambient atmosphere in the reactor. Oxygen as an ambient atmosphere stops all oscillations. This result confirms the assumptions made in the model of Treindl and Noyes[3] that the escaping rate of oxygen from the solution influences the oscillations substantially and that it needs to be taken into account in the modeling of oscillations. The high stirring rate has a similar influence as the oxygen atmosphere. Species HIO_2 and HIO have appeared in CSR simultaneously, indicating a possible equilibrium between them. Activation energies of complex processes on the basis of of preoscillation period and of oscillation frequency were determined by the values 32.3 and 80.4 kJ mol^{-1}, respectively.

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