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ARTICLES

^{1}H NMR Monitoring of Water Behavior during the Bray−Liebhafsky Oscillatory Reaction

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Proton NMR spectroscopy was used to monitor behavior of water during the oscillatiory part of the Bray−Liebhafsky (BL) reaction. A series of ^{1}H NMR spectra showed the complex structure of the water signal with periodic changes of the chemical shift and line splitting, which were in agreement with the periodicity of the BL reaction obtained by potentiometric measurements. An analysis of known intermediates in the BL reaction indicated that oxygen formation both as dissolved and in form of bubbles has the dominant effect on NMR spectra. In addition, certain restructuring of water was observed during oscillations, suggesting the subtle role of water in the mechanism of the BL reaction and pointing out to the importance of the NMR techniques in investigation of the chemical oscillators.

1. Introduction

The Bray−Liebhafsky (BL) oscillatory reaction is one of the simplest oscillatory reactions taking place in an aqueous solution.[1−3] It can be presented by two summarized processes

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

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

which alternately dominate over each other, resulting in periodical evolution of intermediates and catalytic decomposition of hydrogen peroxide

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

Although the reaction has been known and investigated for more than 70 years, its detailed mechanism has not been established yet.[4,5] The main obstacle is a limited number of selective and nondestructive techniques applicable “in situ”.[5−8] ^{1}H NMR spectroscopy offers such a possibility, and it has been applied in studying the mechanism of another oxyhalogen oscillator, i.e., the Belousov Zhabotinsky (BZ) reaction.[9−12] In refs 9−11 the efforts were mainly undertaken to identify organic intermediates and products evolving during the course of the BZ reaction. A thorough investigation of ^{1}H NMR parameters of the solvent water signal during the BZ reaction is presented in ref 12. It has been shown that they are induced by the oscillating behavior of pararmagnetic Mn^{2+}, which was present initially in the reaction mixture as a catalyst at a relatively high concentration ($[Mn^{2+}] = 2.1 \times 10^{-3}$ M). In this work proton high-resolution nuclear magnetic resonance (^{1}H NMR) is, for the first time, applied in monitoring the oscillatory behavior of the water signal during the BL reaction. The study was undertaken not only to analyze the BL reaction itself but also having in mind the great importance of water in living organisms, whose very characteristic is periodicity on a broad time scale.[13]

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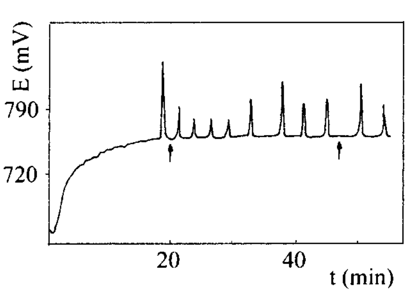

Figure 1. Potentiometric measurements during the Bray−Liebhafsky reaction recorded by a platinum electrode versus an Ag/AgCl reference electrode. Amplitudes and periods of the potentiometrically recorded oscillations vary owing to the absence of stirring. Arrows indicate the time interval during which NMR recordings were performed.

2. Experimental Setup

The BL reaction mixture was prepared at a room temperature. The initial concentrations of the reactants were $[H_2O_2]_0 = 0.22$ mol/dm^3, $[KIO_3]_0 = 7.34 \times 10^{-2}$ mol/dm^3, and $[H_2SO_4]_0 = 4.88 \times 10^{-2}$ mol/dm^3. All reagents were of p.a. grade and were used without further purification. Stock solutions were prepared with deionized water of conductivity $\kappa = 6.0$ S m^{-1}. The mixture was then divided into two reaction vessels (standard glass NMR tubes of a diameter $d = 10$ mm). The volume of the reaction mixture in each of them was $V = 2.55$ mL. In one tube the reaction was followed potentiometrically, while the other was placed in the NMR spectrometer. No stirring was used in either of the experiments. The oscillatory reaction was simultaneously initiated in both tubes by elevating the temperature to 337.1 ± 0.2 K. This temperature was selected from the study of temperature variations of the BL reaction.[14]

Potentiometric measurements were performed by a platinum electrode versus an Ag/AgCl double-junction reference electrode, with a saturated water solution of K_2SO_4 as the outer electrolyte.

NMR measurements were performed on a BRUKER MSL 400 spectrometer at a proton frequency of 400.13 MHz, under the following conditions: recycle delay for the data acquisition 8 s; the spectral width 2 kHz (5 ppm); single-pulse-and-collect sequence with 44 μs pulse width of 90°. Such conditions enabled sufficient time resolution for NMR measurements, i.e., more than 25 spectra per one oscillating period (around 3.5 min). NMR experimental conditions were optimized during the time when the reaction was already in progress but not in the oscillatory mode (see Figure 1). Chemical shifts are in respect to ^{1}H in DSS (sodium 4,4-dimethyl-4-silapentane sulfonate). Changes of T_1 relaxation time of water protons during the BL reaction were followed by monitoring the NMR signal during inversion−recovery pulsed sequence with fixed inversion delay time (so called "NMR titration"[12]). The fitting of the lines was performed using LINESIM.3000 program at the ASPECT 3000 computer. DISMSL program was used for spectral analysis (see Figure 3).

Two separate NMR experiments were performed to investigate the potential effect of oxygen on spectral features observed in the BL reaction. In the first, the NMR spectrum of water protons in deoinized water equilibrated with air was compared with the spectrum of the same sample purged with N_2, in order to determine chemical shift per unit concentration of oxygen. In the second, we investigated whether the oxygen evolution accompanied by bubbles formation (common during the BL reaction) can cause magnetic inhomogeneities. Hence, we recorded NMR spectra in solution where catalytic decomposition of $[H_2O_2]_0 = 0.22$ mol/dm^3 by 0.02 mol/dm^3 tetraacetylethylendiamin[15] at $T = 337.1 \pm 0.2$ K and pH = 8.6. This process is analogous to reaction 3 in the BL reaction but produces more vigorous and continuous evolution of oxygen bubbles.

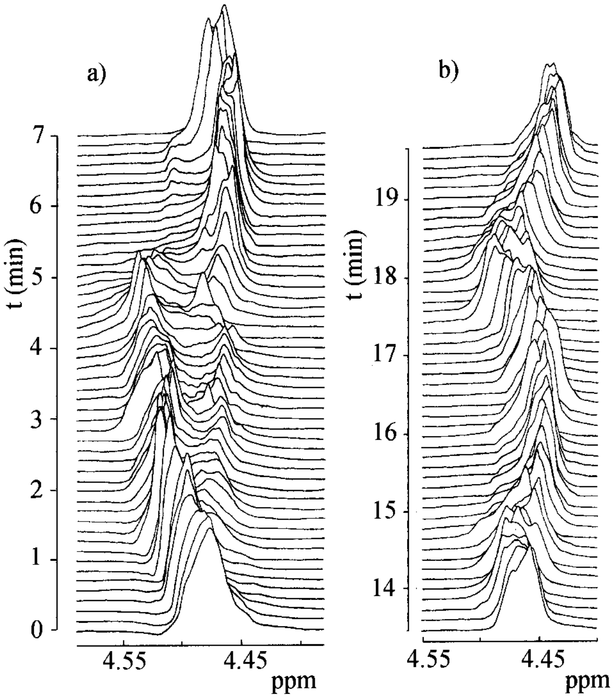

Figure 2. (a) ^{1}H NMR spectra of water protons showing evolution of signals during the first oscillation in the Bray−Liebhafsky reaction. (b) ^{1}H NMR spectra of water during the fourth and fifth oscillations.

3. Results

Potentiometric measurements are presented in Figure 1. Observed variations of the time period between oscillations and irregularity of their amplitudes are probably caused by concentration gradients produced in the absence of stirring. Small leaking of the outer electrolyte from the reference electrode through the ceramic diaphragm of about 5 μL/h compared to the whole volume of 2.55 mL will have only a minor contribution on this effect.

^{1}H NMR spectra of the BL reaction mixture are shown in Figure 2. Only water protons can be observed, owing to the small concentration of other proton-containing species. Figure 2a shows the evolution of the water proton NMR signal into two peaks during the first oscillation. Maximum peak separation was 0.06 ppm. The fourth and fifth oscillations are shown in Figure 2b. The peaks are not so well-resolved as in Figure 2a, but the complex line shape is retained as well as the chemical shift of around 0.05 ppm. The line-shape analysis of all spectra revealed complex combination of Gaussian and Lorentzian lines, whose contribution periodically changes during the oscillation. For example, at the time of maximum line separation (Figure 2a), the low-field line is predominantly Gaussian, while the high-field line is predominantly Lorentzian. This situation is far more complex than in the BZ reaction where a single, Lorentzian line has been observed throughout the reaction.[12] Consequently, the relationship between chemical shift and line width (or T_2) cannot be established. Therefore, we represented temporal evolution of NMR spectra in the manner used in the analysis of 2D NMR spectra.

A contour plot (Figure 3a) shows a complex spread of chemical shift of water protons during the first oscillating period, followed by more regular periodic changes of chemical shifts

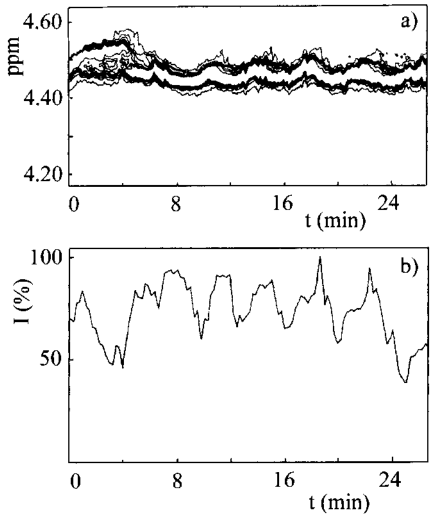

Figure 3. (a) NMR contour plot connecting the limits of certain intensity of all recorded NMR spectra during the reaction. (b) Projection of NMR spectra on the time axis representing the maximal intensity of each of the recorded spectra. Both figures correspond to the time interval indicated by the arrows in Figure 1.

of about 0.05 ppm during consecutive oscillations. Relative changes of the maximum intensity peak in each spectrum are shown in Figure 3b. Since the total area of NMR spectrum remained unchanged throughout the experiment, this parameter reflects changes in line shape and line width, which are too complex to be exactly determined. Nevertheless, periodic changes of the intensity of the signal of about 50% as well as periodic changes of chemical shift (Figure 3a) are obviously related to the time course of the BL reaction as followed by potentiometry (Figure 1).

A control experiment on the effect of dissolved oxygen on the chemical shift of water protons at 337 K revealed a simple shift of 0.07 ppm in aerated water ($[O_2] = 0.12$ mM[16]) vs deoxygenated water, i.e., 0.58 ppm/mM of oxygen.

NMR spectra of solution where catalytic decomposition of H_2O_2 occurs are presented in Figure 4. Again complex time evolution of NMR signal was observed with a maximum chemical shift difference of around 0.1 ppm. An surprising feature in this nonoscillatory reaction is that at the onset of reaction the water peak shifts to high fields while at a certain time point that behavior is reversed. Measurements of $[O_2]$ using oxygen electrode revealed that at the time of maximum line splitting, the amount of oxygen produced in this system is at its maximum and is three times higher than at the corresponding point in the BL reaction.

4. Discussion

Three main features of the water peaks in Figures 2 and 3 are periodic changes of the chemical shift, periodic changes of signal intensity, and their complexity. The changes of NMR parameters have the same oscillating period as chemical changes recorded potentiometrically (Figure 1), which confirms that the variations in the NMR signals reflect changes caused by the oscillatory nature of the BL reaction.

Periodic changes of ^{1}H NMR chemical shift and line width in the BZ reaction[12] have been adequately explained by the oscillating behavior of paramagnetic Mn^{2+}. The situation is more complex in the BL reaction where several oscillating species can potentially influence ^{1}H NMR spectra. Recordings of the most stable intermediate I_2 during BL reaction[3,5,6,7,17] showed that its concentration as well as its maximum variations are of the order of 10^{-4} mol/dm^3. Owing to the high rectivity, concentrations of other intermediates should be much smaller. According to the general stoichimetry (eqs 1 and 2), change of concentration of initial components IO_3^- and H^+ during a single oscillation should be of the same order of magnitude. These changes are unlikely to produce observed changes of the chemical shift, since the highest expected chemical shift induced by H^+ per oscillation should be less than 0.0001 ppm.[18] Another possibility to explain observed shifts is the appearance of some paramagnetic intermediates. Among the free radicals proposed in various mechanisms of the BL reaction,[4d,5] the peroxy radical $HOO^\bullet$ has a somewhat greater stability than other intermediates;[19] however, its concentration is too small and the lifetime is too short to contribute to the observed shifts.

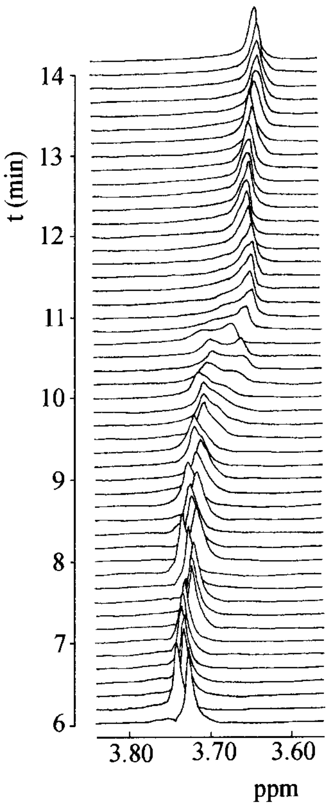

Figure 4. ^{1}H NMR spectra of water showing the time evolution of NMR signal during catalytic decomposition of H_2O_2.

The only paramagnetic species that is present in quantity sufficient to influence the NMR water peak is oxygen. Related to the changes of iodine, increase of $[O_2]$ during one oscillation is around 1 mM (see eqs 1−3). However, the situation here is different from the BZ reaction where manganese oscillates between two states (Mn^{2+}/Mn^{3+}) with different paramagnetic properties creating oscillatory behavior of NMR spectra. In the BL reaction a continuous production of oxygen occurs, and its concentration can be much higher than under normal conditions because of supersaturation.[20] Additional complication arises from oxygen bubble formation due to the absence of stirring.

Complexity of the situation is evident when maximum chemical shifts in BL reaction and catalytic reaction are compared with the shift induced by dissolved oxygen. According to our control experiments in aerated water, maximum chemical shift in the BL reaction should be around 0.6 ppm (around 1 mM of oxygen), while in catalytic decomposition it should be 1.8 ppm. Instead, chemical shifts of 0.05 and 0.1 ppm were observed, respectively. Two explanations are possible. One is that the majority of oxygen is in the form of bubbles, thus reducing its ability to fully contribute to the observed chemical shift. Namely, chemical shift induced by interaction between water protons and dissolved oxygen is a short-range interaction,[21] hence oxygen molecules within bubbles will not contribute to the chemical shift to the same extent as those located at its surface. This situation is analogous to measurements of relaxation effects of iron packed in superparamagnetic particles.[22] On the other hand, Figure 4 indicate that the chemical shift alternates direction at the moment of intense bubble formation, which can be explained only if magnetic inhomogenieties induced by the presence of bubbles counterbalance shift induced by dissolved oxygen. Similar behavior is evident in the BL reaction as well (Figures 2 and 3), only here such behavior is oscillatory. Consequently, observed chemical shifts in BL reactions seem to depend on the complex combination of the effects of bubbles formation and increase in the concentration of dissolved oxygen during oscillation.

Although observed chemical shifts can be explained by the periodic differences in concentration of oxygen, the appearance of multiple lines during the evolution of the BL reaction is difficult to solely explain on that basis. Heterogeneity of the system induced by bubbles formation within the system can create distinctive magnetic environments for water molecules. This could cause the splitting of the water proton NMR signal, as long as the time taken for diffusional exchange of water molecules between these structures is longer than their intrinsic relaxation times (so-called exchange-limited condition). Although this problem is theoretically well-described for other systems,[23] the solution requires knowledge of many parameters (e.g., the median size of bubbles and their spatial distribution), which cannot be measured under the conditions of our experiment. On the other hand, inspection of the time course of line-shape changes in both BL and catalytic reactions suggests that formation of oxygen bubbles may not be solely responsible for the observed line splitting. Bubbles formation started soon after reactions were initiated, yet line splitting was observed only within a limited time interval and was pronounced only when production of oxygen is at its maximum. Complex line shape, i.e., periodical appearance of the combination of Lorentzian and Gaussian lines also suggests some kind of cooperativity and distinct arrangements of water molecules during oscillations. It is possible that this restructuring of hydrogen bonds is due to a periodic release of energy created by highly exo energetic processes during the BL reaction (e.g., $\Delta G^\circ = -467$ kJ/mol and $\Delta G^\circ = -547$ kJ/mol in processes 1 and 2[24]). It is well-known from the theory of processes far from equilibrium[25] that periodic "pumping" of energy can create ordered steady states in bulk water, whose lifetime in this case may be long enough to be distinguished by NMR. The assumption of the importance of bulk water in the overall mechanism is also supported by newly obtained experiments with heavy water.[17]

5. Conclusion

For the first time, behavior of water was monitored during oscillations in the Bray−Liebhafsky reaction by ^{1}H NMR. A series of ^{1}H NMR spectra showed periodic changes of the chemical shift and intensity and complex structure of water peaks. Analysis of NMR spectra showed that oxygen evolution plays a dominant role but also indicated the nontrivial behavior of water during the course of the Bray−Liebhafsky reaction. So far, in studies of the mechanism of the BL reaction, water has been regarded predominately as an structurless medium in which chemical reactions take place, and its role was reduced to balancing their stochiometry. The ^{1}H NMR experiments showed that such an approach is an oversimplification, thus supporting the creation of a subtler approach in modeling the mechanism of the Bray−Liebhafsky oscillatory reaction and providing a new way of investigating the role of water in the overall mechanism.

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