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Excessive Excitation of Hydrogen Peroxide during Oscillatory Chemical Evolution

Dragomir R. Stanisavljev*,† and Miroslav D. Dramićanin‡

Faculty of Physical Chemistry, Studentski trg 12-16, Post Office Box 137, and Institute of Nuclear Sciences "Vinča", Post Office Box 522, University of Belgrade, 11001 Belgrade, Serbia

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The peculiar reaction dynamics of the Bray−Liebhafsky chemical oscillator is connected with the nonequilibrium periodic excitations of hydrogen peroxide embedded in a hydrogen-bonded water network. This was indicated by Raman spectroscopy that showed periodic, isothermal, and excessive excitation of the symmetric vibration of hydrogen peroxide. Since such an excessive excitation should be the result of a specific nonequilibrium energy distribution with the active participation of water, understanding this process can be of considerable importance in other systems in which water is the main constituent.

1. Introduction

Although the phenomena of isothermal spontaneous chemical oscillations have been known for almost a century[1,2] and a number of new oscillatory systems have been discovered,[3] they are still the subject of intensive investigations. Although oscillations exist on thermodynamic principles,[4,5] the detailed mechanisms of the periodic channeling of energy to a specific process are largely unknown. The solution to this problem may be of importance in other systems, including oscillations in living cells.[3,6]

The main difficulties in understanding the mechanism of chemical oscillators are the generation of a number of reactive intermediates (the kinetic parameters of which are known with great uncertainty or are only assumed) and the limited number of fast and selective experimental techniques applicable in vivo. For these reasons our attention was focused on one of the simplest oscillatory systems: the Bray−Liebhafsky (BL) reaction.[1,2,7] This reaction consists initially of only three components dissolved in water: hydrogen peroxide (H_2O_2), potassium iodate (KIO_3), and sulfuric acid (H_2SO_4). Also, it belongs to the surprisingly large class of chemical oscillators containing hydrogen peroxide.[3]

The general stoichiometry of the whole process was proposed by Bray himself:[1]

$$2IO_3^- + 2H^+ + 5H_2O_2 \rightarrow I_2 + 5O_2 + 6H_2O \tag{1}$$

$$I_2 + 5H_2O_2 \rightarrow 2IO_3^- + 2H^+ + 4H_2O \tag{2}$$

The process commences with the reduction of iodate by hydrogen peroxide to iodine (eq 1), followed by the rapid oxidation of the accumulated iodine by (again) hydrogen peroxide back to iodate (eq 2). The most common approach in the attempt to develop a model of the reaction mechanism is the splitting of the complex processes 1 and 2 into more elementary steps. This procedure is not unique and usually introduces a number of possible and extremely reactive components, the kinetic parameters of which are known with great uncertainty or are only assumed. The formal kinetic approach, which became very popular after wide accessibility of computers, consists of fitting the insufficiently known parameters in the proposed differential kinetic equations to obtain the best possible agreement with the experimental findings.

Beside this procedure not being unique, additional phenomena may appear that determine the behavior of the system under nonequilibrium conditions. Far from equilibrium, a possible specific redistribution of energy could change the population of molecular quantum states, changing the rate constants[8] and the reaction dynamics. This assumes a collective functioning of a large number of particles and new properties of the system that are nonexistent for the individual molecules. For a more detailed understanding of the reaction mechanism, formal modeling should be supplemented with considerations of the energy flow through the system. The aim of the present investigation was to show the existence of a submechanism in the BL reaction, which may produce excessive isothermal excitation of peroxide and possibly activate process 2 by a specific distribution of energy.

It is known that iodine and peroxide (without the initial presence of iodate) can remain together for hours,[1,9] indicating a high activation energy of process 2. Contrary to this, being part of the BL reaction, the speed of iodine oxidation (eq 2) periodically exceeds the speed of iodine production (eq 1), despite the fact that process 1 must supply the reactive intermediates for the occurrence of process 2. The domination of the process with the higher activation energy (under isothermal conditions) can be understood if the energy released in process 1 can be selectively channeled to process 2.

In the general scheme of the process, it can be noticed that hydrogen peroxide periodically acts as both the reducing component (eq 1) and the oxidizing component (eq 2). The increase of the oxidative potency of H_2O_2 in process 2 can be favored by the selective excitation of the symmetric OH−OH vibration. Such an excitation could increase the probability of the formation of $OH^\bullet$ radicals, which are among the strongest oxidation agents with a standard reduction potential of $E^0_{OH} =$ 2.813 V.[10] In the present study this possibility was not experimentally investigated but it is discussed as a potential source of nonlinear effects that enable chemical oscillations. Our attention was focused on the detection of vibrationally

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* To whom correspondence should be addressed: e-mail dragisa@ffh.bg.ac.yu.

† Faculty of Physical Chemistry.

‡ Institute of Nuclear Sciences.

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excited peroxide and the related specific nonequilibrium energy distribution, which may give new insight into the reaction mechanism. A suitable technique for the investigation of this possibility is Raman spectroscopy, since the symmetric peroxide vibration is Raman-active[11] ($\tilde{\nu}_{\mathrm{HO-OH}} = 880\ \mathrm{cm}^{-1}$).

2. Experimental Section

The BL reaction was conducted without mechanical stirring in a thermostated cylindrical glass vessel at a temperature of 62 ± 0.5 °C. The volume of the reaction mixture was 8.5 mL with the initial composition $[\mathrm{KIO_3}]_0 = 6.9 \times 10^{-2}$ mol dm^{-3}, $[\mathrm{H_2SO_4}]_0 = 4.7 \times 10^{-2}$ mol dm^{-3}, and $[\mathrm{H_2O_2}]_0 = 6.66 \times 10^{-1}$ mol dm^{-3}. The chemical oscillations were monitored by use of a platinum electrode and a double-junction Ag/AgCl reference electrode. The electrolytic bridge of the reference electrode was filled with a saturated K_2SO_4 solution. Deionized water with a resistivity $\rho = 18$ MΩ·cm was used for the preparation of the solutions. All chemicals were of p.a. grade: $KIO_3$and H_2SO_4 from Merck and H_2O_2 from LaChema.

The Raman scattered spectra were recorded with a R-2001 Raman system with a fiber-optic probe matching $\lambda = 785$ nm diode laser. A linear silicone charge-coupled device (CCD) detector with 2048 elements was used. Spectra were recorded in series with an integration time of 26 s, with the time between recordings being 31.2 s.

3. Results

Identification of the excited states of the symmetric OH−OH vibration was possible, having calculated all the relevant data. The dissociation energy of the HO−OH bond is $D_0 = 207.1$ kJ mol^{-1}.[12] From this, the equilibrium dissociation energy, D_e, and the corresponding wave number, $\tilde{\nu}_\mathrm{e}$, are $D_\mathrm{e} = D_0 + {}^1/_2 h\nu = (3527 \pm 6) \times 10^{-22}$ J/molecule; $\tilde{\nu}_\mathrm{e} = D_\mathrm{e}/hc = (1776 \pm 2) \times 10^3\ \mathrm{m}^{-1}$.

When the anharmonicity of the vibration is taken into account, the differences between adjacent vibration terms are represented[13] by the formula $\Delta G_{v\to v+1} = \omega_\mathrm{e} - 2\omega_\mathrm{e}x_\mathrm{e}(v+1)$, where v is the vibration quantum number of a lower state, ω_e is a constant, and x_e is the anharmonicity constant.

Knowing that ω_e and $\tilde{\nu}_\mathrm{e}$ are connected by $\tilde{\nu}_\mathrm{e} = \omega_\mathrm{e}/4x_\mathrm{e}$ and that transition $0 \to 1$ has $\Delta G_{0\to1} = 880\ \mathrm{cm}^{-1}$, the last two equations are solved for $\omega_\mathrm{e} = 903 \pm 3\ \mathrm{cm}^{-1}$ and $x_\mathrm{e} = (1271 \pm 3) \times 10^{-5}$. Now the frequencies corresponding to the transitions from the excited states can be calculated:

$$\Delta G_{1\to2} = 857 \pm 3\ \mathrm{cm}^{-1} \qquad \Delta G_{2\to3} = 834 \pm 4\ \mathrm{cm}^{-1} \tag{3}$$

The Raman scattered spectrum of the reaction solution showed two well-resolved peaks. By comparison with spectra of the pure components, they are attributed to KIO_3 and H_2O_2. The peak belonging to the H_2O_2 vibration shows a periodically appearing shoulder, corresponding (within the calculation error) to the expected value of 857 cm^{-1}. A satisfactory fit (with ORIGIN 6.0 software) of the recorded spectra is obtained by the nonlinear fitting procedure with three Gaussian peaks positioned at

$$\tilde{\nu}_1 = 801.6 \pm 0.5\ \mathrm{cm}^{-1} \qquad \tilde{\nu}_2 = 859.0 \pm 0.6\ \mathrm{cm}^{-1}$$
$$\tilde{\nu}_3 = 879.9 \pm 0.4\ \mathrm{cm}^{-1} \tag{4}$$

The peak positions $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_3$ represent the mean values from 37 recorded spectra, and all errors in eq 4 represent the 95% confidence limit of the mean.

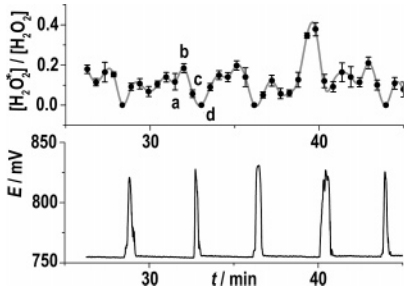

Figure 1. Fraction of excited hydrogen peroxide $[\mathrm{H_2O_2}^*]/[\mathrm{H_2O_2}]$, with the corresponding errors, shown together with the chemical oscillations during the BL reaction. The chemical oscillations are represented by the changes of the potential of a platinum electrode. Recorded spectra at points a−d are given in Figure 2.

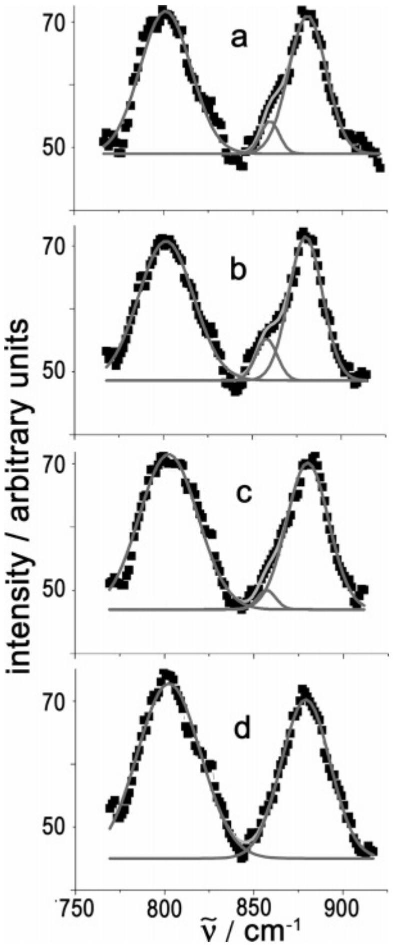

Figure 2. (a−d) Recorded Raman spectra with appropriate fits, corresponding to the marked points in Figure. 1. (■) Experimental points.

The fraction of excited hydrogen peroxide molecules is approximated as the ratio of peak areas A_2/A_3 centered at $\tilde{\nu}_2$ and $\tilde{\nu}_3$. Such a representation minimizes the influences of inhomogeneities in the reaction solution and instrumental instabilities on the different spectra. The periodicity with which peroxide is excited is illustrated in Figure 1, relative to the chemical oscillations recorded with the platinum electrode. The general trends observed from Figure 1 are confirmed with the calculated errors of the ratio of peak areas A_2/A_3 for all recorded spectra. Examples of four spectra with their fits, recorded at the marked points in Figure 1, are represented in Figure 2.

A hint of the transition corresponding to $\Delta G_{1\to2} = 834\ \mathrm{cm}^{-1}$ is observed in Figure 2a,b. Although it is not taken into account due to its small intensity, it is an additional indication that the recorded spectra contain information on the vibration states of peroxide.

Despite the large noise (due to the generally low signal intensity), periodicity of the peroxide excitation is noticeable. A good correlation between the five electrochemical and the five "excitation" oscillations can be established, although the matching of the peak positions is not exact. This can be understood if one bears in mind the experimental conditions under which the spectra were obtained. From Figure 1, the decreasing part of the peroxide oscillations can be estimated to range between 30 and 60 s. The positions and the amplitudes of the recorded peroxide oscillations are dependent on the exact moment when the spectrometer performed the integration during the actual oscillation. Due to the relatively long integration time of 26 s, only one or two points on the decreasing part of the oscillation could be recorded. As a result, some oscillations may be of lower amplitude and the peak minima may vary within 30 s, relative to the electrochemical oscillations.

Since the decrease of the peroxide concentration commences well before the chemical oscillation (Figure 1), characterized by a strong evolution of oxygen bubbles,[14] scattered light by the oxygen bubbles cannot mask the effect. Another important property is that the maximal fraction of excited molecules, $[H_2O_2^*]/[H_2O_2] \approx 0.2$, by far exceeds the consumption of peroxide per oscillation (the number of oscillations is much larger than five since the oscillatory evolution continues for more than an hour). Such excessive peroxide excitation is a solid indication that it is not the result of individual collisions but rather the effect of collective action of a large number of molecules. The existence of a specific mechanism with a nonequilibrium energy distribution is additionally supported, if it is taken into account that a very high temperature is necessary to create vibrational population with $n_1/n_0 = 0.2$ under equilibrium conditions. Since only the ground $G(0)$ and the first vibration term $G(1)$ are considered, the harmonic approximation is used:[13]

$$n_1/n_0 = f_1/f_0 = \exp(-h\nu_e/kT) \tag{5}$$

where the symbols have their usual meanings and f_υ represents the fraction of molecules in the corresponding vibration state, $f_\upsilon = [\exp(-\upsilon h\nu_e/kT)][1 - \exp(-h\nu_e/kT)]$.

The use of the harmonic approximation is justified by the calculation of equilibrium population n_1/n_0 at 62 °C, based on eq 5, and by a more accurate approach taking into account the anharmonicity of the $G(0)$ and $G(1)$ terms. The approximate calculation gives $n_1/n_0 = 0.021$, while the more exact approach gives $n_1/n_0 = 0.019$, showing that the simple harmonic approximation (eq 5) cannot introduce large errors. Accordingly, a temperature of 807 K (534 °C) would be required to maintain population of $n_1/n_0 = 0.2$ under equilibrium conditions. Since the actual temperature of the mixture was maintained at 62 ± 0.5 °C, the existence of nonequilibrium excitation of peroxide is strongly supported.

The agreement between the determined and predicted positions for the vibrational transitions of the peroxide, the large number of excited molecules, and the periodicity of the isothermal peroxide excitation are good indications that a specific energy distribution is related to the reaction mechanism.

4. Discussion

The discussion of the results is based on Figure 1, showing periodic excitation of the symmetric HO−OH vibration. It is derived from the corresponding Raman spectra recorded every 31 s during the experiment. The long duration of the experiment, the possible fluctuation of the instrument electronics, and the irregular scattering of laser light by the inhomogeneities induced by natural convection make comparison of different spectra difficult. These sources of noise are partially eliminated by comparing the relative peak intensities A_1/A_2, but stochastically distributed irregularities are still visible in Figure 1 due to the generally low signal intensity. Despite this, five minima on the $A_1/A_2 = f(t)$ curve are distinguishable, which accompany electrochemical oscillations. As the time evolution of the curve is generally similar during the nonoscillatory regime (between oscillations on the Pt electrode) and the intensity of the noise is less than the observed effect, the periodic excitation of peroxide cannot be the result of a stochastic process, and a good correlation can be established between this process and the electrochemical oscillations. Only by employing more powerful Raman systems can supplementary details (with improved signal/noise ratio) be obtained.

The experiment was conducted without external stirring of the reaction mixture, since large convective flow inevitably creates inhomogeneities and introduces additional noise on the Raman signal. Although such an experimental design improves the signal/noise ratio, temperature inhomogeneities are possible in the reaction mixture. It should be discussed whether regions with increased temperature may be associated with the observed vibrational spectra. However, such an interpretation of the results is improbable for two reasons. The first is that natural convection of fluid from the thermostated vessel walls to the surface (in contact with the atmosphere) minimizes large temperature differences. The second reason comes from statistical thermodynamics.[13] As presented earlier, the temperature necessary to produce a high peroxide excitation of $n_1/n_0 = 0.2$ under equilibrium conditions is 534 °C. Such a high temperature in the aqueous solution is highly improbable. Even if high-temperature regions exist locally, their number should be considerable (to provide $n_1/n_0 = 0.2$), which is not consistent with the measured temperature of 62 ± 0.5 °C. When the obtained results are considered in light of the above discussions, the existence of a specific isothermal nonequilibrium energy distribution producing vibrational excitations of peroxide is highly supported.

Although the chemistry of excited peroxide is not experimentally followed, it is possible to discuss its influence on the reaction dynamics. During process 1, in which peroxide is oxidized to O_2, the HO−OH bond in the peroxide is preserved:[10,15]

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-;\ E^0 = -0.695\ \text{V}$$

On the other hand, being the oxidizing agent in process 2, peroxide is reduced either in two one-electron steps

$$H_2O_2 + e^- + H^+ \rightarrow OH^\bullet + H_2O;\ E^0 = 0.714\ \text{V}$$

$$OH^\bullet + e^- + H^+ \rightarrow H_2O;\ E^0 = 2.813\ \text{V}$$

or in one two-electron step:

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2\ H_2O;\ E^0 = 1.763\ \text{V}$$

In either case, process 2 is related to the breakage of the HO−OH bond; hence excitation of symmetric peroxide vibration should greatly increase the probability of the oxidation branch (eq 2). Facilitating the breakage of a HO−OH bond, a nonequilibrium energy distribution could be involved in the important switching mechanism of changing the reaction dynamics from the reduction branch (eq 1) to the oxidation pathway (eq 2).

Beside the fact that the introduced nonequilibrium energy distribution offers new details for considering chemical oscillations, the possible implications have a broader significance due to the actual mechanism of isothermal peroxide activation. The specific nonequilibrium distribution of energy in the system must be realized by the active involvement of water, which is present in great excess over all other components. The theoretical base of such an energy distribution was already anticipated in the mechanism developed by Fröhlich.[16,17] Accordingly, in systems pumped with energy over some threshold value, special stationary states may exist in which energy is isothermally channeled to the lowest vibration modes. Although such stationary states are characteristic of solidlike structures with a distribution of phonons, their applicability to aqueous solutions became of great significance after numerical calculations performed by Mesquita et al.[18,19] Their results, based on the NESOM formalism,[20] showed that the Fröhlich distribution of energy occurs on a subpicosecond time scale. On such a short time scale, the network of hydrogen bonds (with an average lifetime of $\approx 10^{-11}$ s) may support the existence of phonons, at least in well-connected cooperatively stabilized patches[21] or nuclei,[22,23] and act as a carrier of the Fröhlich process. Hydrogen peroxide, being powerfully incorporated into such temporary structures due to its strong interaction with water,[11,15] changes its energy content according to the altered population of phonons. In favor of the special role of hydrogen-bonded networks are also the large changes of a hydrogen-bonded matrix during chemical oscillations recorded by NMR,[24,25] as well as the possibility of controlling the reaction dynamics by strengthening the hydrogen bonds by use of D_2O as the solvent[26] or loosing them by microwave heating.[27,28] If the dissipation of energy in the surroundings is low and if the exothermal processes supply energy fast enough, a hydrogen-bonded network may preserve its ability to channel energy despite the rearrangement of hydrogen bonds.

According to the obtained results, hydrogen peroxide is excited with 857 $\mathrm{cm^{-1}}$ $\mathrm{molecule^{-1}}$ or 10.3 kJ $\mathrm{mol^{-1}}$. This energy is less than the energy of hydrogen bonds ($\approx$20 kJ $\mathrm{mol^{-1}}$); hence the network of hydrogen bonds is not destroyed by the assumed mechanism. The maximal energy for exciting 0.2 mole fraction of hydrogen peroxide is less than $0.2 \times 0.666 \times 10^{-3}$ (mol $\mathrm{cm^{-3}}$) $\times\ 10.3 \times 10^{3}$ (J $\mathrm{mol^{-1}}$) $= 1.4$ J $\mathrm{cm^{-3}}$ (it is an overestimation since the concentration of peroxide at the beginning of the oscillation is less than the initial value). This value is comparable with the high thermal energy, up to 1.8 J $\mathrm{cm^{-3}}$, released during the few initial seconds of a chemical oscillation.[14,29] Due to the small temperature increase, the dissipation of energy to the surroundings can be represented by a slow Newtonian process[29] (with a long relaxation time of $\approx$100 s). Consequently, exothermal processes can easily maintain a stationary state in which net energy is pumped to the hydrogen-bonded network. If the conditions for the Fröhlich condensation of energy are satisfied, the network can channel energy to the lowest vibrational modes, with excitation of the incorporated peroxide. Below the Fröhlich threshold, the hydrogen-bonded network will efficiently relax all activated molecules and dissipate the energy as heat.

The assumed connection between the obtained experimental results and the theoretical concepts can be of broader interest and requires more detailed investigations. In this sense, chemical oscillators may serve as a simple model system for the investigations of important theories of physics. Also, the given approach may be of interest in other nonequilibrium systems containing water as the main constituent, especially living organisms.

5. Conclusion

The obtained results showed that the energy released in the BL chemical reaction need not be only thermalyzed but, under definite nonequilibrium conditions, may be isothermally channeled to specific processes by selective activation of molecules. This is indicated by Raman spectroscopy showing excessive excitations of the symmetric hydrogen peroxide vibration, preceding chemical oscillations. The process of channeling of energy is assumed to be connected with the active involvement of water through the collective excitation of the hydrogen-bonded water network. This broadens the applicability of the given approach to other systems, particularly living organisms, and justifies further investigations of the effect with the more powerful Raman systems.

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