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PHOTOCHEMISTRY AND MAGNETOCHEMISTRY

On Chemical Reactions in the Laser-Induced Breakdown of a Liquid

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Abstract—It is shown experimentally that a laser-induced breakdown of a liquid is accompanied by chemical reactions initiated by radicals and excited species formed in the spark. It is found that, in water, the laser-induced breakdown is accompanied by the dissociation of water and dissolved nitrogen molecules with the formation of HNO₂ and HNO₃, while, in a FeSO₄ aqueous solution, by the Fe²⁺ \longrightarrow Fe³⁺ oxidation reaction. It is assumed that the mechanism of the process is analogous to that of the action of ionizing radiations and the chemical action of ultrasonically induced cavitation (it is proposed that this mechanism of chemical action of a laser-induced spark proposed be termed indirect). Energy yields of these reactions are found to be of the same order of magnitude as for sonochemical redox reactions. It is shown that the laser-induced breakdown of an aqueous solution of maleic acid is accompanied by its stereoisomerization into fumaric acid, a process catalyzed by small amounts of an alkyl bromide. It is established that, for the formation of fumaric acid in a laser-induced spark, the energy yield is about five orders of magnitude higher than that typical of the above-mentioned redox reactions in the laser-induced spark.

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A high-power laser beam passing through a focusing lens into a gas or liquid produces a spark near the focus. This phenomenon is known as optical breakdown. In a liquid, the optical breakdown gives rise to pulsating bubbles, so-called laser-induced cavitation. The laser-induced breakdown in a medium is similar to electrical breakdown. In the optical range of frequencies, a breakdown in a gas requires very strong electric fields in the light wave (~ 10^8-10^9 V/m) [1] and, in a purified liquid, even several orders of magnitude higher. The laser-induced breakdown of a liquid containing a high concentration of microscopic bubbles requires, as expected, a much lower electric field strength.

The chemical action of laser radiation is usually assumed to initiate photochemical reactions. Unlike classical one-quantum photochemical processes, the chemical action of laser radiation, owing to high concentrations of excited species, is characterized by the occurrence of multiquantum processes [2].

The aim of this work is to study chemical processes in laser-induced breakdowns of water and aqueous solutions by comparing them with ordinary photochemical processes.

In a liquid, low-temperature plasma can be created in several ways. One way is to create an arc discharge using a high-voltage discharger [3]. Another commonly used way is to use ultrasonically induced cavitation: bubble pulsations under the action of high-power ultrasonic waves. In the cavitation, the deformation of bubbles and their splitting are accompanied by charging their surface with the creation of strong electric fields, which, in turn, produces microscopic discharges [4]. An electrical discharge inside a bubble results in excitation, ionization, and dissociation of gases and liquid vapors in the bubble. Under special cavitation conditions, low-temperature plasma arises by another mechanism: the strong compression of an immobile single spherical bubble pulsating at a very high amplitude in the ultrasonic (US) wave field results in heating of the vapor–gas mixture to a temperature higher than 10^4 K. However, in the ordinary multibubble cavitation, strong compression of bubbles does not occur, and the initiation of plasma is due to microscopic electrical discharges in the bubble [4, 5].

The optical breakdown of liquid is similar to the electrical breakdown in many respects. The optical breakdown occurs near the focus, where the electrical field exceeds the critical value due to the presence of microscopic bubbles. Compared to the above cases, an optically induced discharge has some distinctive features. The optical energy is supplied to the plasma without conducting elements, such as electrodes, waveguides, etc. The radiation energy is transported by light immediately through the medium; therefore, using a laser, one can initiate a spark in an arbitrary place far apart from any surfaces. In this case, reaction products are free from impurities.

Another feature of such plasma is a very high temperature in the laser-induced spark (15000–20000 K) even under standard conditions. For other types of discharge, the temperature is much lower—10000 K in arc discharges and below 1000 K for ions during ultrasonically induced multibubble cavitation [5]. Moreover, using a laser-induced spark, one can control the temper-



Fig. 1. A schematic of the setup. For comments, see the text.

ature of the plasma by varying the gas composition. Such high plasma temperatures arising during optical breakdown can be explained by the transparency of the plasma with respect to the laser radiation. Very high temperatures (to 25000–30000 K) are developed in helium at atmospheric pressure, because its ionization potential is very high [1]. Owing to the above-listed features, the laser-induced spark has attracted considerable attention as a promising tool in chemistry and chemical engineering.

EXPERIMENTAL

The experimental setup is schematically represented in Fig. 1. Light beam 1 from YAG : Nd^{3+} pulsed laser 2 with a wavelength of 1.06 µm and a pulse energy of 140 mJ passes through short-focus lens 3 into reactor 4. The laser-induced breakdown of liquid 5 occurs in the region of focal point 6. In some experiments, reactor 4 represented a four-necked glass flask equipped with a jacket for maintaining constant temperature (see Fig. 2a), a thermometer, a reflux condenser, a pipe for gas supply and removal, and a system for degassing of the liquid. The laser beam passed through a tube with glass lens 2 cemented to its end. The tube was mounted so that the lens was in contact with the liquid. In experiments with maleic acid, reactor 4 represented a rectangular cell for photocolorimetry with an optical length of 50 mm (see Figs. 2b, 2c). The reference solution was placed into an analogous cell disposed above the working cell.

The light pulse length was equal to 10 ns, and the pulse interval, 1.2 s. The laser pulse energy was determined by the calorimetric method using an IMO-2N radiation power meter.

HNO₂ was assayed by the colorimetric method with a modified Griess reagent (a mixture of equal volumes of a 1% sulfanilic acid solution in 30% acetic acid, a 0.1% α -naphthylamine solution in 30% acetic acid, and a 10% KBr solution [6]); to 50 ml of the test solution is added ten droplets of the reagent. The concentration of iron (III) ions was determined by the colorimetric method [7] with ammonium rhodanide. Fumaric acid formed was assayed by the weighing method (with allowances made for the water solubility of fumaric acid). All experiments were carried out at 21°C; twice distilled water was used.



Fig. 2. Shapes of laser-induced sparks obtained with lenses with various focal lengths f: (a) 2, (b) 4, and (c) 6 cm; (1) laser-induced sparks, (2) focusing lens.

The first experiments were carried out to determine the optimum shape of the laser-induced spark. Using three focusing lenses with focal lengths of 2, 4, and 6 cm, sparks different in shape were obtained in water: spherical, needle-like, and in the form of a small spark sequence (Fig. 2). Although reactions of interest occurred in all types of spark, the best results were obtained with the lens with a focal length of 4 cm. This lens was used in the experiments described below.

RESULTS AND DISCUSSION

The action of laser radiation on water at room temperature in air results in the formation of nitrogen oxides, which then react with water to yield nitrous and nitric acids. These products are accumulated according to a linear law. In a solution (25 ml) exposed to the laser radiation with a pulse energy of 120 mJ and a pulse interval of 1.2 s, the rate of formation of nitrite was found equal to 1.8×10^{-8} mol l⁻¹ min⁻ ¹. In the optical breakdown of a 0.001 M FeSO₄ solution in 0.4 M H₂SO₄, the oxidation reaction $Fe^{2+} \longrightarrow Fe^{3+}$ occurs. The accumulation of the product also follows a linear law and does not depend on the Fe²⁺ concentration. The rate of formation of Fe³⁺ was found equal to $1.3 \times$ 10⁻⁸ mol l⁻¹ min⁻¹. To our knowledge, such reactions have never been observed under the action of laser radiation on water.

The above-mentioned reactions are due to the formation of a plasma bubble near the focal point in the optical breakdown of liquid. Indeed, when the laser beam is focused at a point above the surface of distilled water or passed through carefully degassed liquid so that no spark occurs, chemical changes in water do not occur too. The experimental results suggest that the mechanism of chemical processes in the laser-induced breakdown is analogous to that for chemical processes in radiolysis of water and aqueous solutions [8] and in the ultrasonically induced cavitation [6]. The mechanism can be represented as follows:

$$H_2O \longrightarrow H + OH, \tag{1}$$

$$H + O_2 \longrightarrow HO_2.$$
 (2)

Here, LIB is the laser-induced breakdown. In an acidic medium containing Fe^{2+} ions, they are oxidized by the reactions

$$OH + Fe^{2+} \longrightarrow OH^{-} + Fe^{3+}, \qquad (3)$$

$$HO_2 + Fe^{2+} + H^+ \longrightarrow H_2O_2 + Fe^{3+}.$$
 (4)

Along with processes (1)–(3) occurring in the radiolysis of water, in the laser-induced plasma bubble in water containing dissolved air, as in the ultrasonically induced cavitation, the dissociation of nitrogen molecules occurs:

$$N_2 \longrightarrow N + N.$$
 (5)

The H, OH, and N radicals formed pass into solution, partially recombine, and react with water to yield a complex mixture of reaction products: H_2 , H_2O_2 , N_2 , NH, HO₂, HNO₂, and HNO₃ [9]. Note that, in radiolysis of water and aqueous solutions, reaction (5) does not occur.

The mechanism of the chemical action of a laserinduced spark involving the dissociation of solvent (water) molecules into radicals, which then pass into solution and interact with a dissolved substance, can be termed indirect (by analogy with the indirect mechanism of the chemical action of radiolysis and ultrasonically induced cavitation).

We used a focused laser beam to initiate the known sonochemical reaction of isomerization of maleic acid into fumaric acid, which is catalyzed by alkyl bromides [6, 9]. This reaction was selected for the following reasons. First, the reaction occurs by a chain mechanism. Second, photochemical stereoisomerization is absent: for example, with bromine water, the reaction could occur under the action of both laser radiation and light. The experiments showed that, in the laser-induced breakdown of a 25% maleic acid aqueous solution containing *n*-butyl bromide, maleic acid undergoes stereoisomerization into fumaric acid, which precipitates in the form of small white crystals. Under irradiation with an unfocused laser beam or exposure to light, the reaction did not occur. It was noticed that the reaction product was formed immediately in the region of the laserinduced breakdown (spark); the white flocs formed were arranged on a radius round the spark (Fig. 3) and then rapidly precipitated to the bottom of the cell. In other regions of the liquid, no chemical change occurred. By analogy with the conclusions made in [6, 9], it can be suggested that, in the optical breakdown at the focal point, alkyl bromide dissociates to yield Br atoms and that other reaction steps are dark. The chain reaction can be represented as follows:

$$C_{4}H_{9}Br \longrightarrow (LIB) \longrightarrow C_{4}H_{9} + Br$$
(6)

$$HC-COOH + Br \longrightarrow BrHC-COOH
HC-COOH + Br \longrightarrow HC-COOH
HC-COOH + Br \longrightarrow HC-COOH
$$\Leftrightarrow \frac{HC-COOH}{HOOC-CH} + Br \text{ and so forth.}$$$$

In principle, these chemical reactions can also be initiated by pulsations of a cavitation bubble formed in the liquid on the laser-induced breakdown, because, at the maximum compression of the bubble, the vaporgas mixture is heated to a high temperature. The laserinduced cavitation bubble is characterized by symmetrical variations of its radius with time in the expansion and compression stages [10] unlike bubbles in an acoustic wave field, which are characterized by slow isothermal expansion and fast compression. The absorbed energy is partially lost by heat conduction and generation of shock waves and cumulative jets, and goes into chemical processes and reradiation; therefore, the maximum temperature and the maximum pressure in the compression of the laser-induced cavitation bubble cannot be higher than the temperature and the pressure in the laser-induced breakdown. Spectral measurements by Williams and coworkers [11] showed that, in the laser-induced breakdown, the temperature of plasma is as high as 16000 K and, at the maximum compression of a cavitation bubble, only 7800 K, i.e., more than two times lower. Therefore, although chemical reactions can be initiated in pulsations of a cavitation bubble, the amount of products formed in the reactions must be many orders of magnitude lower than in the optical breakdown.

Let us estimate the energy yield of reactions described above. In the irradiation of a solution (25 ml) by laser pulses with an energy of 120 mJ at intervals of 1.2 s, the rate of formation of nitrite was found equal to 3.2×10^{-8} mol l⁻¹ min⁻¹. We account for the reflection of the light wave from the air-glass (4%) and glasswater (4%) interfaces. We also account for the linear absorption of light energy in water (by a factor of e at a distance of 7 cm [12]): the laser beam passing through water to a distance of 1.5 cm loses 20% of its light energy. Consequently, the energy supplied to the spark is only $0.96 \times 0.96 \times 0.8 = 73\%$ of the incident radiant energy. It is agreed that the major portion of the energy supplied to the spark is absorbed in it (80–90%); the remainder of the energy is dissipated and goes beyond the region of the focal point. Thus, the plasma bubble absorbs 62% (0.73 × 0.85) of the total radiant energy. The absorbed energy goes into the generation of a shock wave (50–60% of the total energy), vaporization of the liquid, light radiation, heating of plasma, expansion of the cavitation bubble, and chemical processes.

In the determination of the energy yield, the amount of reaction products should be related to the absorbed energy (62% of the incident radiant energy), because the unabsorbed energy has no effect on chemical transformations. This approach (the allowance for only the energy absorbed by the system) is analogous to the Grotthuss–Draper law used in the study of photochemical processes and the approach used in the investigation of sonochemical processes [6, 9]. Since experimental data on recombination coefficients for radicals in the air atmosphere are not available, energy yields were determined in relation to 1 J of the absorbed radiation energy.

The energy yield of nitrite ions $K_{\rm NO_2^-}$ was found equal to 1.2×10^{-10} mol per 1 J of the energy absorbed in the laser-induced spark. For Fe³⁺ ions, analogous calculations yield $K_{\rm Fe^{3+}} = 9 \times 10^{-11}$ mol/J (see table). We also used the data [9] for the multibubble cavitation field. In the nitrogen atmosphere, the yield of Fe³⁺ ions related to



Fig. 3. Formation of fumaric acid (white precipitate) in a 25% maleic acid solution saturated with butyl bromide under the action of a laser-induced spark: (a) (1) the laser-induced spark and (2) a fraction of the precipitate; (b) (2) the precipitate 30 ms after the spark.

the absorbed energy $K_{\text{Fe}^{3+}} = 3.98 \times 10^{-3}/(100 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23}) = 4.1 \times 10^{-10} \text{ mol/J}.$

A comparison between the laser-induced spark and the multibubble cavitation shows that, at the same absorbed power, their energy efficiencies in redox reactions are of the same order. For the reaction of isomer-

Energy yields of reaction products (related to the energy absorbed) for laser-induced spark (I), multibubble cavitation (II), and single-bubble cavitation (III)

Method	$K_{\rm NO_2^-} \times 10^{10}$	$K_{\rm Fe^{3+}} \times 10^{10}$	$K_{\rm OH^-} imes 10^{10}$	$K_{\rm F} \times 10^7$	$K_{\rm hv} imes 10^6$
Ι	1.2	0.9		63	6.0
II	0.17	4.1	0.25	1.4	$10^{-5} - 10^{-6}$
III (20°C)	4.4		0.78		0.47
III (3°C)	10.6		0.88		3.6

Note: The chemical-acoustic efficiency of the multibubble cavitation in the air atmosphere was estimated to be equal to that in a nitrogen atmosphere. The energy yield of photons K_{hv} is given in J/J while the other quantities, in mol/J; F denotes fumaric acid with RBr.

ization of maleic acid, the efficiency of the laserinduced spark was found to be \sim 7 times higher than the efficiency of the multibubble cavitation. Note that the chemical action of the multibubble cavitation is associated with electrical breakdowns inside the bubbles in their deformation and splitting [5].

The chemical action of a single bubble was considered in [13]. It was concluded that the chemical action is associated with the heating of the vapor–gas mixture in the bubble to ~10⁴ K in its compression during the period of acoustic vibration. Energy yields of NO₂⁻ ions and OH radicals in pulsations of a single bubble in airsaturated water at a sound pressure amplitude of 1.5 atm and a US wave frequency of 52 kHz were determined. At 22°C, the maximum radius of the cavitation bubble $R_{\rm m} = 28.9 \,\mu\text{m}$, and amounts of NO₂⁻ ions and OH radicals formed in one period (*N*) were found equal to 3.7×10^6 and 6.6×10^5 , respectively. At the expansion stage, the cavitation bubble accumulates the acoustic field energy, and the total energy accumulated by the bubble is determined by the relation

$$E_1 = (4\pi R_{\rm m}^3/3)(p_{\rm h} + p_{\rm ac} - p_{\rm s}), \qquad (7)$$

where $p_{\rm h} = 1$ atm is the hydrostatic pressure, $p_{\rm ac}$ is the sound pressure averaged over the period of fast compression ($p_{\rm ac} \approx 0.3$ atm), and $p_{\rm s}$ is the saturated vapor pressure ($p_{\rm s} \ll p_{\rm h}$). The energy yield of the product is

$$K = N/(6.02 \times 10^{23} E_1).$$
(8)

Substituting numerical values gives $K_{NO_2^-} = 4.4 \times 10^{-10}$ mol/J (related to the acoustic energy), and $K_{OH} = 7.8 \times 10^{-11}$ mol/J. At 3°C, the bubble is compressed to a higher degree ($R_m = 30.5 \mu m$) because of a lower vapor pressure, which prevents its collapse, and numbers of NO₂⁻ ions and OH radicals formed in the period of laser irradiation are equal to 9.9×10^6 and 8.2×10^5 , respectively; that is, $K_{NO_2^-} = 1.06 \times 10^{-9}$ mol/J (related to the acoustic energy), and $K_{OH} = 8.8 \times 10^{-11}$ mol/J (see table).

After 60 min of exposure of 25 ml of a 25% maleic acid solution saturated with *n*-butyl bromide to the focused laser beam with a pulse energy of 140 mJ and a pulse interval of 1.2 s, $\hat{0}.19$ g (1.64×10^{-3} mol) of fumaric acid was formed (with allowances made for its solubility in 25 ml of water, 0.15 g $(1.1 \times 10^{-3} \text{ mol}))$. Thus, we obtained the stoichiometric amount of fumaric acid, which corresponds to the chain reaction mechanism. The energy yield of the reaction was found to be four to five orders of magnitude higher than those for redox reactions in the irradiation with a focused laser beam, which is an extra argument in supports of the chain reaction mechanism (see table). Note that the energy yield of the ultrasonically initiated chain reaction of stereoisomerization of maleic acid into fumaric acid in the presence of alkyl bromides is also three to four orders of magnitude higher than the energy yield of sonochemical redox reactions [6, 9]. It is believed that such reactions may occur under the action of high-energy particles or products formed under their action (molecules, ions, electrons, radicals, excited species, etc.).

According to estimates [12] the total energy of photons emitted by a laser-induced spark was estimated at $\sim 6 \times 10^{-6}$ of the energy absorbed by the spark. In the single-bubble cavitation, the energy yield of photons at 22°C is equal to 4.7×10^{-7} and, at 3°C, 3.6×10^{-6} [13] (see table). In the multibubble cavitation, the efficiency of conversion of acoustic energy into luminous is very low, 10^{-11} – 10^{-12} [6, 9, 14].

The laser-induced spark and the single-bubble cavi-

tation exhibit much the same energy yields of NO_2^- and efficiencies of conversion of absorbed energy into luminous. In both cases, the temperature of equilibrium plasma is equal to ~10⁴ K. Thus, it is believed that these processes are similar in nature.

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