OTHER PROBLEMS
OF PHYSICAL CHEMISTRY

Iodine–Starch Clathrate Complexes under the Impact of a Low-Frequency Acoustic Field

V. S. Boldyrev, G. N. Fadeev, M. A. Margulis, and B. P. Nazarenko

Bauman Moscow State Technical University, Moscow, 107005 Russia
e-mail: gerfad@mail.ru

Abstract—The results from research on the kinetics of destruction of clathrate complexes (amyloidine, amylopectoiodine and iodinol) in low-frequency acoustic waves from 5 to 25 Hz are presented. Features of the transfer of energy from low-frequency acoustic oscillations are determined. The ability of systems containing biologically active clathrate structures to interact in resonance with external acoustic stimuli according to the energy state of the active part of iodine-containing compexes is confirmed. In the first approximation, such compounds can be regarded as model biochemical systems.

Keywords: acoustic oscillations, resonant frequency, models of biochemical systems, clathrate complexes, amyloidine, amylopectoiodine, iodinol, kinetic parameters of the destabilization of clathrates.

DOI: 10.1134/S0036024413090057

INTRODUCTION

Essential features of the energy transfer and specificity of the effect of low-frequency acoustical vibrations and concomitant factors on the state of biologically active structures were determined in [1−4]. It was shown that such changes are caused by the resonance interaction between the intrinsic frequencies of chemical reactions [4] and an external acoustical field; i.e., there is an intrinsic resonance frequency of acoustical low-frequency vibrations for each chemical system at which such impact is maximal. We have confirmed this experimentally many times for systems that are steps toward biochemical structures.

In [3], important features were determined for the behavior of clathrates (specifically amyloidine and amylopectoiodine); low-molecular components of the investigated compounds resonate under external impact. Changes are related to the resonant interaction between applied vibrations and the frequency of chemical transformation of the active part of a structure. In [1−4], features of interactions between amyloiodine and amylopectoiodine were interpreted as consequences of the different energy states of ions in these compounds; the resonance of external impacts and components of clathrates occurs according to the energy state of iodine molecules that arises after adsorption of iodine.

The aim of this work was to verify the validity of the interpretation given above using a clathrate containing iodine in a similar position. Iodinol satisfies these requirements. In this clathrate, a molecule of polyvinyl alcohol (PVA) has a secondary structure of a polymer chain in the form of a spiral (as does amylose in starch); in contrast with amylose, however, the spiral is single rather than double. According to the data from [5], the iodine in this clathrate bonds to the oxygen atom of the −OH group of polyvinyl alcohol using the middle part of the molecule's atomic bond. Iodine–polyvinyl alcohol complex can interact strongly with electron donor molecules.

EXPERIMENTAL

It was found that at applied external electrical voltages of 3 V for starch and 5 V for iodinol (Fig. 1), the main factor in acoustical impact is not the frequency of the applied vibrations, but their power. At the above voltages, the impact of vibrations is almost identical
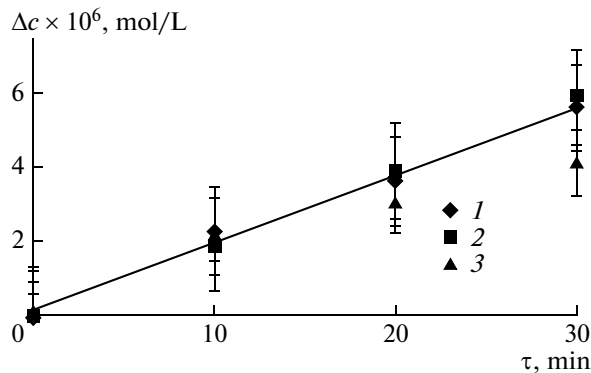

Fig. 1. Kinetics of the destabilization of iodinol at an applied voltage of 5V and frequencies of (*1*) 10, (*2*) 20, and (*3*) 25 Hz.

Table 1. Kinetic characteristics of destabilization of iodine-containing clathrates in a field of low-frequency impact upon introducing polysaccharide to a solution with excess iodine

Clathrate	$E_{destruction}$, kJ/mol	Temperature coefficient, γ	Rate constants $k_0 \times 10^3$, mol L^{-1} s^{-1} ($V = 3$ V)
Iodine–starch	44*, 29**	2.1	0.221
Amylopectoiodine	38—41	1.9—2.1	0.218
Amyloidine	29—31	2.2—2.5	0.305
Iodinol	14—16	1.7—1.9	0.277 0.319***

*Adsorption energy of iodine on amylose; **on amylopectin; *** at $V = 5$ V.

for frequencies of 10, 20, and 25 Hz, the choice of which was determined by the value of the resonance frequencies of the systems under study. The destabilization of both starch and iodinol corresponded to a process with the kinetic parameters given in Table 1. The activation energy of the adsorption of iodine on PVA was 42.64 kJ/mol [6]. This is close to the activation energy of the adsorption of iodine on amylose (44 kJ/mol) and notably exceeds the activation energy of the adsorption of iodine on amylopectin (29 kJ/mol).

Our experimental data confirm that, as in the case of amylose, the strength of iodine adsorption on PVA is not a barrier to the increased activity of iodinol in sonochemical transformation. The rate constants of its destabilization are higher (Table 2) and the activation energy of the destabilization of iodinol $E_{dest} = 16 \pm 2$ kJ/mol is lower than that of amyloiodine ($E_{dest} = 29$—31 kJ/mol). The main factor determining the behavior of the complex is again not its structure, but the state of active part of the clathrate that is able to interact in resonance with an external acoustic impact.

RESULTS AND DISCUSSION

The destabilization of clathrates, which does not depend on the frequencies of applied impacts, indicates that the amount of absorbed energy is the limiting factor under these conditions. A similar effect is observed for photochemical and radiation impacts. We may therefore present with a considerable degree of probability an analogy between the results of a low-frequency acoustical phonon impact and the effect of photochemical or radiation emissions.

Our findings were revealed by acoustical impacts on different (albeit similar) systems: iodine clathrates with starch, amylose, amylopectin, and iodinol. This provides grounds for using the Franc–Rabinovich cell effect for the theoretical rationalization of the above [7, 8] when applied [9] to condensed systems with possible radical polymerization. This analogy is confirmed by the following experimental findings:

(1) the dependence of the destabilization of structures vs. the power of impact, rather than the frequency of applied vibrations;

(2) the changes in the kinetic order of the destabilization of clathrates upon an increase in the power of an acoustical impact;

(3) the irreversible (in contrast with thermal impact) character of the destabilization of the investigated complexes.

The character of dependence of the acoustical energy vs. the effect of the sonochemical process should be noted. There is a power threshold that is unique to a particular clathrate, after the crossing of which the impact of acoustical vibrations is markedly enhanced (Fig. 2). For starch-based clathrates, this transition takes place at a voltage of 5 V; for iodinol, it occurs at 7 V. Assuming we can divide cavitation into undeveloped and developed [10, 11], we refer to this transition as the threshold of developed cavitation (TDC), after the crossing of which another mechanism of the sonochemical process comes into action.

The differences between the action of low-frequency acoustical vibrations from waves of higher frequencies were not clear prior to the results of this work. We now have reason to suggest that the transition from one type of cavitation to another takes place upon an increase in the power of low-frequency vibrations above a certain degree that is unique to each system. This is reflected by a change in the kinetic order of the process (Fig. 3). The TDC for ultrasonic impacts was first determined by R. Eshe. The TDC effect for the low-frequency acoustical vibrations of the infrasound

Table 2. Rate constants ($k \times 10^4$, s^{-1}) of the destabilization of iodine-containing clathrates upon introducing polysaccharide to an iodine solution and at different voltages (V) of impact

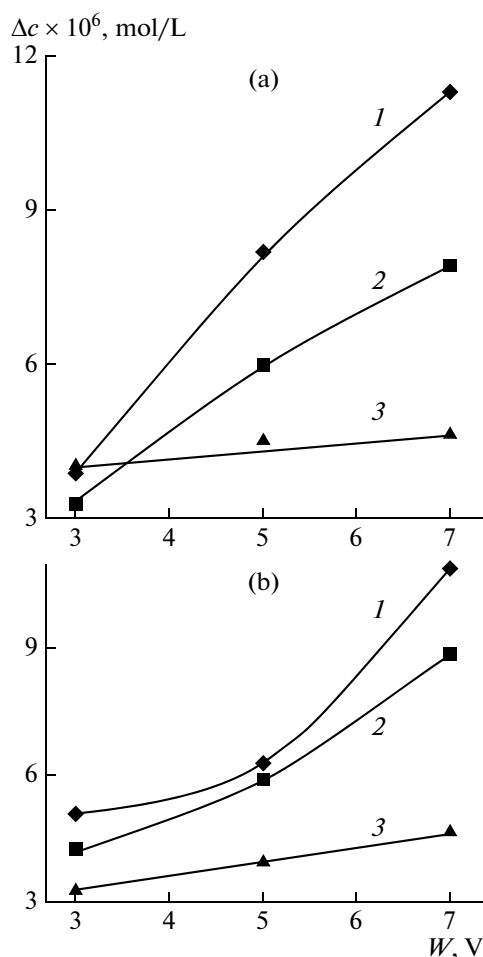| Clathrate	$\nu = 10$ Hz		$\nu = 20$ Hz		$\nu = 25$ Hz	
	$V = 5$ V	$V = 7$ V	$V = 5$ V	$V = 7$ V	$V = 5$ V	$V = 7$ V
Iodine–starch	2.93	6.01	2.78	2.87	1.37	2.16
Amylopectoiodine	1.61	1.75	0.52	1.71	0.75	1.18
Amyloidine	3.7	4.83	0.9	1.13	0.13	0.34
Iodinol	5.66	7.95	4.28	9.33	2.01	4.01

Fig. 2. Kinetics of the destabilization of (a) starch and (b) iodinol upon a change in applied voltages; (*1–3*) see Fig. 1; $\tau = 30$ min.

Fig. 3. Kinetics of the destabilization of iodinol at an applied voltage of 7 V and frequencies of (*1*) 10, (*2*) 20, and (*3*) 25 Hz.

and lower sonic ranges was observed *for the first time in this work*.

Theoretical analysis of our results enabled us to determine the main features of the action of low-frequency vibrations on the processes in microheterogeneous systems representing biologically active structures. Table 2 gives the rate constants of the destabilization of biologically active structures: iodine–starch clathrate complex; clathrate compounds of iodine with components of starch, amyloiodine and amylopectoiodine; and clathrate formations of iodine and polyvinyl alcohol.

Many properties of starch as a high-molecular compound are related to its polydispersity, i.e., to the presence of molecules of various lengths forming aggregates of various sizes. This creates difficulties in interpreting the results from studies of starch. The less complex structure of PVA makes the analysis of these results more precise. Our main conclusions are as follow:
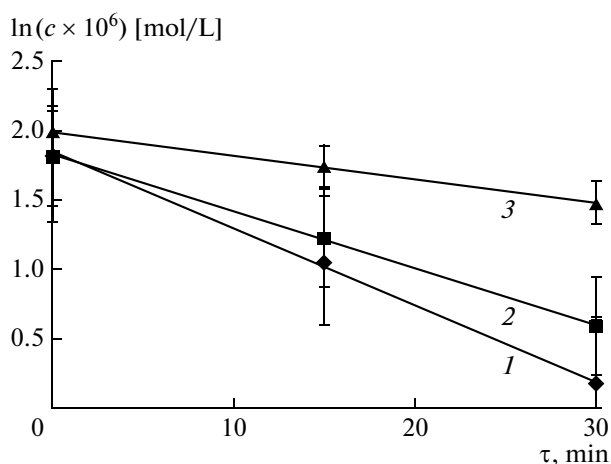
(1) The resonance frequency of the destabilization of iodinol and clathrates of the iodine–starch system lies in the infrasound range.

(2) The strength of the iodine–PVA bond affects iodinol's susception of the resonance of an applied acoustical impact.

(3) In the area of low-frequency acoustical impacts, *the ability of the active part of a clathrate's structure to interact in resonance with an external acoustical impact* is most important and pivotal.

The above features determine the high activity of iodinol in sonochemical transformations. The rate constants of its destabilization are higher than those of amyloiodine (Table 2) and the activation energy of the destabilization of iodinol is lower (Table 1). The conclusion drawn in [1–3] is thus confirmed: upon the absorption of phonons from acoustical emission, the energy state and not the structure of the active part of a biochemical system that responds in resonance with an external acoustical impact is of primary importance.

This opens the door to designing structures that can act as countermeasures against acoustical nonlethal weapons (ANWs). Their operating principle should lie in resonance interaction between the active part of the countermeasure structures and the frequency of an external acoustical impact and the reduction or complete absorption of the energy entering the organism. The clathrates studied in this work are prototypes of such structures. The design of countermeasures against ANWs and any study of the mechanisms of its action should certainly be based on a generalized approach [12]. There is no simple technical solution to this problem [13], meaning that we must integrate the knowledge and cooperative efforts of researchers from a variety of fields, e.g., physics, biochemistry, and medicine.

CONCLUSIONS

The main kinetic parameters of the destabilization of clathrate structures (specifically, amyloiodine, amylopectoiodine, and iodinol) were determined. The relationship between the resonance interaction of active low-molecular clathrates and the frequencies of external acoustical impact was established. It was revealed that amyloiodine, amylopectoiodine, and iodinol clathrate complexes can absorb a substantial part of the energy of low-frequency acoustical vibrations; the active behavior of clathrates is related to the state of iodine, making the complex more sensitive to external impacts. It was found that in principle, the sensitivity of the investigated complexes to the frequency range of acoustical nonlethal weapons makes the use of these structures possible for developing countermeasures against such weapons.

REFERENCES

1. G. N. Fadeev, V. S. Boldyrev, and V. I. Ermolaeva, Dokl. Biochem. Biophys. **446**, 247 (2012).
2. G. N. Fadeev, V. S. Boldyrev, and V. N. Tveritinov, Vestn. Mosc. Tech. Univ. Baumana, Ser. Estestv. Nauki, No. 4, 52 (2012).
3. G. N. Fadeev, V. S. Boldyrev, V. I. Ermolaeva, and N. M. Eliseeva, Russ. J. Phys. Chem. A **87**, 35 (2013).
4. G. N. Fadeev, N. N. Kuznetsov, E. F. Beloborodova, and S. A. Matakova, Russ. J. Phys. Chem. A **84**, 2254 (2010).
5. L. A. Gribov, T. T. Merzlyak, O. B. Zubkova, et al., Zh. Fiz. Khim. **58**, 2529 (1984).
6. www.sev-chem.narod.ru/spravochnik/krahmal.htm
7. J. Franck and E. Rabinowisch, Trans. Faraday Soc. **30** (152, Pt. 2), 120 (1934).
8. R. M. Noyes, J. Am. Chem. Soc. **77**, 2042 (1955); J. Am. Chem. Soc. **78** (3) (1956).
9. S. W. Benson, *Thermochemical Kinetics* (Mir, Moscow, 1954; Wiley, New York, 1968).
10. M. A. Margulis, *Principles of Sonochemistry* (Vysshaya Shkola, Moscow, 1984) [in Russian].
11. M. A. Margulis, *Sonochemical Reactions and Sonoluminescence* (Khimiya, Moscow, 1986) [in Russian].
12. G. Fadeev and V. Ermolaeva, in *Proceedings of the 2nd European Symposiums on Non-Lethal Weapons, Ettlingen, Germany, May 13—14, 2003*.
13. G. N. Fadeev and V. I. Ermolaeva, Vopr. Oboron. Tekh., Ser. 16, Nos. 1—2, 28 (2004).

Translated by A. Muravev