# CHEMICAL KINETICS = AND CATALYSIS

## Destabilization Kinetics of Polyvinylpyrrolidone-Iodine in a Field of Low Frequency Impacts

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**Abstract**—Experimental results on the destabilization kinetics of compounds with chelate structure (polyvinylpyrrolidone-iodine) in the field of the impact of low-frequency vibrations (from 2 to 45 Hz) are presented. The optimum frequencies at which the process rate is greatest are found for different impact modes. Based on the experimental data, conclusions are drawn as to the effect the energy of low-frequency impacts has on the studied clathrate and chelate structures.

*Keywords:* iodine-containing chelates, polyvinylpyrrolidone-iodine, iodine-containing clathrate, polyvinylalcohol-iodine, low-frequency impacts, optimum frequency, destabilization kinetics **DOI:** 10.1134/S0036024416090077

#### INTRODUCTION

It is well known [1-4] that low-frequency vibrations adversely affect the human organism. The interval of frequencies that affect different systems of the organism lies in the infrasonic and bottom ranges of sound: from 2 to 35 Hz. In [5-9], we established the destabilization dependence of biochemically active clathrate complexes on the parameters of external lowfrequency impacts. We concluded that the main role in sonochemical transformations was played by the state of the low molecular part of the complexes (i.e., iodine), which actively responded to external low-frequency impacts [8].

It was of fundamental importance to determine if the studied clathrate structures were exceptional, or if there were other types of compounds that were sensitive to low-frequency impacts. The next step in this direction was to study the effect low-frequency vibrations have on structures of chelate type (i.e., compounds of polyvinyl pyrrolidone with iodine (PVPiodine) that display biochemical activity).

### EXPERIMENTAL

A PE-5400V spectrophotometer (St. Petersburg, Russia) with a measuring range of 335 to 1100 nm was used in our experiments. The accuracy of establishing wavelengths was  $\pm 0.5$  nm; that of establishing absorbance was  $\pm 0.05$  nm. Changes in the absorbance of aqueous solutions of PVP-iodine caused by exposure to low-frequency impacts were determined at a wavelength ( $\lambda$ ) of 500 nm. The absorbances of the solutions were measured before and after exposure to vibrations. The effects of the following frequency intervals were studied:

—infrasound (from 2 to 10 Hz);

-the boundary of the infrasonic and audible sound ranges (from 15 to 20 Hz);

-the range of audible sound (from 25 to 45 Hz).

#### **RESULTS AND DISCUSSION**

When subjected to low-frequency vibrations, the studied chelate was permanently discolored. The optimum frequencies at which the effects of polyvinylpyrrolidone-iodine exposure were maximal lay (Fig. 1) in the infrasonic range of 10-12 Hz. The kinetic parameters we determined were the order of the reactions, the rate constants, and the activation energies. The order of the sonochemical transformations of our PVP-iodine complex was found experimentally over the range of the studied frequencies (from 2 to 45 Hz)

Rate constants ( $k \times 10^4$ , s<sup>-1</sup>) of the sonochemical transformation of PVP-iodine complex in the frequency range of 2 to 45 Hz

<i>U</i> , V	2	5	10	25	35	45
3	0.94	0.47	2.60	0.47	0.50	0.36
5	4.60	4.80	9.78	1.12	1.06	0.50
7	6.78	13.95	11.72	4.73	1.23	1.23



**Fig. 1.** Change in the optical density of PVP-iodine, depending on impact frequency v, Hz, and the applied voltage: (1) 3, (2) 5, (3) 7 V.

and the values of fed voltage *U*: 3, 5, and 7 V. We calculated the rate constants of the transformation of our PVP-iodine complex for the above values of frequency and voltage (see table).

The energy of destabilization ( $E_{dest}$ ,  $\pm 2 \text{ kJ/mol}$ ) is determined for the studied structure of PVP-iodine complex upon sonochemical transformation. A comparison of the values obtained for the destabilization energy of PVP-iodine complex with the same values for clathrate and chelate structures studied earlier in a field of low-frequency impacts at 10 Hz and an intensity of 40 dB are given below:

Amyloiodine A	mylopectoiodine	Iodinol	PVP-iodine	
29-31	38-41	14—16	34-36	

The external energy incident on the complex structures comprising the polymeric part and the low molecular component can be distributed in a variety of ways:

-by being absorbed by the dominant mass of the polymer part of the compound;

—by being divided between the polymer part and low molecular component of the structure;

-by affecting mainly the state of the low molecular compound.

The experimentally determined values of the energy of sonochemical reactions for our PVP-iodine complex were approximately equal to the values for the clathrate structures amyloiodine and amylopectoiodine. The results from our experimental study of the sonochemical transformation of clathrate and chelate structures confirm the assumption made in [3, 5, 8, 9] that *in the sonochemical transformations of the studied*  *iodine-containing clathrates and chelates, the main role is played by changes in the state of low molecular weight component* (iodine) upon a slight change in the polymer part of the complexes' structures.

Raman spectra were recorded to clarify the details of energy transfer during sonochemical transformations that occur in biochemically active structures in the field of action of low-frequency vibrations. A Ntegra Spectra atomic force probe microscope was used employing confocal microscopy and Raman spectroscopy with a resolution of  $0.4 \,\mu\text{m}$ .

For the clathrate compound, the results for iodinol are shown in Fig. 2; the spectrum of the chelate structure of polyvinylpyrrolidone-iodine is shown in Fig. 3. Notable differences are visible in the spectra before and after exposure to low-frequency vibrations with the optimum frequency of 10 Hz and an intensity of sound pressure of 55 dB. The change in the nature of the iodinol spectrum in the range of  $1.3 \times 10^{-3}$  and  $2.4 \times 10^{-3}$  cm<sup>-1</sup>, along with the appearance of peak in the Raman spectrum of PVP-iodine in Fig. 3 in the region of  $(0.4-0.7) \times 10^{-3}$  cm<sup>-1</sup> were probably associated with the change in the state of iodine present in the structure of these compounds.

In iodinol, the intermolecular bonds are of the guest-host type. In polyvinylpyrrolidone-iodine, the bonds of the donor-acceptor mechanism are the basis of intermolecular interactions. The authors of [12–16] believed that both types of bonds allow iodine to form chains of types -I-I-I-I [12],  $-I-I^--I-I-I^--I-$  [15], and even longer (up to  $(I_{24})^{2-}$ ) [14]. Using Raman and Mössbauer spectroscopy, iodine-containing complexes (trimesic acid  $\cdot$  H<sub>2</sub>O)<sub>10</sub>H<sup>+</sup>  $\cdot$  I<sub>5</sub><sup>-</sup> were found [14] in the polycrystalline structure of trimesic (1,3,5-benzene-tricarboxylic) acid with iodine [14]. All these compounds contain helical and partially crosslinked



**Fig. 2.** Raman spectra of the clathrate complex of polyvinylalcohol-iodine (iodinol): (a) initial sample, (b) after the action of acoustic vibrations at a frequency of 10 Hz and an intensity of 55 dB.

parts that include activated iodine in the form of chains. The distance between iodine atoms in these chains are the same at 0.306 nm, which is considerably greater than the distance (0.250 nm) between the atoms in an iodine molecule.

The sonochemical activity of the studied structures of both the clathrate and chelate types is mainly determined by the state of the low molecular component (i.e., iodine). Using Frank and Rabinovich's concept of the cage effect [10, 11], we may assume that not only does the configuration of the polymer part of the compound change under the impact of external energy, but the chains formed by atomized iodine are ruptured as well. For the investigated chelating structure, this is accompanied by an increase in the acidity of the aqueous solution of PVP-iodine as a result of low-frequency impacts from pH 3.6–4.0 to pH 2.8–3.0. The liberation of  $H^+$  cations into the solution weakens the bond between the groups of iodine ions and the polymer part of the molecule, thereby changing the initial configuration of the chains of atomized iodine.

#### CONCLUSIONS

Polyvinylpyrrolidone—iodine, a biochemically active compound belonging to the class of chelates, is sensitive to low-frequency impacts. The optimum frequencies of the sonochemical transformation of this compound with different modes of exposure in the infrasonic and audible sound ranges were experimentally established. Kinetic parameters of these transformations were determined: the kinetic order, the rate constants at different frequencies and intensities of exposure to sound, and the activation energy at a frequency of 10 Hz and an intensity of sound exposure of



Fig. 3. Raman spectra of the chelate complex of polyvinylpyrrolidone-iodine: (a) initial sample, (b) after the action of acoustic vibrations at a frequency of 10 Hz and an intensity of 55 dB.

40 dB. It was established that the main feature of the studied clathrate and chelate structures that determines their sensitivity to low-frequency impact was a change in the state of iodine. Our perception of the energy of low-frequency impacts is due to intermolecular changes that lead to absorption of the energy of external low-frequency vibrations.

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