On the problem of "mysterious" adducts in the Belousov—Zhabotinsky reaction

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The formation of an adduct between *o*-phenanthroline and bromine, a feasible intermediate in the Belousov—Zhabotinsky reaction (BZ) catalyzed by ferroin, was studied. The stability constant of the adduct was determined. One of the assumptions on the composition of the "red precipitate," the substance to which several differences between the behavior of the ferroin and cerium BZ reactions are due, was confirmed.

Key words: Belousov—Zhabotinsky reaction, ferroin, *o*-phenanthroline.

The Belousov—Zhabotinsky reaction (BZ), *i.e.*, catalytic oxidation of malonic acid by bromate in an acidic medium, is an oscillation reaction that has been studied in great detail. When using cerium(III) as a catalyst, the inorganic part of the mechanism can be considered as completely established.[1—3] However, if cerium is replaced by tris(*o*-phenanthroline)iron(II), ferroin, many obscure facts associated with abundant products of oxidation, dissociation, and complexation of iron compounds appear in the mechanism. In particular, it is not clear why oscillations,[4,5] which are not observed in the cerium system, become possible in a ferroin system without an organic substrate in a batch reactor.

In this case an important role might be played by a poorly studied, scantily soluble substance[4,5] that precipitates as a "red precipitate" from the BZ-system at high concentrations of ferroin and bromate; the substance could serve as a ferroin reservoir, providing replenishment of the system and making possible the oscillations. Two formulas of the substance were reported in the literature: $Fe(phen)_3(Br_3)_2$[4,5] and $Fe(phen)_2Br_2$.[6,7] An assumption has been made that it is a bromination product of *o*-phenanthroline in ferroin.[5,8] The substance in question was not studied in detail. When simulating BZ kinetics, a stage with one of the suggested formulas and arbitrary rate constants is commonly included; the rate constants are chosen in such a way that the model would satisfactorily describe the experiment. In the present work we give a description of one more adduct whose formation is possible in this system; its properties will help in drawing a conclusion about the composition of the red precipitate.

Experimental

The following reagents were used: H_2SO_4, KBr, $KBrO_3$, $FeSO_4 \cdot 7H_2O$ (all analytical grade), *o*-phenanthroline (phen) (Wako, "reagent grade"). A water solution of Br_2 was prepared by mixing acid solutions of $KBrO_3$ and KBr in the stoichiometric ratio with the 10 % excess of the latter. A solution of ferroin was prepared by mixing $FeSO_4$ and phen solutions in a 1 : 3 ratio.

The experiments on determination of the stability constant were carried out in an open glass cell (10 mL) at 22 °C and pH 2.5. The concentration of Br_2 was recorded photometrically (ε_{396} = 164 cm^{-1} mol^{-1} L). The concentration of Br_2 was varied from 3 to 8 mmol L^{-1}; that of phen was varied from 0 to 30 mmol L^{-1}.

Results and Discussion

Not only ferroin but also phen was found to react with Br_2 in water solution to give a loose yellow precipitate, whose solubility in water is ~1 g L^{-1}. Needle-shaped greenish-yellow crystals precipitate from the dilute solution upon standing. The precipitate becomes orange with aging. The "yellow precipitate" can be alternately dissolved and precipitated from the same portion of solution by a simple change in pH: at pH > 8 or pH ≤ 2 the precipitate is not formed (or is dissolved, if precipitated previously). Dissolution in an acidic medium gives a yellow solution (due to the formation of Br_2); that in an alkaline medium gives a colorless solution. The possibility of such a sequence of rapidly alternating dissolutions-precipitations indicates that the obtained substance is not a product of bromination of aromatic rings, which

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 379—381, February, 1996.

would hardly be possible under such mild conditions,[9,10] but rather is a molecular complex.[11] The following reactions were suggested to take place during its formation and dissolution:

$$\text{phen} + Br_2 \longleftrightarrow \text{phen}\cdot Br_2 \qquad \text{(formation)}$$

$$\text{phen}\cdot Br_2 + 2\,OH^- \longrightarrow \text{phen} + Br^- + BrO^- + H_2O \qquad \text{(alkaline dissolution}$$

$$\text{phen}\cdot Br_2 + H^+ \longrightarrow \text{phen}\cdot H^+ + Br_2 \text{ (acidic dissolution)}$$

Analogous complexes (mostly with I_2) with nitrogen containing heterocycles have already been described.[11,12,13] They usually have the 1:1 stoichiometry and are n,σ-complexes, *i.e.*, the unshared electron pair of the nitrogen atom passes into the antibonding σ-orbital of the halogen molecule.

The stability constant of the adduct in aqueous solution was determined using the Br_2 capability of volatilizing from the solution. The aqueous solution of phen was added in portions to the bromine solution while changes in the volatilization rate of Br_2 were recorded. Assuming that only non-bonded bromine can evaporate from the solution (following the $d[Br_2]/dt = -k_0[Br_2]$), its concentration was found after adding successive portion of phen

$$[Br_2] = (-d[Br_2]/dt)/(k_0\exp(-k_0\Delta t_s)),$$

where k_0 is the rate constant of volatilization, which was determined before adding the first portion of phen; Δt_s is the time interval chosen in such a way that an increase in solution turbidity, caused by adduct formation, is stopped at the moment of measuring $d[Br_2]/dt$. The overall bromine concentration was calculated from its initial concentration taking into account its decrease due to evaporation during the experiment; the concentration of the complex was determined as the difference between the overall concentration of bromine and the concentration of the non-bonded bromine. We used this method of determination of the Br_2 concentration (not described in the literature) to avoid the necessity to distinguish two similar spectra: the spectrum of the adduct and the spectral sum of its components as well as to work with a strongly diluted transparent solution and small concentrations of reagents, since it could result in decreasing the accuracy of the method which is not high.

If only two reactions are assumed to proceed in this system

$$\text{phen} + H^+ \longleftrightarrow \text{phen}\cdot H^+,$$

$$\text{phen} + Br_2 \longleftrightarrow \text{phen}\cdot Br_2,$$

and the equilibrium constant of the first reaction $\log K_b = 4.9$ (see Ref. 14), then the stability constant of the adduct at 22 °C is $K_c = 2400 \pm 1000$ mol^{-1} L. We could not find a description of the stability constants for n,σ-complexes of amines and nitrogen-containing heterocycles with halogens in water (or in other polar solvents); therefore we propose several data for the iodine complexes in nonpolar solvents for comparison: $C_5H_5N \cdot I_2$ — 159 mol^{-1} L (heptane),[15] quinoline $\cdot\, I_2$ — 312 mol^{-1} L (benzene),[16] phen $\cdot\, I_2$ — 170 mol^{-1} L (CCl_4),[17] $Et_3N \cdot I_2$ — 4646 mol^{-1} L (heptane).[18]

The value of the stability constant we found is by an order of magnitude higher than that for analogous complex phen $\cdot\, I_2$ in CCl_4,[17] which might be explained from the viewpoint of the empiric principle of hard and soft acids and bases.[19] Though Br_2 and I_2 are soft Lewis acids, Br_2 is a harder acid and must form more stable complexes with *N*-heterocycles than I_2. Additionally, in a polar solvent, the formation of charge transfer complex having the dipole moment which exceeds those of the donor and acceptor[12] must result in an additional gain in energy.

We did not measure the rate constant of complex formation k_{rc} because of the above mentioned spectral similarity, but we estimated $k_{rc} \geq 100$ mol^{-1} L s^{-1} from the rate of solution turbiditiration during complex formation.

Studies of peculiarities of formation of the yellow precipitate allowed us to come to conclusion that the red precipitate is not the product of bromination of phen in the ferroin molecule. Usually the bromination of aromatic compounds proceeds according to the mechanism of the electrophilic substitution[20] S_EAr. In phenanthroline, bonded to iron in the complex, the unshared electron pairs of nitrogen atoms partly pass into the vacant d-orbitals of Fe^{2+}; the electron density in the aromatic rings decreases as well as capability for the S_EAr reaction. Thus, a coordinated phen must be a less attractive object for the electrophilic attack than a non-bonded phen.

Simple experiments allow us to confirm the suggestion that the red precipitate contains a ferroin formula unit. It does not dissolve in 4 mol L^{-1} H_2SO_4; however, it dissolves, yielding a blue solution of tris(*o*-phenanthroline)iron(III), — ferriin, with liberation of gaseous bromine, after adding dry not to dilute the solution $NaBrO_3$:

$$\{Fe(\text{phen})_3Br_{2n}\}^{2+} + BrO_3^- + H^+ \longrightarrow$$

$$\longrightarrow Fe(\text{phen})_3^{3+} + nBr_2 + \ldots$$

Neither ferroin nor ferriin in 4 mol L^{-1} H_2SO_4 are formed because of the ligand protonation;[14] therefore, one can conclude that the red precipitate contains an intact formula (and structural) unit of ferroin (without phenanthroline deficiency) and can not be a substance of the $Fe(\text{phen})_2Br_2$ type, since the addition of one more ligand molecule is impossible under such conditions.

The red precipitate readily dissolves in alkaline solutions (in our experiments pH > 10); the first compound formed is ferroin which then dissociates to form $Fe(OH)_2$

$$\{Fe(phen)_3Br_{2n}\}^{2+} + OH^- \longrightarrow Fe(phen)_3^{2+} + Br^- + BrO^- \longrightarrow$$

$$\longrightarrow Fe(OH)_2 + 3\ phen$$

which also confirms the conclusion drawn.

Thus, the experimental results are in agreement with the suggestions made in several papers[4,5] that the adduct of ferroin with bromine (the red precipitate) is a complex of the $Fe(phen)_3(Br_3)_2$ type.

The yellow precipitate described in this work can, as well as the red precipitate, affect the kinetics; if, for instance, the BZ reaction controlled by the bromine hydrolysis is carried out during long time interval and an essential portion of ferroin (ferriin) has managed to dissociate in acid medium,[21] the phen formed will eliminate Br_2 in parallel with its volatilization into the atmosphere, reducing the oscillation period or the induction period.

It is possible that the yellowish-green precipitate with a tentative formula $[Fe^{+3}(phen)_3Br_2]^{3+}$, observed by other researchers[4] in the reaction of ferroin with Br_2, was the adduct of phen and Br_2.

This work was financially supported by the International Science Foundation (Grant MQC 000) and the Russian Foundation for Basic Research (Project No. 93-03-04090).

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Received July 3, 1995