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LETTERS

Mechanism and Mathematical Model of the Oscillating Bromate--Ferroin-Bromomalonic Acid Reaction

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A mechanism for the oscillatory reaction of the ferroin-catalyzed bromomalonic acid oxidation by bromate is proposed. The mechanism involves eleven steps. The corresponding mathematical model is reduced to a second-order system of differential equations. The model obtained is in good agreement with experiment.

The development and propagation of waves in homogeneous nonequilibrium media is a subject of considerable interest.^{1,2} Most of the chemical-wave studies have been made on the oscillatory bromate-ferroin-bromomalonic (malonic) acid system.¹⁻⁷ Therefore it is highly interesting to elucidate the mechanism and to obtain a mathematical model of these oscillations. However, the analysis of the mechanism and the mathematical modeling of oscillating bromate reactions have been confined almost entirely to cerium-catalyzed systems.^{2,8-11} Here we present a mechanism for ferroin-catalyzed oxidation of bromomalonic acid by bromate,

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which differs from the cerium-catalyzed case in some important details. A simple two-variable mathematical model is derived from the mechanism. The model fits the experimental data well.

Experimental Section

Bromomalonic acid was prepared as described in ref 3. The concentration of $Fe(phen)_3^{3+}$ was followed spectrophotometrically at $\lambda = 630$ nm (maximum absorbance of Fe(phen)₃³⁺) under continuous stirring. The temperature was 40 °C.

Mechanism and Model

Oscillations in the ferroin-catalyzed system are rather different from those in the cerium system.¹² There are two main reasons for the distinction. The first is the difference in redox potentials of the Fe(phen) $_{3}^{2+}$ /Fe(phen) $_{3}^{3+}$ (1.14 V) and of Ce³⁺/Ce⁴⁺ (1.61 V) couples,¹³ and the second is the presence of ligands in ferroin which themselves can take part in oxidation-reduction process. As shown in separate studies of metal-ion oxidation by bromate and of metal-ion reduction by bromomalonic acid,14,15 only the

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difference in potentials plays a significant role under conditions of oscillatory reaction. Due to the low redox potential of the ferroin/ferriin couple the equilibrium of elementary steps should be shifted to the oxidized state $Fe(phen)_3^{3+}$.

It seems reasonable that the same should be true for the oscillating system. Therefore we assume the modified FKN scheme^{8,16} as a skeleton mechanism:

$$H^{+} + HBrO_{3} + HBrO_{2} \rightleftharpoons HBrO_{2}^{+} + BrO_{2} + H_{2}O \quad (1)$$

$$BrO_2 + H^+ \rightleftharpoons HBrO_2^+$$
 (2)

$$Fe(phen)_{3}^{2+} + HBrO_{2}^{+} \rightleftharpoons Fe(phen)_{3}^{3+} + HBrO_{2} \quad (3)$$

$$2HBrO_2 \rightleftharpoons HOBr + HBrO_3 \tag{4}$$

$$H^{+} + Br^{-} + HBrO_{2} \rightleftharpoons 2HOBr$$
 (5)

$$H^{+} + Br^{-} + HOBr \Longrightarrow Br_{2} + H_{2}O$$
 (6)

$$H^{+} + Br^{-} + HBrO_{3} \Longrightarrow HBrO_{2} + HOBr$$
(7)

 $Fe(phen)_3^{3+} + CHBr(COOH)_2 \rightleftharpoons$ $Fe(phen)_2^{2+} + H^+ + \cdot CBr(COOH)_2$ (8)

 $H_2O + \cdot CBr(COOH), \rightleftharpoons H^+ + Br^- + \cdot COH(COOH),$ (9)

 $HOBr + CHBr(COOH)_2 \rightleftharpoons CBr_2(COOH)_2 + H_2O$ (10)

 $Br_2 + CHBr(COOH)_2 \rightleftharpoons CBr_2(COOH)_2 + H^+ + Br^-$ (11)

This scheme does not involve unknown details of the interactions of organic substances: •COH(COOH)₂, HCOH(COOH)₂, etc. with ferroin ions, CHBr(COH)₂, and HOBr. According to FKN^{8,9} this part of the mechanism is accounted for by the stoichiometric factor q connecting the ferriin reduction rate with the rate of the **Br**⁻ production.

If we assume HOBr and Br_2 to be rapidly removed through steps 6, 10, and 11 the following system of equations can be obtained:

$$\dot{X} = k_3 U(C - Z) - k_{-3} X Z - k_1 h_0 A X + k_{-1} U^2 - 2k_4 h_0 X^2 - k_5 h_0 X Y + k_7 h_0 A Y$$

$$\dot{Y} = qk_9R - k_7h_0AY - k_5h_0XY$$
$$\dot{Z} = k_3U(C - Z) - k_{-3}XZ - k_8BZ + k_{-8}h_0R(C - Z)$$
(12)

$$\dot{U} = k_3 U(C - Z) + k_{-3} X Z + 2k_1 h_0 A X - 2k_{-1} U^2$$

$$\dot{R} = k_8 B Z - k_{-8} h_0 (C - Z) R - k_9 R$$

where $X = [HBrO_2], Y = [Br^-], Z = [Fe(phen)_3^{3+}], U =$ $[HBrO_2^+], R = [\cdot CBr(COH)_2], A = [HBrO_3], B = [CHBr(C-HBrO_3)], B = [CHBr(C-HBrO_3)], B = [CHBrO_3], B =$ OOH)₂], $C = [Fe(phen)_3^{2+}] + [Fe(phen)_3^{3+}]$, h_0 is the acidity function $(lgh_0 = -H_0)$, and q is the stoichiometric factor.

As was indicated earlier (Rovinsky and Zhabotinsky,¹⁷ Sullivan and Thompson,¹⁸ Tyson²), the FKN rate constants for steps 1-5 (with cerium instead of ferroin) are not accurate. Therefore we have reestimated the constants $k_{\pm 1} - k_{\pm 5}$ by adjusting the model of the cerium oxidation by bromate (that is model 12 with B =0, Y = 0, R = 0) to experiment¹⁹ using the Marquardt technique.²⁰ The values obtained are as follows: $k_1 = 90, k_{-1} = 1.2 \times 10^5, k_3$

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= 7.8×10^3 , $k_{-3} = 2 \times 10^4$, $k_4 = 1.7 \times 10^4$ (k_3 and k_{-3} are given here for cerous/ceric couple). These values are consistent with the Tyson estimates.²

Detailed comparison of experimental curves with calculations based on models of ferroin oxidation by bromate¹⁴ and ferriin reduction by bromomalonic acid¹⁵ shows that for the ferroin/ferriin couple

$$k_3 >> k_{-3}$$
 (13a)

$$k_{-8} >> k_9 >> k_8$$
 (13b)

Due to the first of the inequalities, the U variable remains small and consequently rapid unless $1 - (Z/C) \le 1.^{14}$ The R variable is also rapid because of (13b).¹⁵ Therefore the methods of singular perturbation theory can be used to reduce system 12 to the X, Y, and Z variables. Furthermore, the term $k_{-1}U^2$ can be omitted and the term k_9 can be neglected as compared with $k_{-8}h_0(C-Z)$. Thus system 12 becomes

$$X = k_1 h_0 A X + k_7 h_0 A Y - k_5 h_0 X Y - 2k_4 h_0 X^2$$
$$\dot{Y} = q \frac{K_8 B Z}{h_0 (C - Z)} - k_5 h_0 X Y - k_7 H A Y$$
(14)

$$\dot{Z} = 2k_1h_0AX - \frac{K_8BZ}{h_0(C-Z)}$$

where $K_8 = k_8 k_9 / k_{-8}$.

Based on the experimental data of ref 15, 19, and 21, we have made the additional estimates:

$$k_7 \approx 10 \text{ M}^{-1} \text{ s}^{-1}$$
 $k_5 \approx 10^7 \text{ M}^{-1} \text{ s}^{-1}$
 $K_8 \approx 2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$

Further analysis reveals that at the values of the parameters C~ 10^{-3} M, A ~ 10^{-2} M, B ~ 10^{-1} M, h_0 ~ 1 M, the X and Y variables are fast as compared with Z and their time scales are approximately the same.

The reduction to X, Z variables yields the model:

$$\epsilon \frac{\mathrm{d}x}{\mathrm{d}\tau} = x(1-x) - 2q\alpha \frac{z}{1-z} \frac{x-\mu}{x+\mu}$$
(15)
$$\frac{\mathrm{d}z}{\mathrm{d}\tau} = x - \alpha \frac{z}{1-z}$$

where

$$X = \frac{k_1 A}{2k_4} x \qquad Z = Cz \qquad \epsilon = \frac{k_1 A}{k_4 C} \qquad \alpha = \frac{k_4 K_8 B}{k_1^2 A^2 h_0^2}$$
$$\mu = \frac{2k_4 k_7}{k_1 k_5} \qquad t = \frac{k_4 C}{k_1^2 A^2 h_0^2} \tau$$

The Gear technique²² was used for numerical investigation of model 15.

The following values of the rate constants were chosen:

$$k_1 = 100 \qquad k_4 = 1.7 \times 10^4 \qquad k_5 = 10^7 \qquad k_7 = 15$$
$$K_8 = 2 \times 10^{-5} \qquad q = 0.5$$

Model 15 produces the oscillations of $[Fe(phen)_3^{3+}]$ with extremes proportional to the total ferroin concentration C. That corresponds well to the experiment. The dependence of the extremes and period of the oscillations on the other parameters A, B, h_0 agrees satisfactorily with experimental data as well. Figure

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Figure 1. Oscillations in the bromate-ferroin-bromomalonic acid sytem: experiment, solid line; model 15, broken line. A = 0.025 M, C = 0.001M, $[H_2SO_4] = 1.25$ M ($h_0 = 2.5$ M), (a) B = 0.05 M, (b) B = 0.2 M, (c) B = 0.4 M.



Figure 2. The same as in Figure 1: A = 0.05 M, $[H_2SO_4] = 1.1$ M $(h_0$ = 2.1 M; (a) B = 0.1 M; (b) B = 0.2 M; (c) B = 0.37 M.

 $[Fe(phen)_{3}^{3*}] \cdot 10^{3}$



Figure 3. Nullclines and limit cycle of system 15: A = 0.025, B = 0.2, $C = 0.001, h_0 = 2.5, q = 0.5.$

1 and 2 show the oscillations in the real bromate-ferroin-bromomalonic acid system along with those simulated by model 15 at corresponding values of the parameters. The nullclines of system 15 and the limit cycle are shown in Figure 3.

It is interesting to see how the total model 12 changes its dynamics when k_3 , k_{-3} and k_8 , k_{-8} constants are changed from the ferroin to the cerium values. Figure 4 shows such an evolution. It should be noted that for the ferroin/ferriin couple none of the separate values of k_3 , k_{-3} , k_8 , k_{-8} , k_9 are known except that $k_3 >> k_{-3}$, $k_{-8} >> k_9 >> k_8$, and $k_8 k_9 / k_{-8} \approx 2 \times 10^{-5}$. Model 12 practically does not depend on them if these relations are valid. Therefore they were chosen arbitrarily keeping, however, these relations true.



Figure 4. Evolution of the solution of system 12 with alteration k_3 , k_{-3} and k_8 , k_{-8} constants: $k_1 = 100$, $k_{-1} = 1.2 \times 10^5$, $k_4 = 1.7 \times 10^4$, $k_5 = 10^7$, $k_7 = 7$, $k_9 = 2 \times 10^3$. A = 0.05, B = 0.2, C = 0.001, $h_0 = 2$. Solid line (ferroin case): $k_3 = 10^7$, $k_{-3} = 10^3$, $k_8 = 2$, $k_{-8} = 2 \times 10^8$. Broken line (intermediate case): $k_3 = 8 \times 10^4$, $k_{-3} = 2 \times 10^4$, $k_8 = 1$, $k_{-8} = 2$ × 10⁶. Dotted line (cerium case): $k_3 = 7.8 \times 10^3$, $k_{-3} = 2 \times 10^4$, $k_8 =$ $0.7, k_{-8} = 0.$

Discussion

It was mentioned earlier²³ that the system with bromomalonic acid is simpler than that with malonic acid both in its composition and behavior. In particular, in the bromomalonic acid system both with ferroin or cerium ion as catalyst, self-oscillations begin immediately after mixing reagents without an induction period. Therefore we have chosen this system for quantitative comparison of mathematical models with experimental data.

The paper¹² and the experimental results presented here show that there are two obvious distinctions between the ferroin- and the cerium-catalyzed oscillations. First, the maximum ferriin concentration approaches nearly the total catalyst concentration and is almost independent of [HBrO₃] and [CHBr(COOH)₂] while in the cerium case the maximum [Ce⁴⁺] depends strongly on bromate and bromomalonic acid concentration and may vary from several percent to 80% of the total catalyst concentration.²⁴ Second, the phase of ferroin oxidation is very fast while the phase of ferriin reduction is rather slow; for cerium oscillations the corresponding phases are comparable in their duration in most of the oscillation domain.²⁴ Figures 1 and 2 show that model 15 reproduces both pecularities of the ferroin system.

On the other hand, the mathematical model based on the complete FKN mechanism does not simulate the shape of oscillations of [Ce⁴⁺] when the ratio [HBrO₃]/[CHBr(COOH)₂] is not small. (See for instance the dotted line in Figure 4. Oscillations with such a smooth transition from the oxidation to the reduction phase have never been seen experimentally.) It was impossible to reach satisfactory coincidence with experimental data even after variation of the rate constants over a wide range.¹¹ Moreover, the direct experiment²¹ shows that the FKN assumptions concerning the stoichiometric connection between ceric reduction and Br⁻ production are not valid. Thus, it seems very probable that for the cerium system the FKN mechanism needs significant modification in the part concerning Br⁻ production. This problem was discussed recently.25-27

At the same time, the FKN mechanism with minor modifications allows one to obtain a simple quantitative model for ferroin system which is very like the well-known Oregonator.⁹ The essential distinction between the two models is connected with the term describing the rate of catalyst ion reduction. In model 14

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for the ferroin system this term is the following: $K_8BX/h_0(C - C)$ X); in the Oregonator the corresponding term is kBX. As a result the Oregonator does not contain the important parameter C and permits the ceric ion concentration to exceed the total concentration of cerium in the system.

It was suggested earlier^{12,28,29} that due to the presence of ligands

the mechanism of ferroin-catalyzed oscillations may be much different from cerium oscillations. Ganapthisubramanian and Noyes²⁰ put forward the proposal that the oxidation of organic substrate may involve a Fe(IV) species. However, the simple FKN mechanism, which leads to great discrepancies between models and experiment for the cerium system, leads to a simple and adequate model for the ferroin-catalyzed oscillating reaction.

Registry No. CHBr(COOH)₂, 600-31-7; bromate, 15541-45-4; ferroin, 14708-99-7.

Kinetics of I_2 Following ArF Laser Excitation: Thermal Dissociation of the A'(2_u) State

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The quenching of the lowest excited state of I_2 by I_2 , Ar, and N_2 is studied by a delayed absorption probe technique following excimer laser photolysis. The resulting rate constants (units cm³/s; $T = 296 \pm 3$ K) are $k_{1,} = 8.3$ (1.0) $\times 10^{-11}$, $k_{Ar} = 2.8$ (2) × 10⁻¹⁴, and $k_{N_2} = 7.2$ (7) × 10⁻¹⁴. The latter two are interpreted as thermal dissociation, but the I₂ self-quenching is tentatively ascribed to the process $I_2(A') + I_2 \rightarrow I_3 + I$.

Introduction

One of the simplest termolecular chemical reactions is the three-body recombination of atoms to form a diatomic molecule, and one of the most studied such reactions is the iodine atom recombination.1,2

$$\mathbf{I} + \mathbf{I} + \mathbf{M} \to \mathbf{I}_2 + \mathbf{M} \tag{1}$$

This reaction was first studied quantitatively by Rabinowitch and Wood in 1936.³ When these authors extended their gas-phase experiments to inert liquid solvents,⁴ they observed very efficient recombination, which they attributed to the "cage effect", whereby photodissociated I atoms are forced back together by a solvent cage. Recently the cage effect has come back into prominence, as it has become possible to study it dynamically by using picosecond laser techniques.⁵⁻¹⁰ At the same time the gas-phase studies have been extended to an inert gas density regime comparable to that for liquids, permitting observation of the cage effect in the gas phase.^{11,12}

An interesting point about reaction 1 is that most experiments have yielded only phenomenological rate constants, since they have involved indirect measurements—namely the detection of changes

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in the absorption by ground-state I₂ molecules. Such experiments can say little about the mechanism by which the atoms initially recombine. For example, the ground state of I₂ accounts for only 1/16 of the statistical degeneracy of two ground-state I(${}^{2}P_{3/2}$) atoms, so most I + I collisions occur on one of the other nine Hund's case c electronic states which correlate with the lowest atomic limit. Theoretical calculations, principally classical trajectory studies, have done much to enhance our understanding of the recombination process.^{13–15} One of the results of such studies is that weakly bound excited states play only a minor role in the recombination. However, since two of the relevant excited states of I_2 —A'($2_u^3\Pi$) and A($1_u^3\Pi$)—are now known to be moderately bound,¹⁶ these states could be important in the recombination mechanism.

In the present work we have carried out what we believe to be the first gas-phase kinetics study of the lowest excited state in I_2 , the A' state. Specifically we have prepared this state by ArF laser excitation of I_2 in N_2 and Ar buffer gases at pressures of 50–900 torr and measured the depopulation rate of the A' state by a delayed laser-probe absorption technique. The resulting rates appear to be first order with respect to all three gases. The N_2 and Ar results are interpreted as thermal dissociation. The I_2 results, on the other hand, force us to the speculative conclusion that quenching occurs via the reaction

$$I_2(A') + I_2 \rightarrow I_3 + I \tag{2}$$

Spectroscopic Background

Iodine absorbs light very strongly in the vacuum-UV region via the charge-transfer transition $D(O_u^+) \leftarrow X({}^1\Sigma_g^+)$. Spectro-scopic analysis of the D state¹⁷ shows that, at the 1930-Å wavelength of the ArF laser, the absorption originates mainly in v'' = 1 and terminates in $v' \approx 149$. At low pressure the D state depopulates very rapidly ($\tau = 15.5 \text{ ns}^{18}$) through fluorescence back

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