Kinetic Study of the Autocatalytic Nitric Acid–Bromide Reaction and Its Reverse, the Nitrous Acid–Bromine Reaction

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The kinetics of the forward and backward processes of the reaction $NO_3^- + 2Br^- + 3H^+ \rightleftharpoons Br_2 + HNO_2 + H_2O$ have been studied. The overall process is a true dynamic equilibrium. The same equilibrium position can be reached from either side and can be shifted by changing any of the species involved. The equilibrium constant was found to be $K_1 = (1.6 \pm 0.3) \times 10^{-6}$ M^{-4}. The oxidation of bromide by moderately concentrated nitric acid in batch is autocatalytic, nitrous acid being the catalyst. The influence of initial concentration of nitric acid, bromide, and nitrous acid was determined. In a continuously stirred tank reactor the reaction exhibits bistability. The reaction between bromine and nitrous acid has regular kinetics. A seven-step mechanism with intermediates NO, NO$_2$, BrNO$_2$, BrNO, and HOBr is proposed, which accounts for the stoichiometry, equilibrium nature, and kinetic behavior of the reaction. The agreement between experiments and calculations is generally satisfactory and in some cases excellent.

Introduction

There are many autocatalytic reactions among nitric acid oxidations with both inorganic[1] and organic[2] substrates. Recently attention has been focused on the autocatalytic processes taking place in batch and flow reactors, because some exotic kinetic phenomena were discovered during these investigations.[3] Bistability and hysteresis were found in the oxidation of iron(II)[4] and thiocyanate oxidations in a continuously stirred tank reactor (CSTR), and similar phenomena are expected in other systems. In our laboratory systematic investigations are in progress to explore the kinetics and mechanism of nitric acid oxidations. This work is a part of these investigations.

The stoichiometry of the title reactions is simple and well defined:

$$NO_3^- + 2Br^- + 3H^+ \rightleftharpoons Br_2 + HNO_2 + H_2O \qquad (1)$$
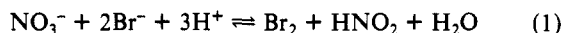
(Hereafter reaction (+1) will refer to the oxidation of bromide and reaction (−1) to the bromine–nitrite interaction.)

The standard redox potentials of the two redox couples are close to each other:[6]

$$NO_3^- + 3H^+ + 2e^- = HNO_2 + H_2O \qquad E = 0.940 \text{ V} \qquad (2)$$

$$Br_2 + 2e^- = 2Br^- \qquad E = 1.087 \text{ V} \qquad (3)$$
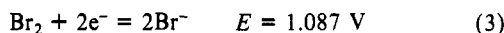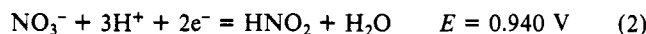
Therefore this reaction is reversible: the same equilibrium position can be reached starting from either side of reaction 1, and the equilibrium reached can be shifted by adding or removing any of the compounds involved. The forward process (+1) is autocatalytic, as noted but not exhaustively studied by Longstaff[7] and Feilchenfeld et al.[8] The reverse reaction (−1) was investigated by Pendlebury and Smith[9] in the pH range 0.8–5.8. In spite of these papers, it seemed necessary to reinvestigate the kinetics of reaction 1 and to extend the experiments to explain both the autocatalytic and reversible character in a batch reactor and the bistable behavior in a continuously stirred tank reactor.

Experimental Section

Materials. Highest grade commercially available HNO$_3$ (Carlo Erba), HClO$_4$ (Rudi Point, VEB Laborchemie, Apolda), Br$_2$

(Merck), and NaBr, NaNO$_2$, and NaNO$_3$ (Reanal) were used without further purification. Nitric acid solutions were prepared by dilution and purged with nitrogen gas for 1 h to remove dissolved gases, particularly nitrogen oxides, because these compounds exhibit a catalytic effect and influence the kinetics of the reaction. To eliminate this problem in CSTR experiments, we used sodium nitrate + perchloric acid and in other cases a mixture of nitric acid and perchloric acid. Saturated solutions of bromine were freshly diluted to the desired concentration before kinetic runs. The concentration of Br$_2$ was determined iodometrically and photometrically.[10] NaBr, NaNO$_2$, and NaNO$_3$ solutions were prepared by weighing the proper amount of the compounds.

Kinetic Runs. Measurements were made on a Hitachi 150-20 spectrophotometer and on a Hitachi 100-60 spectrophotometer, equipped with a homemade rapid-mixing device based on the stopped-flow principle. The mixing time or dead time was ∼1 s, negligible even in the case of the shortest reaction times during the study of reaction +1. However, this delay was too long for some kinetic runs on the reverse reaction (−1). The flow-through cell had no empty gas space in order to eliminate evaporation of bromine or nitrogen oxides. The reaction was followed by continuous recording of the absorbance of bromine at 441 or 467 nm, where molar absorbances are 130 and 85 M^{-1} cm^{-1}, respectively. At these wavelengths the absorption of nitrous acid is negligible. The path length of the cell was 0.5 cm. The cell was thermostated at 25 °C. At higher nitric acid concentrations the heat of dilution increased the temperature of the reaction mixture; therefore the reactant solutions were precooled to compensate for this effect. This certainly reduced the accuracy of measurements. In the case of the bromine + nitrite reaction, we were not able to follow the kinetics at acid concentrations higher than 2 M because the reaction is fairly fast and there is not enough time to establish thermal equilibrium, so the initial rate is very irreproducible.

The CSTR apparatus consisted of a thermostated glass flow reactor with premixer and magnetic stirrer. It was connected to a DESAGA PLG 132100 peristaltic pump. Potentiometric measurements were performed by using a bright Pt electrode against SCE.

Results

Stoichiometric and Equilibrium Studies. On the basis of the stoichiometry of the title reaction given by eq 1 the equilibrium constant is defined as

$$K_1 = \frac{[HNO_2][Br_2]}{[NO_3^-][Br^-]^2 h^3} \qquad (4)$$

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TABLE I: Equilibrium Constants of Reaction 1 at Different Initial Reactant Concentrations

expt no.	$[H^+]$, M	$[NO_3^-]$, M	$[Br^-]_0$, M	$[HNO_2]_0$, 10^4 M	$[Br_2]_0$, 10^3 M	$K_1(H)$, M^{-1}	$K_1 \times 10^6$, M^{-4}	H this work	H ref 13
1	4.0	0.075	0.01	1.0		0.276	1.8	1.73	1.63
2	4.0	0.1	0.0.1	1.0		0.266	1.7	1.73	1.63
3	4.0	0.2	0.01	1.0		0.245	1.6	1.73	1.63
4	4.0	0.3	0.01	1.0		0.263	1.7	1.73	1.63
5	4.0	0.5	0.01	1.0		0.235	1.5	1.73	1.63
6	4.0	0.75	0.01	1.0		0.276	1.8	1.73	1.63
7	4.0	0.5	0.003	1.0		0.202	1.3	1.73	1.63
8	4.0	0.5	0.005	1.0		0.243	1.6	1.73	1.63
9	4.0	0.5	0.01	1.0		0.235	1.5	1.73	1.63
10	4.0	0.5	0.02	1.0		0.264	1.7	1.73	1.63
11	4.0	0.5	0.03	1.0		0.294	1.9	1.73	1.63
12	4.0	0.5	0.01	0.2		0.221	1.4	1.73	1.63
13	4.0	0.5	0.01	0.5		0.230	1.5	1.73	1.63
14	4.0	0.5	0.01	1.0		0.235	1.5	1.73	1.63
15	4.0	0.5	0.01	2.0		0.228	1.5	1.73	1.63
16	4.0	0.5	0.01	5.0		0.234	1.5	1.73	1.63
17	4.0	0.5	0.01	10.0		0.253	1.7	1.73	1.63
18	3.5	0.5	0.01	1.0		0.041	1.6	1.47	1.46
19	4.0	0.5		0.01	1.0	0.235	1.5	1.73	1.63
20	4.5	0.5	0.01	1.0		0.871	1.6	1.91	1.80
21	5.0	0.5	0.01	1.0		2.596	1.6	2.07	1.97
22	5.5	0.5	0.01	1.0		5.026	1.6	2.17	2.15
23	4.0	4.0		100.0	10.3	0.0288	1.7	1.41	1.41
24	4.0	4.0		100.0	9.4	0.0248	1.5	1.41	1.41
25	4.0	4.0		100.0	6.0	0.0228	1.3	1.41	1.41
26	4.0	4.0		100.0	4.5	0.0240	1.4	1.41	1.41

At constant proton concentration we can separate a proton-independent equilibrium constant $K_1(H)$:

$$K_1(H) = \frac{[HNO_2][Br_2]}{[NO_3^-][Br^-]^2}$$

so we can treat the problem of hydrogen ion activity separately.

In order to determine equilibrium concentrations after the reaction took place, we measured the absorbance of the solution. We were not able to find a proper analytical method to measure the concentration of HNO_2 in such a reactive equilibrium mixture.[11] In the range 350–400 nm both HNO_2 and bromine species absorb and it is not possible to separate their contribution to the measured absorbance. At wavelengths >400 nm HNO_2 does not absorb. At first we neglected the absorbance due to tribromide ion, but the differences between calculated mass balances at different wavelengths were as high as 20–80%. It turned out that Br_3^- makes a significant contribution to the measured absorbance. It is present in an equilibrium mixture according to eq 5:[12]

$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad K_5 = 17 \ M^{-1} \qquad (5)$$
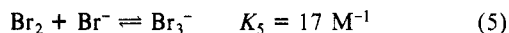
Therefore, we determined the spectrum of Br_3^- in perchloric acid. The isosbestic point of Br_2 and Br_3^- is at 441 nm, where $\epsilon = 130$. The concentrations of the bromine-containing species were calculated in the following way.

The total bromine concentration (T_{Br_2}) can be determined from the absorbance at 441 nm. It is evident that

$$T_{Br_2} = [Br_2] + [Br_3^-]$$

The total bromide concentration is

$$T_{Br^-} = [Br^-] + [Br_3^-] = [Br^-]_0 - 2T_{Br}$$

The concentration of Br_3^- can be calculated from T_{Br_2} and T_{Br^-} using the value of K_5. (We assumed the same value at different acid concentrations.) Having these values the equilibrium concentration of HNO_2 can be deduced from the measured absorbance and the equilibrium constant $K_1(H)$ can be calculated. The $K_1(H)$ values at different initial concentrations are given in Table I.

To calculate the value of K_1, we had to consider the hydrogen ion concentration or the acidity of the medium. Since calculations
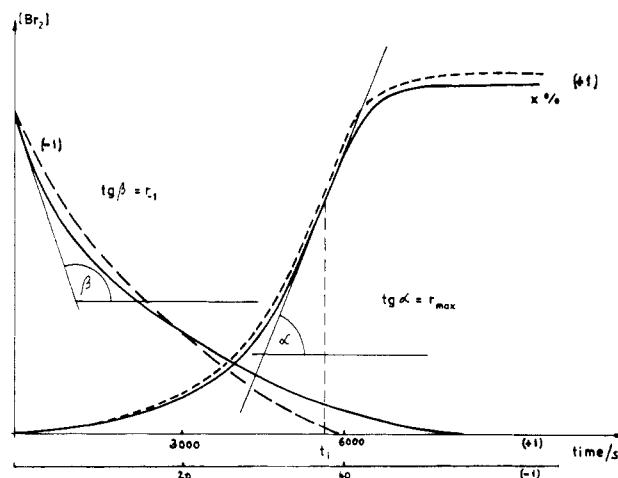

Figure 1. Experimental (—) and calculated (- - -) concentration vs time curves of reaction 1. In reaction +1 $[NO_3^-]_0 = 0.5$ M, $[HClO_4]_0 = 4.5$ M, $[Br^-]_0 = 0.01$ M, and $[HNO_2]_0 = 5 \times 10^{-5}$ M. In reaction −1 $[HNO_2]_0 = 5 \times 10^{-5}$ M, $[Br_2]_0 = 2.37 \times 10^{-3}$ M, and $[HClO_4]_0 = 1$ M.

of $K_1(H)$ with the analytical acid concentration did not give a single constant value, we tried to find a suitable acidity function of perchloric acid for effective $[H^+]$ calculation. There are rather different scales depending on the structure of the indicator set used for their determination. None of those gave satisfying results. But using a slightly modified H values determined by means of amide indicators[13] resulted in a relatively good constancy of K_1 data. This H scale is given in column 9 of Table I. The acidity function of HNO_3 was taken from ref 14. The values of equilibrium constants calculated from the reverse (−1) reaction in HNO_3 are in good agreement with those from the forward (+1) reaction in $HClO_4$. The mean value of equilibrium constant of reaction 1 at 25 °C, determined under 26 different initial conditions, with the variance of the mean is

$$K_1 = (1.6 \pm 0.3) \times 10^{-6} \ M^{-4}$$

Kinetic Studies. Kinetic curves of the forward (+1) and reverse (−1) reactions are rather different: the (+1) curves exhibit the

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characteristic S-shaped autocatalytic behavior; the (−1) ones have a "regular" shape. In Figure 1 we present the two types of the curves, in both cases showing an experimental and a calculated one. The S-shaped autocatalytic curves were characterized by three parameters: the length of the induction period (t_i), which is at the inflection point of the curve; the maximum rate of the reaction (r_{max}), (read at t_i per definition); the extent of the reaction at the final state (expressed in conversion $X\%$ or x). The "regular" curves were evaluated as usual by determining the initial rate of bromine consumption from $\Delta A/\Delta t$ slopes. There was no indication of autocatalysis, and there were no distinguishable stages on the monitored curves.

Reaction between Nitric Acid and Bromide. Experiments in Closed System. Effect of $[H^+]_0$. The most dramatic influence on all three parameters of the reaction is exerted by changing the acid concentration. Below 3.5 M the reaction is extremely slow. Increasing $[H^+]_0$ from 3.5 to 5.5 M, values of t_i are decreased by a factor of more than 20, while r_{max} is increased by 2 orders of magnitude. The conversion changed from 20% to 75%. The influence of acidity was interpreted in the calculations using the same h functions as in the equilibrium calculations.

Effect of $[NO_3^-]_0$. The influence of initial nitrate concentration was studied in the range 0.075–0.75 M at constant $[HClO_4]_0$ = 4.5 M, $[Br_2]_0$ = 0.01 M, and $[HNO_2]_0$ = 1 × 10⁻⁴ M concentrations. Conversion and maximum rate increase and inflection time decrease with increasing nitrate concentration. Bromide ion is not oxidized without nitrate in 3–6 M perchloric acid. The formal order of nitrate is 1 from the plot of r_{max} vs $[NO_3^-]$.

Effect of $[Br^-]_0$. The influence of initial bromide concentration was studied in the range 0.003–0.03 M, at constant $[HClO_4]$ = 4.5 and $[HNO_2]_0$ = 1 × 10⁻² M values. With increasing $[Br^-]_0$ the length of induction period decreases and the maximum rate increases considerably.

Effect of $[HNO_2]_0$. The length of t_i values depends very strongly on the initial concentration of nitrous acid. (It is introduced as sodium nitrite but is present in the form of HNO_2 at these acid concentrations.) The influence of $[HNO_2]_0$ was studied in the range 1 × 10⁻⁵–1 × 10⁻³ M at $[HClO_4]$ = 4.5 and $[Br^-]_0$ = 0.01 M concentrations. Added nitrogen dioxide accelerates the oxidation of bromide, decreasing the induction period, similarly as HNO_2 does. If traces of HNO_2 and NO_2 are removed from the nitric acid solution by means of chemical methods (adding small amounts of nitrite scavengers, hydrazine, or azide), the reaction is retarded for a long period of time. If $NaNO_2$ or NO_2 in small excess is added to the scavenged mixture, reaction +1 starts and takes place.

To within experimental error the highest rate and the value of conversion ($X\%$) are independent of initial nitrous acid concentration if $[HNO_2]$ < 5 × 10⁻⁵ M. At higher $[HNO_2]$ the situation changes because the amount of HNO_2 becomes comparable to that of initial bromide and consequently to HNO_2 formed in the reaction. In accordance with the equilibrium character of reaction 1, if excess nitrite is added to the equilibrium reaction mixture, the equilibrium is shifted back; i.e., some bromine is converted to bromide.

All these results are summarized in Table II.

Reaction between Nitrous Acid and Bromine. Effect of $[Br_2]_0$. The influence of the initial bromine concentration on the initial rate of reaction −1 is shown in Figure 2a. The slope of the van't Hoff plot in the range $[Br_2]_0$ = (1.9–18) × 10⁻³ M is 0.47 ± 0.04, which indicates that the rate is half-order in bromine.

Effect of $[HNO_2]_0$. The rate is found to be first order in nitrous acid in the range of (5–200) × 10⁻⁴ (Figure 2b).

Effect of $[H^+]_0$. On increasing the initial proton concentration from 0.2 to 2.0 M the rate of reaction −1 decreases (Figure 2c). This behavior can be described by

$$r_{-1} = const[Br_2]^{0.5}[HNO_2]h^{-0.5} \qquad (6)$$

At these acidities, the conversion of bromine reduction is greater than 90%.

Experiments in a CSTR. Autocatalytic reactions can show bistability and hysteresis in a continuously stirred tank reactor.

TABLE II: Experimental and Calculated Data of Kinetic Curves of Reaction +1 (Number of Experiments as in Table I)

expt no.	t_i, min		r_{max}, M s⁻¹		X, %	
	exptl	calcd	exptl	calcd	exptl	calcd
1	158	138	1.2	1.1	22.2	20.8
2	146	122	1.7	1.6	25.6	23.4
3	99	90	2.9	2.9	30.6	30.4
4	76	73	4.9	4.7	35.8	35.1
5	60	60	7.3	7.1	40.4	41.4
6	46	49	12.0	11.0	47.2	46.6
7	118	135	0.6	0.5	37.0	38.9
8	105	96	1.5	1.5	40.1	40.1
9	60	60	7.3	7.1	40.4	41.4
10	41	37	32.0	28.0	42.3	43.2
11	35	30	83.0	72.0	43.8	44.8
12	159	146	6.0	6.2	40.1	41.9
13	93	88	6.5	6.2	40.4	41.7
14	60	60	7.3	7.1	40.4	41.4
15	41	38	7.4	7.4	39.5	40.8
16	19	19	8.8	8.8	38.3	39.0
17	7	8	13.0	13.0	37.3	36.2
18	175	150	1.0	1.3	22.2	22.1
19	60	60	7.3	7.1	40.4	41.4
20	26	36	28.0	23.0	56.2	56.2
21	13	19	77.0	51.0	68.5	68.5
22	6	10	170.0	110.0	75.0	75.0

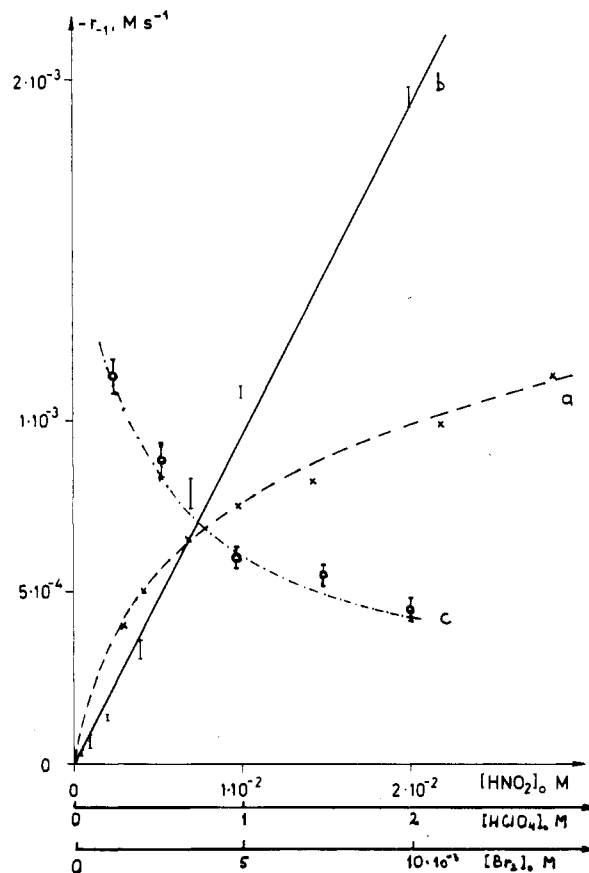**Figure 2.** Dependence of r_{-1} on initial concentration of (a) bromine (at $[HNO_2]_0$ = 5 × 10⁻³ M, $[HClO_4]_0$ = 1 M); (b) nitrous acid (at $[Br_2]_0$ = 2.37 × 10⁻³ M, $[HClO_4]_0$ = 1 M); (c) perchloric acid (at $[Br_2]_0$ = 4.46 × 10⁻³ M, $[HNO_2]_0$ = 5 × 10⁻³ M).

A series of experiments were carried out to determine whether and over what range of constraints the acidic nitrate–bromide system exhibits this behavior. In one such experiment the input concentrations of proton, nitrate, bromide, and nitrite were held constant and the flow rate k_0 (reciprocal of the residence time) was increased stepwise from 0 to 1.5 × 10⁻² s⁻¹ and then decreased back to 0. Figure 3 shows the hysteresis behaviour for a typical experiment. SS1 denotes the high potential (brown colored) steady state at low flow rate (thermodynamic branch); SS2 denotes the
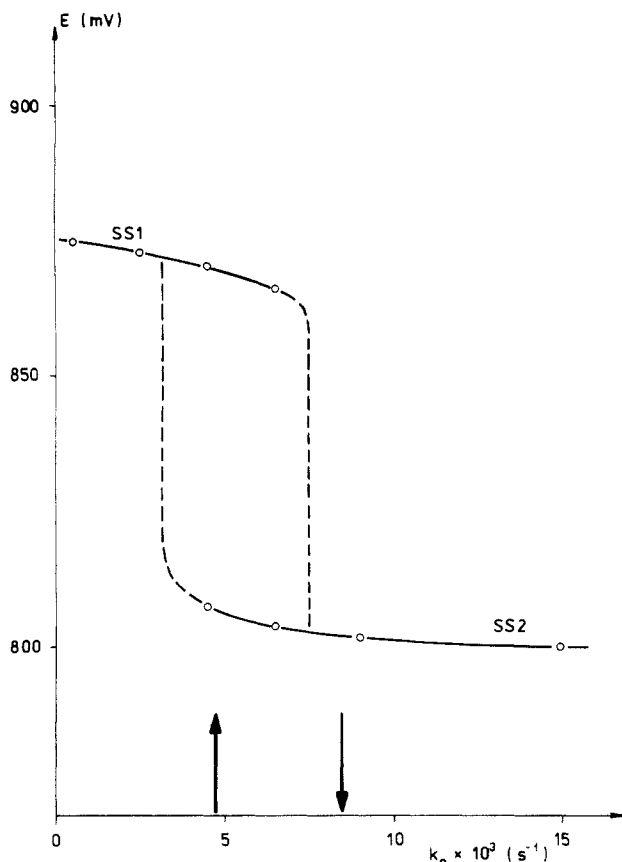
Figure 3. Hysteresis curve of reaction +1 in CSTR with initial concentrations $[HNO_3]_0 = 3.7$ M, $[HClO_4]_0 = 1$ M, $[Br^-]_0 = 0.03$ M, and $[HNO_2]_0 = 1 \times 10^{-4}$ M. Arrows indicate the calculated transitions.

low potential (colorless) steady state (flow branch). Hydrazinium sulfate (in SS1) and sodium nitrite solutions (in SS2) were used as perturbation agents. Within the bistability region, if one applies a small perturbation in either steady state, the system relaxes back to the unperturbed state. However, a large enough perturbation results in transition to the other steady state. Hydrazinium ions react with nitrous acid and give N_2 and N_2O which are inert in this system, so they remove the autocatalyst and push the system to the flow branch. Excess sodium nitrite (i.e., nitrous acid) accelerates the reaction and brings the system to the thermodynamic branch.

Discussion (Mechanistic Considerations)

We are looking for a mechanism that accounts for (a) the stoichiometry and equilibrium data of reaction 1, (b) the autocatalytic behavior of process +1 in batch, (c) its bistability in a CSTR, and (d) the "regular" kinetics of process −1. Certainly in cases b and d both the concentration dependences of initial rates and the shape of the individual kinetic curves must be accounted for.

Let us first consider briefly point a, mainly the question of equilibrium. From the difference of the standard potentials (1.087 and 0.94 V) of the two redox couples (2) and (3), respectively, one obtains a value for $K_1 = 1.5 \times 10^{-5}$ M^{-4}. This is higher than our experimental value $K_1 = 1.6 \times 10^{-6}$. The latter corresponds to a difference of 0.130 V instead of 0.107 V. In our opinion the main reason for this difference is that the standard redox potential of the bromine/bromide couple was not determined at high acid concentrations as high as those used here. Monk and Ellingham[15] showed that when the nitric acid concentration is increased from 1 to 3 M the potential of the Pt electrode increases about 70 mV, independent of the HNO_2 content of the acid. The electrochemical equations use activities, but we had to use acidity function to describe the equilibrium states and the kinetics.

The equilibrium character of the overall reaction (1) in the model to be constructed requires that all of its steps must be reversible and that detailed balance should hold.

The autocatalytic nature of reaction +1, point b, can be explained by considering the results of earlier studies. The role of nitrous acid was first explained by Abel and Schmid[16] in the nitric acid oxidation of nitrogen oxide. In the results of Longstaff[7] there is some indication of the autocatalytic nature of the reaction, but this behavior was not considered by him in treating the experimental data and the derived rate law, although the range of initial concentrations used there covers those of this work. We wrote down about 30 steps, speculating on several possible paths for the reaction. There are no quantitative conclusions and no calculations based on the scheme. Feilchenfeld et al.[8] realized the autocatalytic nature of reaction +1 although this behavior is not dominant under their reaction conditions. The mechanism they propose involves 11 reaction steps and 6 intermediates, but NO appears only as a product, which contradicts the stoichiometry (1) accepted by them, too. The basic considerations of Abel and Schmid[16] were not treated in these works.

Construction of the Mechanism. Bazsa and Epstein in a recent review[1] point out that all autocatalytic nitric acid oxidations may be described by a single general scheme. We tried to apply this scheme in the case of bromide oxidation. According to this, the first step is a reaction between nitric and nitrous acid

$$NO_3^- + HNO_2 + 2H^+ = 2NO_2 + H_2O \qquad (M1)$$
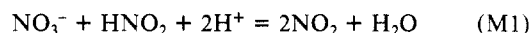
In the next step NO_2 oxidizes bromide in some way, and the N(IV) is reduced to N(III), which appears finally in the form HNO_2. Because two NO_2 are formed from one HNO_2 (and from one HNO_3) in step M1, these produce two HNO_2 molecules, so the autocatalysis is explained. The question is how this oxidation takes place. A separate and exact kinetic study of oxidations by NO_2 in strong acidic medium is generally not possible, because its disproportionation (reaction −M1) is extremely rapid. In this situation one has to try to consider chemically reasonable reactions, and insofar as calculations based on such a mechanism agree well with experimental results, the proposed steps can be accepted.

Certainly independently known steps or rapid equilibria must be taken into account. We have here at least two of the latter type processes: the reversible formation of nitrosyl bromide (BrNO) and the tribromide equilibrium (5). Step 5 is an extremely rapid process, so it exists at any time as an equilibrium. The amount of Br_3^- increases along the reaction coordinate both in reactions +1 and −1 to a maximum and thereafter usually decreases to the equilibrium value. Its maximum concentration could involve 5–10% of bromine and bromide present at that moment. Although it is reasonable to assume that the reactivity of Br_3^- is different from that of Br_2 or Br^- because of the different size, electronic structure, and charge, we never got better results by considering such differences in the calculations. We could not find any data about different reactivity of Br_3^-/Br_2 or Br_3^-/Br^- in the literature. Consequently, we neglected the tribromide formation in the kinetic calculations, but it was taken into account in the calculation of equilibrium concentrations mentioned earlier.

In contrast to Br_3^- the role of the intermediate BrNO is crucial in the kinetics of bromide oxidation.

$$HNO_2 + Br^- + H^+ = BrNO + H_2O \qquad (M3)$$

Our experience in explaining the bistable behavior of autocatalytic nitric acid oxidations predicts that bistability in the CSTR appears only if NO_2 oxidizes the substrate via an intermediate like BrNO, but not if the oxidation proceeds via direct reaction between NO_2 and substrate only. The former case pertains in the oxidation of thiocyanate,[5] where ONSCNH$^+$ plays a key role in the kinetics of the oxidation. FeNO^{2+} has a somewhat different, but similarly crucial role in the bistability found in the nitric acid oxidation of iron(II).[4] Because bistability was found here, we have good

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(16) Abel, E.; Schmid, H. *Z. Phys. Chem.* **1928**, *132*, 55, 64; *Ibid.* **1928**, *134*, 273; *Ibid.* **1928**, *136*, 135, 419, 430.

(17) Schmid, H.; Fouad, E. *Monatsh. Chem.* **1957**, *88*, 631.

reason to include equilibrium M3 and the oxidation of BrNO by NO_2 in our mechanism. Formation of XNO-type compounds is general between nitrous acid and halogenides (Cl^-, Br^-, I^-) and some other anions (SCN^-, $S_2O_3^{2-}$).

We thus assume a reaction between nitrosyl bromide and nitrogen dioxide:

$$BrNO + NO_2 = BrNO_2 + NO \qquad (M4)$$
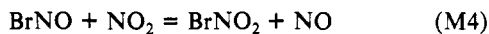
$BrNO_2$ is known to exists[18] and this fact gives good reason to involve it into the mechanism. $BrNO_2$ reacts further. It may decompose in a hydrolytic process to HNO_2 and $HOBr$:

$$BrNO_2 + H_2O = HNO_2 + HOBr \qquad (M5)$$
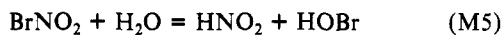
$HOBr$ is again a reactive species and its reaction with bromide ion results in bromine, one of the final products of reaction +1:

$$HOBr + Br^- + H^+ = Br_2 + H_2O \qquad (M6)$$
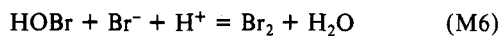
Nitrogen oxide, the other species formed in step M4, is not a final product of the reaction under our conditions. It is known from the literature[16] that NO and NO_2 synproportionate and that this process leads to the other final product of reaction +1:

$$NO + NO_2 + H_2O = 2HNO_2 \qquad (M7)$$
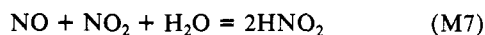
The reverse reaction (−M7) is the disproportionation of HNO_2. One can already see that these reverse steps account for the bromine–nitrite reaction, and so the mechanism may describe both directions of reaction 1.

However, we cannot neglect the *direct* reduction of nitrogen dioxide by bromide ion. If we do not wish to increase the number of postulated intermediates, then we can write this process in the form

$$2NO_2 + Br^- + H^+ = BrNO_2 + HNO_2 \qquad (M2)$$

Reaction M2 in this form is not an elementary step, but this equation simplifies the calculations. It is not difficult to resolve it into two steps—in at least two different ways:

$$2NO_2 = N_2O_4 \qquad (M2a)$$

$$N_2O_4 + Br^- + H^+ = BrNO_2 + HNO_2 \qquad (M2b)$$

or

$$NO_2 + Br^- + H^+ = HBrNO_2 \qquad (M2c)$$

$$HBrNO_2 + NO_2 = BrNO_2 + HNO_2 \qquad (M2d)$$

The two ways of reaction (M2) cannot be distinguished kinetically, if the first steps ((M2a) and (M2b)) are fast with respect to the next steps ((M2b) and (M2d)), respectively. This is known for (M2a)[19] and it seems to be a reasonable assumption for (M2c) because here the oxidation number of the elements do not alter. But in the second steps covalent bonds are broken and new bonds are formed, changes in the oxidation states of the elements take place, and these make the overall process (M2) relatively slow. So for the sake of simplicity we write the oxidation of bromide by nitrogen oxide in the form (M2). In the following, the oxidation of Br^- via BrNO will be referred to as an *indirect*, and the reaction between nitrogen dioxide and bromide as the *direct*, oxidation path.

The choice of the above steps was supported by the satisfying results of calculations. Other, somewhat different mechanisms were tried; e.g., the following reactions were tested:

$$2BrNO = 2NO + Br_2 \qquad (7)$$

or

$$BrNO_2 + Br^- + H^+ = HNO_2 + Br_2 \qquad (8)$$
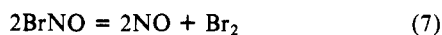
Although these attempts were unsuccessful, it is probable that

TABLE III: Mechanism of Reaction 1 and Rate Equations of the Elementary Steps[a]

$$NO_3^- + HNO_2 + H^+ = 2NO_2 + H_2O \quad (M1)$$

$r_1 = k_1[NO_3^-][HNO_2]h$	$k_1 = 0.015\ M^{-2}\ s^{-1}$
$r_{-1} = k_{-1}[NO_2]^2$	$k_{-1} = 1 \times 10^8\ M^{-1}\ s^{-1}$

$$2NO_2 + Br^- + H^+ = BrNO_2 + HNO_2 \quad (M2)$$

$r_2 = k_2[NO_2]^2[Br^-]h$	$k_2 = 1 \times 10^4\ M^{-3}\ s^{-1}$
$r_{-2} = k_{-2}[BrNO_2][HNO_2]$	$k_{-2} = 1.125 \times 10^4\ M^{-1}\ s^{-1}$

$$HNO_2 + Br^- + H^+ = BrNO + H_2O \quad (M3)$$

$r_3 = k_3[HNO_2][Br^-]h$	$k_3 = 1 \times 10^4\ M^{-2}\ s^{-1}$
$r_{-3} = k_{-3}[BrNO]$	$k_{-3} = 5 \times 10^4\ s^{-1}$

$$BrNO + NO_2 = BrNO_2 + NO \quad (M4)$$

$r_4 = k_4[BrNO][NO_2]$	$k_4 = 8 \times 10^3\ M^{-1}\ s^{-1}$
$r_{-4} = k_{-4}[BrNO_2][NO]$	$k_{-4} = 6.2 \times 10^9\ M^{-1}\ s^{-1}$

$$BrNO_2 + H_2O = HNO_2 + HOBr \quad (M5)$$

$r_5 = k_5[BrNO_2]$	$k_5 = 1 \times 10^4\ s^{-1}$
$r_{-5} = k_{-5}[HNO_2][HOBr]$	$k_{-5} = 1.2 \times 10^8\ M^{-1}\ s^{-1}$

$$HOBr + Br^- + H^+ = Br_2 + H_2O \quad (M6)$$

$r_6 = k_6[HOBr][Br^-]h$	$k_6 = 1.6 \times 10^{10}\ M^{-2}\ s^{-1}$
$r_{-6} = k_{-6}[Br_2]$	$k_{-6} = 110\ s^{-1}$

$$NO + NO_2 + H_2O = 2HNO_2 \quad (M7)$$

$r_7 = k_7[NO][NO_2]$	$k_7 = 2 \times 10^7\ M^{-1}\ s^{-1}$
$r_{-7} = k_{-7}[HNO_2]^2$	$k_{-7} = 5.8\ M^{-1}\ s^{-1}$

[a] Remarks for rate constants, see text.

other kinetic models may be relevant. The mechanism which gave the best fit together with the rate equations of the elementary steps used in our calculations are summarized in Table III.

The set of reactions M1–M7 first reflects the stoichiometry of reaction 1. Second, it describes the equilibrium nature of the overall process. As shown above, there are two pathways. The *direct* oxidation takes place via reactions M1, M2, M5, and M6. The steps of the *indirect* oxidation are M1, M3, M4, M5, M6, and M7. Both routes independently account for reaction −1, too. According to detailed balance, the following relations must hold:

$$K_1 = K_{M1}K_{M2}K_{M5}K_{M6} \qquad (9)$$

and

$$K_1 = K_{M1}K_{M3}K_{M4}K_{M5}K_{M6}K_{M7} \qquad (10)$$

Simplifying the relations, we get

$$K_{M2} = K_{M3}K_{M4}K_{M7}$$

which governs the freedom in choosing parameters in the calculations.

Selection of the Kinetic Parameters. Let us consider the kinetics of the seven steps. As is clear from Table III, all rate equations correspond to the kinetic mass action law. The hydrogen ion concentration was taken into account according to the acidity scale discussed earlier. The concentration of water was not included into the rate equations. The ratio of the rate constants of forward and reverse processes determines the equilibrium constant of each single step. If the latter is known or fixed, then one of the rate constants can be varied and the other is determined.

Step M1 is the common first step of all autocatalytic nitric acid oxidations.[1] There is general agreement in the literature about the kinetics of the two opposite processes, although the values of k_1 vary somewhat around 1×10^{-2} M s⁻¹. The k_1 and k_{-1} values given in Table III were used successfully in describing other nitric acid oxidations.[4,19,20]

The hydrolysis of bromine, step −M6, was studied by Eigen and Kustin.[21] Kinetic and equilibrium data are available for step M7.[4,16] We adopted the data for steps M1, M6, and M7 from these publications without any change.

Data are known for the kinetics and equilibrium of step M3, although they are of indirect origin; namely, they were calculated

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(18) *Comprehensive Inorganic Chemistry*; Bailar, J. C., Emelius, H. J., Nyholm, R., Eds.; Pergamon Press: Oxford, 1973; Vol. II, p 300.

(19) Schmid, G.; Bahr, G. *Z. Phys. Chem. (Munich)* **1964**, *41*, 8.

(20) Lengyel, I.; Barna, T.; Bazsa, Gy. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 229.

(21) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355.

from the catalytic effect of bromide in nitrosation reactions. Instead of $K_{M3} = 0.05$[17] we had to use a value $K_{M3} = 0.2$ M^{-1}. The rate constants k_3 and k_{-3} should be high enough to ensure that process M3 is always at equilibrium. This is fulfilled by the given values, which, according to this requirement, represent only lower limits for these rate constants. An increase in the values of k_3 and k_{-3} has no further effect on the calculated kinetic curves.

As far as we know step M2 has not been studied previously. Forward rate constants are known for similar reactions, the oxidation of iodide,[22] sulfite,[23] etc. by nitrogen dioxide, but under different conditions. In calculations on other nitric acid oxidations the order of magnitude of the rate constant of NO_2 oxidations was 10^4 M^{-1} s^{-1}.[4,5,20] The value $k_2 = 1 \times 10^4$ M^{-3} s^{-1}, which has primary importance in quantitative describing bistability in CSTR, fits well into this range. The reverse rate constant k_{-2} was chosen as a plausible one to fit the experimental results, mainly the conversion ($X\%$).

Steps M4 and M5 have not been investigated separately. Because neither BrNO nor $BrNO_2$ accumulates in high concentrations during reaction 1, these steps should be characterized by small equilibrium constants. The values used in this calculations ensure conditions 9 and 10, but there is no direct evidence for their concrete values. The rate of reaction +M4 has a crucial function in determining the t_i values in batch, so the value of $K_{M3}k_4$ may be varied in a very narrow range.

Calculations. Let us now see the kinetic "capability" of this mechanism. The system of nine differential equations was solved by numerical integration using a semi-implicit Runge–Kutta method.[24] The initial concentrations of the reactants were chosen according to the experiments; those of intermediates and products were instead of 0 very small ($\sim 10^{-20}$) as required by the program. It turned out in the preliminary calculations that a mechanism with only *indirect* oxidation can describe the shape of the individual kinetic curves, but not the concentration dependences. It gives bistability in the calculations but at flow rates 2 orders of magnitude larger than the experimental values. To describe the kinetics of reaction +1, both the *direct* and *indirect* oxidation pathways must be considered. The calculations confirmed the chemical anticipation that the proportion of the two pathways of oxidation by NO_2 depends on the $k_2:(K_{M3}k_4)$ relation. The variability of these two rate constants is not more than $\pm 10\%$. Less certainty can be stated about the k_{-2} and k_{-4} values.

As it was mentioned, steps M3 and M5 should ensure that neither BrNO nor $BrNO_2$ will appear in high concentration in the calculations. This requires relatively large rate and relatively small equilibrium constants in both cases. The values of rate constants represent only *lower limits*; a 10-fold or a 100-fold increase of their values does not modify the calculated data significantly.

The mechanism (M1)–(M7) proposed describes well the dependences of the kinetic parameters t_i, r_{max}, and $X\%$ of the autocatalytic reaction (+1). Their experimental and calculated values vs initial concentrations of nitrate, hydrogen ion, bromide, and nitrous acid are presented in Table II. The acidity scale derived from the equilibrium data was used here, too.

The fitting procedure in this system is a tremendous process. Once the mechanism reflects well the observed stoichiometry, *four more different sets* of experimental data are to be account for: the equilibrium concentrations, the kinetic parameters of the autocatalytic reaction in batch, that of the reverse process (also in batch), and the bistable behavior in CSTR. A program for a systematic minimizing of differences between measured and calculated data of so various types is not known by us, and we hardly believe whether such a one may be created. Sensitivity analysis resulted in minor information. To overcome this hard task, we looked for reasonable functions between initial concentrations and measured values. When such a link was found, the
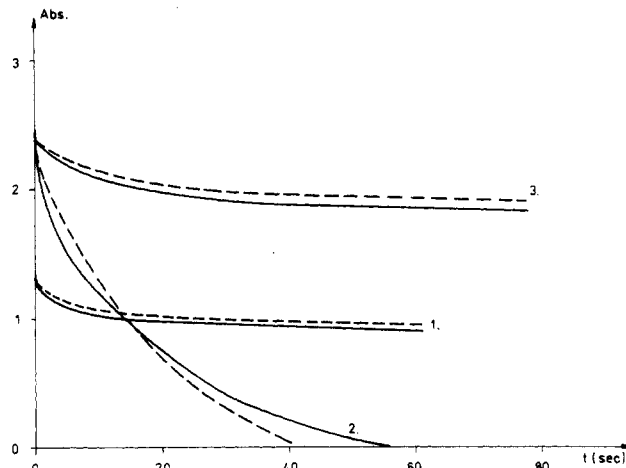
(22) Forni, L. G.; Mora-Arellano, V. O.; Packer, J. E.; Wilson, R. L. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1.

(23) Huie, R. E.; Neta, P. *J. Phys. Chem.* **1986**, *90*, 1193.

(24) Kaps, P.; Rentrop, P. *Numer. Math.* **1979**, *33*, 55.

Figure 4. Experimental (—) and calculated (---) absorbance curves of reaction –1 with initial concentrations (1) $[HNO_2]_0 = 5 \times 10^{-4}$ M, $[Br_2]_0 = 1.8 \times 10^{-3}$ M; (2) $[HNO_2]_0 = 5 \times 10^{-3}$ M, $[Br_2]_0 = 2.37 \times 10^{-3}$ M; (3) $[HNO_2]_0 = 5 \times 10^{-4}$ M, $[Br_2]_0 = 2.37 \times 10^{-3}$ M.

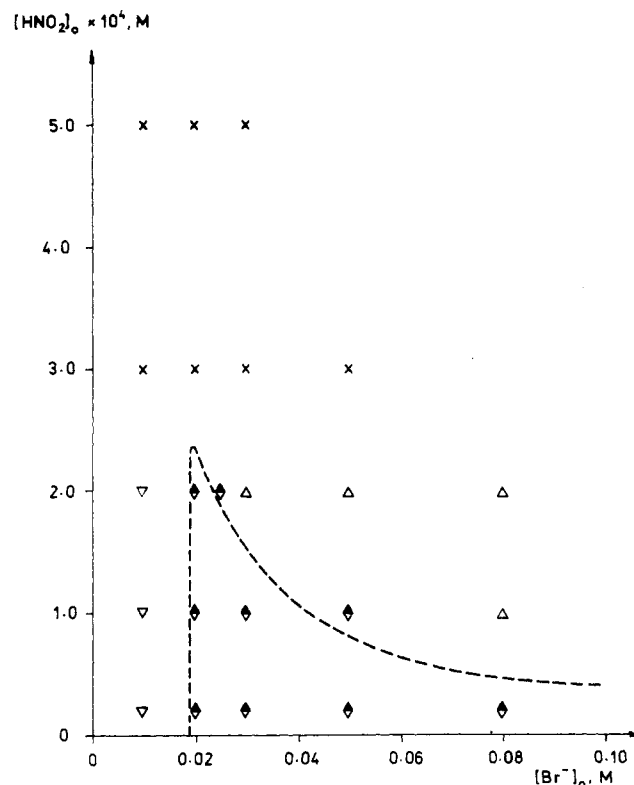**Figure 5.** Phase diagram in the $[Br^-]_0$–$[HNO_2]_0$ plane with $k_0 = 4.5 \times 10^{-3}$ s^{-1}, $[HNO_3]_0 = 2$ M, and $[HClO_4]_0 = 3$ M. The curve (---) indicates the calculated region of bistability. $\triangledown$, low potential steady state; $\blacktriangle$, high potential steady state; $\blacksquare$, bistability; $\times$, monostability.

experimental data were evaluated by linear or nonlinear least squares and we tried to get results of similar quality in the calculations. Let us present three examples. The nitrate concentration influences the conversion x. This can be expressed with the function $x^2/(1 - x) = 0.0238 + (0.522 \pm 0.016)[NO_3^-]$ on the basis of experimental data (Table II, experiments 1–6), with regression coefficient $r = 0.9964$ for the slope. The calculated x values result in $x^2/(1 - x) = 0.0322 + (0.514 \pm 0.019)[NO_3^-]$, with $r = 0.9946$. The effect of initial bromide (Table II, experiments 7–11) is expressed in the form $\ln (r_{max}) = (2.17 \pm 0.04) \ln [Br^-]$ ($r = 0.9991$) for experiments and $\ln (r_{max}) = (2.18 \pm 0.04) \ln [Br^-]$ ($r = 0.9990$) for calculations. In these two examples the agreement is excellent, but it is less good in other cases, e.g., $\ln (r_{max})_{exptl} = (2.64 \pm 0.05) \ln (h)$ ($r = 0.9987$) and $\ln (r_{max})_{calcd} = (3.14 \pm 0.04) \ln (h)$ ($r = 0.9994$) (Table II, experiments 18–22). Differences exceeding experimental error only occurred at varying

acidities. We were not able to find a better fit in this case.

To test the mechanism for describing the kinetics of the *reverse* reaction (−1), we used the same nine rate equations and rate constants. First, we calculated the kinetic curves at the experimental initial bromine, nitrite, and acid concentrations. From these curves we derived the orders for the reactants in the same way (method of initial rates) as we did in treating real experimental data. The rate law found in this way is

$$r_{-1}(\text{calcd}) = \text{const}'[\text{HNO}_2]^{1.2}[\text{Br}_2]^{0.2}[\text{H}^+]^{-0.3} \quad (11)$$

This is not a particularly good agreement. But if we consider the shape of individual kinetic curves at *fairly different* initial concentrations, the calculated curves strongly resemble the experimental ones, and this kind of agreement is in most cases very good (Figure 4). A possible explanation of this result is that the initial rate on the *calculated* curves is poorly defined because they have a very fast section (up to about 5% of conversion within the first second) and a second regular one. In the experiments we were not able to observe these two stages; the ∼1-s "dead time" of our mixing device is larger than this first part of the reaction. The initial rate was taken after the first fast part of reaction −1.

Finally, we treated the CSTR experiment numerically. The experimentally determined and calculated [HNO$_2$] vs [Br$^-$] phase portrait of the system is shown at $k_0 = 4.5 \times 10^{-3}$, [HNO$_3$]$_0$ = 2 M, and [HClO$_4$]$_0'$ = 3 M in Figure 5. No bistability was found if the inflow concentration of nitrous acid was >2.5 × 10^{-4} M. The calculated and experimental regions of bistability (Figure 3) agree excellently. If the system in a CSTR (conditions of Figure 3, k_0 = 0.007 s^{-1}) being in SS2 stationary state was perturbed by added nitrite solution ([HNO$_2$] = 0.01 mol dm^{-3}), then a transition occurred to SS1 with a 4-min half-time. The calculated value of $t_{1/2}$ is the same. This is strong support of the validity of the model. (The opposite transition can be achieved by applying the hydrazine solution, but calculations would require the knowledge of kinetics of this interaction.)

Conclusions

In this paper we presented a complete example where an autocatalytic redox reaction and its reverse were investigated and treated from the stoichiometric, equilibrium, and kinetic points of view. The overall process (1) is a true dynamic equilibrium reaction, and it was successfully described according to the mass action law. The oxidation of bromide in moderately concentrated nitric acid is an autocatalytic process, nitrous acid being the catalyst. In a continuously stirred tank reactor it shows bistability and hysteresis. Its reverse, the reduction of bromine by nitrous acid, has regular kinetics. On the basis of the experimental results, a seven-step mechanism was formulated together with rate equations for the steps. This mechanism describes all these behaviors, and the agreement between measured and calculated data in all cases is fairly good, in some respects excellent.

The long-term aim of these studies is to test such autocatalytic reactions for bistable behavior in a CSTR and then to seek for a proper feedback reaction to produce oscillation. This last goal has not yet been reached, but such work is in progress in our laboratory.

Design of a Permanganate Chemical Oscillator with Hydrogen Peroxide

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The permanganate chemical oscillator with hydrogen peroxide in the presence of phosphoric acid in a continuously stirred tank reactor is described in more detail. Three types of bistabilities and a tristability have been revealed on the basis of the phase diagrams in [H$_3$PO$_4$]$_0$–k_0, [H$_2$O$_2$]$_0$–k_0, and [KMnO$_4$]$_0$–k_0 planes. The reaction scheme of this permanganate chemical oscillator, stressing the crucial role of phosphoric acid in stabilization of colloidal MnO$_2$ species, is outlined.

Introduction

In a homogeneous chemical reaction maintained far from equilibrium where the reaction mechanism contains coupled feedback steps, oscillations in the concentrations of certain intermediates are possible. At the beginning of the 1980s an efficient experimental method was proposed[1-3] to elaborate and to design new homogeneous oscillators. Epstein et al.[4] using this method based on a continuously stirred tank reactor (CSTR) technique succeeded in discovering several new oscillators, first of all the group of chlorite oscillators, and thus broadened the great family of the homogeneous oscillatory reactions based on the chemistry of oxyhalogen anions.

Oscillating systems with no halogen compounds also have been observed.[5] So far they form a relatively small group of homogeneous chemical oscillators. In 1986 we briefly described a new member of this group, the first permanganate chemical oscillator.[6] It consists of an aqueous solution of permanganate ions, hydrogen peroxide, and phosphoric acid. A second permanganate chemical oscillator based on the reaction between permanganate ion and ninhydrin also has been described.[7] Although a kinetic bistability in the permanganate oxidation of hydrogen peroxide or of oxalate in CSTR has been observed[8-10] and the reaction between per-

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