$$\text{Tryp}^{\bullet} + \text{PhOH} \rightleftarrows \text{TrypH} + \text{PhO}^{\bullet} \qquad (6)$$

Consequently, we attempted to observe vestiges of some equilibrium reaction at pH 7. In solutions containing 0.1 M $N_3^-$ and equal amounts ($5 \times 10^{-3}$ M) of tryptophan and phenol the 520-nm absorbance of the tryptophyl radical initially generated was found to decay completely while a new absorbance arose. The latter distinctly differed from the absorbance of the phenoxy radical. This is clearly seen in Figure 3. In yet another experiment at the same pH, phenoxy radicals were initially produced by $OH^{\bullet}$ in the presence of 0.1 M phenol and $5 \times 10^{-3}$ M tryptophan. The absorbance of the phenoxy radical disappeared to yield a spectrum identical with the one observed after the decay of the tryptophyl absorbance in the previous experiment. Thus, we conclude that phenoxy radicals form an adduct to tryptophan (and probably to other indoles as well) according to the scheme

$$\text{Tryp}^{\bullet} + \text{PhOH} \xrightarrow{k_1} \text{PhO}^{\bullet} + \text{TrypH} \xrightarrow{k_2} \text{adduct}$$

From the above experiments $k_1$ and $k_2$ have been evaluated to be $(2.4 \pm 0.4) \times 10^5$ $M^{-1}$ $s^{-1}$ and $(1.8 \pm 0.3) \times 10^{-5}$ $M^{-1}$ $s^{-1}$, respectively. Without thorough spectral comparison the above experiments could be misinterpreted as implying a redox equilibrium. In the absence of sufficient experimental information in ref 14 we can only surmise that such is the likely reason for the very low redox potentials of tryptophan obtained at pH 7 and 13.5 where the above authors utilize *p*-methoxyphenol as reference. In all events, the redox potential[20,21] of *p*-methoxyphenol appears to be firmly established and can thus be ruled out as a source of error. In concluding we note that according to the $E°$ values in the present work the reaction

$$\text{Tryp}^{\bullet} + \text{TyrOH} \rightarrow \text{TrypH} + \text{TyrO}^{\bullet}$$

is thermodynamically favored at any realistic pH value. This rationalizes the experimental observations of several authors.[13,22]

The $E° = 1.14 \pm 0.2$ V reported by Butler et al.[13] for the tryptophyl radical cation has a large error range. The latter resides entirely in the uncertainty of the accepted $E°$ values for the $SCN^{\bullet}/SCN^-$ and $(SCN)_2^{\bullet -}/2SCN^-$ couples, respectively.

If our $E°$ value for tryptophan is combined with the equilibrium constants determined in ref 11 and 23, the redox potentials of the above couples can be evaluated more precisely. These values are collected in Table II. The present work thus revises several redox potentials hitherto accepted. While not necessarily the final version, our values have at least the virtue of being based on a single reference whose redox potential is known with great accuracy.

*Acknowledgment.* The financial support of the Swedish Natural Science Research Council is gratefully acknowledged.

**Registry No.** Ind, 120-72-9; *N*-MeInd, 603-76-9; 2-MeInd, 95-20-5; 3-MeInd, 83-34-1; 2,3-diMe, 91-55-4; TrypH, 73-22-3; $IndH^{\bullet +}$, 57212-28-9; *N*-$MeInd^{\bullet +}$, 110774-31-7; 2-$MeIndH^{\bullet +}$, 99322-93-7; 3-$MeIndH^{\bullet +}$, 109154-80-5; 2,3-$diMeIndH^{\bullet +}$, 110774-32-8; $TrypH^{\bullet +}$, 63148-28-7; $Tryp^{\bullet}$, 104419-69-4; $SO_3^{2-}$, 14265-45-3; $SO_3^{\bullet -}$, 12210-38-7; $(SCN)_2^{\bullet -}$, 34504-17-1; $SCN^-$, 302-04-5; $SCN^{\bullet}$, 15941-77-2; $PhO^{\bullet}$, 2122-46-5; phenolate, 3229-70-7.

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# Kinetics and Mechanism of Oxidation of Nitrous Acid by Chlorite Ion

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Although the oxidation of nitrite by chlorite both stoichiometrically and kinetically is a fairly simple reaction when nitrite is in excess and the pH is above 4, it becomes exceedingly complex in acidic solution containing chlorite in excess. $Cl_2O_2$ appears to be a key intermediate, the transitory formation of which explains both the formation of $ClO_2$ and peculiar three-extrema $E$ versus time curve. Assuming that the electrode process on the bright Pt electrode is $HOCl + e^- + H^+ = Cl_2 + H_2O$, the reaction is an oligooscillatory one in which the concentration of HOCl exhibits three extrema at most.

## Introduction

The oxidation of nitrite ion by chlorite ion was recently studied by Emeish and Howlett and by Nagaishi et al.[1,2] The overall rate equations determined by these two teams are substantially different which is partly due to the difference in conditions. According to Emeish and Howlett[1] in the pH range 3.4–4.4 and rather low concentrations of the reactants ($[NO_2^-]_0 = (1\text{–}10) \times 10^{-4}$ M; $[ClO_2^-]_0 = (0.5\text{–}5) \times 10^{-4}$ M) the rate of the reaction expressed as the rate of the decrease of concentration of nitrite ion is given by

$$-d[NO_2^-]/dt = k_I[NO_2^-]^{1.5}[ClO_2^-]^{0.5}[H^+]^{1.5} + k_I'[NO_2^-]^{1.5}[ClO_2^-]^{0.5}[H^+]^{1.5}[Cl^-] \qquad (I)$$

while Nagaishi, Nozaki, and Matsumoto[2] found in a somewhat less acidic solution (pH 5–6) and higher absolute concentrations of the reactants ($[NO_2^-]_0 = 0.05\text{–}0.2$ M; $[ClO_2^-]_0 = 0.02\text{–}0.15$ M) the following rate law:

$$-d[NO_2^-]/dt = k_{II}[H^+]^2[ClO_2^-][NO_2^-] \qquad (II)$$

Neither of these rate laws are valid in more acidic solution and in the excess of chlorite ion. In this latter case clock behavior is observed: after an induction period chlorine dioxide is formed. The most interesting feature of the reaction in slightly acidic medium (pH < 4.5) is that the potential of a bright Pt electrode exhibits three extrema indicating the possibility of an oligooscillatory reaction. These findings made necessary a more thorough study of the title reaction.

## Experimental Section

All chemicals, except $NaClO_2$ were of analytical grade; they were used without further purification. Commercial $NaClO_2$ (89%) was purified by precipitating $CO_3^{2-}$ and $SO_4^{2-}$ by $BaCl_2$. The $Ba^{2+}$ excess was precipitated by an equivalent amount of

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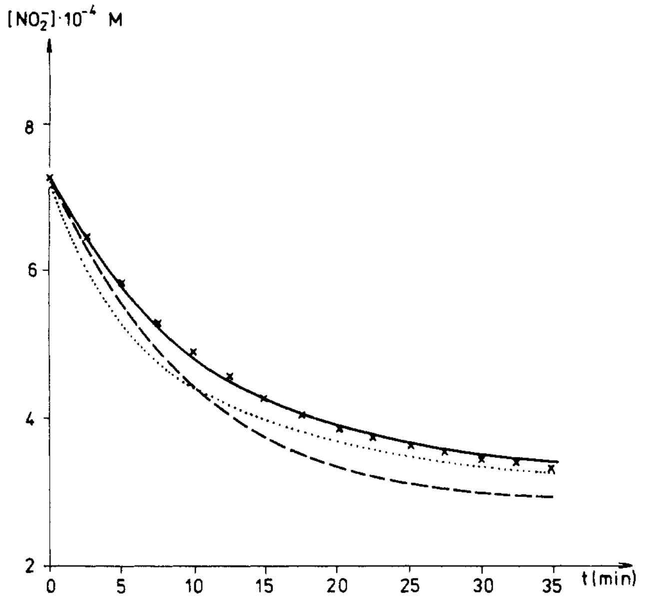

**Figure 1.** Change in nitrite concentration with time for the chlorite–nitrite reaction: $[NO_2^-]_0 = 3.7 \times 10^{-3}$ M, $[ClO_2^-]_0 = 2.25 \times 10^{-3}$ M, $[H^+]_0 = 8.6 \times 10^{-5}$ M; (+) experimental values; (—) calculated from our mechanism; (– – –) calculated after Emeish and Howlett; (···) calculated after Nagaishi et al.

$Na_2SO_4$ and then was twice recrystallized from a 1:3 mixture of water and ethanol at −30 °C to remove the chloride impurity. $NaClO_2$ was then $Cl^-$ free and its purity was over 99% determined iodometrically. pH was adjusted by acetate and sulfate buffers.

The reaction was started by the injection of acidic buffer to the mixture of slightly alkaline chlorite and nitrite solution. SCE reference electrode was used in the potentiometric measurements and the redox electrodes were bright Pt and Au. Both redox electrodes behave the same way in the system. A Hitachi 150-20 spectrophotometer was applied for photometric determinations.

The mixing time of our home-made stopped-flow equipment applied for determining the kinetics of oxidation of nitrous acid by chlorine is about 5 ms. The wavelength was 280 nm where the molar absorptivity of $HNO_2$ and $NO_3^-$ is the same.

HOCl was prepared using the method of Cady.[3]

In the sampling experiments $NO_2^-$ was determined by Griess-Ilosvay reagent.[4]

## Results and Discussion

*Stoichiometry.* In the case of an excess of nitrite ($[NO_2^-] > 2[ClO_2^-]$) there is a simple stoichiometry of the reaction in agreement with the former studies:

$$2NO_2^- + ClO_2^- = 2NO_3^- + Cl^-$$

However, the formation of chlorine dioxide is found when chlorite ion is in excess. The amount of chlorine dioxide formed increases with increasing excess of chlorite. As was mentioned in the Introduction, the formation of $ClO_2$ occurs after a certain induction period; the reaction in case of excess chlorite is in fact a clock reaction.

*The Rate of Consumption of Nitrite.* The decrease of concentration of nitrite was followed above pH 4 only, since below this pH the reaction is too fast to apply the sampling technique. Figure 1 shows the experimentally observed decrease of nitrite concentration in time, together with the $[NO_2^-]$ versus time curves calculated by the rate equations suggested,[1,2] and by our mechanism, the details of which will be discussed later.

*Potentiometric Studies.* The potential of a bright Pt electrode in rather broad concentration ranges of chlorite and nitrite ions is not a monotonic function of time. In a certain pH range (2.4 < pH < 4.5) there are as many as three extrema on the *E* versus time curves (Figure 2). The shape of the *E* versus time curves depends on the initial concentration of the reactants. The curves

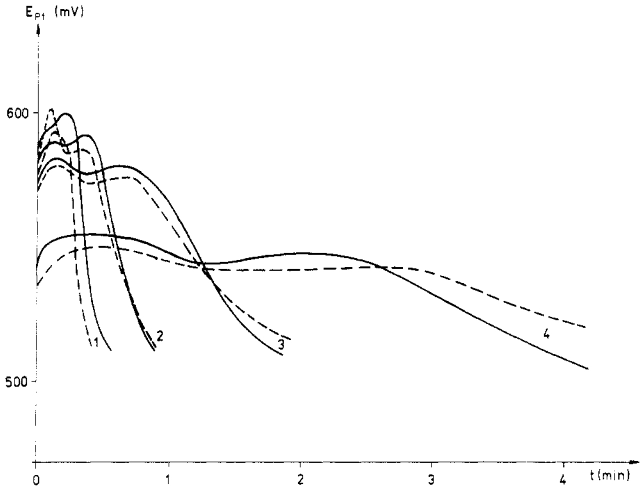

**Figure 2.** Change in redox potential with time for the chlorite–nitrite reaction: measured (– – –) and calculated (- - -) curves. Dependence on the pH. $[NO_2^-]_0 = 3.5 \times 10^{-3}$ M, $[ClO_2^-]_0 = 1.4 \times 10^{-3}$ M; (1) pH 2.4; (2) pH 2.8; (3) pH 3.6; (4) pH 4.0.

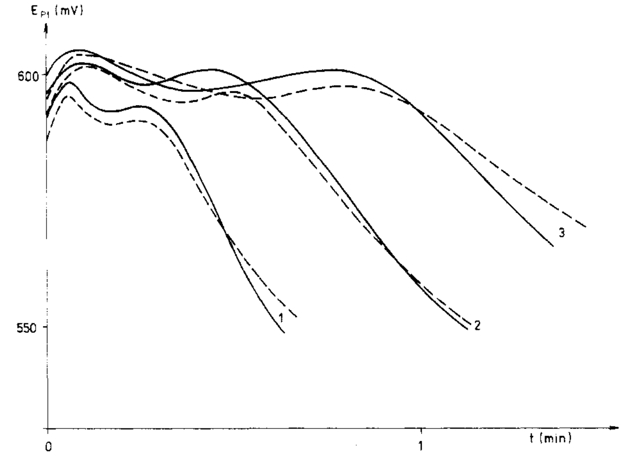

**Figure 3.** Change in redox potential with time for the chlorite–nitrite reactant: measured (– – –) and calculated (- - -) curves. Dependence on the concentration of nitrite. pH 3.2; $[ClO_2^-]_0 = 3 \times 10^{-3}$ M. Nitrite concentrations: (1) $1.25 \times 10^{-2}$ M; (2) $1 \times 10^{-2}$ M; (3) $7.3 \times 10^{-2}$ M.

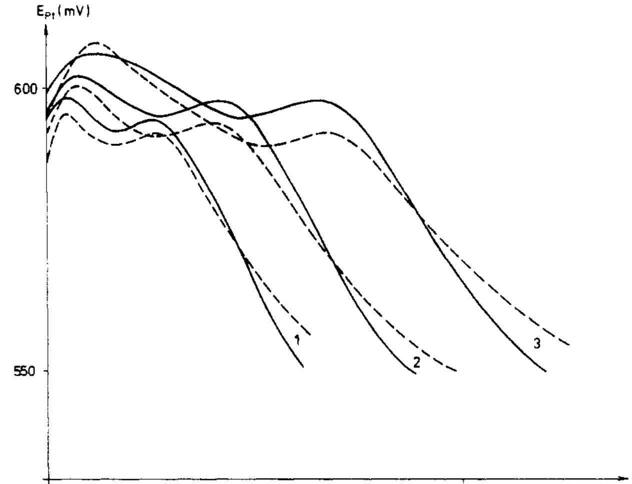

**Figure 4.** Change in redox potential with time for the chlorite–nitrite reaction: measured (– – –) and calculated (- - -) curves. Dependence on the concentration of chlorite. pH 3.2, $[NO_2^-]_0 = 1.25 \times 10^{-2}$ M. Chlorite concentrations: (1) $3 \times 10^{-3}$ M; (2) $4 \times 10^{-3}$ M; (3) $5 \times 10^{-3}$ M.

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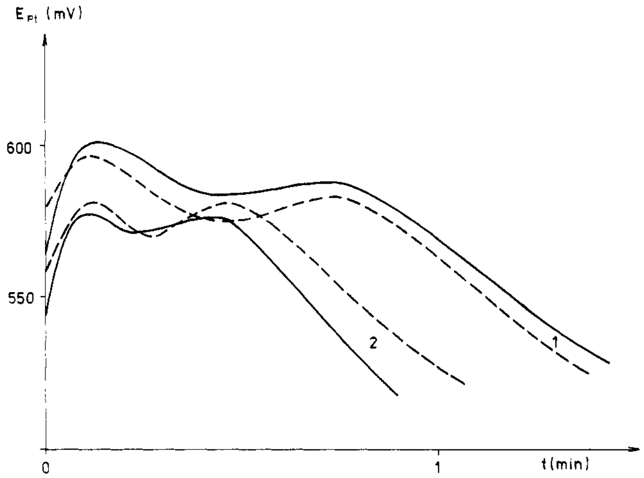

**Figure 5.** Change in redox potential with time for the chlorite–nitrite reaction: measured (–––) and calculated (- - -) curves. Dependence on the chloride concentration. $[NO_2^-]_0 = 1 \times 10^{-2}$ M; $[ClO_2^-]_0 = 3 \times 10^{-3}$ M. Chloride concentrations (1) 0; (2) 0.1 M.

of Figure 3 shows that at constant initial concentration of chlorite ion, the extrema are shifted to the left by increasing the initial concentration of nitrite ion, which is in agreement with the earlier findings concerning the effect of nitrite concentration on the overall rate. As it appears from the curves of Figure 4, the positions of extrema are shifted to the left by decreasing the initial concentration of chlorite, but in this case the height of the curves exhibits a more complicated function. The shapes of the curves depend on the initial concentration of chloride ion, but not to the same extent as on the concentration of the reactants (Figure 5).

*The Rate of the Oxidation of Nitrous Acid by Chlorine and Hypochlorous Acid.* The two-electron reductions of chlorite result in the formation of hypochlorous acid and chloride. Hypochlorous acid oxidizes chloride and chlorine is formed. Therefore it is important to get information on the rate of oxidation of nitrous acid by both HOCl and $Cl_2$. To avoid the hydrolysis of chlorine the reaction must be studied in strongly acidic medium. In 0.1–0.5 M sulfuric acid solution the reaction is first order in both chlorine and nitrous acid, but the rate is independent of the sulfuric acid concentration. The second-order rate constant is $(3.3 \pm 0.4) \times 10^3$ $M^{-1}\,s^{-1}$. No information can be obtained from these experiments on the rate of the oxidation of nitrite ion by chlorine, but it seems obvious that it is much smaller than the rate of the oxidation of nitrous acid.

Unfortunately, the rate law and the rate constant of the oxidation of nitrous acid (nitrite) by hypochlorous acid cannot be determined with the same exactness. According to our measurements the value of the rate constant is about $(0.5–2) \times 10^6$ $M^{-2}\,s^{-1}$ taking the hydrogen ion concentration into account. The reason for the uncertainty is that the spectra of $HNO_2$, $NO_2^-$, and HOCl are overlapping. However, the mechanism does not require knowledge of the exact value of this rate constant.

## Mechanism

The following features of the reaction must be explained by a mechanism: (i) the change of concentration of nitrite in time; (ii) the formation of $ClO_2$ when chlorite ion is in excess; (iii) the peculiar change of the redox potential in time, including the effect of concentrations of nitrous acid, chlorite, and chloride on the shape of $E$ versus time curves.

Obviously, first the oxidation of nitrous acid by chlorite ion and hypochlorous acid must be taken into consideration.

$$ClO_2^- + HNO_2 \rightarrow NO_3^- + HOCl \tag{1}$$

$$HOCl + HNO_2 \rightarrow NO_3^- + Cl^- + 2H^+ \tag{2}$$

The fast reversible reaction between HOCl and $Cl^-$ then makes it necessary to include the reaction between $Cl_2$ and nitrous acid.

$$HOCl + Cl^- + H^+ \rightleftharpoons Cl_2 + H_2O \tag{3f, 3r}$$

$$Cl_2 + HNO_2 + H_2O \rightarrow NO_3^- + 2Cl^- + 3H^+ \tag{4}$$

The reaction of chlorite ion with either hypochlorous acid or chlorine leads to the formation of chlorine dioxide via formation of $Cl_2O_2$.[5]

$$HOCl + ClO_2^- + H^+ \rightarrow Cl_2O_2 + H_2O \tag{5}$$

$$Cl_2 + ClO_2^- \rightarrow Cl_2O_2 + Cl^- \tag{6}$$

$$2Cl_2O_2 \rightarrow Cl_2 + 2ClO_2 \tag{7}$$

Finally, a reaction between nitrous acid and dichlorine dioxide is necessary to assume to explain that there is no formation of $ClO_2$ when nitrous acid is in excess.

$$Cl_2O_2 + HNO_2 \rightarrow NO_3^- + Cl_2O + H^+ \tag{8}$$

Then $Cl_2O$ hydrolyzes producing hypochlorous acid.[6]

$$Cl_2O + H_2O \rightarrow 2HOCl \tag{9}$$

Another explanation of the absence of $ClO_2$ in the excess of nitrite could be a rapid reaction between $ClO_2$ and nitrite. However, the rate of this reaction is too small.

To derive a simple rate law from this reaction mechanism requires some simplifications. Since the rate of reaction 7 is proportional to the square of the concentration of $Cl_2O_2$, rather complicated relations should be considered. However, if nitrite is in excess the rate of reaction 8 is much bigger than that of reaction 7, and therefore this latter reaction can be disregarded. If the initial concentration of chloride ion is not big and the hydrogen ion concentration is smaller than $10^{-4}$ M, the rate of reaction 3f is small enough to neglect reactions of chlorine. The simplified mechanism consists of reactions 1, 2, 5, 8, and 9 only, and applying the steady-state approach to HOCl, $Cl_2O_2$, and $Cl_2O$ the rate of change of the total concentration of nitrite ions and nitrous acid ($T_{NO_2^-} = [NO_2^-] + [HNO_2]$) is as follows:

$$-\frac{dT_{NO_2^-}}{dt} = 2k_1k_2[ClO_2^-]T_{NO_2^-}\frac{[H^+]^2}{K + [H^+]} \times \left(\frac{T_{NO_2^-}\dfrac{[H^+]}{K + [H^+]}}{k_2T_{NO_2^-}\dfrac{[H^+]}{K + [H^+]} - k_5[ClO_2^-][H^+]}\right) \tag{III}$$

$K$ stands for the acid dissociation constant of nitrous acid. In all reactions of N(III) nitrous acid only is regarded as reactive; that is, the corresponding reactions of nitrite ion are neglected. Since in the expression in parentheses the first term in the denominator is much bigger than the second one when nitrite is in excess, eq III can be further simplified:

$$-\frac{dT_{NO_2^-}}{dT} = 2k_1[ClO_2^-]\ T_{NO_2^-}\frac{[H^+]^2}{K + [H^+]} \tag{IV}$$

Obviously, when $K \gg [H^+]$, that is when pH > 4.5, this equation agrees with that found by Nagaishi et al. The empirical rate equation found by Emeish and Howlett cannot be obtained from the mechanism suggested by us, but can be approximately valid in a narrow range of concentration.

However, this steady-state treatment fails to describe the rather structured $E$ versus time curves. Assuming that the redox potential is determined by the reaction

$$HOCl + e^- + H^+ = {}^1/_2Cl_2 + H_2O$$

the calculated $E$ versus time curves rather well agree with the experimentally found ones (see Figures 2–5.) The calculations were performed by the Gear method using the rate equations and

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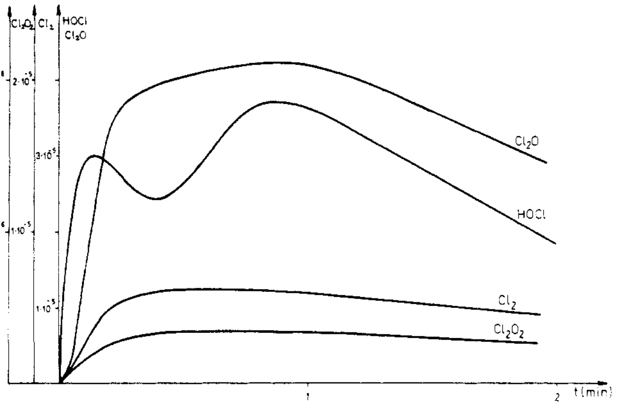

**Figure 6.** Calculated concentration curves of the intermediates in the oxidation of nitrite by chlorite in an excess of nitrite. Initial concentrations: $[NO_2^-] = 3.5 \times 10^{-3}$ M; $[ClO_2^-] = 1.4 \times 10^{-3}$ M; $[H^+] = 2.5 \times 10^{-4}$ M. The conditions are the same as in the case of curve of Figure 2.

**TABLE I**

| rate equation[a] | rate const | dimension |
|---|---|---|
| $v_1 = \alpha k_1[ClO_2^-]T_{NO_2^-}[H^+]$ | $5 \times 10^9$ | $M^{-2}\ s^{-1}$ |
| $v_2 = \alpha k_2[HOCl]T_{NO_2^-}$ | $1 \times 10^6$ | $M^{-1}\ s^{-1}$ |
| $v_{3f} = k_{3f}[HOCl][Cl^-][H^+]$ | $1.8 \times 10^4$ | $M^{-2}\ s^{-1}$ |
| $v_{3r} = k_{3r}[Cl_2]$ | $1 \times 10^1$ | $s^{-1}$ |
| $v_4 = \alpha k_4[Cl_2]T_{NO_2^-}$ | $3 \times 10^3$ | $M^{-1}\ s^{-1}$ |
| $v_5 = k_5[ClO_2][HOCl][H^+]$ | $1 \times 10^4$ | $M^{-2}\ s^{-1}$ |
| $v_6 = k_6[ClO_2][Cl_2]$ | $2 \times 10^3$ | $M^{-1}\ s^{-1}$ |
| $v_7 = k_7[Cl_2O_2]^2$ | $1 \times 10^4$ | $M^{-1}\ s^{-1}$ |
| $v_8 = ak_8[Cl_2O_2]T_{NO_2^-}$ | $1 \times 10^6$ | $M^{-1}\ s^{-1}$ |
| $v_9 = k_9[Cl_2O]$ | $1.5 \times 10^{-1}$ | $s^{-1}$ |

[a] $\alpha = [H^+]/(K + [H^+])$, $K = 5 \times 10^{-4}$.

constants summarized in Table I. Figure 6 shows the calculated concentrations of HOCl, $Cl_2O$, $Cl_2$, and $Cl_2O_2$ as a function of time at a typical experiment. Therefore, according to this interpretation, the chlorite oxidation of nitrous acid is an oligooscillatory reaction in which the concentration of HOCl may exhibit as many as three extrema in time.

Recently a number of oligooscillatory reactions of different types were discovered.[7-9] Reactions involving chlorite ions appear particularly interesting from the point of view of oligooscillatory behavior. So far three reactions involving oxidation by chlorite were found exhibiting oligooscillatory kinetics, and each of them represents different types. Dateo et al.[10] found that under certain conditions when iodide ion is oxidized by chlorite ion, the concentration of iodine shows two extrema: after a sharp maximum a minimum appears on the kinetic curve. This observation can be explained by the oxidation of iodine into I(I) and its subsequent disproportionation to I(V) and $I_2$.[11] Alamgir and Epstein[12] discovered that the concentration of chlorine dioxide exhibits four extrema in time under certain favorable conditions. No mechanism is given for the obviously very complicated reaction. The oxidation of nitrous acid by chlorite seems to be a third type of oligooscillatory reactions involving chlorite.

Our experiments in performing this reaction in a CSTR failed to detect either bistability or oscillatory behavior.

*Acknowledgment.* We are grateful to Dr. Gyula Râbai for discussions concerning the mechanism of the reaction, to the Hungarian Academy of Sciences for supporting this work by research grants No. A-MM-268 and OTKA 156, and to the Soros Foundation for promoting the publication.

**Registry No.** $NO_2^-$, 14797-65-0; $ClO_2^-$, 14998-27-7.

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