Consequently, we attempted to observe vestiges of some equilibrium reaction at pH 7. In solutions containing 0.1 M N<sub>2</sub><sup>-</sup> and equal amounts (5 × 10<sup>-3</sup> 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<sup>*</sup> in the presence of 0.1 M phenol and 5 × 10<sup>-3</sup> 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

\[
\text{Tryp}^* + \text{PhOH} \rightarrow \text{PhO}^* + \text{TrypH} \rightarrow \text{adduct}
\]

From the above experiments \( k_1 \) and \( k_2 \) have been evaluated to be (2.4 ± 0.4) × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> and (1.8 ± 0.3) × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>, 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 other indoles as well) according to the scheme

\[
\text{Tryp}^* + \text{PhOH} \rightarrow \text{PhO}^* + \text{TrypH} \rightarrow \text{adduct}
\]

In all events, the redox potential 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 \( E^0 \) values in the present work the reaction

\[
\text{Tryp}^* + \text{TyroH} \rightarrow \text{TrypH} + \text{TyroO}^*
\]

is thermodynamically favored at any realistic pH value. This rationalizes the experimental observations of several authors.\(^{1 5,2 1}\)

The \( E^0 \) = 1.14 ± 0.2 V reported by Butler et al.\(^{1 3}\) for the tryptophol radical cation has a large error range. The latter resides entirely in the uncertainty of the accepted \( E^0 \) values for the SCN<sup>-</sup>/SCN<sup>-</sup> and (SCN)<sup>2</sup>-/ZSCN<sup>-</sup> couples, respectively.

If our \( E^0 \) value for tryptophol 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-Melnd, 603-76-9; 2-Melnd, 95-20-5; 3-Melnd, 83-34-1; 2,3-diMe, 91-55-4; TrypH, 73-22-3; IndH<sup>+</sup>, 57212-28-9; N-Melnd<sup>+</sup>, 110774-31-7; 2-MelndH<sup>+</sup>, 99322-93-7; 3-MelndH<sup>+</sup>, 1091-84-9; 2,3-diMelndH<sup>+</sup>, 110774-32-8; TrypH<sup>+</sup>, 63148-28-7; Tryp<sup>+</sup>, 104419-69-4; SO<sub>3</sub><sup>2-</sup>, 14265-45-3; SO<sub>3</sub><sup>-</sup>, 12310-38-7; (SCN)<sup>-</sup>, 34504-17-1; SCN<sup>-</sup>, 302-04-5; SCN<sup>+</sup>, 15941-77-2; PhO<sup>-</sup>, 2122-46-5; phenolate, 3229-70-7.

---


---

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

István Lengyel, Vilmos Gáspar, and Mihály T. Beck*

Department of Physical Chemistry, Kossuth Lajos University, Debrecen, 10, Hungary 4010

(Received: April 28, 1987; In Final Form: July 24, 1987)

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. ClO<sub>2</sub> appears to be a key intermediate, the transitory formation of which explains both the formation of ClO<sub>2</sub> and peculiar three-extrema \( E \) versus time curve. Assuming that the electrode process on the bright Pt electrode is HOCl + e<sup>-</sup> + H<sup>+</sup> = Cl<sub>2</sub> + H<sub>2</sub>O, 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\(^{2}\) in the pH range 3.4-4.4 and rather low concentrations of the reactants ([NO<sub>2</sub>]<sup>-</sup> = (1-10) × 10<sup>-4</sup> M; [ClO<sub>2</sub>]<sup>-</sup> = (0.5-5) × 10<sup>-4</sup> M) the rate of the reaction expressed as the rate of decrease of concentration of nitrite is given by

\[
-d[NO_2^-]/dt = k_{III}[H^+]^2[ClO_2^-][NO_2^-] + k_{IV}[NO_2^-][ClO_2^-][H^+]^1[Cl^-] \quad (I)
\]

while Nagaishi, Nozaki, and Matsumoto\(^3\) found in a somewhat less acidic solution (pH 5-6) and higher absolute concentrations of the reactants ([NO<sub>2</sub>]<sup>-</sup> = 0.05-0.2 M; [ClO<sub>2</sub>]<sup>-</sup> = 0.02-0.15 M) the following rate law:

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

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<sub>2</sub> were of analytical grade; they were used without further purification. Commercial NaClO<sub>2</sub> (89%) was purified by precipitating CO<sub>2</sub><sup>-</sup> and SO<sub>4</sub><sup>-</sup> by BaCl<sub>2</sub>. The Ba<sup>2+</sup> excess was precipitated by an equivalent amount of

---

Na₂SO₄ and then was twice recrystallized from a 1:3 mixture of water and ethanol at -30 °C to remove the chloride impurity. NaClO₂ 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 HN₂O and NO₃⁻ is the same.

HOC₁ was prepared using the method of Cady.³

In the sampling experiments NO₂⁻ was determined by Griess-Ilosvay reagent.⁴

Results and Discussion

Stoichiometry. In the case of an excess of nitrite ([NO₂⁻] > 2[C₁O₂⁻]) there is a simple stoichiometry of the reaction in agreement with the former studies:

\[2NO₂⁻ + C₁O₂⁻ = 2NO₃⁻ + Cl⁻\]

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 ClO₂ 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 [NO₂⁻] versus time curves calculated by the rate equations suggested,¹ 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

---


---

The reaction of chlorite ion with either hypochlorous acid or chlorine leads to the formation of chlorine dioxide via formation of Cl₂O₂⁻:

\[
\text{Cl}_2 + \text{HNO}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2\text{Cl}^- + 3\text{H}^+ \quad (4)
\]

The reaction of chlorite ion with either hypochlorous acid or chlorine leads to the formation of chlorine dioxide via formation of Cl₂O₂⁻:

\[
\text{HOCl} + \text{ClO}_2^- + \text{H}^+ \rightarrow \text{Cl}_2\text{O}_2 + \text{H}_2\text{O} \quad (5)
\]

\[
\text{Cl}_2 + \text{ClO}_2^- \rightarrow \text{Cl}_2\text{O}_2 + \text{Cl}^- \quad (6)
\]

\[
2\text{Cl}_2\text{O}_2^- \rightarrow \text{Cl}_2 + 2\text{ClO}_2 \quad (7)
\]

Finally, a reaction between nitric acid and dichlorine dioxide is necessary to assume that there is no formation of ClO₂ when nitric acid is in excess.

\[
\text{Cl}_2\text{O}_2 + \text{HNO}_2 \rightarrow \text{NO}_3^- + \text{Cl}_2\text{O} + \text{H}^+ \quad (8)
\]

Then Cl₂O₄ hydrolyzes producing hypochlorous acid.

\[
\text{Cl}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow 2\text{HOCl} \quad (9)
\]

Another explanation of the absence of ClO₂ in the excess of nitrite could be a rapid reaction between ClO₂ 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 Cl₂O₂⁻, 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, Cl₂O₂⁻, and Cl₂O the rate of change of the total concentration of nitrite ions and nitric acid (\(\text{[NO}_2^-\) = \([\text{NO}_2^-]+[\text{HNO}_2]\))) is as follows:

\[
\frac{d\text{[NO}_2^-\}}{dt} = 2k_1k_2\text{[ClO}_2^-\]T_{\text{NO}_2^-}\frac{[\text{H}^+]^2}{K + [\text{H}^+]} \times \left( \frac{T_{\text{NO}_2^-}}{K + [\text{H}^+] - k_2T_{\text{NO}_2^-}} \right) \quad (III)
\]

\(K\) stands for the acid dissociation constant of nitrous acid. In all reactions of N(III) nitric 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:

\[
\frac{d\text{[NO}_2^-\}}{dT} = 2k_1k_2\text{[ClO}_2^-\]T_{\text{NO}_2^-}\frac{[\text{H}^+]^2}{K + [\text{H}^+]} \quad (IV)
\]

Obviously, when \(K >> [\text{H}^+]\), that is when \(\text{pH} > 4.5\), this equation agrees with that found by Nagaishi et al. The empirical rate equation found by Emesh 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

\[
\text{HOC}^- + e^- + \text{H}^+ = \text{1/2Cl}_2 + \text{H}_2\text{O}
\]

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


Figure 6. Calculated concentration curves of the intermediates in the oxidation of nitrite by chlorite in an excess of nitrite. Initial concentrations: \([\text{NO}_2^-] = 3.5 \times 10^{-3} \text{ M; } [\text{ClO}_2^-] = 1.4 \times 10^{-3} \text{ M; } [\text{H}^+] = 2.5 \times 10^{-4} \text{ M.}\) The conditions are the same as in the case of curve of Figure 2.


TABLE I

<table>
<thead>
<tr>
<th>rate equation</th>
<th>rate const</th>
<th>dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>(e_1 = \alpha \text{[ClO}<em>2^-]T</em>{\text{NO}_2^-}[\text{H}^+])</td>
<td>(5 \times 10^9)</td>
<td>(\text{M}^{-2} \text{s}^{-1})</td>
</tr>
<tr>
<td>(e_2 = \alpha k_1 \text{[HOCI]}T_{\text{NO}_2^-})</td>
<td>(1 \times 10^6)</td>
<td>(\text{M}^{-1} \text{s}^{-1})</td>
</tr>
<tr>
<td>(e_3 = k_3 \text{[HOCI]}[\text{Cl}^-][\text{H}^+])</td>
<td>(1.8 \times 10^4)</td>
<td>(\text{M}^{-2} \text{s}^{-1})</td>
</tr>
<tr>
<td>(e_4 = k_4 \text{[Cl]})</td>
<td>(1 \times 10^4)</td>
<td>(\text{s}^{-1})</td>
</tr>
<tr>
<td>(e_5 = \alpha k_5 \text{[Cl]}T_{\text{NO}_2^-})</td>
<td>(3 \times 10^3)</td>
<td>(\text{M}^{-1} \text{s}^{-1})</td>
</tr>
<tr>
<td>(e_6 = k_6 \text{[Cl]ClO}_2^-)</td>
<td>(1 \times 10^3)</td>
<td>(\text{M}^{-1} \text{s}^{-1})</td>
</tr>
<tr>
<td>(e_7 = k_7 \text{[ClO}_2^-]\text{[H}^+])</td>
<td>(2 \times 10^3)</td>
<td>(\text{M}^{-1} \text{s}^{-1})</td>
</tr>
<tr>
<td>(e_8 = k_8 \text{[Cl]}\text{[ClO}_2^-])</td>
<td>(1 \times 10^3)</td>
<td>(\text{M}^{-1} \text{s}^{-1})</td>
</tr>
<tr>
<td>(e_9 = k_9 \text{[ClO}<em>2^-]T</em>{\text{NO}_2^-})</td>
<td>(1 \times 10^4)</td>
<td>(\text{M}^{-1} \text{s}^{-1})</td>
</tr>
<tr>
<td>(e_{10} = k_{10} \text{[ClO}_2^-])</td>
<td>(1.5 \times 10^{-1})</td>
<td>(\text{s}^{-1})</td>
</tr>
</tbody>
</table>

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


Acknowledgment. We are grateful to Dr. Gyula Rábai 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. \(\text{NO}_2^-, 14797-65-0; \text{ClO}_2^-, 14998-27-7.\)