and starting material. This reaction can be expressed as

$$(olefin-OH)^* \longrightarrow product$$
 (4)

The activation energy of this reaction should be less than or equal to that of the back-reaction of (1). The reaction of the energy-rich adduct would then not reform OH, and thus we would not see a decrease in the rate. We would then get the kinetic expression for the apparent rate constant from reactions 1-4.

$$k = k_3 + \frac{k_1}{1 + \frac{k_{-1}}{k_2[\mathbf{M}] + k_4}}$$
(IV)

Data in the literature strongly suggest the existence of such a reaction for allene.¹³ By use of high-intensity, crossed molecular beams and detecting fragments with a photoionization mass spectrometer, C_3H_3 , CH_3 , and H_2C_2O were measured. C_3H_3 is evidence for reaction 3, the H-atom abstraction. It was proposed that CH_3 and H_2C_2O are products of the reaction

$$OH + C_3H_4 \rightleftharpoons (C_3H_4OH)^* \rightarrow CH_3 + H_2C_2O$$

Since the work was carried out in a molecular beam, product formation requires an efficient unimolecular process.

Since there is little falloff at high temperature and the rate of OH addition to allene is large, the H-atom abstraction reaction could not be seen. However, a careful analysis of the Arrhenius plot for both the experimental and computer-simulated data shows evidence that the H-atom abstraction is of probably of the same order of magnitude in allene as it is in ethylene. The curvature of this plot above 800 K could be due to the effect of this reaction. Since the same curvature occurs in all three curves as seen in Figure 6, it may indeed be a real effect. This curvature occurs because of the increased contribution of reaction 3 to the total

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rate constant. The effect appears largest in allene because the back-reaction of (1) does not cause a curvature in the reverse direction. An upper limit for the reaction rate can also be determined for allene in the same fashion as for 1,3-butadiene, and the rate constant is no more than a factor of 2 greater than that which one would predict from ethylene.

Conclusions

It was not possible to measure the rate of hydrogen abstraction from either allene or 1,3-butadiene because of both the larger rate of the addition reaction and the weaker decrease in the rate of the addition reaction in comparison with the reaction of ethylene. However, an upper limit of about twice the predicted rate for H abstraction from ethylene can be inferred from these data.

The reactions of the three olefins ethylene, 1,3-butadiene, and allene are similar in that the reaction at low temperatures takes place through addition. At higher temperatures, differences appear. The increased stability of the intermediate 1,3-butadiene adduct may allow a longer time for stabilization of the energy-rich adduct; that is, k_{-1} is decreased. For allene, other reaction channels may open up so that the effect of the back-reaction of the intermediate adduct to form the OH radical is diminished. Both of these effects increase the apparent rate at high temperatures which comes from the addition channel and thus make it possible to give only an upper limit to the H-atom abstraction reaction.

A fuller description of these reactions require experiments as a function of buffer gas and pressure as well as temperature. Studies at lower pressures would slow the addition-initiated reactions reaction and may make it possible to observe directly the abstraction reaction.

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Registry No. Hydroxyl radical, 3352-57-6; 1,3-butadiene, 106-99-0; allene, 463-49-0.

Electron Transfer from Indoles, Phenol, and Sulfite (SO_3^{2-}) to Chlorine Dioxide (ClO_2^{\bullet})

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With the ClO₂/ClO₂⁻ couple as reference the one-electron-reduction potentials have been determined for four methylated indolyl radical cations. Their E° values are 1.23 V (N-Me), 1.10 V (2-Me), 1.07 V (3-Me), and 0.93 V (2,3-diMe). E° values were also measured for the following: tryptophyl $H^{*+}/trypH 1.24 V$, SO₃^{*-}/SO₃²⁻ 0.76 V, and phenoxy^{*}/phenolate 0.80 V. The redox potentials were obtained from purely kinetic data (for tryptophan and 2-, 3-, and N-methylindole) or from combined kinetic and thermodynamic measurements.

Introduction

The reliability of determined one-electron-reduction potentials of transient species hinges on the confidence we can place in the accepted E° value of the reference couple. While transient measurements, unlike their stable EMF counterparts, always contain a sizeable uncertainty, failure to utilize correct reference values may play havoc with whole series of determinations. The problem of uncertain reference values is particularly pronounced in the vicinity of 1 V.

Not surprisingly then, the reduction potentials of indoles and unsubstituted phenol are still far from settled. In view of the

interest in the possible electron transfer between tryptophan and tyrosine in biology it would be desirable to reach consensus about the redox properties of the title compounds. One of the few stable radicals known is chlorine dioxide (ClO₂*). The redox potential of the ClO_2^{-}/ClO_2^{-} couple has been measured by several workers¹⁻³ using standard EMF techniques. Therefore, the accepted value³ of 0.936 \pm 0.003 V at 25 °C has an accuracy and reliability unparalleled in transient measurements. The magnitude of the E° value of ClO₂ makes it the ideal reference partner in transient

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TABLE I: Rates and Equilibria^a for the General Reaction $A^z + ClO_2^* \Rightarrow A^{*z+1} + ClO_2^-$

A ^z	$pK_a(IndH^{+})$	$k_{\rm f}, {\rm M}^{-1} {\rm s}^{-1}$	$k_{\rm r}, {\rm M}^{-1} {\rm s}^{-1}$	$k_{\rm f}/k_{ m r}$	Kmeasd	K _{therm}
indole	4.9 ± 0.1	$(1.2 \pm 0.6) \times 10^4$	$(7.3 \pm 0.3) \times 10^8$	1.6×10^{-5}		7.6 × 10 ⁻⁶
N-MeInd		$(1.6 \pm 0.8) \times 10^4$	$(1.4 \pm 0.1) \times 10^9$	1.1×10^{-5}		9.1×10^{-6}
2-MeInd	5.7 ± 0.1	$(8.1 \pm 4.0) \times 10^{5}$	$(2.7 \pm 0.1) \times 10^8$	3.3×10^{-3}		1.5×10^{-3}
3-MeInd	5.0 ± 0.1	$(1.9 \pm 0.9) \times 10^{6}$	$(1.9 \pm 0.1) \times 10^8$	1.1×10^{-2}		5.5×10^{-3}
2.3-diMe	6.1 ± 0.2	$(1.1 \pm 0.3) \times 10^8$	$(5.0 \pm 0.2) \times 10^7$	2.2	1.6	1.2
TrypH	4.3 ^b	$(8.8 \pm 3.1) \times 10^3$	$(5.5 \pm 0.2) \times 10^8$	1.6×10^{-5}		8.1 × 10 ^{−6}
phenolate		$(1.6 \pm 0.3) \times 10^7$	$(6.3 \pm 1.2) \times 10^4$	2.5×10^{2}	2.2×10^{2}	2.4×10^{2}
SO ₃ ²⁻		$(2.6 \pm 0.4) \times 10^{6}$	$(1.3 \pm 0.2) \times 10^3$	2.0×10^{3}	2.1×10^{3}	9.1×10^2

^a Unless otherwise noted the pK_a values, the k_f rates for the indoles, and k_r for unsubstituted indole are taken from ref 10. ^b From ref 11.

determinations of redox potentials around 1 V. In addition, ClO₂• appears to be a pure one-electron oxidant and there is no evidence for its propensity to form adducts with any substance.⁴⁻⁶ No less important, the redox potential of the couple is constant above pH 2.0, the pK_a of HClO₂.

In the present work we shall attempt to determine the redox potentials of six indoles including tryptophan as well as of phenol against the ClO_2/ClO_2^- couple. From the values obtained some inferences will be drawn on other systems and some previously reported values will be critically assessed.

Experimental Section

The pulse radiolysis equipment and its computerized detection system have been described elsewhere.^{7,8} The solutions were prepared in triply distilled water and all experiments were carried out after saturation with N_2O . When the oxidation of tryptophan by ClO₂[•] was studied, very high doses (ca. 300 Gy) were utilized in a 1-cm cell and the reaction was monitored at 380 nm where mainly ClO_2^{\bullet} absorbs. The rate constants of ClO_2^{-} with the cation radicals of tryptophan, N-methylindole, 2-methylindole, and 3methylindole were also measured in a 1-cm cell but with doses around 10 Gy. These rates were monitored at 580 nm where only the radical cations absorb. In all other experiments reported here a 10-cm cell was employed and the applied doses were around 1 Gy.

All chemicals were of the highest purity available and were used without purification. NaClO₂, technical grade, was purified according to ref 9. In solutions containing <0.01 M ClO₂⁻ the G value of primary oxidants was assumed 5.4 ± 0.2 . At high chlorite concentrations $G(ClO_2^{\bullet})$ was taken from ref 9.

Results and Discussion

Table I summarizes the measured rates and equilibrium constants determined in this work. The rates and equilibria refer to the general reaction

$$A^{z} + ClO_{2} \cdot \frac{k_{f}}{k_{r}} A^{z+1} + ClO_{2}^{-}$$
(1)

where z is the charge on the parent compound in question and can be 0, -1, or -2 according to the species studied.

For the indoles the reaction of interest is

$$IndH + ClO_2^{\bullet} \Rightarrow IndH^{\bullet+} + ClO_2^{-}$$
(2)

Except for tryptophan the $k_{\rm f}$ values for the indoles were taken from ref 10 where their evaluation has been described in detail. The rate of the reaction between tryptophan and ClO_2 was determined in the same way. The disappearance of the ClO₂. absorbance was monitored at 380 nm as a function of tryptophan concentration between pH 7 and 10. The employed dose was around 300 Gy/pulse. Thus, the back reaction was negligible in

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Figure 1. A log-log diagram representing the ratio $ClO_2^{\bullet}/2,3$ -diMeIndH⁺⁺ as a function of the corresponding ratio between ClO_2^- and 2,3dimethylindole. The absorbance was measured at 580 nm and OD_{max} is the absorbance measured in the absence of ClO_2^- . Conditions: dose/ pulse 1.4 Gy, cell length 10 cm, pH 4.0, 0.1 M Br⁻, 5×10^{-4} M 2,3dimethylindole, and N₂O saturation.

TABLE II: One-Electron-Reduction Potentials Based on the ClO₂[•]/ClO₂⁻ Couple

radical	E^0	radical	<i>E</i> ⁰
IndH ^{•+}	1.24 ± 0.01	Tryp [•] (pH 7)	1.08 ± 0.02
N-MeInd ⁺⁺	1.23 ± 0.01	PhO•/PhO-	0.80 ± 0.02
2-MeIndH ^{•+}	1.10 ± 0.01	SO3 •-/SO32-	0.76 ± 0.02
3-MeIndH*+	1.07 ± 0.01	$(SCN)_2^{-}/2SCN^{-}$	1.35 ± 0.02
2,3-diMeIndH ^{•+}	0.93 ± 0.01	SCN [•] /SCN ⁻	1.66 ± 0.02
TrypH**	1.24 ± 0.02		

comparison to the recombination between ClO₂[•] and the tryptophyl radical to form the final products. For this reason the true $k_{\rm f}$ values are half the measured ones. The rate constant $k_{\rm f}$ was constant between pH 7 and 8.5 while it increased above pH 9 to attain a value about tenfold higher than the low pH equivalent. The $k_{\rm f}$ in Table I is the rate constant measured below pH 8.5 as it refers to neutral tryptophan with the side chain in the zwitterionic form.

The rate constants of the reverse reaction k_r were measured in the presence of 0.1–0.5 M Br⁻ in the pH interval 3–4, i.e.; well below the pK_a of HClO₂. The exception is N-methylindole since its radical is a cation at all pH values. For the latter compound $k_{\rm r}$ was measured at pH 9.3 in the presence of 0.01 M N₃⁻. The $k_{\rm r}$ values in Table I are the measured ones corrected for the above pK_a values.

With 2,3-dimethylindole the attainment of equilibrium was observed at pH 4, where the ClO_2^- concentration was varied with the indole concentration held constant. The variation of the absorbance at 580 nm (due to the indolyl radical cation) with chlorite is shown in Figure 1. In these experiments both the individual rate constants and the equilibrium constant were determined simultaneously. The forward rate constant $k_{\rm f}$ measured here agreed with the value determined previously under nonequilibrium conditions. In most experiments high ionic strengths (0.1 M or more) had to be employed. In order to ensure the transferability of redox potentials to different ionic media it was felt desirable to correct for the ionic strength. Thus K_{therm} in Table I is the calculated thermodynamic equilibrium constant for the

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Figure 2. A log-log diagram representing the ratio $SO_3^{\bullet-}/ClO_2^{\bullet}$ as a function of the concentration of added SO_3^{2-} . The absorbance was measured at 380 nm and OD_{max} is the absorbance measured in the absence of SO_3^{2-} . Conditions: dose/pulse 2.7 Gy, cell length 10 cm, pH 11.0, 1 M ClO_2^{-} , and N₂O saturation.

general reaction (1). Table II presents the E° values as calculated from K_{therm} and $E^{\circ} = 0.936$ V for the $\text{ClO}_2/\text{ClO}_2^-$ couple.

From Table I it is seen that the forward rate constants k_f vary by 4 orders of magnitude. This strong variation clearly points to an electron-transfer process rather than addition as the latter mode of reaction would surely be much less sensitive toward methyl substitution. The variation in k_r is only a factor of ca. 20. Now, after extrapolation to zero ionic strength, the k_r values with indole, tryptophan, and N-methylindole are about the same, namely $(1.5 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This rate appears to be controlled by diffusion. On the other hand, 2-, 3-, and 2,3-dimethylindole have k_r values significantly lower than the diffusion-controlled limit. Applying the Marcus equation

$$\Delta G = \lambda^0 / (1 + (\Delta G^{\circ} + w_{\rm p}) / \lambda^0)^2$$

to the latter three compounds a $\lambda^0 = 20 \pm 2$ kcal/mol is calculated. Here, w_p is the Coulomb attraction between ClO_2^- and the indolyl radical cation. It was assumed to be ca. -0.8 kcal/mol corresponding to an encounter distance of 5 Å. On the assumption that reaction 2 is an outer-sphere electron transfer a similar mean distance is predicted from the equation

$$\lambda^0 = e^2 (1/D_{\rm op} - 1/D_{\rm st}) (\frac{1}{2}r_1 + \frac{1}{2}r_2 - 1/(r_1 + r_2))$$

The self-exchange rate constant k_{ex} for indoles is unknown. A realistic value would be ca. 10⁹ M⁻¹ s⁻¹. From this value k_{ex} for $ClO_2^{\bullet}/ClO_2^{-}$ is predicted to be 7 × 10⁵ M⁻¹ s⁻¹. Even assuming k_{ex} for the indoles as high as 10^{11} M⁻¹ s⁻¹ the corresponding value for ClO₂[•] would come out as ca. 10⁴ M⁻¹ s⁻¹. Thus it would seem that in the indole reactions the $ClO_2^{\bullet}/ClO_2^{-}$ couple has a much higher apparent self-exchange rate than in its reactions with metal ion complexes.¹² The E° values for the indolyl radical cations in Table II are seen to range from 1.24 to 0.93 V. The value 1.24 \pm 0.02 V for the tryptophyl radical cation is in fair agreement with 1.14 ± 0.2 V reported by Butler et al.¹³ However, it is much higher than the value claimed in ref 14 (0.93 V at pH 3). The discrepancy is even higher at pH 7 where we calculate the value 1.08 ± 0.02 V for the tryptophyl radical while the alleged value in ref 14 is merely 0.64 V. In the above work tryptophan was reacted with the SO3⁻/SO3²⁻ couple at pH 3. In view of the said discrepancy we remeasured the redox potential of the SO_3°/SO_3^{2-} couple against $ClO_2^{\bullet}/ClO_2^{-}$. The attainment of equilibrium was observed at pH 11 in solutions containing 1 M ClO₂⁻ with the SO_3^{2-} concentration varying from 10^{-4} to 1.5×10^{-3} M. The equilibrium was monitored at 380 nm where only ClO₂[•] absorbs.



Figure 3. Spectra obtained upon delivering 1.4-Gy pulses to a 10-cm cell containing N₂O-saturated aqueous N₃⁻ (0.1 M) solutions. Dotted line: spectrum recorded 10 μ s after the electron pulse. The solution contained 5 × 10⁻³ M each of tryptophan and phenol and was held at pH 7.0. Broken line: same as above but recorded after 3 ms. Full line: spectrum of the phenoxy radical obtained at pH 11 in the presence of 10⁻³ M phenol.

Figure 2 shows the plot from which the equilibrium constant was evaluated. At the same time the rate constants k_f and k_r for reaction 3 were also obtained.

$$\mathrm{SO}_3^{2-} + \mathrm{ClO}_2^{\bullet} \rightleftharpoons \mathrm{SO}_3^{\bullet-} + \mathrm{ClO}_2^{-} \tag{3}$$

The values are presented in Tables I and II. It is seen that our E° value is 0.76 V which exceeds by 0.13 V the value reported in ref 15 (0.63 V). We note that roughly the same discrepancy is found by the above authors in the E° value of N,N-dimethylaniline depending on whether they measure^{16,17} it against ClO₂• or SO₃•⁻. The E° value of the phenoxy radical has been given¹⁵ as 0.72 V. As this value was based on the SO₃•⁻/SO₃²⁻ couple we remeasured it by studying reaction 4. The measure

$$PhO^{-} + ClO_{2}^{\bullet} \rightleftharpoons PhO^{\bullet} + ClO_{2}^{-}$$
 (4)

ments were made at pH 13 by monitoring the absorbance of the phenoxy radical at 405 nm (with minor corrections for the absorbance of ClO_2^{\bullet}) while varying the ratio between chlorite and phenolate. The rates and the E° value thus determined are presented in Tables I and II. Combining our E° values for the $SO_3^{\bullet-}/SO_3^{2-}$ and the PhO[•]/PhO⁻ couples we calculate the thermodynamic equilibrium constant for reaction 5 to be ca. 5. This is in good agreement with

$$PhO^{\bullet} + SO_3^{2-} \rightleftharpoons PhO^{-} + SO_3^{\bullet-}$$
(5)

 $K = 17 \pm 5$ measured by Huie and Neta¹⁵ if allowance is made for the ionic strength employed by them (0.1–0.3 M). The self-exchange rate constant k_{ex} for PhO[•]/PhO⁻ has been measured¹⁸ to be $1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. From this value the corresponding k_{ex} for SO₃^{•-}/SO₃²⁻ was calculated to be $3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Using these rate constants and our E° values the apparent self-exchange rate constants for ClO₂[•] are calculated to be 2×10^5 and 8×10^3 $\text{M}^{-1} \text{ s}^{-1}$ in reactions 3 and 4, respectively. Thus, this rate seems to vary somewhat from reaction to reaction in accordance with what has been suggested in ref 19. However, the k_{ex} values estimated in this work are all much higher (by ca. 2 orders of magnitude) than the value obtained in the reaction of ClO₂[•] with metal ion complexes.¹²

Returning to tryptophan it is noted that even after raising E° for sulfite to 0.76 the discrepancy between the reported¹⁴ redox potential and the present value still persists. Combining our E° values for tryptophan and phenol and allowing for the pertinent pK_a values we calculate the thermodynamic equilibrium constant for reaction 6 to be ca. 60 between pH 5 and 9.

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$$Tryp^{\bullet} + PhOH \rightleftharpoons TrypH + PhO^{\bullet}$$
(6)

Consequently, we attempted to observe vestiges of some equilibrium reaction at pH 7. In solutions containing 0.1 M N₃⁻ and equal amounts (5×10^{-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[•] in the presence of 0.1 M phenol and 5×10^{-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

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

From the above experiments k_1 and k_2 have been evaluated to be $(2.4 \pm 0.4) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $(1.8 \pm 0.3) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, 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

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error. In concluding we note that according to the E° values in the present work the reaction

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

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

The $E^{\circ} = 1.14 \pm 0.2$ 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[•]/SCN⁻ and (SCN)₂^{•-}/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.

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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*⁺, 57212-28-9; *N*-MeInd*⁺, 110774-31-7; 2-MeIndH*⁺, 99322-93-7; 3-MeIndH*⁺, 109154-80-5; 2,3-diMeIndH*⁺, 110774-32-8; TrypH*⁺, 63148-28-7; Tryp*, 104419-69-4; SO₃²⁻, 14265-45-3; SO₃⁻⁻, 12210-38-7; (SCN)₂⁻⁻, 34504-17-1; SCN⁻, 302-04-5; SCN*, 15941-77-2; PhO*, 2122-46-5; phenolate, 3229-70-7.

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 Howlett¹ in the pH range 3.4-4.4 and rather low concentrations of the reactants ($[NO_2^{-7}]_0 = (1-10) \times 10^{-4} \text{ M}$; $[ClO_2^{-7}]_0 = (0.5-5) \times 10^{-4} \text{ M}$) the rate of the reaction expressed as the rate of the decrease of concentration of nitrite ion is given by

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

while Nagaishi, Nozaki, and Matsumoto² found in a somewhat

less acidic solution (pH 5-6) and higher absolute concentrations of the reactants ($[NO_2^-]_0 = 0.05-0.2 \text{ M}$; $[ClO_2^-]_0 = 0.02-0.15 \text{ M}$) the following rate law:

$$-d[NO_2^{-}]/dt = k_{II}[H^+]^2[ClO_2^{-}][NO_2^{-}]$$
(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 NaClO₂ were of analytical grade; they were used without further purification. Commercial NaClO₂ (89%) was purified by precipitating CO_3^{2-} and SO_4^{2-} by BaCl₂. The Ba²⁺ excess was precipitated by an equivalent amount of

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