

Oxidations of Amines. X.¹ Detailed Kinetics in the Reaction of Chlorine Dioxide with Triethylenediamine

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Abstract: Stopped-flow kinetics of disappearance of chlorine dioxide and appearance and disappearance of the intermediate cation radical have been analyzed for constants in terms of a proposed mechanism. Presteady state kinetics of chlorine dioxide and the cation radical allowed determination of k_1 (eq 11) and the extinction coefficient (eq 12) of the cation radical (eq A, B). Kinetics of disappearance of the cation radical at constant excess chlorite concentration allowed calculation of k_2 (eq 8), with the prior knowledge of the cation radical extinction coefficient. From the composite constant (eq 3), obtained from kinetics of disappearance of chlorine dioxide, k_{-1} was then calculated. Kinetic justification for identification of the species absorbing at $465\text{ m}\mu$ as the cation radical is presented. Properties of the cation radical are discussed.

Evidence has previously been presented which defines two basic mechanisms for the chlorine dioxide oxidation of amines,² electron abstraction and hydrogen atom abstraction. A more specialized *oxidative fragmentation* mechanism has been described for triethylenediamine and certain other amines in which atoms bearing nonbonded electrons are joined by two-carbon bridges.³ In the latter paper,^{3b} it was shown that the cation radical of triethylenediamine could be detected as an intermediate in the oxidation of triethylenediamine. A transient red species absorbing with $\lambda_{\text{max}} 465\text{ m}\mu$ was observed, and it was proposed that this species was, in fact, the same cation radical. A detailed mechanism was proposed, but many of the relationships within the postulated model were unexplored at that time. Acquisition of a refined stopped-flow kinetics apparatus has now made the latter possible.

In the present paper, the mechanistic model has been developed more fully with respect to available relationships surrounding the intermediate cation radical. The results are fully consistent with identification of the red colored species as the cation radical. Some additional properties of the cation radical have been obtained.

Results

Essentially, the following mechanism had previously been proposed³ for oxidation of triethylenediamine by chlorine dioxide in aqueous solution (see eq A and B). Steady state solutions to this model are readily available in the differential or integral form. For data obtained in the absence of added chlorite, we have preferred to use the differential form, *i.e.*

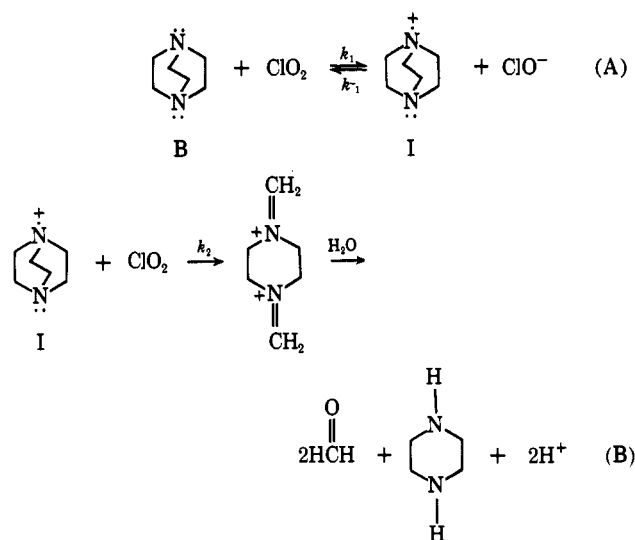
$$-\frac{dt}{d \ln [\text{ClO}_2]} = \frac{k_{-1}}{2k_1k_2[\text{B}]} \frac{[\text{ClO}_2^-]}{[\text{ClO}_2]} + \frac{1}{2k_1[\text{B}]} \quad (1)$$

Thus, the instantaneous slopes on the left were determined graphically and plotted *vs.* the chlorite-chlorine

(1) Paper IX of this series: L. A. Hull, G. T. Davis, and D. H. Rosenblatt, *J. Amer. Chem. Soc.*, **91**, 6247 (1969).

(2) L. A. Hull, G. T. Davis, D. H. Rosenblatt, H. K. R. Williams, and R. C. Weglein, *ibid.*, **89**, 1163 (1967).

(3) (a) W. H. Dennis, Jr., L. A. Hull, and D. H. Rosenblatt, *J. Org. Chem.*, **32**, 3783 (1967); (b) L. A. Hull, D. H. Rosenblatt, W. P. Giordano, G. T. Davis, C. K. Mann, and S. B. Milliken, *J. Phys. Chem.*, **73**, 2147 (1969).



dioxide quotient. Linear plots gave the composite constant, k_{-1}/k_1k_2 (shown inverted in Table I), but

Table I. Rate Constants for Reaction of Triethylenediamine with Chlorine Dioxide near pH 7.2 at 25.0° and Ionic Strength = 0.200

[Triethylenediamine] ^a	[Initial ClO ₂] ^a	pH	k_2k_1/k_{-1} , $M^{-1}\text{ sec}^{-1}$
0.0100	5.218×10^{-4}	7.25	0.99×10^8
0.0100	5.158×10^{-4}	7.20	1.03×10^8
0.0100	5.158×10^{-4}	7.20	0.96×10^8
0.0100	5.158×10^{-4}	7.20	0.91×10^8
0.0200	5.218×10^{-4}	7.23	1.05×10^8
0.0200	5.218×10^{-4}	7.23	1.25×10^8
			Mean 1.03 ± 0.07 $\times 10^8$

^a Molar concentrations.

accurate values for the intercepts could not be obtained. At pH 7, a reasonable approximation to steady state conditions was believed to be obtained, giving reliable constants. However, at pH 9, studies of the intermediate species showed that *substantial* concentrations of the free radical are built up, leading to possible deviations from steady state behavior (Table II).

Table II. Rate Constants for Reaction of Chlorine Dioxide with Triethylenediamine at pH 9.04, 25.0°, and Ionic Strength $\mu = 0.200$ (High Ratio of Cation Radical to Chlorine Dioxide)

[Triethylenediamine], M	[Initial ClO ₂], M	k_2k_1/k_{-1} , M ⁻¹ sec ⁻¹	k_1 , M ⁻¹ sec ⁻¹	k_2/k_{-1}
0.0100	5.494×10^{-4}	1.69×10^3	0.617×10^3	2.73
0.0100	5.494×10^{-4}	1.72×10^3	0.592×10^3	2.90
0.0100	5.494×10^{-4}	1.89×10^3	0.806×10^3	2.35
0.0100	5.322×10^{-4}	1.93×10^3	0.807×10^3	2.39
		Mean $1.81 \pm 0.10 \times 10^3$	$0.70 \pm 0.10 \times 10^3$	2.59 ± 0.22

Nevertheless, plots according to eq 1 were linear at both pH 9 and 7.

In Table III, results are presented for studies with added chlorite ion at pH 9.04. Data were obtained both at 357 m μ (for disappearance of chlorine dioxide) and at 465 m μ (for disappearance of the intermediate cation radical). Under these conditions (added chlorite) the

Table III. Data for Reaction of Chlorine Dioxide with Triethylenediamine in the Presence of Added Chlorite at pH 9.04, at 25.0°, and $\mu = 0.200$

[Added ClO ₂ ⁻], M	[Triethylenediamine], M	[Initial ClO ₂], M	k_2k_1/k_{-1} , M ⁻¹ sec ⁻¹	k_2/ϵ_1
0.0100	0.0400	5.499×10^{-4}	1.241×10^3	5.79
0.0100	0.0400	5.371×10^{-4}	1.121×10^3	a
0.0200	0.0400	5.499×10^{-4}	1.241×10^3	8.35
0.0200	0.0400	5.371×10^{-4}	1.430×10^3	a
0.0300	0.0400	4.73×10^{-4}	1.357×10^3	5.48
0.0400	0.0400	4.73×10^{-4}	1.363×10^3	5.25
0.0100	0.0200	5.51×10^{-4}	1.495×10^3	6.21
0.0100	0.0200	5.51×10^{-4}	b	6.76
0.0100	0.0200	5.51×10^{-4}	b	8.16

^a Not run at 465 m μ . ^b Not run at 357 m μ .

intermediate radical was present in concentrations low enough to allow the steady state assumption to be applied with greater confidence. With this assumption, the equation for disappearance of chlorine dioxide becomes accurately second order in chlorine dioxide (as was observed), since the chlorite concentration does not sensibly change during the course of the reaction.

$$-\frac{d[\text{ClO}_2]}{dt} = \frac{2k_1k_2[\text{ClO}_2]^2[\text{B}]}{k_{-1}[\text{ClO}_2^-]_0} \quad (2)$$

$$\frac{1}{[\text{ClO}_2]} = \frac{2k_1k_2[\text{B}]t}{k_{-1}[\text{ClO}_2^-]_0} + \frac{1}{[\text{ClO}_2]_0} \quad (3)$$

From linear plots according to (3), values for k_1k_2/k_{-1} were obtained which tended to run somewhat higher than those of Table I. The reason for this variation is not understood, since the variation slightly exceeds the variation predicted by the precision of these experiments.

From the steady state assumption

$$[\text{I}] = k_1[\text{ClO}_2][\text{B}]/(k_{-1}[\text{ClO}_2^-] + k_2[\text{ClO}_2]) \quad (4)$$

With added chlorite

$$[\text{I}] = k_1[\text{ClO}_2][\text{B}]/k_{-1}[\text{ClO}_2^-]_0 \quad (5)$$

Thus, in terms of the absorbancy of [I] at 465 m μ , A_I , and the molar extinction coefficient, ϵ_I

$$A_I = k_1[\text{ClO}_2][\text{B}]\epsilon_I/k_{-1}[\text{ClO}_2^-]_0 \quad (6)$$

$$[\text{ClO}_2] = k_{-1}[\text{ClO}_2^-]_0 A_I/k_1[\text{B}]\epsilon_I \quad (7)$$

Substitution of eq 7 in eq 3 gives, on simplification

$$\frac{1}{A_I} = \frac{2k_2t}{\epsilon_I} + \frac{k_{-1}[\text{ClO}_2^-]_0}{k_1\epsilon_I[\text{B}][\text{ClO}_2]_0} \quad (8)$$

Equation 8 provides the method for treatment of data at 465 m μ for the presumed cation radical. Further it provides a test for the intermediacy of the substance absorbing at 465 m μ , serving to characterize the behavior as that of the cation radical. Data obtained at 465 m μ fully agreed with the model represented by eq 8. Thus, plots of $1/A_I$ vs. time were linear, characterizing the disappearance as a second-order process. Secondly, the slopes obtained ($2k_2/\epsilon_I$ from eq 8) were independent of chlorite concentration. Thirdly, the slopes obtained were independent of triethylenediamine concentration (see Table III).

The data of Table IV were obtained under conditions similar to those of Table I. However, in the pH region and with the concentrations of Table IV, very rapid sweep rates after mixing allowed observation of the formation of the intermediate cation radical at 465 m μ . Owing to the extreme exactness with which the stopped-flow apparatus reproduced mixing and kinetics, it was possible to obtain parallel studies at 357 m μ with the identical solutions employed at 465 m μ . Though the observed changes were very small (necessitating scale expansion in some runs), the precision of the runs was remarkably good. Under these conditions, the initial chlorine dioxide disappearance could be treated as zero order, and a useful approximation was assumed as follows.

$$-d[\text{ClO}_2]/dt = k_1[\text{ClO}_2][\text{B}] \quad (9)$$

For negligibly small changes in $[\text{ClO}_2]$ and $[\text{B}]$

$$[\text{ClO}_2] = -k_1[\text{ClO}_2]_0[\text{B}]_0t + [\text{ClO}_2]_0 \quad (10)$$

Thus, data at 357 m μ allowed the determination of k_1 for the mechanism initially depicted.

In a similar way, data at 465 m μ gave approximately zero-order plots, and were assumed to fit the equation

$$d[\text{I}]/dt = k_1[\text{ClO}_2][\text{B}] \quad (11)$$

or the equivalent, after integration

$$A_I = k_1\epsilon_I[\text{ClO}_2]_0[\text{B}]_0t \quad (12)$$

Application of eq 12 in conjunction with the value of k_1 determined by use of eq 10 allowed estimation of ϵ_I , the molar extinction coefficient for the triethylenediamine cation radical.

Utilization of the constants determined under the various conditions permits dissection of the reaction

Table IV. Determination of k_1 and ϵ_1 for Reaction of Triethylenediamine with Chlorine Dioxide at 25.0° and $\mu = 0.200$ (No Chlorite Added)

[Initial ClO ₂], <i>M</i>	[Triethylenediamine], <i>M</i>	pH	k_1	$k_1\epsilon_1$	ϵ_1
5.158×10^{-4}	0.0100	7.20	4.19×10^4	1.04×10^8	2470
4.688×10^{-4}	0.0100	7.19	3.81×10^4	6.67×10^7	1751
4.543×10^{-4}	0.0200	7.17	4.62×10^4	8.86×10^7	1982
4.543×10^{-4}	0.0200	7.17	4.13×10^4		2145
4.688×10^{-4}	0.0200	7.19	2.46×10^4	5.88×10^7	2389
4.688×10^{-4}	0.0400	6.84	5.08×10^4	9.59×10^7	1887
			Mean $4.05 \times 10^4 \pm 0.61$	$8.27 \times 10^7 \pm 1.69$	2104 ± 231

completely into fundamental constants or formation of various composite constants from the separate constants (Table V). From the composite constant k_1/k_{-1}

Table V. Summary of Best Values for Various Simple and Composite Constants in the Reaction of Triethylenediamine with Chlorine Dioxide

Constant	Value
k_1	$4.05 \times 10^4 M^{-1} \text{sec}^{-1}$
k_{-1}	$4.57 \times 10^6 M^{-1} \text{sec}^{-1}$
k_2	$1.31 \times 10^4 M^{-1} \text{sec}^{-1}$
k_2/k_{-1}	0.0286
$k_1/k_{-1} = K$	0.0886
k_2k_1/k_{-1}	$1.16 \times 10^3 M^{-1} \text{sec}^{-1}$
$\epsilon_1 (M^{-1} \text{cm}^{-1})$	2104 ± 231
E_0 (cation radical)	-1.01 V
$\text{p}K_{a1}$ (triethylenediamine at $\mu = 0.200$)	8.93
$\text{p}K_{a2}$ (triethylenediamine at $\mu = 0.200$)	2.98

= K , standard expressions can be used to relate the single electrode potential of chlorine dioxide to that of the triethylenediamine cation radical. Since the chlorine dioxide potential is known¹ to be -0.95, the single electrode oxidation potential of triethylenediamine cation radical can be estimated.

Discussion

The postulated mechanism of reaction of triethylenediamine with chlorine dioxide involves a reversible formation of chlorite and aminium cation radical followed by attack of the cation radical by a second molecule of chlorine dioxide in an irreversible fragmentation process. In accordance with this mechanism, we found eq 1 to account adequately for the rate of disappearance of chlorine dioxide in the absence of added chlorite. In the presence of added chlorite, eq 3 accurately describes the disappearance of chlorine dioxide, as predicted by the model.

The species which absorbs at 465 m μ has been definitely characterized as the triethylenediamine cation radical by the kinetic studies described here. Both this intermediacy of a cation radical (see eq 8) and the existence of a charge-transfer complex in competitive equilibrium⁴ would permit second-order kinetics in the presence of added chlorite ion, as is observed.

(4) The competitive equilibrium would be $\text{ClO}_2 + \text{I} \rightleftharpoons \text{complex}$ (K_c). Thus $[\text{complex}] = K_c[\text{B}][\text{ClO}_2]$. The disappearance of complex would be second order since the disappearance of ClO_2 (see eq 3) is experimentally second order and charge-transfer equilibria are established almost instantaneously, according to C. F. Bernasconi, *J. Amer. Chem. Soc.*, **92**, 129 (1970).

The slopes of the observed second-order plots, however, are independent of added chlorite concentration or free triethylenediamine concentration in agreement with eq 8, but not with eq 13, which governs the disappearance

$$\frac{1}{[\text{complex}]} = \frac{2k_1k_2t}{K_c k_{-1} [\text{ClO}_2]_0} + \frac{1}{K_c [\text{ClO}_2]_0 [\text{B}]} \quad (13)$$

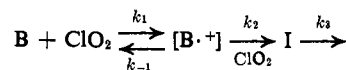
of the competitive charge-transfer complex. The appearance of a charge-transfer complex as an intermediate prior to the cation radical would result in the same kinetics as with competitive equilibrium⁵ and is thus also excluded. The appearance of an absorbing species subsequent to the reaction of a second molecule of chlorine dioxide with the cation radical would give kinetics dependent on concentrations of both free triethylenediamine and chlorite.⁶

Determination of all of the reaction constants for the triethylenediamine-chlorine dioxide system at 25° has been possible. Together with the $\text{p}K_a$ of triethylenediamine, they allow consideration of some fundamental ideas on the formation of aminium cation radicals in aqueous solution by reaction of amines with oxidants such as chlorine dioxide.

The $\text{p}K_a$ of triethylenediamine is 8.93 at ionic strength 0.200. By way of contrast, the $\text{p}K_a$ of another bridgehead amine, quinuclidine, is 11.07 at ionic strength 0.200. If the relationships of Hall⁷ are presumed to be valid, $\Sigma\sigma^*$ could be calculated for the structural elements surrounding the nitrogen with the assumption that simple Taft polar substituent effects determine the $\text{p}K_a$'s of these two amines. The values of $\Sigma\sigma^*$ so calculated are +0.297 for triethylenediamine⁸ and -0.441 for quinuclidine. There are several reasons for supposing that these two amines may deviate from the normal relationship, however. In the case of quinuclidine, the usual degree of freedom associated with rapid inversion about the lone pair electrons is not present in the free base. This inversion is normally frozen out on amine protonation. The lack of such entropy

(5) S. D. Ross and I. Kuntz, *ibid.*, **76**, 3000 (1954).

(6) For the model



where $[\text{B}^+]$ and I are both in steady state equilibrium, the rate expression is $-d[\text{I}]/dt = -d[\text{ClO}_2]/dt$ as expressed in eq 3. If $[\text{I}]$ were not in steady state equilibrium, the kinetics would be expressed as a sum of the terms of eq 3 and a first-order term independent of chlorine species. In the extreme case where the final step was very slow compared to other steps, I would appear rapidly and then disappear by first-order kinetics. In any case, the analytical form would not be similar to eq 8.

(7) H. K. Hall, Jr., *J. Amer. Chem. Soc.*, **79**, 5441 (1957).

(8) Statistical correction of -0.30 was applied.

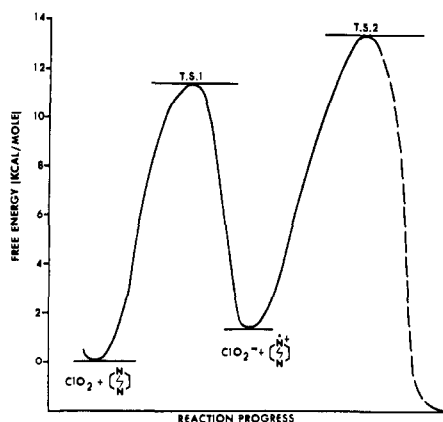


Figure 1. Schematic of reaction energy profile for chlorine dioxide and triethylenediamine.

change for quinuclidine should lead to a structural increase in pK_a greater than the simple polar effect. The case with triethylenediamine would seem to be even more complicated. Here, Hoffmann, Imamura, and Hehre⁹ have shown that the four lone pair electrons of triethylenediamine, when considered in the context of simple molecular orbital theory, are split into two energetically nonequivalent sets. The levels, however, should be split, to a first approximation, equally above and below the center of gravity represented by hypothetical noninteracting lone pairs, and there should be little effect upon pK_a .

Despite factors which would operate to cause deviations from normal correlations where the structural factors are derived from pK_a , by use of statistical correction for the reaction of triethylenediamine, we predict $k_1 = 8.94 \times 10^3 M^{-1} \text{sec}^{-1}$ from the third relationship of ref 1. The actual value (Table V) is $4.05 \times 10^4 M^{-1} \text{sec}^{-1}$. The precision of this correlation is not high, and the agreement is surprisingly good, which is probably fortuitous. A better and more precise relationship is the equation of Figure 2 of ref 10. Using this equation, k_1 is calculated to be $8.32 \times 10^2 M^{-1} \text{sec}^{-1}$. Thus k_1 for triethylenediamine shows *positive* deviations from the usual linear free-energy correlations of rates of amine oxidations with various structural parameters related to pK_a .

We attribute the principal cause of *positive* deviations observed to net stabilization of the cation radical structure relative to the free amine. The bicyclic structure undoubtedly imposes some *strain* on the cation radical system since this latter system tends toward *planar* σ orbitals around the nitrogen atom.¹¹ However, the orbital splitting factor and consequent delocalization of electrons in the free base and in the cation radical act to *stabilize* the cation radical relative to the free base. Thus the four lone pair electrons are split above and below a center of gravity represented by noninteracting lone pairs. The upper (more energetic) pair reacts with the oxidant, leaving one *pair* of electrons in the *lower energy set* and only one electron in the higher energy orbital. The cation radical is thus stabilized by the energy of displacement of one electron

(9) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

(10) L. A. Hull, G. T. Davis, D. H. Rosenblatt, and C. K. Mann, *J. Phys. Chem.*, **73**, 2142 (1969).

(11) A. J. Tench, *J. Chem. Phys.*, **38**, 593 (1963).

from the center of gravity (the original position for a hypothetical noninteracting system) of the system to the new level which it occupies in the free base when allowance is made for the interactions of the lone pair electrons. Evidently, this stabilization energy (about 0.78 eV) is greater than the additional internal strain in the triethylenediamine cation radical. The crude energy levels of the Hückel calculation of ref 9 also may be used to calculate three possible electronic transitions for the triethylenediamine cation radical. For the cation radical, the transition $a_2'' \rightarrow e'$ (designation of ref 9) corresponds to an $A' \rightarrow E''$ transition in C_{3h} symmetry and is "forbidden." This transition occurs at 10.165 eV (122 $m\mu$). The transition $a_1' \rightarrow e'$ for the cation radical is an $A' \rightarrow E'$ transition and is allowed. It is predicted to be at 8.592 eV (144 $m\mu$). The transition $a_2'' \rightarrow a_1'$ for the cation radical is an $A' \rightarrow A''$ transition, allowed, and is predicted to be at 1.573 eV (788 $m\mu$). The experimental maximum is 2.666 eV (465 $m\mu$). Clear identification of the transition cannot be made, owing to neglect of repulsions in the calculated energy levels for the polyelectronic system, but the transition nominally predicted at 788 $m\mu$ seems more closely related to the observed band than the transitions at 122 and 144 $m\mu$.

The data of Table V allow construction of a reasonably good schematic for the reaction energy profile of the chlorine dioxide-triethylenediamine kinetic system (Figure 1). In this picture, the barrier heights are depicted in free energy units and do not seem unreasonable for this system. Calculation of the equilibrium constant for the first process of Figure 1 permits further estimation of an interesting property of the cation radical, the single electrode oxidation potential for this species. In theory, this oxidation potential now allows evaluation of the equilibrium constant of the first process for any other oxidant whose single electrode potential is known. This information is of limited value since the equilibrium constant throws no light on the kinetic processes. However, a driving force for this reaction is well represented by the composite constant, k_2k_1/k_{-1} , which is a product of the equilibrium constant for the first process with the rate coefficient of the second step. We would expect the rate coefficient of the second step for a variety of oxidants to be correlatable by extrathermodynamic relationships with the oxidation potential of a given oxidant,¹⁰ but the establishment of such a relationship would be tedious, even if found to be experimentally feasible.

Experimental Section

Materials. Water was triply distilled from acid permanganate.² The 1,4-diazabicyclo[2.2.2]octane (triethylenediamine), obtained from Matheson Coleman and Bell, was recrystallized three times from 60–90° petroleum ether; its monoperchlorate salt was then prepared by adding the calculated quantity of 0.5 *M* perchloric acid to the free base, adding excess ethanol and ether to precipitate the salt, and recrystallizing the salt six times from methyl alcohol. The salt was dried *in vacuo* over phosphorus pentoxide.

Chlorine dioxide solutions were prepared, stored, and analyzed as described previously.³ Sodium chlorite (analytical grade, 20 mesh) was used without further purification. Solutions were freshly prepared and used without delay. Commercial sodium tetraborate and phosphate salts were used to prepare buffers. Sodium chloride was added to maintain constant ionic strength.

Solutions of chlorine dioxide were made up from concentrated stock solutions by dilution, and the concentration was determined (ϵ

$1240 M^{-1} \text{ cm}^{-1}$) at $357 \text{ m}\mu$ directly on an Aminco-Morrow stopped-flow apparatus with Beckman DU-2 optics. (This method was checked by independent determinations on a Cary Model 14 spectrophotometer, and good agreement, 1-2%, was found.) Mixing was accomplished with two pneumatically driven syringes, giving 1:1 dilution of the separate reaction components. Mixing times were of the order of 2-5 msec. Chlorine dioxide disappearance was monitored at widely varying sweep rates in order to study in detail small portions of the reaction (such as initial formation of the cation radical). Photographic records of the oscilloscope tracings were obtained at both 357^{12} and $465 \text{ m}\mu$, using identical solutions and sweep rates at the two wavelengths; these records were enlarged by projection, readings converted from transmittancy to absorbancy, and thence, where appropriate, to concentrations, for the various calculations. Data were evaluated graphically in all cases.

Slight discrepancies were obtained for k_2k_1/k_{-1} as compared with ref 3. These are probably attributable to the different wavelength ($380 \text{ m}\mu$) used in the previous work. It is probable that appreciable absorption by the cation radical occurs at that wavelength. In the present work, readings at $465 \text{ m}\mu$ were corrected for chlorine dioxide absorbancy at that wavelength from parallel identical runs monitored at $357 \text{ m}\mu^{12}$ ($\epsilon_{\text{ClO}_2} = 1240 M^{-1} \text{ cm}^{-1}$ at $357 \text{ m}\mu$; $\epsilon_{\text{ClO}_2} = 17.2 M^{-1} \text{ cm}^{-1}$ at $465 \text{ m}\mu$). The stopped flow apparatus was thermostated at $25.00 \pm 0.02^\circ$ (temperature of the circulating water bath).

Criteria for Use of Steady State Assumption with Selected Data and Characterization of Data of Table II as Nonsteady State. Initially, it was observed that substantial and virtually instantaneous drops in chlorine dioxide concentration were obtained on mixing the reactants under the conditions of Table II. (The concentration drop was frequently greater than 50% of the initial chlorine dioxide concentrations.) This concentration drop was much smaller at lower pH values or with added initial chlorite ion. Further, the disagreement of data obtained under the conditions of Table II with those of Table I and Table III led to doubts of applicability of the steady state assumption.¹³ In addition, as the radical con-

centration begins to exceed that of the equilibrium concentration of chlorine dioxide at any point in the reaction (data in Table II had ratios of $[\text{I}]/[\text{ClO}_2]$ exceeding 1), there is greater chance for reactions competitive with the second step of the model mechanism to influence the value of the rate constants obtained. For example, the redox disproportionation of I is suspected as a possible interference with the reaction represented by k_2 when [I] becomes large compared with $[\text{ClO}_2]$. Therefore, we concentrated on obtaining data (Tables I and III) under conditions favoring low concentrations of the intermediate cation radical (as low as possible, consonant with reasonably accurate analysis of data for this species). As final justification for use of the steady state assumption with the latter "selected" data, we used the derived constants to estimate steady state concentrations of the intermediate cation radical for given instantaneous concentrations of chlorite and chlorine dioxide. Reasonably good agreement (within 10%) was found for runs under the conditions of Table III, even at the beginnings of the runs and reasonable agreement (within about 20%) under the conditions of Table I beyond about 10-20% reaction. (The presteady state condition lasted for about 10-20% reaction for these runs, as expected.) Under conditions of the runs of Table I and Table III, the most unfavorable cases included (those with higher concentrations of cation radical) produced maximum concentrations of the cation radical amounting to as much as 20% of the available chlorine dioxide. Remarkably, the data of Table II also gave good agreement at any time with the experimentally found concentration. This does not negate the possible interference of a reaction competitive with that associated with k_2 , since the values of the cation radical concentration, after arrival at the steady state, depend almost exclusively upon $k_1[\text{ClO}_2][\text{B}]/k_{-1}[\text{ClO}_2^-]$ with a negligible contribution from $k_2[\text{ClO}_2]$ in the denominator. It should be noted that presteady state conditions prevailed for the runs of Table II up to about 60% reaction. (This portion of the reaction was not directly observable, owing to its rapidity.)

(13) Nonsteady state solutions to the kinetic system were sought. It is, indeed, possible to formulate a differential equation relating the concentrations of chlorine dioxide, chlorite, and the cation radical with time eliminated. The equation has the form

$$(ax + by)(dx + dy) + xy(cdx + fdy) = 0$$

where x and y are the only variables of the system. However, an integrated expression could not be obtained.

(12) At the absorption maximum for chlorine dioxide, $357 \text{ m}\mu$, the cation radical must be virtually nonabsorbing in these experiments; otherwise, under the variety of conditions obtained by variations in chlorite and triethylenediamine concentrations, the chlorine dioxide disappearance kinetics would have deviated considerably from second order and would not have yielded constants.