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Electron Transfer between Azide and Chlorine Dioxide: The Effect of Solvent Barrier Nonadditivity

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Abstract: The reaction of chlorine dioxide with excess azide in aqueous media proceeds with complex kinetics and produces N_2, N_2O, NO_3^-, Cl^-, and ClO_2^-. In the presence of the spin trap PBN, the reaction is much simpler, and the rate law is $-d[ClO_2]/dt = k_1[ClO_2][N_3^-][PBN]/([PBN] + [ClO_2^-]k_{-1}/k_2)$, with $k_1 = 809$ M^{-1} s^{-1} and $k_{-1}/k_2 = 19.0$ at 25 °C. The inferred mechanism implies that k_1 is the rate constant of electron transfer between ClO_2 and N_3^-, k_{-1} is the reverse rate constant (N_3 with ClO_2^-), and k_2 is the rate constant for reaction of N_3 with PBN. A dramatically lower value for k_1 of 0.62 M^{-1} s^{-1} is calculated from the Marcus cross relationship and literature values for the self-exchange rates. The discrepancy is attributed to systematic errors in the literature self-exchange rates that were derived by applying the Marcus cross relationship to reactions of coordination complexes with N_3^- and ClO_2. Such errors develop whenever this method is applied to reactions between species of widely differing size. Correcting for this effect leads to a calculated value of 56 M^{-1} s^{-1} for k_1, which is in much improved agreement with the observed value. Similar corrections lead to greatly improved correlations for the self-exchange reaction of NO_2 with NO_2^- and the electron-transfer reaction of ClO_2 with NO_2^-.

Introduction

There have been a large number of recent reports on the kinetics of aqueous electron-transfer reactions between substitution-inert metal complexes and small nonmetal compounds, and there have been many attempts to correlate these rates with Marcus theory.[1–11] By employing the Marcus[12] cross relationship, effective self-exchange rate constants have been estimated for couples such as O_2/O_2^-,[7] ClO_2/ClO_2^-,[13] N_3/N_3^-,[10] and NO_2/NO_2^-.[6] In the cases of the NO_2/NO_2^- and O_2/O_2^- systems, the calculated self-exchange rate constants are substantially smaller than the experimentally obtained self-exchange rate constants.[6,14,15] A similar discrepancy was reported for the rate of electron transfer from NO_2^- to ClO_2, where the experimental rate constant was measured at 153 M^{-1} s^{-1}, but that calculated by applying the Marcus cross relation to the effective self-exchange rate constants was 0.2 M^{-1} s^{-1}.[16] It is not clear whether these three discrepancies have various origins or whether they indicate a systematic trend. Some of the factors that have been suggested are nuclear tunneling,[13] strong orbital overlap in the transition state,[6] and solvent barrier nonadditivity.[15,17]

In an effort to gain more data to assess these issues, the present paper reports on the reaction of ClO_2 with N_3^-. This reaction was selected because both of the ClO_2/ClO_2^- and N_3/N_3^- redox couples have been the subject of prior scrutiny, their standard reduction potentials are well established, and reasonable estimates of their self-exchange rate constants have been derived from cross reactions with coordination complexes.[10,13] Moreover, the reverse process, electron transfer from ClO_2^- to N_3, has been investigated by use of pulse radiolysis.[17,18] We find that the electron-transfer rate constant substantially exceeds the predictions of simple Marcus theory, and that much of the difference can be eliminated by correcting for the effects of solvent barrier nonadditivity.

Experimental Section

Reagents and Solutions. PBN (*N-tert*-butyl-α-phenyl nitrone) was used as supplied by Aldrich. $NaClO_2$ (Kodak) was recrystallized as before.[13] $NaClO_4$ (GFS) was recrystallized by dissolving 250 g in 60 mL of water at 90 °C;[19] after the hot solution was filtered, 40 mL of ethanol was added, and the solution was cooled to obtain crystals, which were dried under vacuum at room temperature. NaN_3 (Fisher) was recrystallized as described previously.[10] Water was distilled with a Barnsted Fi-streem all-glass still. Stock ClO_2 solutions were prepared as described previously.[20] Solutions were prepared daily in volumetric flasks by weighing the reagents (except for ClO_2); they were protected from room light by covering with aluminum foil.

Analytical Methods. Ion chromatography experiments for anion analysis were preformed on a Wescan ion chromatography system equipped with a silica-based anion-exchange column 269-013. The eluent was 4 mM phthalate solution at pH 4.00. Calibration curves were obtained by measuring peak heights for samples of known concentrations. Peaks were identified by comparing their elution times with those of standards.

UV–vis spectra were obtained with an HP8452 spectrophotometer and 10-mm quartz cells. pH measurements were performed at room temperature on a Corning pH meter Model 130 with a Ross combination electrode filled with a saturated NaCl solution.

N_2O yields were determined by gas-phase IR spectroscopy. An IR gas cell was constructed with KBr windows and was equipped with two outlets with stopcocks. One could be attached to a vacuum line and the other to a 50-mL round-bottom flask. A 10-mL sample of NaN_3 solution

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Table I. Kinetic Data for the Reaction of ClO_2 with N_3^- in the Presence of PBN[a]

k_{obs}, s^{-1}	[PBN], mM	[N_3^-], mM	[ClO_2^-], mM
0.573(1)	9.27	60.2	40.4
0.769(2)	9.27	60.2	29.9
1.155(4)	9.27	60.2	19.8
2.17(1)	9.27	60.2	10.3
3.93(1)	9.27	60.3	5.58
5.19(2)	4.65	60.2	2.04
9.47(1)	9.32	60.2	2.04
13.94(3)	9.27	60.3	1.23
48.6(1)[b]	8.64	60.4	0.0
7.92(5)	37.1	60.0	10.1
4.34(2)	18.5	60.0	10.1
2.233(5)	9.28	60.0	10.1
1.821(5)	7.42	60.0	10.1
1.17(1)	4.64	60.0	10.1
0.364(4)	8.95	10.0	10.0
1.11(1)	8.96	30.4	9.99
1.822(6)	8.96	50.3	9.99
2.544(5)	8.96	69.9	9.99
3.26(2)	8.96	89.9	9.99

[a] 25.0 °C, $\mu = 0.10$ M ($NaClO_4$), $[ClO_2]_0 = 8 \times 10^{-5}$ M, and natural pH (7 ± 1). [b] This result not included in fit of eq 4.

was mixed with 10 mL of a ClO_2 solution in the flask, which was then attached to the IR cell. The IR cell was evacuated, and then the vacuum connection was closed. The solution was allowed to react and achieve gas equilibrium with the headspace; then the round-bottom flask was placed in a dry ice/acetone bath in order to freeze the solution. The stopcock between the IR cell and the flask was then opened, allowing the headspace gas to flow into the IR cell. IR spectra were obtained with an IBM Instruments FTIR spectrophotometer.

Kinetic Methods. Initial ClO_2 concentrations were determined by the UV–vis absorbance of ClO_2 at 360 nm ($\epsilon = 1200$ M^{-1} cm^{-1}).[13] The ionic strength was maintained at 0.10 M by addition of $NaClO_4$ as a background electrolyte. The reactions were monitored at 360 nm. For the reaction of N_3^- with ClO_2 in the presence of PBN, the kinetic data were obtained using a Hi-Tech Scientific Model SF-51 stopped-flow apparatus equipped with a SU-40 spectrophotometer and a C-400 circulating water bath; a Zenith-based OLIS Model 4300S system was used for data acquisition and analysis. Pseudo-first-order rate constants were evaluated by OLIS subroutines and are listed in Table I. The value of each rate constant is the average of at least 4 shots, with the uncertainties in parentheses. The temperature was maintained at 25.0 ± 0.1 °C. For the slow reaction of N_3^- with ClO_2 without PBN, the data were obtained using an HP8452 UV–vis spectrophotometer by mixing 2 mL of 1.2×10^{-3} M ClO_2 with 2 mL of 0.2 M N_3^- in a 10-mm quartz cell maintained at 25.0 ± 0.1 °C.

The Los Alamos nonlinear least-squares computer program was used to fit the rate law to the values of k_{obs}.[21] The data were weighted as the inverse square of the dependent variable. Uncertainties given in parentheses represent one standard deviation. Numerical integrations were performed with a local implementation of Hindmarsh and Byrne's subroutine EPISODE (Lawrence Livermore Laboratory, 1977). A Macintosh Plus computer was used in these calculations.

Results

Stoichiometry. The stoichiometry of the reaction of N_3^- with ClO_2 was examined by ion chromatography and by IR spectroscopy. Ion chromatography experiments were conducted on a solution prepared by mixing 25 mL of 7.6×10^{-4} M ClO_2 ($\epsilon = 1200$ M^{-1} cm^{-1}) with 25 mL of 2.1×10^{-3} M NaN_3 in a 100-mL flask at room temperature. The flask was covered by aluminum foil to prevent exposure to room light, and the reaction was monitored at 360 nm to ensure that ClO_2 was completely consumed before product analysis. Anionic products were identified as Cl^-, ClO_2^-, and NO_3^-. Quantitation by peak-height analysis of N_3^- consumption and product yields, relative to ClO_2 consumption, gave the following results:

$$ClO_2 + 1.01(3)N_3^- \rightarrow 0.81(3)Cl^- + 0.20(1)ClO_2^- + 0.50(1)NO_3^- \quad (1)$$

Thus, ion chromatography shows mass balance for chlorine but not for nitrogen.

Gaseous products were examined by IR spectroscopy. A sample of 10 mL of 5.87×10^{-2} M N_3^- was mixed with 10 mL of 1.81×10^{-3} M ClO_2 in a 50-mL round-bottom flask and allowed to react. A component of the gas above the product solution was identified as N_2O by its three IR bands (590, 1300, and 2222 cm^{-1}).[22] The amount of N_2O produced was estimated by preparing a saturated solution of N_2O and diluting portions of it to 20 mL in the same apparatus as was used for the product study. IR absorbance measurements from these solutions were used to construct a calibration curve that was based on a solubility value of 2.4×10^{-2} M atm^{-1} for N_2O.[23] Under the above conditions the ratio of the moles of N_2O produced to the moles of ClO_2 consumed ($\Delta n_{N_2O}/\Delta n_{ClO_2}$) was 0.25 ± 0.02. In another experiment, when equal volumes of 3.75×10^{-3} M N_3^- and 1.54×10^{-3} M ClO_2 were mixed, the ratio was 0.20 ± 0.01. Thus, the yield of N_2O appears to be independent of the concentration of excess N_3^-. A complete summary of these stoichiometry results is given by

$$ClO_2 + 1.01(3)N_3^- \rightarrow 0.81(3)Cl^- + 0.20(1)ClO_2^- + 0.50(1)NO_3^- + 0.23(3)N_2O \quad (2)$$

The relationship between this (eq 2) and a balanced chemical equation is deferred to the Discussion.

Ion chromatography was also used to determine the stoichiometry of the reaction of ClO_2 with N_3^- in the presence of the spin trap PBN. A 25-mL sample containing 2.49×10^{-3} M of N_3^- and 5.25×10^{-3} M of PBN was mixed with a 25-mL sample containing 7.33×10^{-4} M of ClO_2 at room temperature. The only anionic product observed was ClO_2^-, the yield of Cl^- and NO_3^- being undetectably low. A quantitative determination of the consumption of N_3^- gave a value of 1.02(1) for $\Delta[N_3^-]/\Delta[ClO_2]$. Harbour and Issler[24] and Kalyanaraman et al.[25] observed by ESR that PBN reacts with N_3 to form a stable spin adduct ($PBNN_3$). Consequently, we infer that the overall stoichiometry in the presence of PBN is

$$PBN + ClO_2 + N_3^- \rightarrow ClO_2^- + PBNN_3 \quad (3)$$

Kinetics. The kinetics of the reaction of ClO_2 with excess N_3^- was investigated at natural pH (~7) in H_2O at 25 °C. It shows extreme deviations from pseudo-first-order behavior, appearing almost biphasic: with 0.1 M N_3^- and an initial ClO_2 concentration of 0.6 mM, the first half-life was 6 s, whereas the second was 50 s. An example of this behavior is shown in the main graph in Figure 1; because of the long time scale of the overall reaction, the first half-life is not even recorded. In the presence of ClO_2^-, the decay of ClO_2 was strongly inhibited. For example, when the reaction was conducted under the above conditions but in the presence of 0.01 M ClO_2^-, the first half-life increased from 6 to 1750 s. Under these conditions the general appearance of the decays was monophasic rather than biphasic. The decays could be fit with no simple-order expression, although they most closely resembled second order. In blank tests we found that there was no reaction between ClO_2 and ClO_2^- or between N_3^- and ClO_2^- at typical concentrations on the time frame of the above studies.

In the presence of the spin trap PBN, the reduction of ClO_2 by N_3^- is much faster and different in character. As shown in

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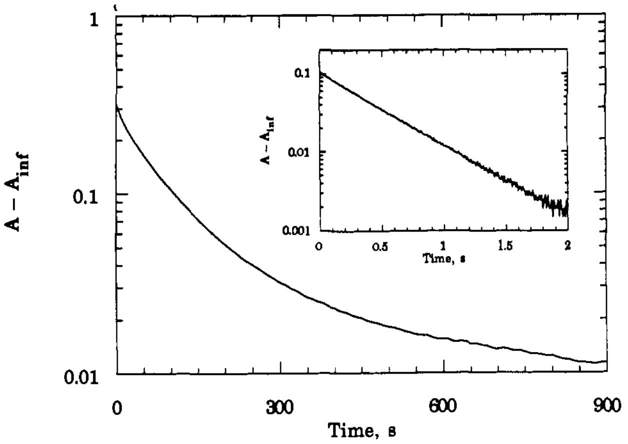

Figure 1. Semilog plots of $(A - A_\infty)$ at 360 nm as a function of time for the reaction of ClO_2 with excess N_3^- in water at 25 °C. Main figure has $[ClO_2]_0 = 6.0 \times 10^{-4}$ M and $[N_3^-] = 0.1$ M. Inset shows the effect of PBN: $[ClO_2]_0 = 8.0 \times 10^{-5}$ M, $[N_3^-] = 0.06$ M, $[ClO_2^-] = 0.01$ M, and $[PBN] = 9.3 \times 10^{-3}$ M.

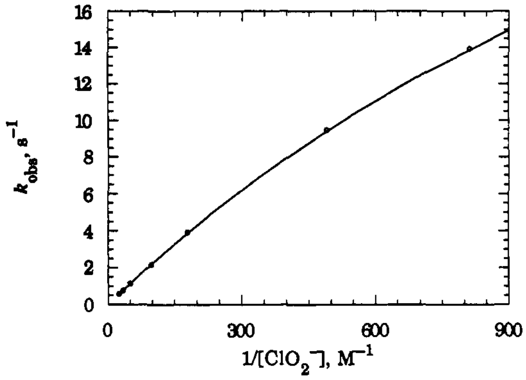

Figure 2. Plot of k_{obs} versus $1/[ClO_2^-]$ at 60 mM N_3^- and 9.3 mM PBN. Solid line is the fit according to eq 4 with parameters as specified in the text.

the inset in Figure 1, the reaction obeys pseudo-first-order kinetics under conditions of excess N_3^- and PBN. This effect is obviously not due to the much slower direct reaction of PBN with ClO_2, which has a pseudo-first-order rate constant of about 1×10^{-4} s^{-1} when 5×10^{-4} M ClO_2 is mixed with 1×10^{-3} M PBN. Values of k_{obs}, the pseudo-first-order rate constants for the reaction of ClO_2 with N_3^-, were quite sensitive to the concentrations of N_3^-, ClO_2^-, and PBN and have been summarized in Table I.

A plot of k_{obs} versus $[N_3^-]$ at constant [PBN] and $[ClO_2^-]$ is linear with a zero intercept, showing that the rate law is simply first order with respect to $[N_3^-]$. However, the dependences on [PBN] and $[ClO_2^-]$ are more complex. The rates generally increase with increasing [PBN] at constant $[N_3^-]$ and $[ClO_2^-]$, but a plot of k_{obs} versus [PBN] is not strictly linear; a plot of $1/k_{obs}$ versus 1/[PBN] is linear and has a nonzero intercept, which indicates that the rates are saturating with respect to [PBN]. ClO_2^- has a generally inhibitory effect, but curvature in the plot of k_{obs} versus $1/[ClO_2^-]$ (shown in Figure 2) indicates that the rate law is not simply inverse with respect to $[ClO_2^-]$. The correct dependence is shown in Figure 3, which is a plot of $1/k_{obs}$ versus $[ClO_2^-]$ that is linear and has a nonzero intercept. These considerations suggest that the rate law is

$$k_{obs} = \frac{k'[PBN][N_3^-]}{[PBN] + K'[ClO_2^-]} \qquad (4)$$

An excellent fit of the data in Table I was obtained with eq 4 and gave values of $k' = 809(9)$ M^{-1} s^{-1} and $K' = 19.0(2)$.

In some blank tests the effects of ionic strength and pH were investigated. The reaction of ClO_2 with 0.010 M N_3^- in the presence of 0.010 M ClO_2^- and 8.95 mM PBN at 25 °C had k_{obs} values of 0.367(2), 0.36(1), and 0.365(3) s^{-1} at $\mu = 0.20$, 0.10, and 0.020 M, respectively. Therefore, within experimental error the rate constants are not influenced by ionic strength. Studies of the pH dependence were conducted with 0.011 M ClO_2^-, 0.060 M N_3^-, and 9.3 mM PBN by use of sodium phosphate as a buffer. Under these conditions the pseudo-first-order rate constants were 2.188(7) and 2.20(1) s^{-1} at pH 6.8 and 8.0, respectively. These results indicate that the rates are independent of pH over the range studied.

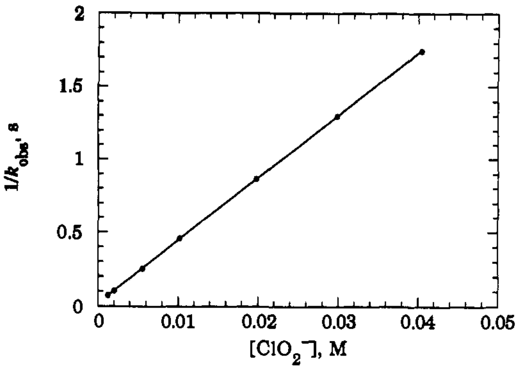

Figure 3. Plot of $1/k_{obs}$ versus $[ClO_2^-]$ in water at 25 °C. $[N_3^-] = 0.06$ M and $[PBN] = 9.3 \times 10^{-3}$ M at $\mu = 0.10$ M and $[ClO_2]_0 = 8 \times 10^{-5}$ M. Solid line is a linear least-squares fit.

Discussion

Mechanism with PBN. The reaction of azide with chlorine dioxide in aqueous media without PBN proceeds with complex kinetics and stoichiometry. In the presence of PBN the reaction is highly simplified. Since our understanding of the reaction in the presence of PBN places substantial constraints on models of the direct reaction, we first discuss the reaction in the presence of PBN.

A simple two-step mechanism is proposed for the reaction in the presence of PBN:

$$ClO_2 + N_3^- \rightleftharpoons ClO_2^- + N_3 \qquad k_1, k_{-1}, K_1 \qquad (5)$$

$$PBN + N_3 \rightarrow PBNN_3 \qquad k_2 \qquad (6)$$

This mechanism leads to a stoichiometry consistent with the experimental results in eq 3, and, if the steady-state approximation is applied to the concentration of the azidyl radical, then the derived rate law is

$$-\frac{d[ClO_2]}{dt} = \frac{k_1[PBN][N_3^-][ClO_2]}{[PBN] + (k_{-1}/k_2)[ClO_2^-]} \qquad (7)$$

This is equivalent to the observed rate law reported in eq 4, and thus we identify k' as k_1 and K' as k_{-1}/k_2. This mechanism and rate law are also consistent with the observed independence of the rates on ionic strength. Moreover, since HN_3 and $HClO_2$ have pK_a values of 4.4 and 1.8, respectively, the fact that the observed rates are constant over the pH range from 6.8 to 8.0 is as expected.

There is strong independent support for the above mechanism. From the published[26-28] reduction potentials of 0.934 V for the ClO_2/ClO_2^- couple and 1.33 V for the N_3/N_3^- couple, a value of 2.0×10^{-7} for K_1 (eq 5) can be calculated. By use of this result, the experimental value of k_1 obtained in this study, and the relationship $K_1 = k_1/k_{-1}$, a value of 4.0×10^9 M^{-1} s^{-1} for k_{-1} can

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be derived. Hence the rate constant for trapping of the azidyl radical by PBN, k_2, is 2.1×10^8 M^{-1} s^{-1}, which is an entirely reasonable result in view of PBN's use as a N_3 spin trap. Shoute et al.[18] investigated the reaction of ClO_2^- with N_3 by use of pulse radiolysis; they found that ClO_2 is produced in the reaction, and they used its absorbance to obtain values of 3.2×10^9 M^{-1} s^{-1} and 3.5×10^9 M^{-1} s^{-1} at 17 and 33 °C for k_{-1}. Merényi et al. using the same techniques obtained a value of 1.9×10^9 M^{-1} s^{-1} for k_{-1},[17] which is in reasonable agreement with that reported by Shoute et al. The agreement between this measured value for k_{-1} and our derived value is excellent, and it can be taken as proof that our measured value of $k'(k_1)$ corresponds to the rate constant for electron transfer between N_3^- and ClO_2.

The above mechanism is essentially the same as that proposed previously for the reactions of N_3^- with $IrCl_6^{2-}$, $IrBr_6^{2-}$, and $[Fe(bpy)_3]^{3+}$.[10] However, rate law 4 differs from that found for the coordination complexes, which was simply first order with respect to the concentrations of the oxidants and N_3^-. The difference arises for two reasons. One is that the reactions of the coordination complexes were conducted under saturating conditions, i.e., at low concentrations of the reduced complexes. The other is that k_{-1} is larger for the reaction of ClO_2 than it is for the reactions of the coordination compounds.

Mechanism without PBN. As can be seen from the products and from the kinetic behavior, the reaction between ClO_2 and N_3^- without PBN is much more complex than in the presence of PBN. Some degree of clarification can be achieved by examining the stoichiometry in more detail.

The results expressed in eq 2 do not achieve mass balance for nitrogen. However, as has been seen, for example, in the reaction of N_3^- with $IrCl_6^{2-}$, N_2 is a common product in oxidations of N_3^-.[10] It is reasonable to assume that N_2 is among the products of the reaction of N_3^- with ClO_2 (although we did not check for this possibility). With this assumption the overall reaction can be considered as the weighted sum of three limiting stoichiometries:

$$10ClO_2 + 10N_3^- + 4H_2O \rightarrow 10Cl^- + 8NO_3^- + 11N_2 + 8H^+ \quad (8)$$

$$8ClO_2 + 8N_3^- + H_2O \rightarrow 8Cl^- + 2NO_3^- + 11N_2O + 2H^+ \quad (9)$$

$$2ClO_2 + 2N_3^- \rightarrow 2ClO_2^- + 3N_2 \quad (10)$$

If these three reactions are combined so as to maintain the experimentally observed ratios of $\Delta[N_2O]/\Delta[NO_3^-] = 0.5$ and $\Delta[ClO_2^-]/\Delta[Cl^-] = 0.2$, then the overall stoichiometry is

$$ClO_2 + N_3^- + 0.278H_2O \rightarrow 0.833Cl^- + 0.167ClO_2^- + 0.555NO_3^- + 0.278N_2O + 0.943N_2 + 0.555H^+ \quad (11)$$

The coefficients in the above equation are reasonably close to the observed results given in eq 2.

The normal outcome of oxidation of N_3^- is quantitative formation of N_2.[10] However, more complex behavior is not unheard of. Pertinent examples include the reaction with potassium permanganate: as summarized by Audrieth, the products include N_2, O_2, and NO_3^-.[29] Thompson observed the formation of N_2 and N_2O from the reaction of bromate with hydrazoic acid,[30] and these products were seen in the reaction of HSO_5^- with azide.[31] The reaction of ozone with azide is reported to give N_2, N_2O, NO_3^-, and NO_2^- as products.[32]

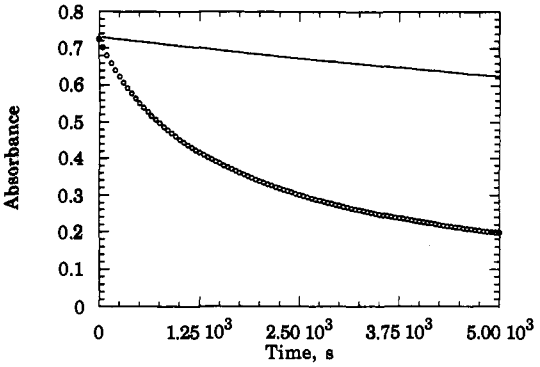

Figure 4. Plot of absorbance versus time for the reaction of ClO_2 with 0.1 M N_3^- in the presence of 0.01 M ClO_2^-: circles = experimental results; solid line = results from numerical integration assuming a mechanism with reversible electron transfer followed by self-reaction of N_3 (parameters as specified in the text).

Although reaction 10 is clearly insufficient to describe the overall reaction, we have used it as a starting point in developing a mechanism of the reaction. By analogy with the well-established oxidation of N_3^- by $IrCl_6^{2-}$,[10] reaction 10 would be expected to have the mechanism

$$ClO_2 + N_3^- \rightleftarrows ClO_2^- + N_3 \qquad k_1, k_{-1} \quad (12)$$

$$2N_3 \rightarrow 3N_2 \qquad k_3 \quad (13)$$

The present study provides a value of 809 M^{-1} s^{-1} for k_1. Values of 3×10^9 M^{-1} s^{-1} for k_{-1} and 4.5×10^9 M^{-1} s^{-1} for k_3 are available from pulse radiolysis studies.[17,18,33,34] These rate constants and eqs 12 and 13 were used as input in numerical integrations designed to simulate the observed kinetics. As shown in Figure 4, the predicted decay of ClO_2 is much slower than that observed experimentally. It can be concluded that kinetic inhibition by ClO_2^- of the above mechanism allows other pathways to become important. These other pathways would prevent ClO_2^- from exerting its full inhibitory effect, and they could provide routes to the additional products found.

Two classes of mechanisms can be envisioned that would meet these requirements. One would have N_3 react in some other way than with itself as in eq 13. The other would have ClO_2 reacting with N_3^- with a rate constant less than k_1 to give products other than those deriving from electron transfer.

Within the first class, the most likely possibility is that N_3 reacts with ClO_2 as in

$$N_3 + ClO_2 \rightarrow N_3ClO_2 \qquad k_4 \quad (14)$$

followed by

$$N_3ClO_2 + H_2O \rightarrow NO_2^- + N_2 + OCl^- + 2H^+ \qquad \text{fast} \quad (15)$$

and

$$N_3ClO_2 \rightarrow N_2O + NOCl \qquad \text{fast} \quad (16)$$

Subsequent reactions of NO_2^-, OCl^-, and NOCl would lead to the observed products.

The second class of mechanisms could begin with an oxygen atom transfer reaction as in

$$ClO_2 + N_3^- \rightarrow ClO + N_3O^- \qquad k_5 \quad (17)$$

ClO is known to be highly reactive and reacts rapidly with N_3^-.[35] There is some evidence that N_3O^- can exist, and that it is a good oxidant; this evidence comes from studies of the reactions of MnO_4^- and O_3 with N_3^-, in which product solutions are generated that have oxidizing properties.[29] N_3O^- would then react to give the observed species.

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In principle, the two mechanisms would lead to different kinetics, which would provide a means to distinguish between them. Numerical simulations of the first mechanism, consisting of eqs 12, 13, and 14, were fairly successful at reproducing the data in Figure 4 when a value of 1.5×10^5 M^{-1} s^{-1} was used for k_4. Similar investigations of the second mechanism (eqs 12, 13, and 17) showed that there is no value for k_5 that could lead to a decay having the proper time scale as well as the correct shape. These results appear to support the first mechanism. However, there are potential complications in these matters. One is that N_3 reacts with N_3^- to form N_6^- with an equilibrium constant of 0.33 M^{-1}.[36] Another is that subsequent reactions of the intermediates could consume additional ClO_2. For these reasons we do not feel confident in selecting one mechanism over the other.

Marcus Theory.[12,37,38] As discussed above, the weight of evidence strongly supports the assignment of k_1 as the rate constant of electron transfer between ClO_2 and N_3^-. The corresponding value of k_{-1}, 4×10^9 M^{-1} s^{-1}, is rather large, but perhaps less than the diffusion-controlled limit of 1.2×10^{10} M^{-1} s^{-1}. It is of interest to compare these results with the predictions of Marcus theory. The cross relationship of Marcus theory is particularly germane, because all of the parameters required are available from the literature, and because it provides an estimate of k_1 under the assumption that electron transfer is the rate-limiting step. The usual form of the cross relationship is given as

$$k_{12} = \sqrt{(k_{11}k_{22}K_{12}f)} \tag{18}$$

$$\ln(f) = \frac{(\ln K_{12})^2}{4\ln(k_{11}k_{22}/Z^2)} \tag{19}$$

In the present case k_{12} is k_1, K_{12} is the equilibrium constant for the electron-transfer reaction (K_1), k_{11} and k_{22} are the self-exchange rate constants for the ClO_2/ClO_2^- and N_3/N_3^- couples, and Z is the collision rate, taken as 1×10^{11} M^{-1} s^{-1}. Work terms are omitted because in all reactions (both forward and reverse) one of the reactants is uncharged. As noted above, a value for K_{12} of 2×10^{-7} can be calculated from the pertinent reduction potentials. Values of $k_{11} = 200$ M^{-1} s^{-1} and $k_{22} = 4 \times 10^4$ M^{-1} s^{-1} are available from studies in which they were determined by applying the Marcus cross relationship to reactions of ClO_2^- and N_3^- with substitution-inert coordination compounds.[10,13] With use of these data a calculated value of $k_1 = 0.62$ M^{-1} s^{-1} is obtained, which is about a factor of 1000 less than observed.

Deviations of this sort for main-group/main-group electron-transfer reactions have been observed in *every* case where comparisons have been made between measured rate constants and those deduced from the Marcus cross relationship. There are four such cases: (1) the present reaction. (2) The cross reaction of NO_2^- with ClO_2 has a rate constant of 153 M^{-1} s^{-1}, but a value of 0.2 M^{-1} s^{-1} was derived from the Marcus cross relationship on the basis of self-exchange rate constants that were obtained by applying the cross relationship to reactions with coordination complexes.[16] (3) The self-exchange reaction of NO_2 with NO_2^- has a rate constant of 580 M^{-1} s^{-1}, but a value 0.3 M^{-1} s^{-1} was inferred from cross reactions with coordination complexes.[6,14] (4) The self-exchange reaction of O_2 with O_2^- has a rate constant of 450 M^{-1} s^{-1}, but that inferred from cross reactions was 2 M^{-1} s^{-1}.[7,15,17] These four sets of comparisons reveal a consistent pattern in which the experimental rate constants exceed the calculated rate constants by a factor of about 1000. A plausible explanation for this behavior is that there is strong orbital overlap in the transition states for the measured reactions, which reduces the barrier relative to that implicit in the Marcus model. Another explanation, suggested in qualitative terms by Lind et al., and more quantitatively by Merényi et al., is that applying the Marcus cross relationship to reactions between small molecules and coordination complexes leads to systematic errors because of "solvent nonadditivity".[15,17]

Lind et al.[15] and Merényi et al.[17] cited Eberson's book[39] in explanation of solvent nonadditivity, but the book is not clear as to the origins of the concept. The actual source is eq 93 of a paper by Marcus.[12] According to Marcus, the cross relationship is derived under the approximation that

$$\lambda_{o,12} = {}^1/_2(\lambda_{o,11} + \lambda_{o,22}) \tag{20}$$

i.e., that the solvent reorganizational barrier for the cross reaction can be taken as the average of the barriers for the two self-exchange reactions. If the fractional error, y, introduced by this approximation is defined as

$$y = \frac{\lambda_{o,12} - {}^1/_2(\lambda_{o,11} + \lambda_{o,22})}{\lambda_{o,11}} \tag{21}$$

then according to Marcus it can be calculated by the simple relationship

$$y = \left(1 - \frac{r_1}{r_2}\right)^2 \Big/ 2\left(1 + \frac{r_1}{r_2}\right) \tag{22}$$

where r_1 and r_2 are the radii of the two reactants.

We have developed a method that uses eqs 21 and 22 to correct results obtained by applying the traditional Marcus cross relationship (eqs 18 and 19). We start with the general equations of Marcus

$$\Delta G^*_{12} = \frac{1}{4}\lambda_{12}\left[1 + \frac{\Delta G^\circ_{12}}{\lambda_{12}}\right]^2 \tag{23}$$

and

$$k_{12} = Z\exp(-\Delta G^*_{12}/RT) \tag{24}$$

We now define ΔG^*_{er} by the equation

$$4\Delta G^*_{er} = \lambda_{o,12} - {}^1/_2(\lambda_{o,11} + \lambda_{o,22}) \tag{25}$$

and thus

$$y = 4\Delta G^*_{er}/\lambda_{o,11} = \Delta G^*_{er}/\Delta G^*_{o,11} \tag{26}$$

It is customary to separate the inner- and outer-shell contributions as in

$$\lambda_{12} = \lambda_{in,12} + \lambda_{o,12} \tag{27}$$

and to approximate $\lambda_{in,12}$ as ${}^1/_2(\lambda_{in,11} + \lambda_{in,22})$. Combining this approximation with eqs 25 and 27 leads to

$$\lambda_{12} = {}^1/_2(\lambda_{11} + \lambda_{22}) + 4\Delta G^*_{er} \tag{28}$$

When this is inserted into eq 23, the result is

$$\Delta G^*_{12} = \frac{1}{2}[\Delta G^*_{11} + \Delta G^*_{22} + \Delta G^\circ_{12}] + \Delta G^*_{er} + \left[\frac{(\Delta G^\circ_{12})^2}{8(\Delta G^*_{11} + \Delta G^*_{22}) + 16\Delta G^*_{er}}\right] \tag{29}$$

so that

$$k_{12} = \sqrt{(k''_{11}k_{22}K_{12}f'')} \tag{30}$$

$$\ln(f'') = \frac{(\ln K_{12})^2}{4\ln(k''_{11}k_{22}/Z^2)} \tag{31}$$

and

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$$k''_{11} = Z \exp\left(\frac{-(\Delta G^*_{\mathrm{in},11} + \Delta G^*_{\mathrm{o},11} + 2\Delta G^*_{\mathrm{er}})}{RT}\right) \quad (32)$$

Equation 32 shows that the values of k_{11} that have been evaluated previously by applying the usual Marcus cross relationship to reactions with coordination compounds are in error and are actually values of k''_{11}. Corrected values of k_{11} can be derived from reported values of k''_{11} by using eq 32 to calculate the sum of $\Delta G^*_{\mathrm{in},11} + \Delta G^*_{\mathrm{o},11} + 2\Delta G^*_{\mathrm{er}}$. The value of $\Delta G^*_{\mathrm{in},11}$ (estimated elsewhere) is subtracted from this sum to obtain $\Delta G^*_{\mathrm{o},11} + 2\Delta G^*_{\mathrm{er}}$; the corresponding value of y (calculated from eq 22) is substituted into eq 26, which leads to a pair of simultaneous equations with $\Delta G^*_{\mathrm{o},11}$ and ΔG^*_{er} as unknowns. By solving this pair of equations a value of $\Delta G^*_{\mathrm{o},11}$ is obtained, so that finally k_{11} is calculated by

$$k_{11} = Z \exp(-(\Delta G^*_{\mathrm{o},11} + \Delta G^*_{\mathrm{in},11})/RT) \quad (33)$$

Application of the above equations to the reactions of ClO_2 and of N_3^- is as follows. We use a value of 13.36 kJ mol^{-1} for $\Delta G^*_{\mathrm{in},11}$ for the ClO_2/ClO_2^- system, which was estimated in a previous study by use of the known geometries and vibrational force constants of ClO_2 and ClO_2^-.[13] As is shown in Table II, there are three reactions of coordination complexes with the ClO_2/ClO_2^- system that are pertinent, and literature values of k''_{11} are available for these three reactions. By use of the above equations and estimated values of r_1 and r_2, the tabulated values of k_{11} and ΔG^*_{er} have been obtained. This procedure leads to values of k_{11} that are significantly greater and are somewhat more self-consistent than the original k''_{11} values. The average value of k_{11} so obtained is 3.3×10^4 M^{-1} s^{-1}.

In the case of the N_3/N_3^- system, structures of both N_3 and N_3^- are available from high-resolution gas-phase spectroscopy. The azide anion has the same symmetry ($D_{\infty h}$) as the azidyl radical, and the bond lengths differ by only 0.0073 Å.[40,41] Therefore, $\Delta G^*_{\mathrm{in},22}$ for the N_3/N_3^- system is approximated as zero. Results of the ensuing corrections are shown in Table III. Here too, the corrections lead to greater and more consistent values of k_{22}, and an average of 3.7×10^6 M^{-1} s^{-1} is obtained for this parameter; this result is our best current estimate, although the scatter in the data suggests that it has considerable latitude for refinement.

We believe that these corrected self-exchange rate constants more accurately reflect the intrinsic rate constants than the uncorrected rate constants. They should be appropriate in calculating the rate of outer-sphere electron transfer from N_3^- to ClO_2 by use of the simple Marcus cross relation (eqs 18 and 19) because these reactants are of similar size. This calculation leads to a value of 56 M^{-1} s^{-1} for k_{12}. This is much closer to the experimentally obtained value of 809 M^{-1} s^{-1} than was the value obtained without correction (0.62 M^{-1} s^{-1}). The agreement between the experimental and corrected-Marcus results is close enough to suggest that the electron-transfer reaction between N_3^- and ClO_2 may be reasonably modelled by an outer-sphere mechanism. The residual discrepancy may be due to a degree of strong overlap (inner-sphere mechanism), but it is not large enough to merit further discussion until a more reliable value of k_{22} becomes available.

Table II. Corrected Self-Exchange Rate Constant for ClO_2/ClO_2^- Couple

oxidant	r,[a] Å	k''_{11},[a] M^{-1} s^{-1}	ΔG^*_{er},[b] kJ	k_{11},[b] M^{-1} s^{-1}
$IrCl_6^{2-}$	4.4	1.1×10^3	3.9	2.6×10^4
$[Co(terpy)_2]^{2+}$	6.0	2.4×10^2	5.6	2.1×10^4
$[Fe(phen)_3]^{2+}$	6.0	1.0×10^2	6.2	6.7×10^4

[a] From ref 13. [b] Calculated as described in text, using $r_{ClO_2} = 1.5$ Å;[13] avg $k_{11} = 3.3 \times 10^4$ M^{-1} s^{-1}.

Table III. Corrected Self-Exchange Rate Constant for N_3/N_3^- Couple

oxidant	r,[a] Å	k''_{22},[a] M^{-1} s^{-1}	ΔG^*_{er},[b] kJ	k_{22},[b] M^{-1} s^{-1}
$IrCl_6^{2-}$	4.4	1.4×10^6	2.4	9.3×10^6
$[Fe(bpy)_3]^{3+}$	6.0	5.0×10^4	4.6	1.6×10^6
$IrBr_6^{2-}$	4.7	1.4×10^4	3.7	2.7×10^5

[a] Data from ref 10. [b] Calculated as described in text using $r_{N_3} = 2.0$ Å;[42,43] avg value of $k_{22} = 3.7 \times 10^6$ M^{-1} s^{-1}.

Table IV. Corrected Self-Exchange Rate Constant for NO_2/NO_2^- Couple

oxidant	r,[a] Å	k''_{33},[a] M^{-1} s^{-1}	ΔG^*_{er},[b] kJ	k_{33},[b] M^{-1} s^{-1}
$[Fe(tmp)_3]^{3+}$	6.5	0.81	4.0	21
$[Fe(bpy)_3]^{3+}$	6.0	0.18	4.3	5.7
$Fe(CN)_6^{3-}$	4.5	0.12	3.2	1.6
$IrCl_6^{2-}$	4.4	0.21	3.0	2.3
$Ru(CN)_6^{3-}$	4.7	0.55	3.0	6.3
$[Ni(tacn)_2]^{3+}$	3.8	5.1	1.7	21

[a] All data from ref 6 and references therein. [b] Calculated as described in text, using $r_{NO_2} = 1.9$ Å;[13] avg value of $k_{33} = 9.6$ M^{-1} s^{-1}.

To test further our method of correcting for size differences, similar calculations were performed for reactions involving the NO_2/NO_2^- redox couple. We used a value for $\Delta G^*_{\mathrm{in},33}$ of 34.3 kJ mol^{-1}, which was estimated in prior work by use of known structures and force constants.[13] The original and corrected self-exchange rate constants are listed in Table IV, and lead to an average effective self-exchange rate constant of 9.6 M^{-1} s^{-1}. Once again, the corrected rate constants are larger and more self-consistent than the uncorrected rate constants. An experimentally measured self-exchange rate constant of 580 M^{-1} s^{-1} has been reported.[14] Thus the process of correcting the effective self-exchange rate constants leads to greater agreement between the experimental and calculated rate constants. When the experimentally measured NO_2/NO_2^- self-exchange rate constant was first published, it was compared with a value of 0.02 M^{-1} s^{-1} that had been derived from the uncorrected Marcus formalism.[14] The large discrepancy was attributed to strong overlap (an inner-sphere mechanism) occurring in the direct self-exchange reaction. In a subsequent publication, the Marcus-derived rate constant was adjusted upward to 0.3 M^{-1} s^{-1}, primarily because of an improvement in the value of $E°$ used for the NO_2/NO_2^- couple.[6] Our present calculations lead to yet another upward adjustment to the calculated rate constant; it is no longer clear that the discrepancy between it and the experimental self-exchange rate constant can be attributed to strong overlap. We must seriously consider the possibility that complete agreement could be obtained with further refinements (perhaps by improving the solvation model or by including nuclear tunneling).

Another comparison concerns the rate of electron transfer from NO_2^- to ClO_2. The experimental rate constant is 153 M^{-1} s^{-1},[16] and that calculated by applying the Marcus relation to the above-corrected self-exchange rate constants is 50 M^{-1} s^{-1}. This is a great improvement relative to the value of 0.2 M^{-1} s^{-1} previously obtained from the Marcus relation.

Similar conclusions have been reached regarding reactions involving the O_2/O_2^- redox couple.[15,17]

The above discussion shows that solvent nonadditivity must be taken into account in applying Marcus theory to reactions between molecules of widely disparate size. Moreover, when this is done, the calculations can provide a reasonable base-line estimate for outer-sphere electron-transfer rate constants between small molecules. While such calculations will never be sufficient to provide unambiguous evidence for an outer-sphere mechanism, they should prove useful in signaling anomalous reactions.

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Conclusions

In the absence of spin traps, the reaction of ClO_2 with N_3^- is strongly inhibited by ClO_2^- because of rapid back-electron transfer; this leads to additional mechanistic pathways, complex kinetics, and an unusual set of products. By use of spin traps to scavenge N_3, the effects of back-electron transfer can be eliminated, which enables measurement of the rate of electron transfer from N_3^- to ClO_2. This deduction receives strong support from pulse-radiolysis studies of the reverse process.

Effective self-exchange rate constants have been deduced previously for the component redox couples by applying the simple Marcus cross relation to reactions of these species with coordination complexes. Rather poor agreement is obtained when these effective self-exchange rates are used with the Marcus relation to estimate the rate of electron transfer from N_3^- to ClO_2. Part of the disagreement stems from an approximation in the Marcus relation regarding additivity of the solvent barrier. This approximation breaks down significantly for reactions between small molecules and coordination complexes, where the radius ratio can exceed 4. Correcting for this effect leads to much improved correlation between theory and experiment for electron transfer from N_3^- to ClO_2, from NO_2^- to NO_2, and from NO_2^- to ClO_2.

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