

Slow Electron Transfer between Main-Group Species: Oxidation of Nitrite by Chlorine Dioxide

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A detailed study of the reaction of ClO₂ with NO₂⁻ in aqueous media has been carried out. With excess NO₂⁻ the reaction gives ClO₂⁻ and NO₃⁻ as products; ClO₂⁻ reacts with NO₂⁻ to give Cl⁻ and NO₃⁻ in a slower phase. The rate law for the first phase is first order with respect to both [ClO₂] and [NO₂⁻], with $k = 153 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, $\Delta H^\ddagger = 56.5 \pm 1.1 \text{ kJ mol}^{-1}$, and $\Delta S^\ddagger = -14 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$. ClO₂⁻ inhibits the rate of the reaction, and its effect has been modeled by a mechanism involving reversible electron transfer to form NO₂ and ClO₂⁻ as primary products, followed by disproportionation of NO₂. The electron-transfer rate constant, although much less than diffusion controlled, is 3 orders of magnitude greater than that predicted by the cross relationship of Marcus' theory, implying a strong-overlap mechanism.

Introduction

Electron-transfer reactions involving simple main-group compounds have been a topic of longstanding interest in our laboratories. The general approach that has been taken is to investigate reactions between substitution-inert coordination complexes and the main-group substrates. The value of the approach is that the reactivity of the coordination complexes is well-known, which means that only one partner in the reaction, the main-group species, has largely unknown properties. By use of these methods it has been possible to determine the one-electron-reduction potentials for species such as N₃, NO₂, and I.¹⁻³ It has also been shown that the rates of reactions involving couples such as SO₂/SO₂⁻,⁴ N₃/N₃⁻,¹ NO₂/NO₂⁻,⁵ and ClO₂/ClO₂⁻⁶ may be discussed profitably in terms of Marcus' theory of electron transfer. There are many cases in which the rates exceed the predictions of Marcus' theory, and these can usually be attributed to significant bonding between the reactants in the transition state. There are also a few cases that are anomalously slow, especially for the O₂/O₂⁻ system, and these are still not fully understood.⁷ Nevertheless, the situation has now advanced to the stage that many reactions appear to be consistent with Marcus' theory, and effective self-exchange rate constants have been assigned to several main-group redox couples.

Considerably less effort has been directed at investigating the rates of electron-transfer reactions between two main-group redox couples. The accumulation of data from the studies of reactions between coordination complexes and main-group species mentioned above has finally reached the stage where such studies can be meaningful. These reactions may differ from those involving coordination complexes because the redox orbitals of main-group species are not protected by a ligand sphere, and so there is ample opportunity for strong orbital overlap between the reactants. A possible outcome of this situation is that all such reactions will have essentially no kinetic barrier and proceed at diffusion-controlled rates. Indeed, there are many examples where this is the situation. To our knowledge there is no report of a reaction between two main-group species for which both the reduction potentials and self-exchange rate constants have been reported, for which the rate constant is substantially less than diffusion controlled (i.e. less than $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), and for which an electron-transfer mechanism has been established.

This paper reports on the reaction between ClO₂ and NO₂⁻ in aqueous media, which may reasonably be anticipated to involve electron transfer to generate ClO₂⁻ and NO₂. In a brief investigation of this reaction it was reported that the rate constant is $110 \text{ M}^{-1} \text{ s}^{-1}$, i.e., much less than that for a diffusion-controlled reaction.⁸ Since reduction potentials for both ClO₂ and NO₂ are known, and since effective self-exchange rate constants for both redox couples have been reported, the reaction is a candidate in the search for main-group electron-transfer reactions having

significant kinetic barriers. The present study is more extensive than the prior report, including an investigation of the products, a determination of the activation parameters, and the detection of kinetic inhibition by ClO₂⁻.

Experimental Section

NaNO₂ (MCB) was recrystallized twice from a hot 50% aqueous ethanol mixture. The crystals were washed sparingly with cold 95% ethanol, dried overnight in an Abderhalden pistol, and stored in a vacuum desiccator. NaClO₄ was prepared by neutralization of HClO₄ (Baker) with Na₂CO₃ (Baker) and recrystallization twice from hot water. NaClO₂ (Kodak) was recrystallized by adding 15 g of NaClO₂ to 10 mL of H₂O at 38 °C and allowing the mixture to cool to 25 °C. All solutions were made with distilled deionized water. Purified Na₄P₂O₇·10H₂O crystals were available from a previous investigation.⁵ Solutions of ClO₂ were prepared from NaClO₂ and K₂S₂O₈ as previously described⁹ and were protected from light.

Solutions of NaNO₂ were prepared by weight, as standardization with ferrous ammonium sulfate showed this to be sufficiently accurate. ClO₂ solutions were standardized by spectrophotometry on a Cary 210 UV-vis spectrophotometer at 360 nm assuming $\epsilon = 1200 \text{ M}^{-1} \text{ cm}^{-1}$.⁶ NaClO₄ solutions were standardized by passing an aliquot down a Dowex 50W-X8 cation exchange column in the H⁺ form and titrating with standard NaOH.

Fast-kinetics studies were performed on an Aminco-Morrow stopped-flow instrument as previously described,^{6,9} while the slower reactions were monitored on the Cary 210. Product analyses were performed on a Wescan ion analyzer as previously described.¹ The eluent was a phosphate buffer at pH 3.2 at $5 \times 10^{-3} \text{ M}$.

For the reactions at pH > 3 with no added ClO₂⁻ good pseudo-first-order kinetics was observed. Semilog plots of the time-dependent absorbances, which were linear for at least 3 half-lives, were used to obtain the observed rate constants. In the studies with added ClO₂⁻ the potential effects of the direct reaction of ClO₂⁻ with NO₂⁻ were minimized by mixing solutions of NO₂⁻ with solutions of ClO₂ plus ClO₂⁻. When the reactions were conducted with [NO₂⁻] > $4 \times 10^{-2} \text{ M}$, departure from the first-order dependence on [NO₂⁻] was seen. Under these conditions the order with respect to [NO₂⁻] was substantially greater than unity, and the absorbance changes were significantly less than expected, as though there were a rapid prior consumption of ClO₂. Detailed investigation of these effects was hampered by the large and increasing absorbance due to NO₂⁻; however, some blank tests were run that showed the effect to be independent of the observation wavelength, slit width, pH, buffer

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[†] Portions of this research were conducted at Rice University.

Table I. Kinetics Data from the Reaction of ClO₂ with NO₂^{-a}

[NO ₂ ⁻], M	k _{obs} , s ⁻¹	T, °C	[NO ₂ ⁻], M	k _{obs} , s ⁻¹	T, °C
0.0040	0.55	25.0	0.072	14.8	25.0
0.0060	0.83	25.0	0.080	17.2	25.0
0.0080	1.15	25.0	0.010	1.49 ^b	25.0
0.010	1.45	25.0	0.020	1.12 ^b	13.2
0.020	2.9	25.0	0.020	1.28 ^b	15.8
0.032	4.9	25.0	0.020	2.95 ^b	25.3
0.040	6.6	25.0	0.020	4.39 ^b	29.9
0.052	8.7	25.0	0.020	6.45 ^b	35.1
0.060	10.8	25.0	0.020	8.86 ^b	39.9

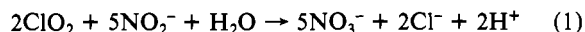
^a [ClO₂]₀ = 4.3 × 10⁻⁴ M, μ = 0.2 M (NaClO₄), 1 mM P₂O₇⁴⁻ buffer, pH 6.0, 1.0-cm path length. ^b [ClO₂]₀ = 2.6 × 10⁻⁴ M, μ = 0.5 M, pH 6.5.

concentration, and added NO₃⁻, Cl⁻, or O₂.

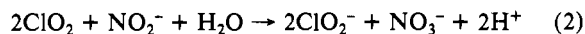
The second-order rate constant, activation parameters, and standard deviations were calculated by using the Los Alamos nonlinear least-squares program. Numerical integrations were performed by using Hindmarsh and Byrne's subroutine EPISODE (Lawrence Livermore Laboratory, 1977). All calculations were performed on a Macintosh Plus computer.

Results

Stoichiometry. In the prior study of the reaction between NO₂⁻ and ClO₂ no results were reported concerning the products.⁸ In the present study the stoichiometry was examined by use of single-column anion chromatography with conductivity and amperometric detection. In one set of experiments a mixture of 8 × 10⁻⁴ M NaNO₂ and 5 × 10⁻⁴ M ClO₂ was prepared and injected into the chromatograph after various time intervals. The first chromatogram showed formation of 2.3 × 10⁻⁴ M ClO₂⁻ and a corresponding amount of NO₃⁻. In subsequent chromatograms the ClO₂⁻ peak diminished, the NO₃⁻ peak increased, and a Cl⁻ peak appeared. In a second set of experiments at 5 × 10⁻³ M NaNO₂ and 5 × 10⁻⁴ M ClO₂ the first chromatogram showed only a small amount of ClO₂⁻ but substantial amounts of Cl⁻ and NO₃⁻. In subsequent chromatograms ClO₂⁻ was absent and the NO₃⁻ peak attained a stable intensity. Quantitative comparison of the peak heights with those of standard solutions indicated that the stoichiometry at long times is given as



It is apparent that ClO₂⁻ is formed at shorter times but that it reacts with NO₂⁻ on a longer time-scale to give the above stoichiometry. We can infer that at short times the stoichiometry is given by



The reaction of NO₂⁻ with ClO₂⁻ has recently been discussed by Beck and co-workers.¹⁰ Its rate law shows catalysis by H⁺ and Cl⁻. This behavior is consistent with our observations. Since our stoichiometry studies were performed with unbuffered solutions, and since H⁺ is a product in both reactions 1 and 2, we may assume that, under the buffered conditions of the kinetics studies described below, reaction 2 properly describes the process studied.

Kinetics. The kinetics of the reaction between NO₂⁻ and ClO₂ was studied at μ = 0.2 and 0.5 M (NaClO₄), 25 °C. Solutions were buffered with 1 mM P₂O₇⁴⁻, and the conditions generally held NO₂⁻ in large excess. The reactions were monitored by stopped-flow methods by observing the loss of absorbance due to ClO₂. These were best observed at 360 nm, but at high concentrations of NO₂⁻ the background absorbance of NO₂⁻ was so high that results were determined at 394 nm. Under most conditions excellent pseudo-first-order behavior was obtained; the data are listed in Table I. The reaction demonstrated an excellent first-order dependence on [NO₂⁻] over the range from 4 to 40 mM. The rate of the reaction was independent of pH over the range from pH 7.5 to 4.9. It was not affected by ionic strength over the range 0.2–0.5 M, and additions of 1 mM ClO₃⁻, 1 mM Cl⁻,

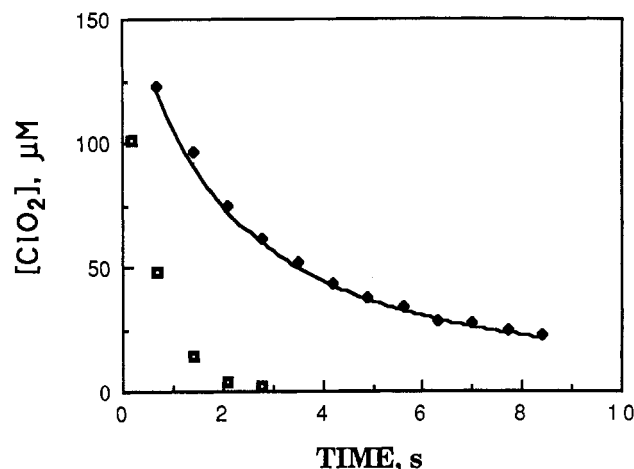


Figure 1. [ClO₂] as a function of time in the reaction with NO₂⁻, illustrating the effect of ClO₂⁻. The solid diamonds are experimental data under the conditions of [ClO₂]₀ = 1.67 × 10⁻⁴ M, [NO₂⁻] = 0.01 M, [ClO₂⁻] = 0.025 M, 25 °C, μ = 0.5 M (NaClO₄), pH 6.4, and 1 mM P₂O₇²⁻ as buffer. The open squares are experimental data under identical conditions except that there is no ClO₂⁻ initially in the mixture. The solid line is a simulation of the reaction with added ClO₂⁻ according to the mechanism and rate constants discussed in the text.

or 1 mM NO₃⁻ had no effect. Thus under these conditions the rate law is simply

$$-d[\text{ClO}_2]/dt = k[\text{ClO}_2][\text{NO}_2^-] \quad (3)$$

with $k = 153 \pm 4 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0 °C. The temperature dependence of the kinetics was determined over the temperature range from 13 to 40 °C at pH 6.5 with [NO₂⁻] = 0.020 M, [ClO₂]₀ = 2.6 × 10⁻⁴ M, and μ = 0.46 M. The data, when treated according to the Eyring equation, gave $\Delta H^\ddagger = 56.5 \pm 1.1 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -14 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$.

The prior study of this reaction⁸ reported pseudo-first-order kinetics with NO₂⁻ in excess over the range [NO₂⁻] = 0.09–1.1 mM. A first-order dependence on [NO₂⁻] was found over this range, and the rates were found to be independent of pH over the range from 10 to 4. A value of 110 M⁻¹ s⁻¹ was reported for the rate constant; the mild discrepancy from our result is not disturbing because the temperature was not specified in the prior study. In conclusion, insofar as our experiments overlap with the prior study, they are in agreement.

The effect of added ClO₂⁻ on the kinetics of the reaction between ClO₂ and NO₂⁻ was significant. A series of experiments was conducted at μ = 0.5 M, [NO₂⁻] = 0.010 M, and [ClO₂]₀ = 2.8 × 10⁻⁴ M with varying concentrations of ClO₂⁻. Under these conditions the semilog plots were nonlinear, showing curvature characteristic of a reaction order greater than unity. Pseudo-first-order rate constants extracted from the initial portions of these curves decreased with increasing concentration of ClO₂⁻, with values of 0.95, 0.35, 0.092, and 0.069 s⁻¹ for [ClO₂⁻] = 0.0063, 0.025, 0.05, and 0.10 M, respectively. These results may be compared with the pseudo-first-order rate constant of 1.4 s⁻¹ that is obtained under these conditions without added ClO₂⁻. A typical example illustrating the inhibitory effect of ClO₂⁻ is presented in Figure 1. The direct reaction of ClO₂⁻ with NO₂⁻, as noted above, is catalyzed by Cl⁻ and H⁺, and so with proper buffering and the low [Cl⁻] present in the reactant solutions, the ClO₂⁻/NO₂⁻ reaction is not a problem. Thus, the kinetic inhibition by ClO₂⁻ is mechanistically significant.

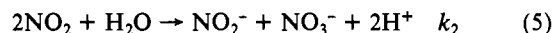
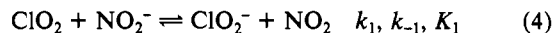
Qualitatively different behavior was observed in acidic media. In a series of experiments at pH 2.0 with [ClO₂]₀ = 3 × 10⁻⁴ M and [N(III)] varying between 8.0 × 10⁻³ and 4.0 × 10⁻² M, the loss of ClO₂ occurred with zero-order kinetics. Although the data were not of high quality, there appeared to be a second-order dependence on [N(III)] with a rate constant of about 20 M⁻¹ s⁻¹. It was clear that these results were due to the chemistry of nitrous acid, presumably reflecting the rate-limiting second-order de-

composition of HNO_2 to produce NO and NO_2 ,² the studies were not pursued further.

At concentrations of NO_2^- higher than 0.040 M there were deviations to higher rates. These observations are not understood and are described in the Experimental Section.

Discussion

The first stage in the reaction of ClO_2 with NO_2^- , when the concentrations of NO_2^- , ClO_2^- , and H^+ are not too high, yields of NO_3^- and ClO_2^- according to reaction 2 with simple mixed second-order kinetics. The kinetic inhibition at higher concentrations of ClO_2^- is taken as an important clue to the reaction mechanism. The mechanism we propose is given as



which is analogous to the mechanism previously proposed for the reaction of $[\text{Fe}(\text{TMP})_3]^{3+}$ (TMP = 4,5,7,8-tetramethylphenanthroline) with NO_2^- .⁵ Disproportionation of NO_2 as in reaction 5 is well established, having a rate constant of $5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ as the presently accepted value.¹¹ Thus, k_2 is sufficiently rapid to ensure that the steady-state approximation is valid. Unfortunately, the steady-state solution is a complicated quadratic function that cannot be linearized. Under conditions of low $[\text{ClO}_2^-]$ the reverse step, k_{-1} , can be neglected, and this leads to the observed rate law in eq 3, with $k = k_1$.

The observed kinetic inhibition by ClO_2^- can be treated as follows. Reduction potentials for ClO_2 and NO_2 are currently recognized to have values of 0.934 and 1.04 V, respectively.¹² These potentials lead to a value of 1.6×10^{-2} for the equilibrium constant K_1 . From the relationship $K_1 = k_1/k_{-1}$ our values for K_1 and k_1 lead to a value of $9.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for k_{-1} , which is probably accurate within a factor of 2. The differential equations arising from reactions 4 and 5 were solved by numeric integration, and the experimental results were adequately reproduced when the rate constants cited above were used. A slightly better fit was obtained by adjusting the value of k_{-1} to $7.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, which is well within the uncertainty of our estimate. Figure 1 illustrates such a simulation as a solid curve that accurately overlies the experimental results. Analysis of the results from the numerical integrations showed that at high concentrations of ClO_2^- the rate law can be fairly closely approximated by assuming that the electron-transfer step occurs as a rapid preequilibrium prior to disproportionation; however, at the lower concentrations of ClO_2^- the preequilibrium approximation breaks down and the numerical method is required. In conclusion, strong support for the proposed mechanism and derived rate constants can be inferred from the success of these simulations in reproducing the real data.

From the above arguments it is clear that the second-order rate constant determined under conditions of low $[\text{ClO}_2^-]$ is the rate constant of an electron-transfer process between ClO_2 and NO_2^- . Further support for this deduction comes from the activation parameters. For an adiabatic electron-transfer reaction involving at least one uncharged reactant, it is expected that the entropy of activation will be close to zero; the experimental value of $-14 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$ is reasonably close to expectations.

It is fairly rare for reactions between main-group compounds to be demonstrated to proceed by an electron-transfer mechanism. Two other processes that can occur in reactions between main-group compounds are adduct formation and atom transfer. For example, O_2 adds to SO_3^{2-} ,¹³ and it has been argued that NO_2 reacts with SO_3^{2-} by oxygen atom transfer.¹⁴ It is of some interest to examine in terms of Marcus' theory those reactions that have been shown to proceed by an electron-transfer mechanism for which electron self-exchange rate constants have been estimated.

The list of main-group redox couples for which self-exchange rate constants have been estimated presently includes O_2/O_2^- ,⁷ $\text{HO}_2/\text{HO}_2^-$,¹⁵ $\text{ON}(\text{SO}_3)_2^{2-}/\text{ON}(\text{SO}_3)_2^{3-}$,¹⁶ $\text{NO}_2/\text{NO}_2^-$,⁵ $\text{ClO}_2/\text{ClO}_2^-$,⁶ $\text{SO}_2/\text{SO}_2^-$,⁴ $\text{SO}_3^-/\text{SO}_3^{2-}$,¹⁴ N_3/N_3^- ,¹ $\text{CO}_2/\text{CO}_2^-$,¹⁷ $\text{Cl}_2/\text{Cl}_2^-$,¹⁸ $\text{Br}_2/\text{Br}_2^-$,¹⁸ I_2/I_2^- ,¹⁹ and I/I^- .²⁰ The matrix of reactions between these couples has 169 rate constants, of which 13 are self-exchange rate constants that have been inferred but never measured. Of the remaining 156, half are related to the other half by the principle of microscopic reversibility, which leads to 78 unique cross-reactions. Of those that may proceed by electron transfer, many have rate constants in either the forward or reverse direction that are close to diffusion controlled and that are therefore not particularly good tests of the Marcus cross relationship.

There are five cross-reactions that bear closer scrutiny in terms of the cross relationship of Marcus' theory. One of these is the reaction of ClO_2 with HO_2^- , which was studied in a pulse radiolysis experiment by monitoring the loss of ClO_2^- .²¹ Another of these is the reaction of N_3 with I^- , in which the formation of I_2^- was monitored.²² It is not certain that either of these reactions proceeds by electron transfer. Another is the reaction of O_2^- with HO_2 , and this is problematic because of uncertainties as to the correct self-exchange rate constant for the O_2/O_2^- couple.⁷ The fourth reaction is that between CO_2^- and SO_2 with $k = 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, which is only marginally less than diffusion controlled.²³ The fifth is that between ClO_2 and NO_2^- , which is described here. These last two reactions appear to be the only reported main-group reactions that are suitable as tests of the cross relationship of Marcus' theory. The value of the calculated electron-transfer rate constant for the $\text{CO}_2^-/\text{SO}_2$ reaction is $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, while that for the $\text{NO}_2^-/\text{ClO}_2$ reaction is $0.2 \text{ M}^{-1} \text{ s}^{-1}$.²⁴ The former is 2.5-fold less than observed, whereas the latter is 3 orders of magnitude less than observed. Because of considerable uncertainties in the values of E° and the self-exchange rate constant for the $\text{CO}_2/\text{CO}_2^-$ couple,¹² the calculation for the $\text{NO}_2^-/\text{ClO}_2$ system is the more meaningful of the two.

If we disregard the uncertainties associated with the other three cross-reactions discussed above and apply the Marcus equation, we find that all the observed rate constants are orders of magnitude greater than predicted. Furthermore, the reactions of Br_2 or I_2 with O_2^- ,²⁵ O_2 with SO_2^- ,²⁶ and N_3 with HO_2^- ²⁷ all proceed plausibly by electron transfer at rates close to diffusion controlled; however, the rates calculated from the Marcus equation for these reactions are generally 2–3 orders of magnitude less than observed. An extreme case is the reaction of SO_2^- with O_2 , which is more than 5 orders of magnitude faster than predicted. It is difficult to make generalizations on the basis of the few firm data presently in hand, but the apparent trend suggests that the outer-sphere model may not be appropriate for reactions between simple main-group compounds and that, when electron transfer occurs, it does so by a more efficient strong-overlap mechanism. Such a mechanism is analogous to the inner-sphere mechanism of co-

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(24) Calculations use the equation $k = (k_{11}k_{22}K_{eq})^{1/2}$ with $\log f = (\log K_{eq})^2 / (4 \log(k_{11}k_{22}/Z^2))$, $Z = 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, $k_{11}(\text{ClO}_2/\text{ClO}_2^-) = 1.6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, $k_{22}(\text{NO}_2/\text{NO}_2^-) = 2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, $k_{11}(\text{SO}_2/\text{SO}_2^-) = 1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $k_{22}(\text{CO}_2/\text{CO}_2^-) = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $E^\circ(\text{SO}_2) = -0.26 \text{ V}$, and $E^\circ(\text{CO}_2) = 1.8 \text{ V}$. The self-exchange rate constants are from the references indicated in the text, and the potentials are from ref 12.

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ordination chemistry, except that solvation of monoanions and neutrals is so weak that the concept of ligand substitution is not very meaningful. The reaction between SO_2^- and O_2 may be the limiting case in which strong overlap leads to adduct formation rather than electron transfer, although Wilkins and co-workers rationalize the data in terms of outer-sphere electron transfer by using very large self-exchange rate constants for both couples.²⁸ The argument in favor of adduct formation is supported by the

observation that SO_2^- supported on TiO_2 binds O_2 .²⁹ Despite the apparent inapplicability of the outer-sphere model to main-group electron-transfer reactions, it is still notable that the title reaction does have a substantial kinetic barrier and thus displays vestiges of the cross relationship of Marcus' theory.

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Registry No. NO_2^- , 14797-65-0; ClO_2 , 10049-04-4.

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Oxidative Addition of Thiols to a Coordinatively Unsaturated Triplatinum Cluster Complex

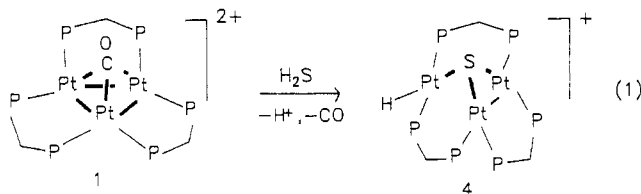
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Reaction of RSH with $[\text{Pt}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][\text{PF}_6]_2$ (**1**, $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) gave CO and $[\text{Pt}_3\text{H}(\mu_3\text{-SR})(\mu\text{-dppm})_3][\text{PF}_6]_2$ (**2a**, $\text{R} = \text{Me}$; **2b**, $\text{R} = \text{Et}$; **2c**, $\text{R} = \text{CH}_2\text{Ph}$; **2d**, $\text{R} = \text{CH}_2\text{CO}_2\text{Et}$; **2e**, $\text{R} = \text{Ph}$; **2f**, $\text{R} = 4\text{-MeC}_6\text{H}_4$) and, when $\text{R} = \text{aryl}$, $[\text{Pt}_3(\text{SR})(\mu_3\text{-SR})(\mu\text{-dppm})_3][\text{PF}_6]_2$ (**3a**, $\text{R} = \text{Ph}$; **3b**, $\text{R} = 4\text{-MeC}_6\text{H}_4$). Reaction of *t*-BuSH with **1** gave the known complex $[\text{Pt}_3\text{H}(\mu_3\text{-S})(\mu\text{-dppm})_3][\text{PF}_6]_2$ (**4**). Mixed-thiolate derivatives $[\text{Pt}_3(\text{SR})(\mu_3\text{-SR}')(\mu\text{-dppm})_3][\text{PF}_6]_2$ (**3c**, $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$; **3d**, $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$) were formed by reaction of **2a** with PhSH. In some cases, thiolate-exchange reactions were observed; for example, **2e** with excess MeSH gave mostly **2a**. PhSeH reacted with **1** to give a mixture of $[\text{Pt}_3\text{H}(\mu_3\text{-SePh})(\mu\text{-dppm})_3][\text{PF}_6]_2$ (**5**) and $[\text{Pt}_3(\text{SePh})(\mu_3\text{-SePh})(\mu\text{-dppm})_3][\text{PF}_6]_2$ (**6**). In the reactions of **1** with EtSH or PhSH, low-temperature ^{31}P and ^{13}C NMR experiments showed the formation of a rapid pre-equilibrium between the reagents and $[\text{Pt}_3(\mu_3\text{-CO})(\text{RSH})(\mu\text{-dppm})_3]^{2+}$ (**7a**, $\text{R} = \text{Et}$; **7b**, $\text{R} = \text{Ph}$) with $\Delta H^\circ = -27 \pm 1$ and -24 ± 1 kJ mol^{-1} and $\Delta S^\circ = -110 \pm 5$ and -73 ± 5 $\text{J K}^{-1} \text{mol}^{-1}$ for formation of **7a** and **7b**, respectively. These reacted further to give **2b** or **2e** on warming to $\sim 0^\circ\text{C}$. PhSeH gave the analogous intermediate $[\text{Pt}_3(\mu_3\text{-CO})(\text{PhSeH})(\mu\text{-dppm})_3]^{2+}$ and, with excess PhSeH, another species, which is probably $[\text{Pt}_3\text{H}_2(\mu\text{-SePh})(\mu\text{-dppm})_3]^{3+}$.

Introduction

The coordinatively unsaturated cluster complex $[\text{Pt}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (**1**, $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) is able to mimic several reactions of a Pt(111) surface.² In particular, the reaction with H_2S gives $[\text{Pt}_3\text{H}(\mu_3\text{-S})(\mu\text{-dppm})_3]^+$ (**4**, eq 1³), a reaction that models the poisoning of a platinum surface catalyst by H_2S .⁴



It was suggested that formation of **4** involved coordination of H_2S to **1** followed by oxidative addition to give $[\text{Pt}_3\text{H}(\mu_3\text{-SH})(\mu\text{-dppm})_3]^{2+}$ and then rapid deprotonation of the $\mu_3\text{-SH}$ ligand to give **4**.³ However, no intermediates could be detected.³ The analogous reactions of RSH and RSeH ($\text{R} = \text{alkyl}$ or aryl) with complex **1** have now been studied, and intermediate RSH complexes have been detected; the mechanisms of these reactions thus

lend support to the proposed mechanism of the reaction of **1** with H_2S . A preliminary account of parts of this work has been published.⁵

Results

Synthesis of New Complexes. The major results from the reaction of $[\text{Pt}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (**1**) are shown in Scheme I. When $\text{R} = \text{alkyl}$, the thiols RSH gave $[\text{Pt}_3\text{H}(\mu_3\text{-SR})(\mu\text{-dppm})_3]^{2+}$ (**2**) as the product obtained at room temperature. The only exception was in the reaction of *t*-BuSH with **1**, which gave $[\text{Pt}_3\text{H}(\mu_3\text{-S})(\mu\text{-dppm})_3]^+$ (**4**), presumably as a result of the relatively good leaving group *t*-Bu⁺ being lost from the intermediate **2**. When $\text{R} = \text{aryl}$, reaction with excess RSH gave $[\text{Pt}_3(\text{SR})(\mu_3\text{-SR})(\mu\text{-dppm})_3]^{2+}$, and it was difficult to isolate the product **2** in pure form from the reaction of equimolar amounts of **1** and RSH due to partial formation of **3** even under these conditions.

The formation of **3** from **2** requires the more acidic arenethiol reagent. For example, **2a** with PhSH gave a mixture of **3c** and **3d** with a trace of **3a**. Reaction of **2e** with MeSH did not yield the above products but gave thiol exchange, with formation of **2a** as major product. Complex **2a** at 0°C with PhSH gave some **2e**. Thus, it is clear that thiol-exchange reactions are faster than reaction of **2** with RSH to give **3**.

Benzeneselenol behaved in a manner similar to that of PhSH and gave a mixture of $[\text{Pt}_3\text{H}(\mu_3\text{-SePh})(\mu\text{-dppm})_3]^{2+}$ (**5**) and $[\text{Pt}_3(\text{SePh})(\mu_3\text{-SePh})(\mu\text{-dppm})_3]^{2+}$ (**6**), as characterized by NMR spectroscopy. In this case the mixture could not be separated,

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