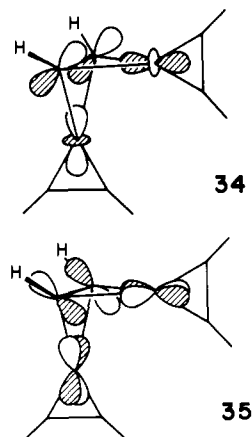


of **32** and **33** reinforces the motion of the isolobal relationship between the alkyne and  $L_2$  ligands in their orthogonal orientation.

The portion,  $Pt(HC_2H)_2$ , has one alkyne prepared for bonding by bending the *cis*-bent hydrogens away from the approaching  $Pt(HC_2H)$ . In this way there are carbon hybrid orbitals produced

which are directed toward the incoming fragment.

A major stabilizing interaction occurs between the HOMO of  $Pt(HC_2H)$ , mainly metal  $d_{xz}$  and the LUMO of  $Pt(HC_2H)_2$ , the out-of-phase combination of the newly hybridized orbitals. The in-phase combination of these hybrids interact with many of the  $a'$  metal orbitals under the low symmetry. The HOMO-LUMO gap produced by such interactions is around 2.5 eV. **34** and **35**



represent the HOMO and LUMO, respectively, of  $Pt_2(\mu-HC_2H)(HC_2H)_2$  and illustrate the  $\pi$  and  $\sigma$  interactions of the carbon hybrid orbitals.

Registry No.  $PtAs_2^{2-}$ , 89088-76-6;  $Pt(HC_2H)^{-}$ , 89088-77-7.

## Outer-Sphere Electron-Transfer Reactions Involving the Chlorite/Chlorine Dioxide Couple. Activation Barriers for Bent Triatomic Species

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Received May 31, 1983

**Abstract:** The kinetics of several redox reactions involving the  $ClO_2/ClO_2^-$  couple have been determined in aqueous solution by stopped-flow spectrophotometry.  $ClO_2$  is reduced by  $[Co(terpy)_2]^{2+}$  to produce  $ClO_2^-$  and  $[Co(terpy)_2]^{3+}$  with simple bimolecular kinetics ( $k = 2.1 \times 10^7 M^{-1} s^{-1}$  at 25 °C,  $\mu = 0.1 M$  ( $NaCF_3SO_3$ )).  $ClO_2^-$  is oxidized by  $IrCl_6^{2-}$  to produce  $ClO_2$  and  $IrCl_6^{3-}$ ; the rate law is  $-d \ln [IrCl_6^{2-}]/dt = k_1 [Cl(III)] / (1 + [H^+]/K_a)$ , with  $k_1 = 1.06 \times 10^4 M^{-1} s^{-1}$  and  $K_a = 1.6 \times 10^{-2} M$ , the acid dissociation constant of  $HClO_2$ . For the reaction of  $ClO_2^-$  with  $IrBr_6^{2-}$   $k_1$  is  $1.86 \times 10^4 M^{-1} s^{-1}$ . Application of the Marcus-Hush cross relationship to these outer-sphere electron-transfer reactions leads to a self-consistent self-exchange rate constant of  $1.6 \times 10^2 M^{-1} s^{-1}$  for the  $ClO_2/ClO_2^-$  couple. An explicit equation for the classical contributions of molecular vibrations to the activation free energy of self-exchange reactions of bent triatomic species has been derived. Calculations of these barriers show that both bending and stretching are important in the activation process. With this equation the activation barriers for the  $ClO_2/ClO_2^-$ ,  $NO_2/NO_2^-$ , and  $SO_2/SO_2^-$  redox couples have been rationalized. Nuclear tunneling introduces a correction to the classical rate constant by a factor of 79 for the  $NO_2/NO_2^-$  couple.

Chlorine dioxide is one of the very limited group of main-group molecules which, as free radicals, are reasonably stable in aqueous solution. Its stability confers upon it great advantage in the study of electron-transfer kinetics of small molecules. Thus, its reduction potential is known unequivocally, its geometry has been determined in the gas phase, and its various spectra rank it among the most carefully studied molecules. Its aqueous solutions are photosensitive and decompose rather quickly when alkaline, but when handled properly aqueous chlorine dioxide is a mild and efficient

oxidant, leading to its use in water treatment and fiber bleaching.<sup>1,2</sup> Notable kinetic and mechanistic studies include its disproportionation,<sup>3</sup> its electron exchange with chlorite,<sup>4</sup> its oxygen exchange with water,<sup>5</sup> and its oxidations of amines,<sup>6</sup> iodide,<sup>7</sup> and sulfite,<sup>8</sup>

(1) Masschelein, W. J. "Chlorine Dioxide"; Ann Arbor Science: Ann Arbor, 1979.

(2) Gordon, G.; Kieffer, R. G.; Rosenblatt, D. H. *Prog. Inorg. Chem.* **1972**, *15*, 201.

(3) Medir, M.; Giralt, F. *Water Res.* **1982**, *16*, 1379.

(4) Dodgen, H.; Taube, H. *J. Am. Chem. Soc.* **1949**, *71*, 2501.

(5) Murrmann, R. K.; Thompson, R. C. *J. Inorg. Nucl. Chem.* **1970**, *32*, 1404.

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and it may well be important in chlorite oscillators.<sup>9</sup> However, as yet no scheme has been developed to predict the rates of its reactions.

The considerable success of Marcus-Hush theory in placing outer-sphere electron-transfer reactions in a predictive context<sup>10</sup> suggests that such reactions of chlorine dioxide may also be correlated. Accordingly, we have embarked on a study of the reductions of chlorine dioxide and the oxidations of chlorite by substitution-inert coordination complexes. Our first study,<sup>11</sup> the reduction of ClO<sub>2</sub> by [Fe(phen)<sub>3</sub>]<sup>2+</sup>, revealed an important property which has constrained all of the subsequent studies: ClO<sub>2</sub> is such a rapid oxidant that it is difficult to find reactions and conditions which are slow enough to be observed with stopped-flow instrumentation. In this paper results are reported on three observable reactions. The oxidation of [Co(terpy)<sub>2</sub>]<sup>2+</sup> (terpy = 2,2',2''-terpyridine) by ClO<sub>2</sub> is particularly noteworthy in that the cobalt complex is a much stronger reducing agent ( $E^\circ = 0.27$  V)<sup>12</sup> than [Fe(phen)<sub>3</sub>]<sup>2+</sup> ( $E^\circ = 1.09$  V).<sup>11</sup> The other two reactions are oxidations of ClO<sub>2</sub><sup>-</sup> by IrCl<sub>6</sub><sup>2-</sup> and IrBr<sub>6</sub><sup>2-</sup>; both IrCl<sub>6</sub><sup>2-</sup> and IrBr<sub>6</sub><sup>2-</sup> are weaker oxidants than ClO<sub>2</sub>, and so their reactions were studied in the uphill direction, driven to effective completion by mass action.

The results of these studies enable the following questions to be addressed. (A) To what degree can the reactions be correlated by the Marcus-Hush cross relationship? (B) Can the barriers to reaction be understood in terms of molecular and solvent reorganizational contributions? (C) Is the classical model of vibrational activation, which has been found fairly useful for coordination complexes, an appropriate description of the transition state for ClO<sub>2</sub>/ClO<sub>2</sub><sup>-</sup> reactions? (D) Do these same questions yield similar conclusions for reactions of other bent triatomic molecules?

### Experimental Section

**Reagents.** CoCl<sub>2</sub>·6H<sub>2</sub>O (Mallinckrodt), 2,2',2''-terpyridine (Sigma), HClO<sub>4</sub> (Baker), and Na<sub>2</sub>IrCl<sub>6</sub>·6H<sub>2</sub>O (Alfa) were used as supplied. Triflic acid (HCF<sub>3</sub>SO<sub>3</sub>) and sodium triflate (NaCF<sub>3</sub>SO<sub>3</sub>) were obtained and prepared in the same way as described previously.<sup>11</sup> NaClO<sub>4</sub> solutions were prepared by neutralization of HClO<sub>4</sub> with NaCO<sub>3</sub> and subsequent recrystallization. K<sub>2</sub>IrBr<sub>6</sub> (Pfalz and Bauer) was purified by Melvin and Haim's procedure.<sup>13</sup> NaClO<sub>2</sub> (MCB, practical flakes) was recrystallized as described by Mellor,<sup>14</sup> followed by dehydration in a vacuum desiccator. Deionized water distilled in a Corning Mega-Pure still was used throughout.

**Synthesis of [Co(terpy)<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>.** The literature procedure<sup>15</sup> for the synthesis of [Co(terpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was modified as follows. A solution of 0.1 g of terpyridine in 3 mL of methanol was added to a solution of 0.04 g of CoCl<sub>2</sub>·6H<sub>2</sub>O in 7 mL of distilled water. The deep red mixture was filtered to remove excess terpy. A saturated aqueous solution of NaCF<sub>3</sub>SO<sub>3</sub> was added dropwise to the filtrate until the first appearance of small crystals. Crystals were grown in a refrigerator for several days before they were collected and washed with toluene and diethyl ether. The crude product was recrystallized by dissolving the crystals in approximately 15 mL of warm (~40 °C) distilled H<sub>2</sub>O. The filtered solution was allowed to cool to room temperature. Approximately 0.5 mL of saturated aqueous NaCF<sub>3</sub>SO<sub>3</sub> solution was added dropwise. Crystals were grown in a refrigerator over several days with ~0.5-mL/day aliquots of saturated NaCF<sub>3</sub>SO<sub>3</sub> being added the first 2 days. The red needles were collected, washed with toluene and diethyl ether, and dried in a vacuum desiccator. Anal. Calcd for C<sub>32</sub>CoF<sub>6</sub>H<sub>22</sub>N<sub>6</sub>O<sub>6</sub>S<sub>2</sub>: C, 46.67; H, 2.69; N, 10.20. Found: C, 46.44; H, 2.84; N, 9.98.

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

(7) Fukutomi, H.; Gordon, G. *J. Am. Chem. Soc.* **1967**, *89*, 1362.

(8) Suzuki, K.; Gordon, G. *Inorg. Chem.* **1978**, *17*, 3115.

(9) Orban, M.; Dateo, C.; De Keper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 5911.

(10) Cannon, R. D. "Electron Transfer Reactions"; Butterworths: Boston, 1980.

(11) Lednický, L. A.; Stanbury, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 3098.

(12) (a) Chen, Y.-W. D.; Santhanam, K. S. V.; Bard, A. J. *J. Electrochem. Soc.* **1982**, *129*, 61. (b) Cummins, D.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5158.

(13) Melvin, W. S.; Haim, A. *Inorg. Chem.* **1977**, *16*, 2016.

(14) Mellor, J. W. "Inorganic and Theoretical Chemistry"; Longmans, Green, and Co: London, 1956; Supplement II, Part I, p 570.

(15) Baker, B. R.; Basolo, F.; Neumann, H. M. *J. Am. Chem. Soc.* **1959**, *63*, 371.

**Instrumentation and Precautions.** Solution pH was determined on a Corning 130 pH meter with a glass electrode and a SCE reference electrode filled with 3.5 M NaCl. Spectra were recorded on a Cary 210 UV/vis spectrophotometer with quartz cuvettes and on a Beckman 4250 IR spectrophotometer with KBr pellets. Kinetics were recorded on the Amino-Morrow stopped-flow as described previously;<sup>11</sup> it was thermostated by a Lauda K-2/R refrigerated circulating water bath, with a water/ethylene glycol circulating fluid. The chamber surrounding the mixing cell was purged with dry N<sub>2</sub> to minimize atmospheric condensation. The temperature at the cell was monitored with a thermistor by using a Digitec digital thermometer. The photometric signal from the RC filter was digitized, recorded, and processed on an OLIS 3820 data acquisition system. Although this system permitted signal averaging of several shots, it was found that this procedure was inadvisable; slight irreproducibility in the time delay between triggering and the stop of the flow resulted in distortion of the initial data for reactions having half-lives less than 15 ms.

Chlorine dioxide stock solutions were prepared as described previously<sup>11</sup> and were protected from light and stored in a refrigerator. These solutions were generally stable for about 3 weeks. All [Co(terpy)<sub>2</sub>]<sup>2+</sup> solutions were prepared immediately before use to ensure that no air oxidation occurred. A cursory investigation of the oxidation of [Co(terpy)<sub>2</sub>]<sup>2+</sup> by O<sub>2</sub> was carried out by preparing a solution in air-saturated water with [Co(terpy)<sub>2</sub>]<sup>2+</sup><sub>0</sub> = 1.0 × 10<sup>-4</sup> M; a portion of the solution was saturated with O<sub>2</sub> ([O<sub>2</sub>]<sub>0</sub> = 1.2 × 10<sup>-3</sup> M at 1 atm O<sub>2</sub>).<sup>16</sup> Over a period of 17 h at ~22 °C the absorbance at 505 nm decreased by 20% for the oxygenated solution, while only a 4% decrease was observed in the air-saturated solution. With the assumption of pseudo-first-order kinetics and Henry's law for the solubility of O<sub>2</sub> (air being 20.98% O<sub>2</sub>),<sup>17</sup> the initial rates gave a second-order rate constant of  $k = 3.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ . This reaction presented no interference with the rapid oxidation of [Co(terpy)<sub>2</sub>]<sup>2+</sup> by ClO<sub>2</sub>.

All solutions were permitted to contact only glass, platinum, and Teflon. Solutions of IrCl<sub>6</sub><sup>2-</sup> and IrBr<sub>6</sub><sup>2-</sup> were protected from light and were used within 1 h of preparation to minimize the effects of hydrolysis.

**Analytical Methods.** Solutions of HCF<sub>3</sub>SO<sub>3</sub> and HClO<sub>4</sub> were standardized by titration against 0.1 N NaOH to a phenolphthalein end point. NaClO<sub>4</sub> stock solution was standardized by evaporation at 110 °C and weighing the anhydrous NaClO<sub>4</sub> residue. NaCF<sub>3</sub>SO<sub>3</sub> stock solution was standardized by passing an aliquot down a cation-exchange column in the acid form (Dowex 50W-X8) and titrating the eluent with 0.1 N NaOH.

NaClO<sub>2</sub> stock solutions were prepared daily, protected from light, and standardized iodometrically by the method of Brown.<sup>18</sup>

Solutions of [Co(terpy)<sub>2</sub>]<sup>2+</sup> were determined spectrophotometrically. The extinction coefficient at 505 nm was found to be 1404 M<sup>-1</sup> cm<sup>-1</sup> ([Co(terpy)<sub>2</sub>]<sup>2+</sup> = 1.70 × 10<sup>-4</sup> M). This value agrees with previously reported values.<sup>19</sup> At 316 nm the extinction coefficient was found to be 3.34 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> (not a local maximum). The C, H, and N analysis was performed by Galbraith Labs (Knoxville, TN).

ClO<sub>2</sub> concentrations were determined spectrophotometrically ( $\epsilon = 1200 \text{ M}^{-1} \text{ cm}^{-1}$  at 358 nm or 529 M<sup>-1</sup> cm<sup>-1</sup> at 316 nm). Contrary to Massehelein,<sup>20</sup> we found that ClO<sub>2</sub> could not reliably be determined iodometrically at neutral pH. An aliquot of freshly prepared ClO<sub>2</sub> solution (~0.02 M) was added to an equal volume of phosphate buffer (~0.02 M) at pH 7, 1 g of KI was added, and the solution was titrated with 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to a starch end point. This method led to molar absorptivities ~10% too low. Furthermore, with a 1.2-fold excess of NaClO<sub>2</sub> added to the ClO<sub>2</sub> solution, an additional 20% of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> was required to reach the end point. It is concluded that ClO<sub>2</sub><sup>-</sup> is oxidized by I<sup>-</sup> even at pH 7; this conclusion is strengthened by the observation that I<sub>2</sub> catalyzes the reaction of I<sup>-</sup> with ClO<sub>2</sub><sup>-</sup>.<sup>21</sup>

**Determination of Stoichiometry.** A solution of 5.41 × 10<sup>-5</sup> M [Co(terpy)<sub>2</sub>]<sup>2+</sup> was prepared, and 2.8 mL was transferred to a 1-cm rectangular quartz cuvette. The absorbance was measured at 505 and 336 nm. To the solution in the cuvette was added 0.2 mL of ClO<sub>2</sub> ([ClO<sub>2</sub>] > 0.01 M), excess ClO<sub>2</sub> then being removed by sparging with Ar. The absorbance was then determined at 336 nm, a local maximum for [Co-

(16) Seidell, A.; Linke, W. F. "Solubilities of Inorganic Compounds", 4th ed.; Van Nostrand: Princeton, NJ, 1964; p 1228.

(17) "The Merck Index", 8th ed.; Merck and Co.: Rahway, NJ, 1968; p 109. **Note Added in Proof:** The rate of reaction of O<sub>2</sub><sup>-</sup> with Co(terpy)<sub>2</sub><sup>3+</sup> has recently been reported: Bradic, Z.; Wilkins, R. G. *J. Am. Chem. Soc.*, in press. The ratio of the rate constant for the O<sub>2</sub> reaction with Co(II) and the O<sub>2</sub><sup>-</sup> reaction with Co(III) is equal to the equilibrium constant as determined from the redox potentials.

(18) Brown, E. G. *Anal. Chim. Acta* **1952**, *7*, 494.

(19) Prasad, J.; Peterson, N. C. *Inorg. Chem.* **1969**, *8*, 1622.

(20) Reference 1, p 91.

(21) Kern, D. M.; Kim, C.-H. *J. Am. Chem. Soc.* **1965**, *87*, 5309.

(terpy)<sub>2</sub>]<sup>3+</sup> ( $\epsilon = 2.10 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ),<sup>22</sup> the contribution from ClO<sub>2</sub><sup>-</sup> being negligible. It was found that 99.2 ± 0.8% of the [Co(terpy)<sub>2</sub>]<sup>2+</sup> was oxidized to [Co(terpy)<sub>2</sub>]<sup>3+</sup>. A similar experiment was performed by oxidizing [Co(terpy)<sub>2</sub>]<sup>2+</sup> with Cl<sub>2</sub> in acid medium, then expelling any dissolved Cl<sub>2</sub> with Ar. The spectra of the product [Co(terpy)<sub>2</sub>]<sup>3+</sup> were identical in both methods of oxidation.

A spectrophotometric titration was performed twice by preparing 50-cm<sup>3</sup> solutions of [Co(terpy)<sub>2</sub>]<sup>2+</sup> ( $1.23 \times 10^{-5}$  and  $3.93 \times 10^{-6}$  mol) and titrating with 1-cm<sup>3</sup> aliquots of ClO<sub>2</sub> solutions ( $1.04 \times 10^{-3}$  and  $1.11 \times 10^{-3}$  M). The change in absorbance was measured at 505 nm in a 1-cm cell. The end point was taken as the break in a plot of *A* vs. volume.

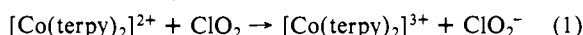
For the reaction of ClO<sub>2</sub><sup>-</sup> with IrCl<sub>6</sub><sup>2-</sup>, IrCl<sub>6</sub><sup>3-</sup> was verified as the product as follows. A solution containing  $2 \times 10^{-3}$  M NaClO<sub>2</sub>,  $2 \times 10^{-5}$  M IrCl<sub>6</sub><sup>2-</sup>, and 0.2 M NaClO<sub>4</sub> was allowed to react. The solution was then acidified with 0.2 M HClO<sub>4</sub> and saturated with Cl<sub>2</sub>. After the brown color characteristic of IrCl<sub>6</sub><sup>2-</sup> returned, excess Cl<sub>2</sub> was sparged from the solution by a stream of Ar. Spectrophotometric analysis of the resulting solution showed quantitative recovery of IrCl<sub>6</sub><sup>2-</sup> by its absorption at 487 nm,  $\epsilon = 4000 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>23</sup>

The yield of ClO<sub>2</sub> from oxidation of ClO<sub>2</sub><sup>-</sup> by IrCl<sub>6</sub><sup>2-</sup> was also determined spectrophotometrically. A solution of  $2 \times 10^{-3}$  M NaClO<sub>2</sub>, 0.1 M NaClO<sub>4</sub>, and  $2 \times 10^{-5}$  M IrCl<sub>6</sub><sup>2-</sup> at pH 5 was prepared and allowed to react. Measuring the absorbance at 360 nm gave a yield of  $0.94 \pm 0.05$  mol of ClO<sub>2</sub> per mol of IrCl<sub>6</sub><sup>2-</sup> consumed.

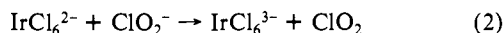
**Kinetics Methods.** The reactions were initiated by mixing equal volumes of solutions in the stopped-flow. Both solutions were maintained at  $\mu = 0.1$  M with background electrolyte, NaCF<sub>3</sub>SO<sub>3</sub> for the Co(II) reactions and NaClO<sub>4</sub> for the Ir(IV) reactions. In cases where the pH was deliberately controlled, NaOH, HClO<sub>4</sub>, or HCF<sub>3</sub>SO<sub>3</sub> was added to the solution containing the metal complex. For the Co(II) reactions, the data were manipulated on the OLIS 3820 to obtain a plot of eq 4 as the ln term vs. time. These plots were generally linear for 2 or 3 half-lives, and the rate constants were obtained from the slopes. For the Ir(IV) reactions the absorbance was monitored at the peak maximum, 487 nm for the IrCl<sub>6</sub><sup>2-</sup> and 588 nm for IrBr<sub>6</sub><sup>2-</sup>; semilog plots were also linear for 3 half-lives, but values of *k*<sub>obsd</sub> were determined by computer fitting the data to an exponential decay.

## Results

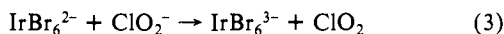
**Stoichiometry.** The reaction of [Co(terpy)<sub>2</sub>]<sup>2+</sup> with ClO<sub>2</sub> quantitatively yields [Co(terpy)<sub>2</sub>]<sup>3+</sup>. Spectrophotometric titrations demonstrate a consumption ratio of 1 mol of [Co(terpy)<sub>2</sub>]<sup>2+</sup> per mol of ClO<sub>2</sub>. Chlorite, the other assumed product, was not directly observed owing to its weak UV absorbance; however, since it is stable in solutions which are not too acidic<sup>24</sup> it is reasonable to write the stoichiometry as



IrCl<sub>6</sub><sup>3-</sup> was determined to be the product of oxidation of ClO<sub>2</sub><sup>-</sup> with IrCl<sub>6</sub><sup>2-</sup> by observing quantitative recovery of IrCl<sub>6</sub><sup>2-</sup> after oxidation with Cl<sub>2</sub>. As determined by its UV absorption, ClO<sub>2</sub> was formed in this reaction in 94% yield. The stoichiometry for this reaction is just the inverse of reaction 1.



The stoichiometry of the oxidation of ClO<sub>2</sub><sup>-</sup> by IrBr<sub>6</sub><sup>2-</sup> was not investigated, but by analogy it must be



ClO<sub>2</sub> is so much more strongly oxidizing ( $E^\circ = 0.936 \text{ V}$ )<sup>25</sup> than [Co(terpy)<sub>2</sub>]<sup>3+</sup> ( $E^\circ = 0.27 \text{ V}$ )<sup>12</sup> that the equilibrium in eq 1 is wholly to the right under all accessible conditions. IrCl<sub>6</sub><sup>2-</sup> ( $E^\circ = 0.892 \text{ V}$ )<sup>26</sup> and IrBr<sub>6</sub><sup>2-</sup> ( $E^\circ = 0.843 \text{ V}$ )<sup>27</sup> are actually weaker oxidants than ClO<sub>2</sub>, and so reactions 2 and 3 were studied with sufficient excess ClO<sub>2</sub><sup>-</sup> to force the equilibria to at least 95% completion.

Table I. Kinetics Data for ClO<sub>2</sub> Reaction with [Co(terpy)<sub>2</sub>]<sup>2+</sup> <sup>a</sup>

[Co(terpy) <sub>2</sub> ] <sup>2+</sup> , M	[ClO <sub>2</sub> ], M	pH	<i>T</i> , °C	<i>k</i> × 10 <sup>-7</sup> , M <sup>-1</sup> s <sup>-1</sup>
7.19 × 10 <sup>-5</sup>	7.50 × 10 <sup>-5</sup>	4.24	10.0	1.77 ± 0.40
9.51 × 10 <sup>-5</sup>	1.36 × 10 <sup>-4</sup>	4.90	10.0	1.19 ± 0.39
9.44 × 10 <sup>-5</sup>	6.04 × 10 <sup>-5</sup>	4.90	10.0	1.34 ± 0.69
3.70 × 10 <sup>-5</sup>	2.81 × 10 <sup>-5</sup>	3.78	10.0	1.90 ± 0.76
3.63 × 10 <sup>-5</sup>	4.13 × 10 <sup>-5</sup>	3.78	10.0	2.06 ± 0.60
1.05 × 10 <sup>-4</sup>	1.26 × 10 <sup>-4</sup>	6.50	10.0	1.11 ± 0.25
8.94 × 10 <sup>-5</sup>	1.23 × 10 <sup>-4</sup>	2.45	10.0	1.10 ± 0.88
8.76 × 10 <sup>-5</sup>	1.04 × 10 <sup>-4</sup>	3.67	10.0	1.50 ± 0.32
2.81 × 10 <sup>-5</sup>	5.38 × 10 <sup>-5</sup>	3.69	10.0	1.60 ± 0.37
6.80 × 10 <sup>-5</sup>	7.74 × 10 <sup>-5</sup>	3.76	10.0	1.20 ± 0.32
6.70 × 10 <sup>-5</sup>	1.33 × 10 <sup>-4</sup>	3.71	10.0	1.55 ± 0.30
1.53 × 10 <sup>-4</sup> <sup>b</sup>	1.53 × 10 <sup>-4</sup>	3.77	5.0	2.28 ± 0.03
1.34 × 10 <sup>-4</sup> <sup>b,c</sup>	1.34 × 10 <sup>-4</sup>	3.72	5.0	2.08 ± 1.0
1.32 × 10 <sup>-4</sup> <sup>b,d</sup>	1.32 × 10 <sup>-4</sup>	2.53	10.0	3.18 ± 0.5
8.26 × 10 <sup>-5</sup> <sup>e</sup>	1.04 × 10 <sup>-4</sup>	3.67	10.0	1.50 ± 0.14
8.33 × 10 <sup>-5</sup> <sup>e</sup>	1.08 × 10 <sup>-4</sup>	3.78	15.0	1.54 ± 0.26
8.33 × 10 <sup>-5</sup> <sup>e</sup>	1.04 × 10 <sup>-4</sup>	3.67	20.0	1.94 ± 0.26
8.19 × 10 <sup>-5</sup> <sup>e</sup>	9.87 × 10 <sup>-5</sup>	3.68	25.0	2.38 ± 0.32
7.98 × 10 <sup>-5</sup> <sup>e</sup>	9.36 × 10 <sup>-5</sup>	3.68	30.0	2.35 ± 0.46

<sup>a</sup>  $\mu = 0.1$  M (NaCF<sub>3</sub>SO<sub>3</sub>);  $\lambda = 316$  nm; eq 4 used to evaluate *k*; *k* values were obtained as averages of five shots, and uncertainties were the standard deviations for the shots. <sup>b</sup>  $\lambda = 505$  nm; eq 5 used to evaluate *k*. <sup>c</sup> Added [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> =  $8.8 \times 10^{-5}$  M. <sup>d</sup> Added [terpy] =  $1.2 \times 10^{-3}$  M. <sup>e</sup> Used to determine the activation parameters.

**Kinetics.** The reaction of ClO<sub>2</sub> with [Co(terpy)<sub>2</sub>]<sup>2+</sup> was found to be extremely fast. Initial experiments were performed by monitoring the substantial absorption band of Co(II) in the visible region. In order for the reaction to be detectable with our apparatus it was necessary to work with very dilute solutions, and conditions of pseudo-first-order kinetics could not be attained. Some advantage was gained by working mostly at 10 °C. However, data of reasonable S/N were not achieved until experiments were performed in the UV; the absorbance changes in the UV were about a factor of 20 greater than in the visible.

Semilog plots of the kinetics data were not linear, nor were simple second-order plots. On the assumption that the kinetics were mixed second order, eq 4 was deemed appropriate.<sup>28</sup>

$$\ln \left( 1 + \frac{\Delta_0}{[A]_0} \frac{\Delta \text{Abs}_0}{\Delta \text{Abs}_t} \right) = \Delta_0 k t + \ln \frac{[B]_0}{[A]_0} \quad (4)$$

In this equation A is the limiting reagent,  $\Delta_0 = [B]_0 - [A]_0$ ,  $\Delta \text{Abs}_0$  is the overall absorbance change,  $\Delta \text{Abs}_t$  is the difference between the absorbance at time *t* and at "infinite" time, and *k* is the second-order rate constant. Rate constants obtained from eq 4 are listed in Table I. This method of determining rate constants is quite imprecise, because small errors in the molar absorptivities of the reactants lead to large errors in  $\Delta_0$ ; hence, there is considerable scatter in the reported rate constants. Some of the earlier experiments, run in the visible under conditions of equal reactant concentrations, were analyzed with eq 5.<sup>28</sup>

$$\Delta \text{Abs}_0 / \Delta \text{Abs}_t = k[A]_0 t + 1 \quad (5)$$

Rate constants so obtained, although even less precise than those obtained by using eq 4, are also listed in Table I. These results demonstrate that the second-order rate constants are independent of pH, added terpy ligand, and added [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>. Clear first-order dependences on [ClO<sub>2</sub>] and [Co(terpy)<sub>2</sub>]<sup>2+</sup> are demonstrated. The rate law for the reaction is

$$-d[\text{Co(terpy)}_2^{2+}] / dt = k[\text{Co(terpy)}_2^{2+}][\text{ClO}_2] \quad (6)$$

The Eyring equation

$$k(T) = \frac{RT}{Nh} \exp \left( \frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \right) \quad (7)$$

(28) Espenson, J. A. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; pp 19-24.

(22) Farina, R.; Wilkins, R. G. *Inorg. Chem.* **1968**, *7*, 514.

(23) Wilmarth, W. K.; Stanbury, D. M.; Byrd, J. E.; Po, H. N.; Chua, C.-P. *Coord. Chem. Rev.* **1983**, *51*, 155.

(24) (a) Kieffer, R. G.; Gordon, G. *Inorg. Chem.* **1968**, *7*, 239. (b) Hong, C. C.; Rapson, W. H. *Can. J. Chem.* **1968**, *46*, 2053.

(25) Troitskaya, N. V.; Mischchenko, K. P.; Flis, I. E. *Russ. J. Phys. Chem.* **1959**, *33*, 77.

(26) Margerum, D. W.; Chellappa, K. L.; Bossu, F. P.; Burce, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 6894.

(27) Stanbury, D. M.; Wilmarth, W. K.; Khalaf, S.; Po, H. N.; Byrd, J. E. *Inorg. Chem.* **1980**, *19*, 2715.

Table II. Kinetics Data for  $\text{ClO}_2^-$  Reaction with  $\text{IrCl}_6^{2-}$ <sup>a</sup>

$[\text{ClO}_2^-]$ , M	pH	$k_{\text{obsd}}$ , $\text{s}^{-1}$	$[\text{ClO}_2^-]$ , M	pH	$k_{\text{obsd}}$ , $\text{s}^{-1}$
$7.35 \times 10^{-3}$	3.98	72.7	$3.84 \times 10^{-3}$	4.0	40.7
$7.35 \times 10^{-3}$	3.86	77.1	$5.67 \times 10^{-3}$	4.0	55.3
$7.35 \times 10^{-3}$	2.42	63.1	$6.72 \times 10^{-3}$	4.0	69.5
$7.35 \times 10^{-3}$	1.69	34.3	$5.75 \times 10^{-3}$	4.0	60.5
$7.35 \times 10^{-3}$	1.38	21.6	$6.70 \times 10^{-3}$	4.0	63.5
$5.00 \times 10^{-3}$ <sup>b</sup>	4.0	55.5	$7.66 \times 10^{-3}$	4.0	86.5
$2.00 \times 10^{-3}$ <sup>b</sup>	4.0	23.7	$8.62 \times 10^{-3}$	4.0	96.1
$1.00 \times 10^{-3}$ <sup>b</sup>	4.0	11.3	$8.62 \times 10^{-3}$	1.36	25.0
$5.00 \times 10^{-4}$ <sup>b</sup>	4.0	6.0	$8.62 \times 10^{-3}$ <sup>c</sup>	4.0	92.2
$2.88 \times 10^{-3}$	4.0	32.6	$5.76 \times 10^{-3}$ <sup>d</sup>	6.2	58.0

<sup>a</sup>  $\mu = 0.10$  M ( $\text{NaClO}_4$ ),  $T = 25^\circ\text{C}$ ,  $[\text{IrCl}_6^{2-}]_0 = 2.0 \times 10^{-5}$  M.  
<sup>b</sup>  $[\text{IrCl}_6^{2-}]_0 = 1.0 \times 10^{-5}$  M. <sup>c</sup> Added  $[\text{Cu}^{2+}] = 1.0 \times 10^{-5}$  M.  
<sup>d</sup> Used purified  $\text{IrCl}_6^{2-}$  as described in text.

Table III. Kinetics Data for  $\text{IrBr}_6^{2-}$  Reaction with  $\text{ClO}_2^-$ <sup>a</sup>

$[\text{ClO}_2^-]$ , M	pH	$k_{\text{obsd}}$ , $\text{s}^{-1}$	$[\text{ClO}_2^-]$ , M	pH	$k_{\text{obsd}}$ , $\text{s}^{-1}$
$4.88 \times 10^{-3}$	5.6	$8.77 \times 10^1$	$5.76 \times 10^{-3}$	4.57	$1.18 \times 10^2$
$5.86 \times 10^{-3}$	5.6	$1.18 \times 10^2$	$1.74 \times 10^{-3}$ <sup>b</sup>	5.0	$3.51 \times 10^1$
$6.84 \times 10^{-3}$	5.6	$1.31 \times 10^2$	$2.17 \times 10^{-3}$ <sup>b</sup>	5.0	$3.95 \times 10^1$
$7.81 \times 10^{-3}$	5.6	$1.60 \times 10^2$	$2.61 \times 10^{-3}$ <sup>b</sup>	5.0	$4.05 \times 10^1$
$8.79 \times 10^{-3}$	5.6	$1.71 \times 10^2$	$3.48 \times 10^{-3}$ <sup>b</sup>	5.0	$5.44 \times 10^1$
$5.76 \times 10^{-3}$	6.23	$1.12 \times 10^2$	$4.35 \times 10^{-3}$ <sup>b</sup>	5.0	$6.84 \times 10^1$
$5.76 \times 10^{-3}$	6.21	$1.08 \times 10^2$	$5.22 \times 10^{-3}$ <sup>b</sup>	5.0	$8.64 \times 10^1$

<sup>a</sup>  $\mu = 0.10$  M ( $\text{NaClO}_4$ ),  $T = 25.0^\circ\text{C}$ ,  $[\text{IrBr}_6^{2-}]_0 = 2 \times 10^{-5}$  M.  
<sup>b</sup>  $[\text{IrBr}_6^{2-}]_0 = 1 \times 10^{-5}$  M.

was used to obtain activation parameters by fitting the temperature-dependent rate constants with a nonlinear least-squares computer routine, each point being equally weighted. This led to  $\Delta H^\ddagger = 16.2 \pm 3.8$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger = -50 \pm 13$  J K<sup>-1</sup> mol<sup>-1</sup>, and a rate constant at 25.0 °C of  $(2.1 \pm 0.4) \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>.

The reaction of  $\text{IrCl}_6^{2-}$  with  $\text{ClO}_2^-$  was studied at 25.0 °C, with a large excess of  $\text{ClO}_2^-$ . Values of the pseudo-first-order rate constants,  $k_{\text{obsd}}$ , are listed in Table II. A first-order dependence on  $[\text{ClO}_2^-]$  is obeyed in weakly acidic media. In more strongly acidic media at fixed total  $[\text{Cl(III)}]$  the rates are inhibited. The data are consistent with the rate law

$$\frac{-d[\text{IrCl}_6^{2-}]}{dt} = \frac{k[\text{IrCl}_6^{2-}][\text{Cl(III)}]}{1 + [\text{H}^+]/K_a} \quad (8)$$

and a nonlinear least-squares fit gives  $k = (1.06 \pm 0.02) \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> and  $K_a = (1.62 \pm 0.13) \times 10^{-2}$  M. This may be compared with the literature value for  $K_a$  of  $1.7 \times 10^{-2}$  M.<sup>24b</sup> One entry in Table II demonstrates that purifying the commercial  $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$  by boiling for several hours in concentrated  $\text{HCl}$ <sup>29</sup> does not significantly affect the results.<sup>30</sup>

$\text{IrBr}_6^{2-}$  was reduced by  $\text{ClO}_2^-$  as well with a large excess of  $\text{ClO}_2^-$ . Table III presents the pseudo-first-order rate constants. A good first-order dependence on  $[\text{ClO}_2^-]$  was found. The pH dependence was studied only in the region far from the  $\text{p}K_a$  of  $\text{HClO}_2$ , and the conclusion is that in this region there is no pH dependence. The observed rate law

$$-d[\text{IrBr}_6^{2-}]/dt = k[\text{IrBr}_6^{2-}][\text{ClO}_2^-] \quad (9)$$

is thus analogous to rate law 8 under conditions of high pH. A least-squares fit of eq 9 gives  $k = (1.86 \pm 0.05) \times 10^4$  M<sup>-1</sup> s<sup>-1</sup>.

(29) Poulsen, I.; Garner, C. G. *J. Am. Chem. Soc.* **1962**, *84*, 2032.

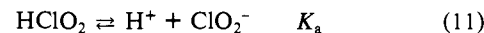
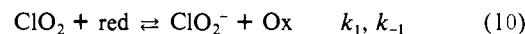
(30) One other rate law was also tried as a fit to the data

$$\frac{-d[\text{IrCl}_6^{2-}]}{dt} = \frac{[\text{IrCl}_6^{2-}][\text{Cl(III)}](k_1K_a + k_2[\text{H}^+])}{(K_a + [\text{H}^+])}$$

The resulting least-squares parameters were  $k_1 = (1.06 \pm 0.02) \times 10^4$  M<sup>-1</sup> s<sup>-1</sup>,  $k_2 = (0.05 \pm 1.02) \times 10^3$  M<sup>-1</sup> s<sup>-1</sup>, and  $K_a = (1.60 \pm 0.51) \times 10^{-2}$  M. The large standard deviation for  $k_2$  indicates that this parameter is not defined by the data, and it suggests an upper limit to  $k_2$  of  $1.0 \times 10^3$  M<sup>-1</sup> s<sup>-1</sup>, i.e., an order of magnitude less than  $k_1$ .

## Discussion

**Cross Relationship.** The three reactions investigated in this study and the previously studied reaction of  $\text{ClO}_2$  with  $[\text{Fe(phen)}_3]^{2+}$  have stoichiometries and rate laws which are consistent with the following general mechanism



Thus when the reducing agent is  $[\text{Co(terpy)}_2]^{2+}$ , the second-order rate constant is  $k_1$ , but when the oxidizing agent is  $\text{IrCl}_6^{2-}$  or  $\text{IrBr}_6^{2-}$  the second-order rate constant is  $k_{-1}$ . The ratio  $k_1/k_{-1}$  for a given system is, by the principle of detailed balancing, equivalent to the equilibrium constant, which is, in turn, defined by the known relevant redox potentials. Table IV collects these results. Although many of the rate constants are very large, none approach the limits of diffusion control within an order of magnitude. Casual inspection reveals two interesting phenomena. The reactions of  $\text{ClO}_2$  with  $[\text{Fe(phen)}_3]^{2+}$  and  $[\text{Co(terpy)}_2]^{2+}$  differ in their equilibrium constants by 14 orders of magnitude, yet their rate constants differ by only 3 orders of magnitude. Of the reactions of  $\text{ClO}_2^-$  with  $\text{IrCl}_6^{2-}$  and  $\text{IrBr}_6^{2-}$  that of  $\text{IrCl}_6^{2-}$  is thermodynamically more favored, but its rate constant is actually less.

The reactions in question proceed without substitution in the octahedral coordination sphere of the transition-metal ions. No evidence was obtained for formation of significant amounts of intermediate species. Furthermore, several reactions of the  $\text{ClO}_2/\text{ClO}_2^-$  couple have been shown to proceed without exchange of oxygen with the solvent water.<sup>33</sup> These observations suggest that the reactions are formally of the outer-sphere type, but they do not rule out a substantial degree of strong overlap.

The cross relationship of Marcus-Hush theory, given in eq 12,<sup>34</sup> is useful in rationalizing rate/equilibrium ratios for outer-sphere electron-transfer reactions.<sup>10</sup> Equation 12 is the usual cross

$$k_{11} = \left( \frac{k_{12}}{W_{12}} \right)^2 \frac{1}{k_{22}K_{12}f_{12}};$$

$$W_{12} = \exp\left( \frac{-(w_{12} + w_{21} - w_{11} - w_{22})}{2RT} \right)$$

$$\ln(f_{12}) = \frac{\left( \ln(K_{12}) + \frac{w_{12} - w_{21}}{RT} \right)^2}{4 \left\{ \ln\left( \frac{k_{11}k_{22}}{Z^2} + \frac{w_{11} + w_{22}}{RT} \right) \right\}}$$

$$w_{ab} = \frac{4.23 \times 10^{-8} Z_A Z_B}{a(1 + 3.28 \times 10^7 a(\mu^{1/2}))} \quad (12)$$

relationship, with work terms,  $w_{ab}$ , explicitly included, and it has been reorganized to yield  $k_{11}$ , the self-exchange rate constant for the  $\text{ClO}_2/\text{ClO}_2^-$  couple. In this equation  $k_{22}$  is the self-exchange rate constant for the transition-metal complex redox couple,  $k_{12}$  is the observed second-order rate constant,  $K_{12}$  is the equilibrium constant,  $Z$  is the collision rate, taken to be  $10^{11}$  M<sup>-1</sup> s<sup>-1</sup>,  $Z_a$  and  $Z_b$  are the ionic charges of the relevant species, and  $a$  is the center-to-center distance in the transition state, taken as the sum of the ionic or van der Waals radii. Since  $f_{12}$  itself is expressed in terms of  $k_{11}$ , values of  $k_{11}$  were determined for each reaction by an iterative procedure. Table IV lists the results of these calculations. The calculated values for  $k_{11}$  have a geometric mean

(31) Ruff, I.; Zimonyi, M. *Electrochim. Acta* **1973**, *18*, 515.

(32) Hurwitz, P.; Kustin, K. *Trans. Faraday Soc.* **1966**, *62*, 427.

(33) Halperin, J.; Taube, H. *J. Am. Chem. Soc.* **1952**, *74*, 375.

(34) Haim, A.; personal communication, 1980. In some earlier publications, ref 11 and 23,  $w_{ab}$  was inadvertently used with an incorrect denominator. This correction revises  $k_{11}$  for the  $\text{Fe(phen)}_3^{2+} + \text{ClO}_2$  reaction from  $6.1 \times 10^1$  to  $1.0 \times 10^2$  M<sup>-1</sup> s<sup>-1</sup>, and  $k_{11}$  for the  $\text{NO}_2/\text{NO}_2^-$  couple is revised from  $1 \times 10^{-2}$  to  $8.1 \times 10^{-3}$  M<sup>-1</sup> s<sup>-1</sup>.

Table IV. Marcus-Hush Cross Relationship for Reactions of  $\text{ClO}_2/\text{ClO}_2^-$ <sup>a</sup>

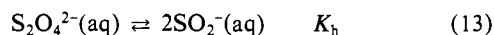
reagent	$E^\circ$ , V	$k_{22}$ , $\text{M}^{-1} \text{s}^{-1}$	$K_{\text{eq}}$	$k_1$ , $\text{M}^{-1} \text{s}^{-1}$	$r_2$ , <sup>j</sup> Å	$k_{-1}$ , $\text{M}^{-1} \text{s}^{-1}$	$k_{11}$ , $\text{M}^{-1} \text{s}^{-1}$ (calcd)
$[\text{Co}(\text{terpy})_2]^{2+}$	0.27 <sup>b</sup>	48 <sup>f</sup>	$1.82 \times 10^{11}$	$2.1 \times 10^7$	6	$1.2 \times 10^{-4}$	$2.4 \times 10^2$
$[\text{1}^{\text{c}}\text{c}(\text{phen})_3]^{2+}$	1.09 <sup>c</sup>	$5 \times 10^8$ <sup>g</sup>	$1.98 \times 10^{-3}$	$4.5 \times 10^4$	6	$2.27 \times 10^7$	$1.0 \times 10^2$
$\text{IrCl}_6^{2-}$	0.892 <sup>d</sup>	$2 \times 10^5$ <sup>h</sup>	5.55	$5.88 \times 10^4$	4.4	$1.06 \times 10^4$	$1.1 \times 10^3$
$\text{IrBr}_6^{2-}$	0.843 <sup>e</sup>	$2 \times 10^8$ <sup>i</sup>	$3.73 \times 10^1$	$6.94 \times 10^5$	4.7	$1.86 \times 10^4$	$2.7 \times 10^1$

<sup>a</sup>  $\mu = 0.1$ ;  $r_1 = 1.5$  Å assumed for  $\text{ClO}_2^-/\text{ClO}_2$ ;  $k_{11}$  calculated with use of eq 12;  $k_1$ ,  $k_{-1}$  as defined in eq 10 and 11, using  $E^\circ = 0.936$  V.<sup>25</sup>  $k_{22}$  is the self-exchange for the metal complex. <sup>b</sup> Reference 12. <sup>c</sup> Reference 11. <sup>d</sup> Reference 26. <sup>e</sup> Reference 27. <sup>f</sup> Reference 22. <sup>g</sup> Reference 31. <sup>h</sup> Reference 32. <sup>i</sup> Reference 27. <sup>j</sup> Estimated.

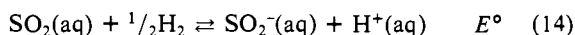
of  $1.6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . Of these the result for  $[\text{Co}(\text{terpy})_2]^{2+}$  is most dubious because its self-exchange rate was measured at very low ionic strength at 0 °C; a more appropriate value would have the effect of reducing  $k_{11}$ . We have used eq 12 to calculate  $k_{11}$  because its value is unknown; in its usual form the cross relationship calculates  $k_{12}$ , which is proportional to  $k_{11}^{1/2}$ . Thus the spread of a factor of 41 in  $k_{11}$  is equivalent to a spread of a factor of 6 in a more conventional treatment. Considering the uncertainties and the range of oxidants and  $\Delta G^\circ$  covered in Table IV, the spread in  $k_{11}$  is large but acceptable, and it is consistent with an outer-sphere mechanism.

Direct measurement of  $k_{11}$  was attempted by Dodgen and Taube using isotope-exchange methods;<sup>4</sup> their data suggest a lower limit to  $k_{11}$  of  $4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . The actual isotope-exchange rate constant may be much greater, and if so, it could be interpreted as involving a strong overlap mechanism. At this point, however, the data are consistent with a weak-overlap (outer-sphere) mechanism both for the four cross reactions and for the actual self-exchange.

How generally do triatomic molecules participate in single-electron transfer reactions which can be treated consistently with the cross relationship? The  $\text{NO}_2^-/\text{NO}_2$  couple is one other example where the cross relationship appears to be appropriate, and an effective self-exchange rate constant of  $8.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  has been derived.<sup>23,34</sup> There are fewer data for the  $\text{SO}_2^-/\text{SO}_2$  couple, but it, too, appears to react consistently with the cross relationship.<sup>35</sup> Unfortunately, the investigators of the  $\text{SO}_2^-/\text{SO}_2$  system inappropriately used  $E^\circ$  for the  $\text{SO}_2^-/\text{HSO}_3^-$  couple when applying the cross relationship.<sup>36</sup> The reactions were oxidations of  $\text{S}_2\text{O}_4^{2-}$  by  $\text{Co}(\text{EDTA})^-$  and  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ . The rate laws were first order in  $[\text{Co}(\text{III})]$  and half order in  $[\text{S}_2\text{O}_4^{2-}]$ , thus implying a pre-equilibrium homolysis of  $\text{S}_2\text{O}_4^{2-}$  followed by rate-limiting reactions of  $\text{SO}_2^-$ . Since the rate laws apparently were zero order in  $[\text{OH}^-]$ , hydrolysis of  $\text{SO}_2$  to  $\text{HSO}_3^-$  must have occurred in a subsequent step.  $\Delta G_f^\circ$  for  $\text{SO}_2^-$  ( $= -65.7$  kcal) can be obtained by using  $\Delta G_f^\circ$  for  $\text{S}_2\text{O}_4^{2-}$ <sup>37</sup> and  $K_h$ , the homolysis constant for  $\text{S}_2\text{O}_4^{2-}$ .<sup>38</sup>



The appropriate  $E^\circ$  ( $= -0.262$  V) defined as



is then obtained from the difference of  $\Delta G_f^\circ$  for  $\text{SO}_2(\text{aq})$ <sup>37</sup> and  $\text{SO}_2^-(\text{aq})$ . The corrected effective self-exchange rate constant is  $3.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , rather than  $1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  as previously reported. These three cases, then, support the applicability of the cross relationship to reactions of triatomic molecules.

However, the  $\text{SCN}^-/\text{SCN}$  redox couple is not effectively treated by using the cross relationship because its reactions are diffusion controlled.<sup>27</sup> Similar arguments, although less compelling, have been advanced regarding the  $\text{N}_3^-/\text{N}_3$  couple.<sup>23</sup> Although numerous kinetic data are available for the  $\text{CO}_2/\text{CO}_2^-$  couple,<sup>39</sup> its  $E^\circ$  is not sufficiently accurately known<sup>40</sup> to test the cross rela-

tionship. Data for the  $\text{BrO}_2^-/\text{BrO}_2$  couple are extremely limited,<sup>41</sup> and do not as yet bear on the issue. In summary, the cross relationship appears to apply to some, but not to all, triatomic redox couples.

**Classical Model.** The conventional "classical" model of Marcus-Hush theory gives the activation barrier for a self-exchange reaction as  $\Delta G^*$  in

$$k = Z \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (15)$$

The form of  $Z$  has been the subject of some discussion, but it is probably not too bad an approximation to assign it a value of  $10^{11} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C in water.<sup>42</sup> There has also been some discussion of whether a preexponential factor  $\kappa$ , reflecting the degree of nonadiabaticity, should be present.<sup>43</sup> However, the concern with these reactions is not that they may be nonadiabatic, but that they may involve strong overlap. In the rest of this paper eq 15 will be assumed to be appropriate. It is further conventional to express  $\Delta G^*$  as

$$\Delta G^* = w + \Delta G_0^* + \Delta G_i^* \quad (16)$$

Since  $\text{ClO}_2$  is not ionic, the work term,  $w$ , is close to zero, leaving  $\Delta G^*$  the sum of  $\Delta G_0^*$ , the solvent reorganizational barrier, and  $\Delta G_i^*$ , the molecular reorganizational barrier.

In the classical model,  $\Delta G_0^*$  derived under the assumption of a dielectric continuum is given by<sup>44</sup>

$$\Delta G_0^* = \frac{(\Delta Z)^2 e^2}{4} \left( \frac{1}{r_1^*} - \frac{1}{r^*} \right) \left( \frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon} \right) \quad (17)$$

Here,  $\Delta Z$  is the number of electrons transferred,  $r_1^*$  is the radius of each reactant in the transition state,  $r^*$  is the center-to-center distance in the transition state,  $\epsilon_{\text{op}}$  is the square of the refractive index of the solvent, and  $\epsilon$  is the solvent's dielectric constant. Equation 17 has been found to be an effective description for many self-exchange reactions of coordination complexes.<sup>42</sup> It is not a priori obvious that it should be equally effective for self-exchange reactions of triatomic redox couples; the high charge/radius ratio for a species such as  $\text{ClO}_2^-$ , its nonspherical geometry, and its small size (comparable to the solvent molecule size) render eq 17 particularly dubious. Practically, to calculate  $\Delta G_0^*$  using eq 17 is error prone for small molecules because errors in  $r_1^*$  and  $r^*$  are magnified by appearing in the denominators.

The classical model for  $\Delta G_i^*$  is frequently written as

$$\Delta G_i^* = \frac{n f_1 f_2 (r_1 - r_2)^2}{2(f_1 + f_2)} \quad (18)$$

with  $n$  as the number of ligands,  $f_1$  and  $f_2$  as the bond stretching force constants for the two oxidation states, and  $r_1$  and  $r_2$  as the bond lengths in the two oxidation states.<sup>44</sup> Equation 18 is derived

(35) (a) Mehrotra, R. N.; Wilkins, R. G. *Inorg. Chem.* **1980**, *19*, 2177.

(b) Scaife, C. W. J.; Wilkins, R. G. *Ibid.* **1980**, *19*, 3245.

(36) Mayhew, S. G. *Eur. J. Biochem.* **1978**, *85*, 535.

(37) *NBS Tech. Note (U.S.)* **1968**, 270-3.

(38) Lambeth, D. O.; Palmer, G. *J. Biol. Chem.* **1973**, *248*, 6095.

(39) Swallow, A. J. *Prog. React. Kinet.* **1978**, *9*, 195.

(40) (a) Henglein, A. *Radiat. Phys. Chem.* **1980**, *15*, 151. (b) Berdnikov, V. M. *Russ J. Phys. Chem.* **1975**, *49*, 1771. (c) Papaconstantinou, E. *Anal. Chem.* **1975**, *47*, 1592.

(41) (a) Sullivan, J. C.; Thompson, R. C. *Inorg. Chem.* **1979**, *18*, 2375. (b) Field, R. J.; Raghavan, N. V.; Brummer, J. G. *J. Phys. Chem.* **1982**, *86*, 2443.

(42) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

(43) Taube, H. In "Bioinorganic Chemistry-II"; Raymond, K. N., Ed.; American Chemical Society: Washington, D.C. 1977; p 127.

(44) Reynolds, W. L.; Lumry, R. W. "Mechanisms of Electron Transfer"; Ronald Press: New York, 1966; p 124.

Table V. Molecular Parameters for Classical Inner-Sphere Calculation

species	$\lambda$ , deg	$r_{m-o}$ , Å	$K_1$ mdyn Å <sup>-1</sup>	$H_1$ mdyn Å <sup>-1</sup>
ClO <sub>2</sub>	117.5 <sup>a</sup>	1.47 <sup>a</sup>	6.815 <sup>b</sup>	0.618 <sup>b</sup>
ClO <sub>2</sub> <sup>-</sup>	111 <sup>a</sup>	1.57 <sup>a</sup>	4.25 <sup>c</sup>	0.55 <sup>c</sup>
NO <sub>2</sub>	134 <sup>a</sup>	1.197 <sup>a</sup>	8.36 <sup>d</sup>	1.59 <sup>d</sup>
NO <sub>2</sub> <sup>-</sup>	115 <sup>a</sup>	1.24 <sup>a</sup>	7.50 <sup>e</sup>	1.67 <sup>e</sup>
SO <sub>2</sub>	119.5 <sup>a</sup>	1.43 <sup>a</sup>	9.97 <sup>f</sup>	0.81 <sup>f</sup>
SO <sub>2</sub> <sup>-</sup>	110 ± 5 <sup>g</sup>	~1.51 <sup>a</sup>	6.36 <sup>h</sup>	1.78 <sup>h</sup>

<sup>a</sup> Reference 46. <sup>b</sup> Reference 47. <sup>c</sup> Reference 48. <sup>d</sup> Calculated from frequencies in ref 49 using the simple valence force field of ref 45, p 169. <sup>e</sup> Reference 50. <sup>f</sup> Reference 45, p 170. <sup>g</sup> References 51 and 52. <sup>h</sup> Reference 52.

for reactions of octahedral molecules under the assumption that the symmetrical breathing mode carries the reaction. Clearly, this is not appropriate for a bent triatomic molecule, and we are unaware of a published solution to this problem. An explicit solution can be derived as follows. The potential energy of a bent triatomic molecule is given by a simple valence force field<sup>45</sup>

$$V = \frac{1}{2}K((\Delta r_1)^2 + (\Delta r_2)^2) + \frac{1}{2}H(r^0\Delta\alpha)^2 \quad (19)$$

$K$  is the stretching force constant,  $\Delta r_1$  and  $\Delta r_2$  are the displacements of the two bond lengths from the equilibrium lengths,  $H$  is the bending force constant,  $r^0$  is the equilibrium bond length, and  $\Delta\alpha$  is the displacement (in radians) of the bond angle from equilibrium.

For simplicity it is assumed that the transition state is symmetrical, and that in it the bond lengths and bond angles are equal. Under these constraints, the potential for the pair of reactants is

$$V_{tot} = K_0(r' - r_0^0)^2 + \frac{1}{2}H_0(r_0^0(\alpha' - \alpha_0^0))^2 + K_-(r' - r_-^0)^2 + \frac{1}{2}H_-(r_-^0(\alpha' - \alpha_-^0))^2 \quad (20)$$

Terms superscripted with primes refer to parameters of the distorted molecules. Terms subscripted with 0 and - refer to the oxidized and reduced species, respectively. The actual transition state is chosen as the geometry under which eq 20 is minimized, and it is found by setting equal to zero the partial derivatives of eq 20 taken with respect to  $r$  and  $\alpha$ . The inner-sphere barrier is then the difference in potential between the transition state and the ground state, and this is given by

$$\Delta G_i^* = \frac{(r_-^0 - r_0^0)^2 K_0 K_+}{K_0 + K_-} + \frac{H H_0 (r_-^0)^2 (r_0^0)^2 (\alpha_-^0 - \alpha_0^0)^2}{2(H_0 (r_0^0)^2 + H_-(r_-^0)^2)} \quad (21)$$

The inner-sphere reorganizational barrier is the sum of a bond-stretching term and a bond-bending term. The ClO<sub>2</sub>/ClO<sub>2</sub><sup>-</sup> and NO<sub>2</sub>/NO<sub>2</sub><sup>-</sup> redox couples are particularly amenable to analysis with eq 21 because all four force constants are known from vibrational spectroscopy studies and the bond lengths and angles are accurately known from X-ray crystallographic or gas-phase spectroscopic studies.

There is more difficulty in applying eq 21 to the SO<sub>2</sub>/SO<sub>2</sub><sup>-</sup> redox couple because the geometry of SO<sub>2</sub><sup>-</sup> is uncertain. Its bond angle can be estimated from ESR and vibrational studies, but the error may be as great as 5°. The bond length has arbitrarily been selected as that found in S<sub>2</sub>O<sub>4</sub><sup>2-</sup>. These molecular parameters, measured and estimated, are presented in Table V. Table VI displays the results of the calculations.

Table VI. Marcus-Hush Self-Exchange Calculations

	ClO <sub>2</sub> / ClO <sub>2</sub> <sup>-</sup>	NO <sub>2</sub> / NO <sub>2</sub> <sup>-</sup>	SO <sub>2</sub> / SO <sub>2</sub> <sup>-</sup>
$\Delta\lambda$ , deg	6.5	19	9.5 (5)
$\Delta r_{m-o}$ , Å	0.10	0.04	0.08
$\Delta G_i^*$ , kJ	17.5	45.3	15.0 (4.6)
$\Delta G_i^*$ , Å/ $\Delta G_i^*$ , r	0.11	9.32	1.17 (0.94)
$\Delta G^*$ , kJ	50.2	74.7	48
$\Delta G_0^*$ , kJ	32.7	29.4	33.0 (4.6)
$r_1^\ddagger$ , Å	2.91	3.23	2.88 (0.35)
$\nu_{in,sym}$ , cm <sup>-1</sup>	867 <sup>b</sup>	1321 <sup>c</sup>	1068 <sup>d</sup>
$\nu_{in,bend}$ , cm <sup>-1</sup>	423 <sup>b</sup>	789 <sup>c</sup>	508 <sup>d</sup>
$\Delta G^*_{in,cor}$ , kJ	13.36	34.3	14.4 (7.0)
$\Delta G^*_{o,cor}$ , kJ	36.8	40.4	33.6 (7.0)
$r_{1,cor}^\ddagger$ , Å	2.58	2.35	2.83 (0.49)
$\Gamma_n$	5.3	79	2.8

<sup>a</sup> Values in parentheses indicate estimate of uncertainty. Parameters subscripted cor have been corrected for nuclear tunneling. <sup>b</sup> References 48 and 53. <sup>c</sup> References 49 and 54. <sup>d</sup> References 52 and 55.

The difference in  $\Delta G_i^*$  for the ClO<sub>2</sub>/ClO<sub>2</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>/NO<sub>2</sub> couples is striking. The ratio  $\Delta G_i^*/\Delta G_i^*r$  is the ratio of the two terms in eq 21; this ratio shows that the bending mode is dominant for the NO<sub>2</sub><sup>-</sup>/NO<sub>2</sub> couple, while the stretching mode is dominant for the ClO<sub>2</sub>/ClO<sub>2</sub><sup>-</sup> couple. These observations stand in contrast to the situation for octahedral coordination complexes, where it is often sufficient to consider only one mode, the symmetric breathing mode.<sup>56</sup> Furthermore, the greater importance of the bending mode for the NO<sub>2</sub><sup>-</sup>/NO<sub>2</sub> couple than the ClO<sub>2</sub>/ClO<sub>2</sub><sup>-</sup> couple may be traced both to the greater change in bond angle and to the larger bending force constants.

The calculated  $\Delta G_i^*$  values are related to the self-exchange rates through eq 16.  $\Delta G_0^*$ , the solvent reorganizational energy, can simply be obtained by subtraction. Since the molecular sizes are not very different for the ClO<sub>2</sub>/ClO<sub>2</sub><sup>-</sup>, NO<sub>2</sub>/NO<sub>2</sub><sup>-</sup>, and SO<sub>2</sub>/SO<sub>2</sub><sup>-</sup> couples, eq 17 would imply that  $\Delta G_0^*$  should be similar for these three couples. This prediction is explored in Table VI, and fairly good agreement is shown. With the assumption that the two partners in the self-exchange reaction are just touching, eq 17, simplifies<sup>44</sup> in aqueous solution at 25 °C to

$$\Delta G_0^* = 95.0(\Delta Z)^2/r_1^\ddagger \quad (22)$$

Reactant radii in Table VI, calculated from eq 22 and the tabulated  $\Delta G_0^*$ , are about 1.5 Å larger than one might have expected; it is difficult to understand why ClO<sub>2</sub>/ClO<sub>2</sub> appears smaller than NO<sub>2</sub>/NO<sub>2</sub><sup>-</sup>. Nevertheless, the classical model does account for the gross difference in reactivity between the NO<sub>2</sub>/NO<sub>2</sub><sup>-</sup> and ClO<sub>2</sub>/ClO<sub>2</sub><sup>-</sup> couples. Also, the results for the SO<sub>2</sub>/SO<sub>2</sub><sup>-</sup> couple seem reasonable.

**Nuclear Tunneling.** Due to the wave mechanical nature of molecular vibrations, the classical treatment of the inner-sphere activation barrier is only an approximation. The conventional picture<sup>44</sup> of the transition state as the minimum on the intersection of reactant and product parabolic energy surfaces is expressed in eq 21. For a reactant pair of a given energy, quantum mechanics predicts that there is a finite probability that the pair will penetrate into the classically forbidden region. This means that in regions where the reactant and product energy surfaces are close, there is a significant probability that a reactant pair may find itself on the product energy surface, i.e., that reaction may occur, and this can happen even for reactant pairs having less energy than the transition state. This phenomenon is called nuclear tunneling.

(45) Herzberg, G. "Infrared and Raman Spectra"; Van Nostrand-Reinhold: Dallas, 1945; p 168.

(46) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Clarendon Press: Oxford, 1975; pp 340, 342, 580, 590, 657.

(47) Sawodny, W. *Angew. Chem., Int. Ed. Engl.* **1965**, *5*, 573.

(48) Tanguy, B.; Frit, B.; Turrell, G.; Hagenmuller, P. *Compt. Rend.* **1967**, *264c*, 301.

(49) St. Louis, R. V.; Crawford, B. L., Jr. *J. Chem. Phys.* **1965**, *42*, 857.

(50) Kato, R.; Rolfe, J. *J. Chem. Phys.* **1967**, *47*, 1901.

(51) Reuveni, A.; Luz, Z.; Silver, B. L. *J. Chem. Phys.* **1970**, *53*, 4619.

(52) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1971**, *55*, 1003.

(53) Nielson, A. H.; Woltz, P. J. H. *J. Chem. Phys.* **1952**, *20*, 1878.

(54) Weston, R. E., Jr.; Brodasky, T. F. *J. Chem. Phys.* **1957**, *27*, 683.

(55) Hastie, J. W.; Hauge, R. H.; Margrave, J. L. *J. Inorg. Nucl. Chem.* **1969**, *31*, 281.

(56) Newton, T. W. *J. Chem. Educ.* **1968**, *45*, 571.

There have recently been several studies of nuclear tunneling.<sup>57,58</sup> The overall degree of nuclear tunneling is not easily experimentally accessible at room temperature, but it can be evaluated theoretically. In the high-temperature limit the problem becomes classical, and so a nuclear tunneling factor may be defined as  $\Gamma_n = k(T)/k(T = \infty)$ .<sup>59</sup> Calculations of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  exchange have led to  $\Gamma_n = 3.5$  at 300 K, while for  $\text{Co}^{2+}/\text{Co}^{3+}$  a  $\Gamma_n \sim 10$  was found. A simple expression due to Holstein<sup>60</sup> relates the classical activation barrier  $\Delta G_i^*$  to the barrier corrected for nuclear tunneling  $\Delta G_{i,\text{tun}}^*$ <sup>57</sup>

$$\Delta G_{i,\text{tun}}^* = \Delta G_i^* \left( \frac{4RT}{Nh\nu_{\text{in}}} \right) \tanh \left( \frac{Nh\nu_{\text{in}}}{4RT} \right) \quad (23)$$

where  $\nu_{\text{in}}$  is the average vibrational frequency for the two oxidation states. Since two vibrational modes contribute to the activation barrier for triatomic molecules, eq 23 is applied as a correction to both terms in eq 21. Table VI shows the results of these corrections. In the case of the  $\text{ClO}_2/\text{ClO}_2^-$  exchange, the correction is substantial, while the correction for the  $\text{NO}_2/\text{NO}_2^-$  case is much greater. Since the correction is effectively a reduction of the inner-sphere barrier, the solvent reorganization barrier is correspondingly larger. Molecular radii calculated from eq 22, also listed in Table VI, are smaller than in the classical model,

(57) (a) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741. (b) Newton, M. D. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1980**, *14*, 363. (c) Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *J. Phys. Chem.* **1981**, *85*, 3759. (d) Chapters by N. Sutin and B. S. Brunschwig, M. D. Newton and N. S. Hush In "Mechanistic Aspects of Inorganic Reactions"; Rorabacher, D. B.; Endicott, J. F. Eds. American Chemical Society: Washington, D.C. 1982; A.C.S. Symp. Ser. No. 198.

(58) (a) Weaver, M. J.; Li, T. T. *J. Phys. Chem.* **1983**, *87*, 1153. (b) Buhks, E.; Bixon, M.; Jortner, J. *Ibid.* **1981**, *85*, 3763.

(59) Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798.

(60) Holstein, T. *Philos. Mag.* **1978**, *37*, 49.

and are closer to expected radii. Note that  $r_1^*$  for the  $\text{NO}_2/\text{NO}_2^-$  couple is significantly less than  $r_1^*$  for the  $\text{ClO}_2/\text{ClO}_2^-$  couple in contrast with the classical result. This observation lends support to the semiclassical model. The nuclear tunneling correction is equivalent to  $\Gamma = 79$  for the  $\text{NO}_2/\text{NO}_2^-$  system; nuclear tunneling can be much more important for reactions of bent triatomic molecules than for octahedral complexes because of the greater vibrational frequencies. A similar degree of nuclear tunneling has recently been calculated for the isomerization of 1,3-cyclobutadiene to 2,4-cyclobutadiene.<sup>61</sup>

### Summary

The kinetics studies of outer-sphere electron-transfer reactions involving the  $\text{ClO}_2/\text{ClO}_2^-$  couple are consistent with the cross relationship for a series of reactions spanning 14 orders of magnitude in equilibrium constant and 7 orders of magnitude in self-exchange rate constants, and involving a diversity of coordination complexes. The classical model of vibrational activation has been found useful in rationalizing the effective self-exchange rate constants for the  $\text{ClO}_2/\text{ClO}_2^-$ ,  $\text{NO}_2/\text{NO}_2^-$ , and  $\text{SO}_2/\text{SO}_2^-$  redox couples. Corrections for nuclear tunneling are substantial and correlate the data even better.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are also pleased to acknowledge support from the Robert A. Welch Foundation and the Research Corporation. This material is based upon work supported by the National Science Foundation under Grant No. CHE-8215501. Professor T. J. Meyer is thanked for his encouragement in the analysis of nuclear tunneling effects.

**Registry No.**  $[\text{Co}(\text{terpy})_2]^{2+}$ , 18308-16-2;  $\text{IrCl}_6^{2-}$ , 16918-91-5;  $\text{IrBr}_6^{2-}$ , 16919-98-5;  $\text{ClO}_2$ , 10049-04-4;  $\text{ClO}_2^-$ , 14998-27-7.

(61) Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700.

## CO Insertion into the Iron-Carbon $\sigma$ Bond in Optically Active $\text{CpFe}(\text{CO})(\text{L})\text{R}$ . Solvent Dependence and Acid Catalysis

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**Abstract:** The insertion of CO into the iron-carbon bond in optically active organoiron complexes  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Et}$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) (**1**) and  $\text{CpFe}(\text{CO})(\text{mtpb})\text{Et}$  ( $\text{mtpb} = \text{P}(\text{OCH}_2)_3\text{CMe}$ ) (**3**) in the presence of CO yields  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COEt}$  (**2**) and  $\text{CpFe}(\text{CO})(\text{mtpb})\text{COEt}$  (**4**), and in the presence of cyclohexyl isocyanide ( $\text{chi}$ ) yields  $\text{CpFe}(\text{chi})(\text{PPh}_3)\text{COEt}$  (**5**) and  $\text{CpFe}(\text{chi})(\text{mtpb})\text{COEt}$  (**6**), respectively. In nitroethane or nitromethane under CO pressure **2** and **4** are formed highly stereospecifically, and in MeCN with much reduced stereospecificity, but all with formal alkyl migration. In HMPA,  $\text{Me}_2\text{SO}$ , DMF, or propylene carbonate the optical purity is moderate to low, and the configuration corresponds to formal CO migration. Mixed-solvent studies, cyclic voltammetry, and UV-vis spectra suggest that a special charge- or electron-transfer mechanism in nitroalkane solvent is unlikely. Use of  $^{13}\text{C}$ -labeled CO results in the expected incorporation of label only in the terminal CO position of **2**. Strong catalysis results from  $\text{BF}_3\cdot\text{Et}_2\text{O}$  addition, but with no change in stereochemistry. Insertion in the presence of  $\text{chi}$  yields **5** and **6** with formal alkyl migration in either nitroethane or HMPA (the configurational assignment of the latter is highly tentative) but with reduced % ee. Operation of the usual reversible first-order insertion followed by second-order ligand uptake in the presence of  $\text{chi}$  is confirmed by a kinetics study of **1** with  $\text{chi}$  in  $\text{Me}_2\text{SO}$  with  $k_1 = 4.9 \times 10^{-4} \text{ s}^{-1}$ , and  $k_2/k_{-1} = 0.54 \text{ L M}^{-1}$ . No intermediates could be detected by IR or NMR in nucleophilic solvents. Possible mechanisms are discussed, including the likely presence of an  $(\eta^2\text{-acyl})\text{iron}$  intermediate in rapid equilibrium with an unsaturated  $(\eta^1\text{-acyl})\text{iron}$  species.

The path of the insertion of CO into the metal-carbon  $\sigma$  bond is well-known to proceed in most cases as shown in eq 1.<sup>1</sup> The

stereochemistry of this important reaction has been a subject of considerable interest and has been extensively reviewed.<sup>1-3</sup> While