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Electron Transfer to Ozone: Outer-Sphere Reactivities of the Ozone/Ozonide and Related Non-Metal Redox Couples

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For the net reaction $O_3 + 2IrCl_6^{3-} + 2H^+ = O_2 + 2IrCl_6^{2-} + H_2O$, $d[IrCl_6^{2-}]/dt = 2k[O_3][IrCl_6^{3-}]$, with $k = 1.7 \times 10^4$ M^{-1} s^{-1} (25 °C), $\Delta H^{\ddagger} = 10.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -4.5$ eu. The initial step appears to be an outer-sphere electron transfer from $IrCl_6^{3-}$ to O_3, followed by rapid protonation of O_3^- and oxidation of a second $IrCl_6^{3-}$ by HO_3 or OH. From a reduction potential of 1.02 V for the O_3/O_3^- couple, its self-exchange rate constant is calculated to be 4 M^{-1} s^{-1}; an estimate of 90 M^{-1} s^{-1} results from a calculation of the primary bond and solvation shell rearrangement energies. Similar approximate agreement is obtained between the self-exchange constants calculated by the relative and absolute Marcus–Hush theories for the O_2/O_2^-, SO_2/SO_2^-, ClO_2/ClO_2^-, NO_2/NO_2^-, and N_3/N_3^- couples so long as cross-reactions with inert metal complexes are employed. In contrast, the cross-reactions O_3/O_2^-, O_3/ClO_2^-, O_3/NO_2^-, ClO_2/NO_2^-, and O_2/SO_2^- are orders of magnitude faster than predicted from these self-exchange constants. These higher reactivities appear attributable to enhanced orbital overlap between two non-metal reactants in the transition state. Oxidative additions of O_3 to U^{4+}(aq) and Fe^{2+}(aq) to yield monodentate ozonide intermediates, from which O_2 or O_3^- is lost, appear likely. Thus, a broad range of redox mechanisms, from weak-overlap, outer-sphere electron transfer through strong orbital overlap in both transition state and product(s), is exhibited by ozone.

Introduction

Ozone is an important oxidant with more than one path for its reduction. Its reactions in the gas phase[1,2] and with organic molecules in solution[3,4] have been studied extensively. In aqueous solution the decomposition of ozone[5-18] and its reactions with predominantly non-metal inorganic reductants[7,17,19-29] have received attention. In these reactions, two-equivalent (2-equiv) reduction processes that involve bond making and bond breaking, especially oxygen atom transfer and cyclic ozonide formation, predominate. The electronic structure of ozone and the observation of the ozonide ion in alkaline solution[30,31] suggest that electron transfer to ozone is a possible reaction pathway with certain reductants. Our experiments were designed to explore this possibility.

An outer-sphere one-electron reduction of ozone should be favored by a reactant that readily undergoes a one-electron, but not a two-electron, oxidation and that does not offer a reactive site for covalent electrophilic attack by ozone (e.g., by oxygen atom transfer). According to these criteria, the hexachloroiridate(III) ion was selected as an attractive and sufficiently characterized reductant. The results of our kinetic study of its reaction with ozone are consistent with an outer-sphere electron transfer as the initial and rate-determining step. From the rate constant an estimate of the O_3/O_3^- self-exchange reactivity was made by using the relative Marcus–Hush theory. Our report concludes with an evaluation of this estimate, a discussion of its significance for understanding the reactivity of ozone in aqueous solution, and reactivity comparisons with the related redox couples O_2/O_2^-, SO_2/SO_2^-, ClO_2/ClO_2^-, NO_2/NO_2^-, N_3/N_3^-, and CO_2/CO_2^-, which have been studied in other laboratories.

Experimental Procedures

Materials. At an oxygen flow rate of 3 L/min and a Variac output of 100 V, an Ozonair electrical discharge generator converted approximately 0.5% by weight of O_2 to O_3. This mixture was passed through a gas wash bottle containing dilute $HClO_4$ and then through a glass frit into the reactant solution. The $Na_3IrCl_6 \cdot xH_2O$ from Alfa was tested for purity by chlorine oxidation to $IrCl_6^{2-}$ in 0.01 M $HClO_4$ followed by spectral analysis.[32] The absorbancies at 418, 434, and 488 nm were in the correct ratios within 1% but indicated a slightly lower water content than the labeled 7%. The concentration of each sample prepared for stoichiometric or kinetic measurements was determined similarly. Deionized water was distilled from alkaline permanganate solution. Reagent grade $HClO_4$ and $NaClO_4$ were from G. F. Smith. Glassware for handling ozone solutions was used exclusively for that purpose.

Techniques. In tests of the identity of the iridium product, four similarly weighed samples of $Na_3IrCl_6 \cdot xH_2O$ were oxidized separately in

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0.01 M $HClO_4$, two with excess Cl_2 and two with excess O_3. No appreciable variations were observed in the four product spectra, and the absorbancies at the maxima were within 3% of those expected for $IrCl_6^{2-}$ based on complete conversion of $IrCl_6^{3-}$. The stoichiometry was established similarly in 0.02 M $HClO_4$ but under conditions of excess $IrCl_6^{3-}$, determining the ozone concentration in its stock solution before each withdrawal by using its absorbance at 259 nm ($\epsilon = 2900$).[18,33]

A thermostated (±0.1 °C) Durrum-Gibson Model D110 stopped-flow spectrophotometer with a Tektronix Model 3A9 differential amplifier and storage oscilloscope was used to record the reproducible decreases in transmittance at 488 nm (due principally to the formation of $IrCl_6^{2-}$) after mixing reactant solutions with $IrCl_6^{3-}$ in at least a 10-fold stoichiometric excess over O_3. (In preliminary experiments with O_3 in excess, the rate of transmittance change decreased with successive trials, indicating a loss of ozone from the close-to-saturated solutions.)

Results

In 27 experiments with $[O_3]_0 = (3\text{–}7) \times 10^{-5}$ M and $[IrCl_6^{3-}]_0$ in 5–7-fold molar excess, the stoichiometric ratio, $[O_3]_0{:}[IrCl_6^{2-}]_\infty$, fell within the range 1.0:2.0 ± 0.1. These results indicate the following net reaction in which the iridium coordination sphere has remained intact:

$$O_3 + 2IrCl_6^{3-} + 2H^+ = O_2 + 2IrCl_6^{2-} + H_2O$$

Kinetic plots of ln $(A_\infty - A_t)$ vs time were linear over 70–80% reaction, establishing a first-order dependence on $[O_3]$. Pseudo-first-order rate constants, k_{obs}, were obtained by dividing the slopes by 2 to account for the stoichiometry. At each of six temperatures, linear plots of k_{obs} vs $[IrCl_6^{3-}]$ with near-zero intercepts yielded second-order rate constants, k_1. At 25 and 16 °C no rate dependence on ionic strength or the concentration of $HClO_4$ was evident over the range 0.010–1.0 M. No indication of inhibition by added $IrCl_6^{2-}$ was evident over the range, $(2\text{–}6) \times 10^{-5}$ M, which was limited by the contribution to the measured transmittance from the added $IrCl_6^{2-}$. Over the range, 10^{-4} M $< [IrCl_6^{3-}] < 10^{-3}$ M, with O_3 in at least 10-fold stoichiometric deficiency, the reaction obeys the rate law

$$d[IrCl_6^{2-}]/dt = 2k_1[O_3][IrCl_6^{3-}]$$

The experimental values for k_1 ($M^{-1}\ s^{-1}$) at the various temperatures were as follows: 2.5 °C, $(4.1 \pm 0.2) \times 10^3$; 7.7 °C, $(5.7 \pm 0.1) \times 10^3$; 16.0 °C, $(1.0 \pm 0.05) \times 10^4$; 25.0 °C, $(1.7 \pm 0.06) \times 10^4$; 30.0 °C, $(2.4 \pm 0.1) \times 10^4$; 33.4 °C, $(3.1 \pm 0.1) \times 10^4$. (At temperatures other than 16 and 25 °C, the ionic medium was usually 0.10 M $HClO_4$ and 0.10 M $NaClO_4$.) These results yielded a linear plot of ln (k_1/T) vs $1/T$, from which the following activation parameters were calculated: $\Delta H_1^\ddagger = 10.3 \pm 0.3$ kcal mol^{-1} and $\Delta S_1^\ddagger = -4.5 \pm 1$ eu.

Discussion

At least three mechanisms can be offered that are consistent with the observed rate law by virtue of having the following initial and rate-determining reaction in common:

$$O_3 + IrCl_6^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_3^- + IrCl_6^{2-} \qquad (1)$$

From $k_1 = 1.7 \times 10^4\ M^{-1}\ s^{-1}$ and $K = 1.1 \times 10^2$ (vide infra) at 25 °C, $k_{-1} = 1.5 \times 10^2\ M^{-1}\ s^{-1}$ is calculated. This initial reaction is prevented from coming to equilibrium by the rapid consumption of O_3^-. The first step is the diffusion-controlled protonation of O_3^- with $k_2 = (5\text{–}9) \times 10^{10}\ M^{-1}\ s^{-1}$:[18,34]

$$O_3^- + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HO_3 \qquad (2)$$

This reaction probably does not come to equilibrium due to rapid consumption of HO_3 by one or both of two related paths.[35] In mechanism A, HO_3 dissociates rapidly, $k_3 \geq 10^5\ s^{-1}$,[18,27a,34] to yield the hydroxyl radical, which oxidizes $IrCl_6^{3-}$ rapidly, $k_4 = (9\text{–}13) \times 10^9\ M^{-1}\ s^{-1}$:[36-38]

$$HO_3 \xrightarrow{k_3} OH + O_2 \qquad (3)$$

$$IrCl_6^{3-} + OH \xrightarrow{k_4} IrCl_6^{2-} + OH^- \qquad (4)$$

$$H^+ + OH^- \xrightarrow{k_6} H_2O \qquad (6)$$

In mechanism B, HO_3 reacts directly with $IrCl_6^{3-}$ so that reactions 3 and 4 coalesce into (5).

$$IrCl_6^{3-} + HO_3 \xrightarrow{k_5} IrCl_6^{2-} + OH^- + O_2 \qquad (5)$$

If H_2O and O_3 acted concertedly to oxidize $IrCl_6^{3-}$, yielding HO_3 and OH^- initially, the observed rate law would result. However, the corresponding action of H_3O^+ and O_3, with 0.82 V greater driving force, is not detectable at acidities as high as 1 M. We conclude that the rate-determining reduction of O_3 by $IrCl_6^{3-}$ is not facilitated by proton transfer from water.

The rate law does not distinguish between mechanisms A and B. Whether the net reaction is consummated by mechanism A or B or both depends on the competition for HO_3 by the first-order reaction (3) vs the second-order reaction (5). For comparable fractions of the reaction to be carried by mechanisms A and B under our conditions ($[IrCl_6^{3-}] \sim 10^{-4}\text{–}10^{-3}$ M), a value for k_5 of at least $10^8\text{–}10^9\ M^{-1}\ s^{-1}$ appears necessary. The substantially lower reactivity of O_3^- as an oxidant relative to O^-[31] suggests a similar fate for HO_3 relative to OH. Nevertheless, the unknown effect of protonation on relative reactivities and the fact that k_4 is diffusion rather than activation controlled leave open the possibility that k_5 might be as high as $10^8\text{–}10^9\ M^{-1}\ s^{-1}$.

Given the rapid consumption of O_3^- by protonation and subsequent reaction in mechanism A and perhaps B, a third pathway in which O_3^- dissociates relatively slowly, $k = 5.0 \times 10^3\ s^{-1}$,[31] into O_2 and O^- (which is protonated rapidly and then reacts by reaction 4) need not be considered under our acidic conditions.

The remainder of our attention will focus on reaction 1, to which our data pertain. While the nature of the $IrCl_6^{3-}$ reactant, the $IrCl_6^{2-}$ product, and the rate law are all consistent with the initial reaction occurring by an outer-sphere electron transfer, one other possibility must be considered which is also consistent with these facts. An oxygen atom transfer from O_3 to $IrCl_6^{3-}$ would be first order in each reactant. Spectral evidence has been presented for a fleeting intermediate, formulated as $Cl_5IrClOH^{3-}$, which arises along one path of the $IrCl_6^{3-}$–OH reaction and yields $IrCl_6^{2-}$ as the ultimate product.[37] The reaction of O_3 with $IrCl_6^{3-}$ to yield Cl_5IrClO^{3-} is, by contrast, a 2-equiv oxidation (which would require a 1-equiv reduction with chlorine–oxygen bond cleavage to release $IrCl_6^{2-}$). A related contrast is provided by the very rapid reaction of OH with Cl^- to yield $HOCl^-$ ($k = 4.3 \times 10^9\ M^{-1}\ s^{-1}$)[39] and the much slower reaction of O_3 with Cl^- to yield OCl^- ($k = 3.1 \times 10^{-3}\ M^{-1}\ s^{-1}$).[22,29] The coordination of Cl^- by Ir(III) might be expected to reduce its susceptibility to electrophilic attack. While this expectation is not realized in the reaction of OH with $IrCl_6^{3-}$ ($k = 10^{10}\ M^{-1}\ s^{-1}$),[37] it is difficult to envisage that reactivity

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(33) $\epsilon = 3300$ has been reported for O_3 at 260 nm: Hart, E. J.; Sehested, K.; Holcman, J. *Anal. Chem.* **1983**, *55*, 46. The use of this value would change our $[O_3]_0{:}[IrCl_6^{2-}]_\infty$ ratio to 1.0:2.3 ± 0.1 but would not affect our kinetic results.

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(35) Revised values of $k_{-2} = 3.3 \times 10^2\ s^{-1}$ and $pK_a(HO_3) = 8.2$ have been reported.[18] Since k_3 for the subsequent dissociation of HO_3 into OH and O_2 is $1.1 \times 10^5\ s^{-1}$,[18] or larger,[34] reaction 2 does not come to equilibrium. Since the pseudo-first-order deprotonation of HO_3 by H_2O and/or HPO_4^{2-} is not competitive with its dissociation into OH and O_2, it is difficult in the absence of a more detailed report to see how these constants could be determined. Nevertheless, all reports agree on a very rapid protonation of O_3^- ($k_2 = (5\text{–}9) \times 10^{10}\ M^{-1}\ s^{-1}$) and a rapid subsequent dissociation of HO_3 into OH and O_2.[18,27,34]

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toward oxygen atom transfer from O_3 would be enhanced by a factor of 10^7 with $IrCl_6^{3-}$ relative to Cl^-. Thus, our rate constant of 1.7×10^4 M^{-1} s^{-1} provides the principal evidence against an oxygen atom transfer in the reaction of O_3 with $IrCl_6^{3-}$.

If (1) is correctly characterized as an outer-sphere electron-transfer reaction, it can be examined within the context of the Marcus–Hush theory.[40,41] In particular, since the reduction potential (0.90 V)[42] and self-exchange rate constant (2×10^5 M^{-1} s^{-1})[43] for the $IrCl_6^{2-}/IrCl_6^{3-}$ couple have been reported, the reduction potential for the O_3/O_3^- couple would make possible a calculation of its effective self-exchange rate constant. This potential is not available directly, but can be calculated from the following thermochemical cycle:

			ΔG, kcal/mol
$O_3(g) + H_2O + 2e^-$	$= O_2(g) + 2OH^-(aq)$	$E° = 1.25$ V	-57.7[44]
$O_3(aq)$	$= O_3(g)$		-2.8[28,44]
$O_2(g)$	$= O_2(aq)$		3.9[44]
$O_2(aq) + O^-(aq)$	$= O_3^-(aq)$	$K = 6.0 \times 10^5$	-7.9[31]
$HO(aq)$	$= O^-(aq) + H^+(aq)$	$K = 10^{-11.9}$	16.2[31]
$OH^-(aq)$	$= OH(aq) + e^-$	$E° = -1.90$ V	43.8[45,28]
$H^+(aq) + OH^-(aq)$	$= H_2O$	$K = 1.0 \times 10^{14}$	-19.1
$O_3(aq) + e^-$	$= O_3^-(aq)$	$E° = 1.02$ V	-23.6

The potential that results is in excellent agreement with a value of 1.01 V calculated from a kinetic determination of K_{eq} for the $O_3(aq) + ClO_2^-(aq) = O_3^-(aq) + ClO_2(aq)$ reaction.[28,46] Values of $E° = 0.12$ V and $K_{eq} = 1.1 \times 10^2$ for reaction 1 are calculated from these data.

From the rate constant, $k_{12} = 1.7 \times 10^4$ M^{-1} s^{-1}, and equilibrium constant, $K_{12} = 1.1 \times 10^2$, for the relabeled cross-reaction (1), k_{11} for the O_3/O_3^- self-exchange can be calculated by using the Marcus–Hush relationships[47]

$$k_{11} = \left(\frac{k_{12}}{W_{12}}\right)^2 \frac{1}{k_{22}K_{12}f_{12}} \tag{7}$$

$$W_{12} = \exp\left(\frac{-(w_{12} + w_{21} - w_{11} - w_{22})}{2RT}\right) \tag{8}$$

$$w_{ij} = \frac{4.23 z_i z_j}{a(1 + 0.329 a I^{1/2})} \tag{9}$$

$$\ln f_{12} = \frac{\left(\ln K_{12} + \dfrac{w_{12} - w_{21}}{RT}\right)^2}{4\left(\ln \dfrac{k_{11}k_{22}}{Z^2} + \dfrac{w_{11} + w_{22}}{RT}\right)} \tag{10}$$

Since the reactions involved have different charge products ($z_i z_j$) and center-to-center distances (a in Å), the work terms (w_{ij} in kcal mol^{-1}) do not cancel in W_{12} and must be included. (While the iterated correction arising from $f = 0.92$ is not significant, W_{12}^2 lowers k_{11} approximately 4-fold.) From the data previously assembled and effective radii of 1.9 and 4.2 Å for each member of the O_3/O_3^- and $IrCl_6^{2-}/IrCl_6^{3-}$ couples, respectively, an effective self-exchange constant of 4 M^{-1} s^{-1} for O_3/O_3^- is calculated. If our conclusion that the $O_3 + IrCl_6^{3-}$ reaction is outer-sphere is incorrect, a still lower estimate for the outer-sphere O_3/O_3^- electron exchange would result. Thus, we estimate k_{11} as 4 M^{-1} s^{-1} if our cross-reaction is outer-sphere and less than 4 M^{-1} s^{-1} if it is not, with the usual reservation about the certainty of a self-exchange constant derived from a single cross-reaction.

The Marcus-Hush theory provides the most promising current model for understanding the magnitude of this rate constant and its difference from those of similar couples. A self-exchange rate constant is expressed within this model as

$$k = Z \exp\left(\frac{-\Delta G^*}{RT}\right) \tag{11}$$

For reactions in which one reactant is uncharged, ΔG^* is given by

$$\Delta G^* = \Delta G_i^* + \Delta G_o^* \tag{12}$$

ΔG_i^* and ΔG_o^* are the free energies required for the reorganization of the primary bond system and the solvation shell, respectively, prior to electron transfer.

For the transfer of one electron between self-exchange partners that are just touching, a dielectric continuum model of aqueous solution as the medium for spherical reactants yields for ΔG_o^*[48]

$$\Delta G_o^* \text{ (kcal mol}^{-1}) = 22.7/r \tag{13}$$

Presumably an effective radius, r, can be employed to overcome limitations in the applicability of this model to small, nonspherical reactants.

Stanbury and Lednicky have applied a simple valence force field to bent triatomic couples with symmetrical transition states in which both reactants have acquired equal bond lengths and angles.[47a] Under the approximation that the primary bond energy is independent of the solvation energy, the energy required for these distortions

$$V_{tot} = K_0(d' - d_0°)^2 + \tfrac{1}{2}H_0[d_0°(\alpha' - \alpha_0°)]^2 + K_-(d' - d_-°)^2 + \tfrac{1}{2}H_-[d_-°(\alpha' - \alpha_-°)]^2 \tag{14}$$

was minimized. K and H designate stretching and bending force constants; d and α designate bond lengths and angles; subscripts designate oxidation states; superscripts designate equilibrium (°) or transition-state (′) values. The approach is analogous to Sutin's simplified treatment of octahedral metal couples.[49] The barrier arising from this reorganization within the primary bond systems is given by

$$\Delta G_i^* = \frac{(d_-° - d_0°)^2 K_- K_0}{K_0 + K_-} + \frac{H_- H_0 (d_-°)^2 (d_0°)^2 (\alpha_-° - \alpha_0°)^2}{2[H_0(d_0°)^2 + H_-(d_-°)^2]} \tag{15}$$

According to this expression, the activation barrier from the primary bond systems consists of cleanly separated terms for bond stretching and angle bending.

Implicit in this derivation is an assumption that the stretch–stretch and stretch–bend interaction constants of the general valence force field[50] contribute negligibly to ΔG_i^*. However, since the stretch–stretch constant ($f_{dd} = 1.52 \times 10^5$ dyn cm^{-1}) and the stretch–bend constant ($f_{d\alpha}/d_0° = 0.332 \times 10^5$ dyn cm^{-1}) for ozone are appreciable relative to the stretching ($f_d = 5.70 \times 10^5$ dyn cm^{-1}) and bending ($f_\alpha/d_0°^2 = 1.28 \times 10^5$ dyn cm^{-1}) force constants,[51] this assumption must be questioned for the O_3/O_3^-

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(46) This reduction potential differs from those calculated by using a similar cycle (Koppenol, W. H. *FEBS Lett.* **1982**, *140*, 169. Koppenol, W. H.; Liebman, J. F. *J. Phys. Chem.* **1984**, *88*, 99) primarily because earlier and, we believe, less accurate values for the $OH(aq)/OH^-(aq)$ potential were used.

(47) (a) Stanbury, D. M.; Lednicky, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 2847. (b) A value of 1×10^{12} M^{-1} s^{-1} for Z, the collision frequency, discussed later in the text, was used in eq 10. For calculations for O_3/O_3^- using eq 9, $I = 0.20$ M was used.

(48) Reynolds, W. L.; Lumry, R. *Mechanisms of Electron Transfer*; Ronald Press: New York, 1966; p 129.

(49) Sutin, N. *Annu. Rev. Nucl. Sci.* **1962**, *12*, 285.

(50) Sawodny, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 573. Note that α should be replaced by $\Delta\alpha$ in the last term in the GVFF equation on p 574.

(51) Pierce, L. *J. Chem. Phys.* **1956**, *24*, 139.

Table I. Kinetic Parameters for Related Non-Metal Self-Exchanges

		O_2/O_2^-		O_3/O_3^-	SO_2/SO_2^-	ClO_2/ClO_2^-	NO_2/NO_2^-	N_3/N_3^-	CO_2/CO_2^-
$d_-^\circ(O_2^-)$	1.30		1.32						
k_{11}(exptl), $M^{-1}\ s^{-1}$		3		4	1×10^4	2×10^2	2×10^{-2}	4×10^4	10^{-5} (10^{-7})
k_{11}(theor), $M^{-1}\ s^{-1}$	44		14	90	1.1×10^3	55	1.6×10^{-3}	5.3×10^3	see text
Γ_n	5		12	3.7	2.6	5.3	79	1	(2300)[a]
ΔG_i^*, kcal mol^{-1}	2.3		3.5	2.5	2.0	4.2	10.8	~0	(18.5)[a]
ΔG_0^*, kcal mol^{-1}		12.8		12.0	10.8	10.8	12.0	11.3	12.0
r, Å		1.77		1.9	2.1	2.1	1.9	2.0	1.9

[a] These values were calculated from k_{11}(exptl) = $10^{-7}\ M^{-1}\ s^{-1}$.[65]

self-exchange. If only the stretch–stretch constant is included in the previous derivation, the same expression for ΔG_i^* is obtained but with K now equal to $(f_d + f_{dd})$. This increases the barrier due to bond stretching by ~20%. If the stretch–bend constant is also included, a substantially more complex expression results for ΔG_i^*, but without significant change in its value, primarily because the angular change is small. Thus, the other three deformation constants for O_3 and O_3^-, together with the bond lengths and angles, are sufficient for an adequate estimate of ΔG_i^* using eq 15.

The addition of an electron to O_3 increases the bond length from 1.278 to 1.35 Å and decreases the bond angle from 116.8 to 114°.[52,53] The lowest unoccupied molecular orbital of ozone has been characterized as antibonding, with the addition of an electron to it predicted to result in longer bonds and a smaller angle.[54] In addition to the experimental support for this characterization which is provided by the above structural changes, the fundamental vibrational frequencies shift from $\nu_1 = 1103$, $\nu_2 = 701$, and $\nu_3 = 1042$ cm^{-1} for O_3 to $\nu_1 = 1010$, $\nu_2 = 590$, and $\nu_3 = 795$ cm^{-1} for O_3^-.[55]

For O_3 the vibrational frequencies have been supplemented by rotational data to yield the four force constants given above.[51] Since neither rotational nor isotopic substitution data are available for O_3^-, we have estimated $f_{d\alpha}/d_-^\circ$ to be 0.30×10^5 dyn cm^{-1}, on the basis of the above experimental value for this constant in O_3, in order to calculate $f_d = 4.7 \times 10^5$, $f_\alpha/d_-^{\circ 2} = 1.0 \times 10^5$, and $f_{dd} = 0.70 \times 10^5$ dyn cm^{-1} from the three vibrational frequencies by using Wilson's **G** and **F** matrices.[56,50] This method was tested with O_3 by using the known value of $f_{d\alpha}/d_0^\circ = 0.33 \times 10^5$ dyn cm^{-1} and the three vibrational frequencies to calculate $f_d = 5.1 \times 10^5$, $f_\alpha/d_0^{\circ 2} = 1.5 \times 10^5$, and $f_{dd} = 0.90 \times 10^5$ dyn cm^{-1} for comparison with the force constants that have been more rigorously defined by the rotational data. When this comparison is made in the context of our objective of estimating a self-exchange rate constant for O_3/O_3^- using ΔG_i^*, the force constants calculated for O_3^- from the vibrational frequencies seem sufficiently accurate.

These constants for O_3^- were used with the more rigorously defined constants for O_3 to calculate $\Delta G_i^* = 2.5$ kcal mol^{-1} for the self-exchange. The contributions of bond stretching and angle bending to this "inner-sphere" barrier stand in the ratio of 93:7.

From an average bond distance of 1.3 Å and a van der Waals radius for oxygen of 1.5 Å, an estimate was made for the volume of each reactant of 30 Å^3, which corresponds to a sphere with a radius of 1.9 Å, and an estimate for ΔG_0^* from eq 13 of 12.0 kcal mol^{-1}. On the basis of a diffusion-controlled rate constant of 10^{10} $M^{-1}\ s^{-1}$ and an estimate of 10^2 collisions in the solvent cage per encounter,[57] we have used $Z = 10^{12}\ M^{-1}\ s^{-1}$ and the resultant $\Delta G^* = 14.5$ kcal mol^{-1} in eq 11 to calculate $k_{11} = 24\ M^{-1}\ s^{-1}$ for the O_3/O_3^- self-exchange. The good correlation between this rate constant and the $k_{11} = 4\ M^{-1}\ s^{-1}$ derived experimentally from our cross-reaction must be subjected to a further consideration.

Since the (geometrically averaged) values of $h\nu$ for stretching (2.10×10^{-20} J/molecule) and bending (1.27×10^{-20} J/molecule) are larger than kT at 298 K (4.11×10^{-21} J/molecule), a more rigorous evaluation would include the effects of nuclear tunneling through the classical inner-sphere barrier. The solvation shell rearrangement can be treated classically, since water is characterized by a frequency of ~30 cm^{-1}, which is less than the value of 207 cm^{-1} corresponding to kT at 298 K. According to the semiclassical theory of Sutin et al.,[58,59] an inner-sphere nuclear tunneling factor, Γ_n, can be calculated from the equations

$$\Delta G_i^*(T) = 4\Delta G_i^*\left(\frac{kT}{h\nu_i}\right)\tanh\left(\frac{h\nu_i}{4kT}\right) \qquad (16)$$

$$\ln \Gamma_n = \frac{\Delta G_i^* - \Delta G_i^*(T)}{RT} \qquad (17)$$

When the resulting Γ_n of 3.7 for the O_3/O_3^- self-exchange is used as an additional preexponential factor in eq 11, a value of 90 $M^{-1}\ s^{-1}$ is calculated for k_{11}.[60a] In view of the uncertainty arising from a spherical model for nonspherical reactants, a semiclassical extension of the Marcus–Hush theory, in which $\Gamma_n = 3.7$, $Z = 10^{12}\ M^{-1}\ s^{-1}$, $\Delta G_i^* = 2.5$ kcal mol^{-1}, and ΔG_0^* is close to that expected from the size of the reactants, provides an acceptable account of our experimentally estimated self-exchange rate constant of 4 $M^{-1}\ s^{-1}$.[60b]

From outer-sphere cross-reactions with metal complexes, relative Marcus theory estimates of self-exchange rate constants have been made for the O_2/O_2^-,[61] SO_2/SO_2^-,[62,63] ClO_2/ClO_2^-,[47a] NO_2/NO_2^-,[64a] N_3/N_3^-,[64b] and CO_2/CO_2^-[65] couples. The procedure

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(52) Hughes, R. D. *J. Chem. Phys.* **1956**, *24*, 131.

(53) Schnick, W.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 54.

(54) (a) Mulliken, R. S. *Rev. Mod. Phys.* **1942**, *14*, 204. (b) Walsh, A. D. *J. Chem. Soc.* **1953**, 2266. (c) Peyerimhoff, S. D.; Buenker, R. J. *J. Chem. Phys.* **1967**, *47*, 1953. (d) Buenker, R. J.; Peyerimhoff, S. D. *Chem. Rev.* **1974**, *74*, 127.

(55) (a) Clough, S. A.; Kneizys, F. X. *J. Chem. Phys.* **1966**, *44*, 1855. (b) Jacox, M. E. *J. Phys. Chem. Ref. Data* **1984**, *13*, 977.

(56) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, 1955; pp 61–76. We thank our colleague Walt Jones for guidance with these calculations.

(57) Sutin, N. *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 15, p 45.

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

(59) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(60) (a) If, for O_3^-, the bond distance is as high as 1.357 Å and the bond angle as low as 113.4° (the values found for KO_3),[53] the corresponding ΔG_i^* of 3.1 kcal mol^{-1} and Γ_n of 5 would combine with a ΔG_0^*(s) of 12.0 kcal mol^{-1} to yield a theoretical expectation for k_{11} of 40 $M^{-1}\ s^{-1}$ rather than 90 $M^{-1}\ s^{-1}$ for the O_3/O_3^- couple. (b) The theoretical and experimental estimates of k_{11} would agree within a factor of 2 if a value of $10^{11}\ M^{-1}\ s^{-1}$ for Z were used. However, this appears to be a less accurate reflection of the effective collision frequency than 10^{12} $M^{-1}\ s^{-1}$, as judged by the apparent applicability of the latter to the related reactions discussed below and by the similarity of the corresponding entropy of association to that obtained from preequilibrium treatments of encounter formation.[59]

(61) (a) Zahir, K.; Espenson, J. H.; Bakac, A. *J. Am. Chem. Soc.* **1988**, *110*, 5059. (b) Stanbury, D. M.; Haas, O.; Taube, H. *Inorg. Chem.* **1980**, *19*, 518. (c) Stanbury, D. M.; Mulac, W. A.; Sullivan, J. C.; Taube, H. *Inorg. Chem.* **1980**, *19*, 3735. (d) Stanbury, D. M.; Gaswick, D.; Brown, G. M.; Taube, H. *Inorg. Chem.* **1983**, *22*, 1975. (e) Creaser, I. I.; Gene, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.

(62) Twelve reductions by SO_2^- yield an average SO_2/SO_2^- self-exchange constant of $8 \times 10^3\ M^{-1}\ s^{-1}$[63a] whereas five oxidations by SO_2 yield an average value of $5 \times 10^4\ M^{-1}\ s^{-1}$[63b] ($2 \times 10^4\ M^{-1}\ s^{-1}$ after recalculation using eqs 7–10). In Table I we have used an intermediate estimate of $1 \times 10^4\ M^{-1}\ s^{-1}$.

(63) (a) Balahura, R. J.; Johnson, M. D. *Inorg. Chem.* **1987**, *26*, 3860. (b) Simmons, C. A.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 581.

(64) (a) Ram, M. S.; Stanbury, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 8136. (b) *J. Phys. Chem.* **1986**, *90*, 3691.

(65) Schwarz, H. A.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1985**, *24*, 433. Using eqs 7–10, we calculate $k_{11} \sim 10^{-7}\ M^{-1}\ s^{-1}$ for the CO_2/CO_2^- couple from their data.

described above for the O_3/O_3^- couple was used to calculate the kinetic parameters in Table I. The equations

$$d' = \frac{K_0 d_0^\circ + K_- d_-^\circ}{K_0 + K_-} \tag{18}$$

$$\Delta G_i^* = {}^1\!/_2 K_0 (d' - d_0^\circ)^2 + {}^1\!/_2 K_- (d_-^\circ - d')^2 \tag{19}$$

$$\Delta G_i^* = \frac{0.5 K_0 K_- (d_-^\circ - d_0^\circ)^2}{K_0 + K_-} \tag{20}$$

were derived for the calculation of ΔG_i^* for the O_2/O_2^- couple from bond distances of d_0° = 1.207 Å[66] and d_-° = 1.30 and 1.32 Å[67] and stretching frequencies of 1556 and 1090 cm^{-1},[66,68] which yield force constants of $K_0 = 1.14 \times 10^6$ and $K_- = 5.61 \times 10^5$ dyn cm^{-1}. When the resulting values for ΔG_i^* of 2.3 and 3.5 kcal mol^{-1} and a geometrically averaged stretching frequency of 1262 cm^{-1} are used in eqs 16 and 17, nuclear tunneling factors of 5 and 12 are calculated. Since no definitive measurements of the bond distance and angle in SO_2^- have been reported, we have relied on Hirao's calculation[71] of the differences in these values of 0.053 Å and −4.3° from those of SO_2, which are known,[72] to calculate ΔG_i^* for the SO_2/SO_2^- couple.[73] A large angular rearrangement energy for the CO_2/CO_2^- couple places it in a separate category, to be discussed below. Stanbury's estimates of ΔG_i^* and Γ_n were used for the other three couples.[47a,64]

Table II. Rate Constant Comparison for Non-Metal Cross-Reactions[a]

ref	reaction	k_{12}(obsd), M^{-1} s^{-1}	k_{12}-(calcd), M^{-1} s^{-1}
27a	$O_3 + O_2^- \rightarrow O_3^- + O_2$	1.5×10^9	2×10^8
28	$O_3 + ClO_2^- \rightarrow O_3^- + ClO_2$	4×10^6	2×10^2
29	$O_3 + NO_2^- \rightarrow O_3^- + NO_2$	3.7×10^5	3×10^{-1}
86	$ClO_2 + NO_2^- \rightarrow ClO_2^- + NO_2$	1.5×10^2	2×10^{-1}
87	$O_2 + SO_2^- \rightarrow O_2^- + SO_2$[b]	$\geq 1 \times 10^8$	1×10^3

[a] To calculate the cross-reaction rate constants, the following reduction potentials were used: O_3/O_3^-, 1.02 V; O_2/O_2^-, −0.16 V;[88] ClO_2/ClO_2^-, 0.93 V;[28] NO_2/NO_2^-, 1.04 V;[86] SO_2/SO_2^-, −0.26 V.[47] [b] Since this reaction follows the rate-determining dissociation of $S_2O_4^{2-}$ and is followed by subsequent reaction, its formulation as an electron transfer is reasonably inferred but not definitively established.

For all of the small non-metal couples of 0/1− charge type in Table I except CO_2/CO_2^-, the semiclassical Marcus–Hush theory estimates self-exchange rate constants that are within factors of 5–20 of the values derived from cross-reactions with metal complexes. These differences between theory and experiment are at least as small as for any family of couples for which this sort of evaluation has been made. Thus, the Marcus–Hush theory appears equally applicable to reactants without ligands, which are less symmetrical and substantially smaller than the metal complexes which have received so much attention. Against this background, several comparisons and deviations are worthy of attention.

The available structural data for the CO_2/CO_2^- couple[75] yield $\Delta G_i^* = \Delta G_{str}^* + \Delta G_{bend}^* = 8 + 24 = 32$ kcal mol^{-1} from eq 15, which, together with Γ_n = 75 000 and ΔG_0^* = 12 kcal mol^{-1}, result in k_{11}(theor) = 2×10^{-16} M^{-1} s^{-1}, which compares poorly with k(exptl) = 10^{-5} (10^{-7}) M^{-1} s^{-1}.[65] Pacansky et al.[77] have calculated detailed energy surfaces for CO_2 and CO_2^- that intersect 17.4 and 9.3 kcal mol^{-1} above the CO_2 and CO_2^- minima, respectively, at d' = 1.20 Å and α' = 149°, and provide a substantially lower ΔG_i^* = 26.7 kcal mol^{-1}. It appears from this that one assumption leading to eq 15, that α' is midway between α_0° = 180° and α_-° = 135°, is invalid for this couple. More critically, force constants derived from much smaller harmonic deformations are not valid throughout such large angular deformations. Even with this improved ΔG_i^* (and a correspondingly decreased Γ_n of 7200), the calculated $k_{11} = 3 \times 10^{-13}$ M^{-1} s^{-1} is substantially below the value derived from the cross-reaction, testimony to the difficulty in calculating activation energies. As if to emphasize this point, a more recent calculation using polarization functions yielded a minimum-energy intersection 29.7 and 3.2 kcal mol^{-1} above the CO_2 and CO_2^- minima, respectively,[80] leading to a ΔG_i^* = 33 kcal mol^{-1}. Two rather ad hoc calculations yield values for ΔG_i^* that approach the experimental value of 18.5 kcal mol^{-1} (Γ_n = 2300), which we calculate from k_{11}(exptl) = 10^{-7} M^{-1} s^{-1} (assuming the $CO_2^-/Co(bpy)_3^{2+}$ reaction is indeed outer-sphere.) If the minimum-energy intersection is 4.8 kcal mol^{-1} above the CO_2^- minimum (England's $\Delta\epsilon$[80]) and the CO_2 minimum is 11.5 ± 2.3 kcal mol^{-1} below it (corresponding to the experimental estimates of the electron affinity of CO_2[81,82]), a value of 21.1 ± 2.3 kcal mol^{-1} is calculated for ΔG_i^*. Alternatively, if the electron affinity of CO_2 is 0.2 eV more positive than the appearance potential measurements indicate, as suggested by Cooper and Compton[81a] and Pacansky et al.,[77] the same calculation would yield ΔG_i^* = 16.5 kcal mol^{-1}. In view of the uncertainties in calculated energies and in the driving force for the cross-reaction,[65] this very approximate agreement between theory and experiment for the

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(66) Herzberg, G. *Spectra of Diatomic Molecules*; D. Van Nostrand: Princeton, NJ, 1950; p 560.

(67) A range of values has been reported for the bond distance in the O_2^- ion, which weighs heavily in the calculation of ΔG_i^*. A value of 1.28 ± 0.07 Å in KO_2 was first reported by: Kassatochkin, W.; Kotow, W. *J. Chem. Phys.* **1936**, *4*, 458. A value of 1.33 ± 0.06 Å in an impure sample of NaO_2 (measured by: Templeton, D. H.; Dauben, C. H. *J. Am. Chem. Soc.* **1950**, *72*, 2251) appears to have been revised to 1.35 ± 0.06 Å on the basis of later work on a single crystal that did not report a new determination of the distance: Carter, G. F.; Templeton, D. H. *J. Am. Chem. Soc.* **1953**, *75*, 5247. The 1.33-Å value was criticized and reported to be 1.31 ± 0.03 Å in the room-temperature form of a purer sample of NaO_2: Zhdanov, G. S.; Zvonkova, Z. V. *Dokl. Akad. Nauk SSSR* **1952**, *82*, 743; *Chem. Abstr.* **1952**, *46*, 6893. A powder specimen of KO_2 was reexamined and a value of 1.28 ± 0.02 Å was reported: Abraham, S. C.; Kalnajs, J. *Acta Crystallogr.* **1955**, *8*, 503. A theoretical evaluation of this result based on the rather large temperature factor and the electronic orbital degeneracy in O_2^- was presented and it was concluded that a value in the range of 1.32–1.35 Å was compatible with the X-ray data for KO_2: Halverson, F. *J. Phys. Chem. Solids* **1962**, *23*, 207. (It appears that this estimate might have been lowered to 1.30–1.33 Å if Halverson had used the 1.31-Å result for NaO_2 in his plot.) In the context of Raman transitions of 1145 ± 2 cm^{-1} for KO_2 and 1142 ± 5 cm^{-1} for NaO_2 (reported by: Creighton, J. A.; Lippincott, E. R. *J. Chem. Phys.* **1964**, *40*, 1779), we note that an oxygen–oxygen distance in O_2^- of 1.29–1.30 Å is compatible with all the experimental reports. Moreover, a plot of vibrational frequency vs bond length for O_2^+ (1145 cm^{-1}, 1.123 Å),[66] O_2 (1556 cm^{-1}, 1.207 Å),[66] O_2^- (1090 cm^{-1}, ~1.31 Å),[68] and O_2^{2-} (842 cm^{-1}, 1.49 Å)[69,70] provides a calibration for the shift in Raman frequency to 1090 cm^{-1} for an isolated O_2^- ion[69] being indicative of a bond length that is ~0.015 Å longer than in KO_2 and NaO_2. The resulting estimate of 1.30–1.32 Å for the bond length in O_2^- fits on a smooth plot of bond order vs bond length for the family of dioxygen species. In order to provide an indication of the sensitivity of the kinetic parameters to variation in this distance, Table I includes the results of calculations based on 1.30 and 1.32 Å.

(68) Rolfe, J.; Holzer, W.; Murphy, W. F.; Bernstein, H. J. *J. Chem. Phys.* **1968**, *49*, 963.

(69) Evans, J. C. *J. Chem. Soc. D* **1969**, 682.

(70) Abrahams, S. C.; Kalnajs, J. *Acta Crystallogr.* **1954**, *7*, 838.

(71) Hirao, K. *J. Chem. Phys.* **1985**, *83*, 1433.

(72) Kivelson, D. *J. Chem. Phys.* **1954**, *22*, 904.

(73) The structural parameters for SO_2 (d_0° = 1.432 Å, α_0° = 119.5°, $f_d = 10.0 \times 10^5$, $f_{dd} = 0.02 \times 10^5$, $f_\alpha/d_0^2 = 0.79 \times 10^5$, and $f_{d\alpha}/d_0 = 0.19 \times 10^5$ dyn cm^{-1})[72] and SO_2^- (d_-° = 1.485 Å, α_-° = 115.2°, $f_d = 6.5 \times 10^5$, $f_{dd} = 0.50 \times 10^5$, $f_\alpha/d_0^2 = 0.77 \times 10^5$ dyn cm^{-1}, the latter three calculated as for O_3^- by the **FG** matrix method by assuming that $f_{d\alpha}/d_0 = 0.19 \times 10^5$ dyn cm^{-1} (the value for SO_2) and using $\nu_1 = 985$, $\nu_2 = 495$, and $\nu_3 = 1042$ cm^{-1})[74] were used for the calculation of ΔG_i^*. The ratio between bond-stretching and angle-bending contributions is 83:17.

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

(75) For CO_2: d_0° = 1.16 Å,[76] α_0° = 180°, $K_0 = 1.73 \times 10^6$, $H_0 = 5.83 \times 10^4$ dyn cm^{-1}.[76] For CO_2^-: d_-° = 1.25 Å, α_-° = 135°,[77–79] $K_- = 1.16 \times 10^6$, $H_- = 1.15 \times 10^5$ dyn cm^{-1}.[77–78]

(76) Suzuki, I. *J. Mol. Spectrosc.* **1968**, *25*, 479. Note that the potential function is defined as *V* rather than the usual 2*V*.

(77) Pacansky, J.; Wahlgren, U.; Bagus, P. S. *J. Chem. Phys.* **1975**, *62*, 2740.

(78) Carmichael, I.; Bentley, J. *J. Phys. Chem.* **1985**, *89*, 2951.

(79) Yoshioka, Y.; Jordan, K. D. *Chem. Phys. Lett.* **1981**, *84*, 370.

(80) England, W. B. *Chem. Phys. Lett.* **1981**, *78*, 607.

(81) (a) Cooper, C. D.; Compton, R. N. (b) *Chem. Phys. Lett.* **1972**, *14*, 29. (c) *J. Chem. Phys.* **1973**, *59*, 4140.

(82) Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1975**, *63*, 3821.

CO_2/CO_2^- couple is as good as can be expected. We conclude that formalisms such as eq 15 that work reasonably well for couples with smaller rearrangement barriers cannot be used reliably to estimate larger rearrangements such as the angular deformation which is predominantly responsible for the slowness of the CO_2/CO_2^- self-exchange. Even so, it seems likely that realistic estimates of self-exchange rate constants can still be made by using the Marcus–Hush theory if ΔG_i^* can be calculated reliably.

We next examine the compatibility of our assessment of the O_2/O_2^- couple with its reversible or quasi-reversible response to cyclic voltammetry in nonaqueous solvents at a scan rate of 0.1 V s^{-1}.[83] For acetonitrile, dimethylformamide, and dimethyl sulfoxide, eq 13 is modified by the differing optical and static dielectric constants[48,84] to yield

$$\Delta G_o^* \text{ (kcal mol}^{-1}) = 21.7/r \text{ (AN)}, 19.1/r \text{ (DMF)}, 18.0/r \text{ (DMSO)} \quad (21)$$

The resulting values of ΔG_o^* for O_2/O_2^- (r = 1.77 Å) of 12.3, 10.8, and 10.2 kcal mol^{-1}, in combination with the other kinetic parameters evaluated for d_-° = 1.30 Å (Table I), yield theoretical estimates for k_{11} of 1×10^2 M^{-1} s^{-1} in acetonitrile, 1×10^3 M^{-1} s^{-1} in DMF, and 4×10^3 M^{-1} s^{-1} in DMSO. These homogeneous rate constants correspond to electrochemical rate constants of 1, 3, and 6 cm s^{-1},[85] which are more than sufficient to account for the reversible cyclic voltammograms. Even if the homogeneous and electrochemical rate constants are lower by factors of 10 and $10^{1/2}$, respectively, reversibility on the cyclic voltammetric time scale would not be compromised. Thus, a self-exchange constant in water as slow as the cross-reaction value of ~3 M^{-1} s^{-1} is not at odds with the available electrochemical evidence.

When the results for the non-metal couples in Table I are compared with those for typical metal complexes, the base level of reactivity is seen to be lower as the result of radii that are smaller and ΔG_o^*'s that are larger by a factor of ~2. For example, the self-exchange constant of 4×10^4 M^{-1} s^{-1} for N_3/N_3^- is at the upper end of the reactivity scale. Below this upper boundary on reactivity, a ~10^{11}-fold variation in rate constant in the present family is due to a range in ΔG_i^* from 0 to 19 kcal mol^{-1}, which is modulated by a range in nuclear tunneling factors from 1 to 2300. This range in ΔG_i^* is similar to that for metal complexes. For both metal complexes and small non-metal couples, the redox electron exerts a sufficiently varied influence on bonding to result in a broad spectrum of reactivity.

Five cross-reactions between couples in Table I have been studied.[27a,28,86,87] Table II contrasts their observed rate constants with those calculated from the self-exchange constants (k_{11}(exptl)) in Table I by using the relative Marcus–Hush theory. With the rate of the O_3/O_2^- reaction approaching diffusion control, it is not possible to determine by how much the activation-limited rate constant exceeds the calculated value and oxygen atom transfer cannot be excluded. Nevertheless, a pattern seems to be emerging[86] in which reactions between two non-metal reactants are faster than predicted from the self-exchange constants consistently pointed to both by cross-reactions with substitution-inert metal complexes and by the absolute Marcus–Hush theory. We subscribe provisionally to the view[86] that the mechanistic difference implied by this pattern consists principally in greater orbital overlap between two non-metal reactants than can occur when one of the reactants is a metal ion shielded by its ligands. Since the cross-reaction relationship requires comparable orbital overlap in the three interrelated reactions and the absolute theory does not take account of strong electronic coupling, self-exchange constants derived either from weak-overlap cross-reactions or from the absolute theory cannot be expected to predict rate constants for reactions involving strong overlap. Particularly important examples of this may prove to be the self-exchange reactions of the non-metal couples. The elegant direct measurement of k_{11} = 5.8×10^2 M^{-1} s^{-1} for the NO_2/NO_2^- self-exchange[89] appears, on comparison with k_{11}(exptl) = 2×10^{-2} M^{-1} s^{-1}, to provide the first example. If, as this and the cross-reactions in Table II raise as a possibility, a self-exchange involves strong overlap, the two approaches considered in this report will provide better estimates of its "weak-overlap" self-exchange constant than a direct measurement. Several serious discrepancies in the cross-reactions of non-metal reactants can perhaps be understood from this perspective. A number of cross-reactions involving SO_2, SO_2^-, and O_2^- are substantially faster[90] than would be consistent with the "weak-overlap" self-exchange constants in Table I. To the extent that they involve strong overlap—and with many of the cross-reactants this appears to be a strong possibility[61c,63]—this behavior is to be expected. Such reactions cannot be used to estimate self-exchange constants.[91]

In addition to the experimental evidence previously described, two converging lines of evidence provide theoretical support for the conclusion that we have measured the rate of an outer-sphere electron transfer from $IrCl_6^{3-}$ to O_3. The most important result is that the structural characteristics of O_3 and O_3^- lead to a Marcus–Hush theoretical self-exchange constant estimate of 90 M^{-1} s^{-1}, which is close to *but greater than* the value of 4 M^{-1} s^{-1} calculated from our cross-reaction. Thus, the theoretically predicted outer-sphere reactivity is actually slightly greater than what we have observed. Confidence in the reasonableness of this prediction is strengthened by the close correlation between theoretical self-exchange estimates for five similar non-metal couples and their experimental reactivities with a variety of inert metal complexes, which is hard to understand except in terms of a common outer-sphere electron-transfer mechanism.

We shift attention now to an interesting contrast between the behavior of ozone toward $IrCl_6^{3-}$ and three labile aquo metal ions. Gordon and Taube established by means of isotopic labeling that one oxygen atom from O_3 is transferred to U^{4+}(aq) in the course of its conversion to the substitution-inert UO_2^{2+} ion.[23] The rate of the reaction was not studied. A similar 2-equiv oxygen atom transfer would account for the 40% of Fe^{2+}(aq) that is converted to $Fe_2(OH)_2^{4+}$, presumably via an Fe(IV) intermediate.[24] The rate constant for the appearance of Fe(III), $(1.7 \pm 0.3) \times 10^5$ M^{-1} s^{-1},[24] is consistent with an inner-sphere mechanism for this 2-equiv process and the competing 1-equiv oxidation, since the rate constant for the substitution of water on $Fe(OH_2)_6^{2+}$ is 4.4 $\times 10^6$ s^{-1}.[92-94] The following mechanism is consistent with the

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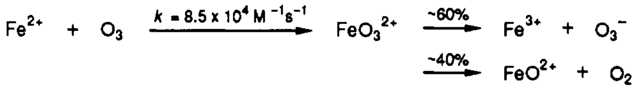
available data:[99]



$$\mathrm{Fe^{2+} + O_3 \xrightarrow{k\,=\,8.5\times10^{4}\ M^{-1}s^{-1}} FeO_3^{2+}} \begin{array}{l} \xrightarrow{\sim 60\%} \mathrm{Fe^{3+} + O_3^-} \\ \xrightarrow{\sim 40\%} \mathrm{FeO^{2+} + O_2} \end{array}$$

Alternatively, the 1-equiv oxidation may involve initially a hydrogen atom abstraction from $Fe(OH_2)_6^{2+}$ by O_3 to yield $(H_2O)_5FeOH^{2+}$ and HO_3 with a rate constant of $\sim 5 \times 10^4\ M^{-1}\ s^{-1}$. In this case the substitution of O_3 on $Fe(OH_2)_6^{2+}$, with a rate constant of $\sim 3.5 \times 10^4\ M^{-1}\ s^{-1}$, would contribute solely to the 2-equiv path. The slowness of this hypothetical substitution relative to that by NO[94] and the fortuitous similarity required of the rate constants for hydrogen atom abstraction and substitution render this alternative less appealing than the first mechanism. In any event, by both 1- and 2-equiv paths O_3 reacts with $Fe(OH_2)_6^{2+}$ substantially more rapidly than the $k_{12} = 2 \times 10^3\ M^{-1}\ s^{-1}$, which is calculated for an outer-sphere process by using eqs 7–10, $k_{22} = 4\ M^{-1}\ s^{-1}$,[100] and $E° = 0.77$ V[101] for the $Fe(OH_2)_6^{3+/2+}$ couple. Similarly, an outer-sphere reaction between O_3 and $Co(OH_2)_6^{2+}$, with a $k_{12} = 5 \times 10^{-8}\ M^{-1}\ s^{-1}$ calculated by using $k_{22} = 3.3\ M^{-1}\ s^{-1}$ [102] and $E° = 1.92$ V[101] for the $Co(OH_2)_6^{3+/2+}$ couple, is excluded by the observed $k = 0.65\ M^{-1}\ s^{-1}$ at 0 °C,[21,22] which is above the diffusion-controlled limit for this highly unfavorable reaction so long as it is considered outer-sphere. The hydrogen atom abstraction suggested by Hill[21] and by Yeatts and Taube[22] is appealing for this reaction. It is worth noting in this context, however, that a wide variety of inorganic acids (e.g., HNO_2) are substantially less reactive toward ozone than their conjugate bases,[29] suggesting that hydrogen atom transfer to ozone requires a careful evaluation, which we will not attempt here.

A certain irony emerges from these collected observations. Despite our apparent success in characterizing an outer-sphere electron transfer to ozone that is in accord with the Marcus–Hush theory, this pathway for ozone reduction appears less reactive than a number of alternatives, all of which involve greater orbital overlap in the transition state. Our view of this behavior has developed congruently with that of Linck.[103] Any reductant–ozone combination implies a one-electron, outer-sphere transition state which, however, can be evaded if a transition state of lower energy involving greater orbital overlap is accessible. Now, ozone is not as strong an oxidant in its reduction to O_3^- as it is in its conversion to other products where new bonds are made. Moreover, the intrinsic outer-sphere reactivity of the O_3/O_3^- couple is rather low. Since these two parameters represent the principal contributions from ozone to the activation barrier for its outer-sphere reduction, this pathway often proves slow relative to the alternatives offered with many reductants. The subtlest gradation in this direction occurs with reductants for which the only difference from idealized outer-sphere transfer arises in the transition state where stronger electronic interactions result in greater reactivity. The reactions of ozone with 1-equiv non-metal reductants such as ClO_2^-, NO_2^-, and O_2^- appear to be strong candidates for this mode of reactivity enhancement. A further step in this direction is provided by reactions in which greater orbital overlap in the transition state persists into the product(s) where the resulting new bond(s) may also increase the net driving force. The oxygen atom transfers established for the O_3–U^{4+} reaction and postulated for the 2-equiv path of the O_3–Fe^{2+} reaction are examples. As postulated for the reaction with Fe^{2+}, an important inner-sphere mechanism may involve a 1-equiv oxidative addition of ozone to the reducing center to yield a monodentate ozonide intermediate.[104] The formation of a cyclic ozonide intermediate from the reaction between ozone and an alkene[3] can be regarded as a related 2-equiv oxidative addition. A net bonding change also occurs in the 1-equiv abstraction of a hydrogen atom from a reductant by O_3. It is clear from this spectrum of behavior that ozone engages in as wide a variety of redox mechanisms as any oxidant studied thus far. The reactions of ozone with inorganic reductants offer abundant opportunity for exploring the expression of this remarkable mechanistic potential.

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