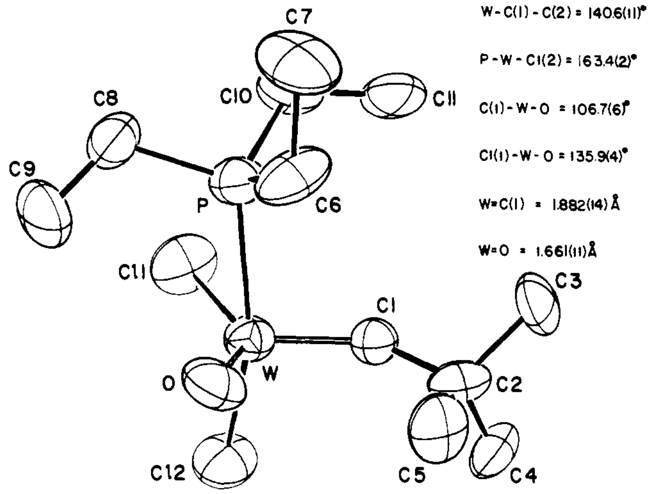


Figure 1. ORTEP drawing of the structure of $W(O)(CHCMe_3)(PEt_3)Cl_2$ showing all nonhydrogen atoms.

half of the data is systematically weak. Discrepancy indices are $R_F = 0.147$ and $R_{wF} = 0.068$ for all 3055 reflections and $R_F = 0.082$ and $R_{wF} = 0.060$ for those 1769 reflections with $|F_{obsd}| > 3\sigma[|F_{obsd}|]$.

The molecular geometry is shown in Figure 1. The molecule is a distorted trigonal bipyramid in which the oxo ligand, C_α and C_β of the neopentylidene ligand, and the chloride ligand all lie in the equatorial plane [$W{=}C(1) = 1.882\ (14)$, $W{=}O = 1.661\ (11)$, and $W{-}Cl(1) = 2.389\ (5)$ Å]. The triethylphosphine ligand and the second chloride ligand occupy the "axial" sites [$W{-}P = 2.518\ (4)$, $W{-}Cl(2) = 2.379\ (5)$ Å]. Although many features of this molecule are worth some discussion we want to comment on only two of them here. The first is the $W{=}C(1)$ bond length; it is intermediate between the tungsten-alkylidene and tungsten-alkylidyne bond lengths found in $W({\equiv}CCMe_3)({=}CHCMe_3)(CH_2CMe_3)(dmpe)$ [$W{=}C = 1.942\ (9)$, $W{\equiv}C = 1.785\ (8)$ Å].[14] The second is the $W{=}C(1){-}C(2)$ angle [140.6 (11)°]; it is the *smallest* of any observed so far in several neopentylidene complexes of Ta[4c,15,16] and W.[14]

We conclude from these studies that alkylidene ligand conformations are more "normal" in electron-deficient[17] Ta or W complexes which contain "hard" alkoxide[18] or oxo ligands, respectively. These complexes are metathesis catalysts.[3] When only "softer" ligands are present (η^5-C_5R_5, Cl, Br, PR_3)[19] and/or when such Ta-alkylidene complexes are formally reduced by two electrons,[20] the alkylidene ligand is distorted such that the $M{-}C_\alpha{-}C_\beta$ angle is 160–170°. These "reduced" alkylidene complexes do not metathesize olefins.[3,19] We have shown[2a,10,21] that, in these cases, the initial metallacyclobutane complex rearranges to an olefin complex too rapidly relative to the rate at which it cleaves to form a new alkylidene complex.

Acknowledgments. We thank the National Science Foundation for support (Grant CHE 77-04981 to M.R.C. and CHE79-05307 to R.R.S.).

References and Notes

(1) Multiple Metal–Carbon Bonds. 16. Part 15: ref 4b.

(2) (a) Schrock, R. R. *Acc. Chem. Res.* **1979,** *12*, 98–104. (b) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978,** *100*, 6774–6776.

(3) Schrock, R. R.; Rocklage, S.; Wengrovius, J. H.; Rupprecht, G. A.; Fellmann, J. D. *J. Mol. Catal.* **1980,** *8*, 73–83.

(4) (a) We have prepared many octahedral neopentylidene and benzylidene complexes. In all cases to date, all evidence[4b] (including structural studies[4c]) suggests that alkylidene ligands are bound to the metal through at least a double bond and that they lie along one of the axes in the octahedron. (b) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.*, in press. (c) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G. A.; Fellmann, J. D. *Ibid.* **1979,** *101*, 1593–1595.

(5) The stereochemistry is based on the fact that the phosphine ligands are equivalent and that the protons on the methylene ligand (which must lie along an axis[4]) are not equivalent. Since the oxo ligand donates its π electrons to the metal so efficiently it uses two of the three available π-type metal d orbitals. For the third π-type metal d orbital to overlap with the alkylidene α-carbon's $2p_z$ orbital, the CHR ligand must lie in the O–W–C plane.

(6) A typical catalyst system consists of 0.25 mmol of W, 0.25 mmol of nonane, 5 mL of solvent, 20–100 equiv of olefin (as needed), and 0.5 equiv of $AlCl_3$. Only a fraction of the $AlCl_3$ actually dissolves. We add 0.5 equiv simply because small amounts cannot be weighed out as easily and accurately. The reaction is slower if only traces of $AlCl_3$ are added and slows down if greater than ~1 equiv is added. The latter may be due either to precipitation of W-containing solids or to faster catalyst deactivation.

(7) Most Nb– and Ta–alkylidene complexes studies so far give β-elimination products,[2a] the exception being complexes containing alkoxide ligands.[3]

(8) The signal for H_α of **1d** is found at δ 12.10.[3] The signals for the two inequivalent methylene protons in **1e** are found at δ 12.34 and δ 11.47.[3] The ratio of **1d** to **1e** is variable since **1e** is not so stable as the others and since the rate of reaction with 1-butene varies considerably depending on how much is allowed to dissolve. In our case we let the reaction volume increase by ~20% with dissolved 1-butene before isolating the reaction vessel from the 1-butene source.

(9) (a) It has been known for some time in "classical" metathesis systems that the rate of degenerate metathesis via α,α'-disubstituted metallacyclobutane complexes of type **2** is faster than the rate of productive metathesis via complexes of type **3**.[9b] (b) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979,** *17*, 449–492, and references therein.

(10) Rupprecht, G. A.; Rocklage, S.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R., manuscript in preparation.

(11) $W(O)(CHCMe_3)(PEt_3)_2Br_2$ can be prepared in a manner analogous to that for preparing **1a**[3] from $Ta(CHCMe_3)(PEt_3)_2Br_3$[4b] and $W(O)(OCMe_3)_4$ in pentane.

(12) **4** crystallizes preferentially on addition of pentane to the toluene solution. Calcd for $WC_{11}H_{25}OCl_2P$: C, 28.78; H, 5.49. Found: C, 29.08; H, 5.59. ^1H NMR (ppm, C_6D_6): 9.80 (d, 1, $^3J_{PH} = 3$ Hz, H_α), 1.50 (poor q, 6, PCH_2CH_3), 1.13 (s, 9, Me), 0.65 (dt, 9, $^2J_{PH} = 16$ Hz, PCH_2CH_3). ^{13}C NMR (ppm, C_6D_6, gated ^1H decoupled): 295.4 (d, $J_{CH} = 115$ Hz, C_α), 45.4 (s, C_β), 31.2 (q, $J_{CH} = 125$ Hz, CMe_3), 17.4 (t, $J_{CH} = 130$ Hz, PCH_2CH_3), 8.05 (q, $J_{CH} = 129$ Hz, PCH_2CH_3); $J_{C\alpha W} = 176$ Hz in the $^{13}C[^1H]$ NMR spectrum. ^{31}P NMR (ppm, C_6D_6, ^1H decoupled): 40.9 ($J_{PW} = 364$ Hz). Mol wt: calcd, 459; found, 436.

(13) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977,** *16*, 265–271.

(14) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979,** *18*, 2454–2458.

(15) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978,** *17*, 1957–1962.

(16) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979,** *18*, 1930–1935.

(17) By electron deficient we mean containing less than 18 valence electrons.

(18) The values for $^1J_{CH\alpha}$ in $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ complexes[3] (M = Nb or Ta) is ~125 Hz. Since $^1J_{CH\alpha}$ inversely correlates in known Ta structures with the $M{-}C_\alpha{-}C_\beta$ angle we assume the angle in the $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ complexes is also on the order of 140–150°.

(19) See ref 2a and references therein.

(20) (a) An example is $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$,[20b] a neutron diffraction study of which[20c] shows that the $Ta{=}C_\alpha{-}C_\beta$ angle is 170.2 (2) and the $Ta{=}C_\alpha{-}H_\alpha$ angle is 78.1 (3)°, the $C_\alpha{-}H_\alpha$ bond length is 1.135 (5) and the $Ta{=}C_\alpha$ bond length is 1.946 (3) Å, and H_α is only 2.042 (5) Å from Ta. (b) Wood, C. D., unpublished results. (c) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R., submitted for publication.

(21) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979,** *101*, 4558–4570.

(22) Camille and Henry Dreyfus Teacher–Scholar Grant awardee, 1978.

Jeffrey H. Wengrovius, Richard R. Schrock*[22]
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Melvyn Rowen Churchill,* Joseph R. Missert
Wiley J. Youngs
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Received February 19, 1980

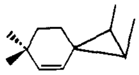
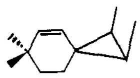
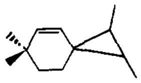
Intermolecular Reactions of 4,4-Dimethylcyclohex-2-enylidene[1]

Sir:

In an important paper describing intramolecular insertion reactions of alkylcarbenes, Chang and Shechter[3] made the suggestion that excited singlet carbenes could be responsible for much of the chemistry occurring on direct irradiation of

0002-7863/80/1502-4516$01.00/0

Table I

olefin + 1	conditions				
trans-2-butene	$h\nu$	0	0	35	65
cis-2-butene	$h\nu$	23	25	0	52
cis-2-butene	$h\nu$, Ph_2CO	29	22	14	35
cis-2-butene	125 °C	34	23	13	30

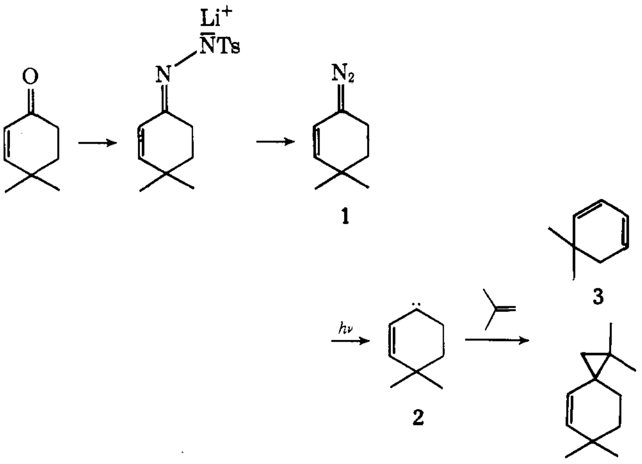
alkyl diazo compounds and diazirines. Chang and Shechter noted that (1) direct irradiation or singlet sensitization produced a carbene more indiscriminate than did either thermal decomposition or triplet photosensitization, and (2) triplet photosensitization and pyrolysis produced an identically behaving pair of intermediates, presumably the triplet and lowest singlet states. As the photosensitization must produce triplet carbene, this implied rapid equilibration through intersystem crossing followed by reaction of the singlet and triplet states with $k_s > k_t$.[4] The authors reasoned that the less discriminating

$$\begin{tikzcd}
\text{thermal decomposition} \arrow[r] & \text{singlet} \arrow[r, shift left, "k_i"] \arrow[d, "k_s"] & \text{triplet} \arrow[l, shift left, "k_{-i}"] \arrow[d, "k_t"] & \text{triplet sensitization} \arrow[l] \\
& \text{singlet products} & \text{triplet products} &
\end{tikzcd}$$

reagent formed by direct irradiation might be an electronically excited singlet state, thus amplifying early suggestions by Frey and his co-workers.[5]

We describe here a complementary study on intermolecular reactions of a vinylcarbene indicating that reactions of excited singlet states may be general, at least for alkylcarbenes.

4,4-Dimethyldiazocyclohex-2-ene (**1**) was synthesized from 4,4-dimethylcyclohex-2-enone via the tosyl hydrazone salt. Although prone to azine formation, **1** proved an adequate source of carbene **2**. Irradiation of **1** in olefins led to **3**, the product of intramolecular insertion and surprising amounts of intermolecular cycloaddition. The isolated yield of **3** is deceptively low, however, as control experiments demonstrated that substantial losses occurred on photolysis and isolation of **3** from olefinic solutions. The adducts are formed in yields (9–50% based on diazo compound not converted into azine) comparable with those produced from 4,4-dimethylcyclohexadienylidene[6] in which intramolecular diversion is difficult. Our first thought was that the adducts might be formed from triplet **2**, whereas the singlet led exclusively to intramolecular insertion to give **3**. Ample precedent for singlet–triplet equilibration exists,[7] and it seemed a logical explanation until we found that the cycloadducts were formed in a *stereospecific* fashion. Thus we were disabused of the notion that triplets were solely responsible for the cycloaddition.



Photosensitized decomposition of **1** (Rayonet reactor, benzophenone as sensitizer) led to a significantly different distribution of stereoisomers. Although addition is still predominantly cis, substantial amounts of trans adduct are also formed. Here a traditional explanation seems sound. Triplet **2** is formed first, but before reaction via k_t forms cyclopropanes equilibration with the lowest singlet state of **2** is established through intersystem crossing. As k_s overwhelms k_t, most of the product is formed stereospecifically from the singlet. Inspired by the experiment of Chang and Shechter,[3,8] we also examined the decomposition of **1** in olefins at 125 °C and found results indistinguishable from those of the *sensitized* photolysis (see Table I). Thus the pattern found for intramolecular insertion is repeated for the intermolecular cycloadditions. The thermal chemistry is the same as that from triplet sensitization and different from that produced by direct irradiation. Access to an equilibrating pair of carbenes is gained via the singlet by thermal decomposition and via the triplet by photosensitized decomposition. Direct irradiation produces a third carbene, possibly the p^2 singlet, completely stereospecific in its addition reactions.

Moreover, it must be admitted that the explanation offered here is quite unconventional. Thus we must posit reactions (intermolecular in our case, intramolecular in that of Chang and Shechter) rapid enough to compete with internal conversion. A point in our explanation's favor is that this effect should appear only in cases in which the delicate balance of k_i, k_{-i}, k_s, and k_t allows products to be formed from *both* singlet and triplet. If k_s is vastly greater than k_t, reactions of a higher singlet will be invisible, as they are indistinguishable from those of the lowest singlet. A similar situation will apply if intersystem crossing is slow.[9]

However, one *caveat* must be mentioned that applies both to our work and that of Chang and Shechter.[3,8] There is growing evidence that a difficulty, often mentioned but usually dismissed, must be reconsidered in a serious way. That is the potential intervention of reactions of excited diazo compounds masquerading as carbenes.[10] In our reactions we must deal with the possibility of pyrazoline formation, which in the thermal decompositions could lead to the trans cyclopropane.[11] It would have to be fortuitous that, within experimental error, the same amount of trans cyclopropane was formed in the thermal and photosensitized reactions, but such an event is clearly possible, if unlikely. Diazomethane, a diazo compound quite reactive in 1,3-dipolar additions,[12] requires 7–10 days to form a pyrazoline with the butenes.[13] Our thermal reactions are complete in <2 h. Thus we feel it unlikely that nitrogenous intermediates are involved, but cannot claim to have removed the possibility.[14]

Acknowledgments. We thank Professor Peter P. Gaspar of Washington University and Professors L. C. Allen, Jeffrey Schwartz, and Jeffrey K. McVey of Princeton for helpful comments.

References and Notes

(1) Support by the National Science Foundation through Grant CHE 77-24625 is gratefully acknowledged.
(2) Allied Fellow, 1978–1979.
(3) Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082. An alter-

nate explanation involved carbene-mimicking reactions of excited diazo compounds.
(4) Gaspar, P. P.; Hammond, G. S. "Carbenes", Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, Chapter 6.
(5) Frey, H. M.; Stevens, I. D. R. *J. Am. Chem. Soc.* **1962,** *84*, 2647. Frey, H. M. *J. Chem. Soc.* **1962**, 2293. Frey, H. M.; Stevens, I. D. R. *Ibid.* **1963,** 3514; **1964,** 4700; **1965,** 3101. Frey, H. M. *Pure Appl. Chem.* **1964,** *9*, 527. Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966,** 1733.
(6) Jones, M., Jr.; Harrison, A. M.; Rettig, K. R. *J. Am. Chem. Soc.* **1969,** *91*, 6411.
(7) Closs, G. L. In ref 4, Chapter 4.
(8) We thank Professor Shechter for prepublication data.
(9) Many irradiations of diazo compounds and diazirines do *not* produce excited intermediates. A referee has suggested two: Moss, R. A.; Pilkiewicz, F. G. *J. Am. Chem. Soc.* **1974,** *96*, 5632.
(10) Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979,** *44*, 3072.
(11) Moore, R.; Mishra, A.; Crawford, R. J. *Can. J. Chem.* **1968,** *46*, 3305.
(12) Huisgen, R.; Grashey, R.; Saver, J. "The Chemistry of Alkenes", Patai, S., Ed.; Wiley: New York, 1964; pp 826–835.
(13) Crawford, R. J.; Ali, L. H. *J. Am. Chem. Soc.* **1967,** *89*, 3908.
(14) A referee has suggested that thermolysis may produce a triplet diazo compound. This would lead to triplet carbenes and thus to results identical with those from photosensitization.

Gregory R. Chambers, Maitland Jones, Jr.*
Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received December 3, 1979

Reaction between Superoxide Ion and the Superoxide Coordinated in a Cobalt(III) Complex

Sir:

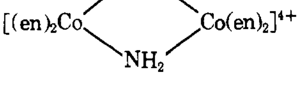
The importance of dioxygen species in biological redox reactions,[1] in photosynthesis and in combustion of materials,[2] is well recognized. One-electron reduction of oxygen produces the superoxide ion, $O_2^{-}\cdot$, and the redox potential observed for the process

$$O_2 + H^+ + e^- \rightarrow HO_2\cdot$$

is −0.33 V which is independent of pH.[2] The reactions of $O_2^{-}\cdot$ are of considerable interest; the spontaneous dismutation reaction

$$2O_2^{-}\cdot + 2H^+ \rightarrow O_2 + H_2O_2$$

is known to be catalyzed by protons. In enzymatic systems, superoxide dismutases which contain transition metal ions such as copper, zinc and manganese bring about this reaction.[3] Several transition-metal complexes have been used to show model behavior of the superoxide dismutase reaction.[4,5] In the cobalt(III) dioxygen complexes the nature of the -O-O- bridge is known to be superoxo or peroxo as determined by ESR[6] and crystallographic studies.[7] One-electron reduction of the superoxo complexes produce the peroxo bridge complexes which are diamagnetic and the process does not reduce the metal center.[8-12] We have investigated the redox reactions between the $O_2^{-}\cdot$ ion and the coordinated $O_2^{-}\cdot$ in the transition-metal complexes, μ-amido-μ-superoxo-bis[bisethylenediamine cobalt(III)] (I) and μ-superoxo-bis(pentacyano)cobalt(III)] (II).



I

II

Superoxide ion was produced pulse radiolytically[13] in aqueous solutions, saturated with oxygen, containing 0.1 M sodium formate. The reaction of $O_2^{-}\cdot$ with the superoxo coordinated complex was followed by monitoring the formation of the peroxo complex using spectrophotometric pulse radiolysis technique.[14] Solutions of the superoxocobalt(III) complexes I or II in 0.1 M sodium formate saturated with oxygen were irradiated with a 10-MeV beam of electrons from Notre Dame linear accelerator. The rate of formation of the peroxo complex was followed at 380 nm and 310 nm for I and II respectively; absorbance increase at 380 nm corresponds to the formation of the μ-amido-μ-peroxo-bis[bisethylenediamine cobalt(III)] complex, whereas absorbance decrease for the cyanide complex at 310 nm is proportional to the formation of the corresponding peroxo complex.[15,16] The rate constants for the reaction of $O_2^{-}\cdot$ with the cobalt(III) superoxo complexes were determined varying the pH and by varying the concentration of the complex in the solution. The bimolecular rate constants which were found to be independent of the concentration of the superoxo complex present in the solution are shown in Figure 1 as a function of pH.

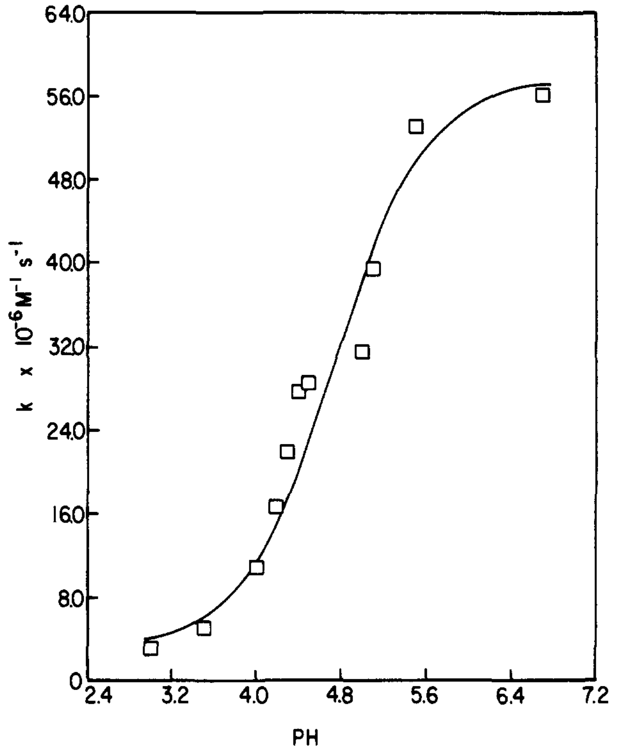


Figure 1. Bimolecular rate constants.

γ radiolysis of the complexes in oxygenated 0.1 M formate solutions produces the peroxo complex quantitatively. No cobalt(II) was detected in the γ-irradiated solution. γ radiolysis of II also shows spectral changes corresponding to the formation of the peroxo complex. However, in this case, the peroxo complex decomposes slowly in aqueous solutions.[15]

With the identification of the peroxo product the reduction of the coordinated superoxide by O_2^- may be formulated as shown in Scheme I. A generalized rate treatment including the hydroperoxy radical as the additional reducing species shows that the bimolecular rate constant k for the reduction process is a sum of the rate constants due to the fraction of $O_2^{-}\cdot$, $f_{O_2^-}$, and the fraction of $HO_2\cdot$, f_{HO_2}, present in the solution:

$$k = (k_{O_2^-} \times f_{O_2^-} + k_{HO_2} \times f_{HO_2})$$

$$= \frac{k_{O_2^-}}{1 + (K/[H^+])} + \frac{k_{HO_2}}{1 + ([H^+]/K)}$$

K is the acid dissociation constant for $HO_2\cdot$ and $k_{O_2^-}$ and k_{HO_2} are the rate constants for the reduction process by $O_2^{-}\cdot$ and $HO_2\cdot$, respectively. The best fit to the data shown in Figure 1 is obtained for $k_{O_2^-} = 5.8 \pm 0.3 \times 10^7$ and $k_{HO_2} = 3.0 \pm 0.5 \times 10^6\ M^{-1}\ s^{-1}$. The p$K_a$ for $HO_2\cdot$ is known[17] to be 4.75 and above pH 5.0 reduction by $O_2^{-}\cdot$ is the predominant pathway. The reaction between two $O_2^{-}\cdot$ ions is negligibly slow compared with that of $O_2^{-}\cdot$ and $HO_2\cdot$ for which a rate constant of

0002-7863/80/1502-4518$01.00/0