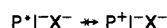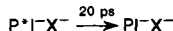*Photosynth.*, 4th, in press.

(15) Support for the assumption that this technique generates I⁻ comes from picosecond flash experiments[5-7] which indicate that, in *R. viridis* reaction centers so treated, photooxidation of P is effectively prevented because all electron acceptors have been reduced:

$$P^* I^- X^- \nrightarrow P^+ I^- X^-$$

and

$$P^* I^- X^- \xrightarrow{20 \text{ ps}} PI^- X^-$$

(16) This value is clearly distinct from that found[4a] for P⁺, $g = 2.0026$. The small variation in the anion values, 2.0033–2.0036, may reflect the tightness of the ion pairs formed by the anion radicals and their gegenions. For a discussion of mechanisms which influence g values of porphyrins, see J. Fajer and M. S. Davis in "The Porphyrins", D. Dolphin, Ed., Academic Press, New York, N.Y., in press.

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(24) (a) Division of Chemical Sciences; (b) Medical Research Center; (c) Department of Biology.

(25) Guggenheim Memorial Fellow, on sabbatical leave from the University of California at Los Angeles.

J. Fajer,*[24a] M. S. Davis,[24a] D. C. Brune[24a]
A. Forman,[24b] J. P. Thornber[24c,25]

Brookhaven National Laboratory
Upton, New York 11973
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Figure 1. Absorption spectrum of MnO_2^+ (●) at pH 6.0 and 23.5 °C in an air-saturated 0.5 mM sodium formate solution containing a small amount of phosphate buffer. Absorption spectrum of $Mn(OH)^{2+}$ (○) at pH 6.3 and 23.5 °C in an N_2O-saturated solution containing sodium phosphate and perchloric acid.

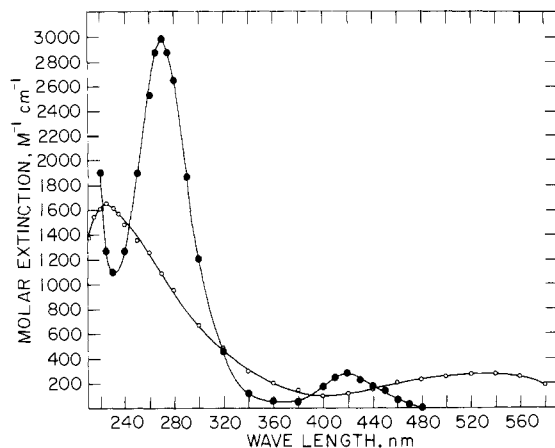## Products of Reaction of Superoxide and Hydroxyl Radicals with Mn²⁺ Cation

Sir:

We would like to report the absorption spectra of MnO_2^+ and $Mn(OH)^{2+}$ which are the products of the interaction of the Mn^{2+} cation with superoxide and hydroxyl radicals:

$$Mn^{2+} + O_2^- \rightarrow MnO_2^+ \qquad (1)$$

$$Mn^{2+} + OH \rightarrow Mn(OH)^{2+} \qquad (2)$$
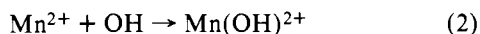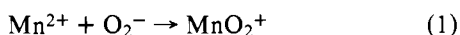
Although the formation of these species had been correctly diagnosed in an earlier pulse radiolysis study,[1,2] the reported spectra were not well resolved (see Figure 2 in ref 1) and hardly differed from each other. Because of the importance of these species in biological reactions,[3,4] where it had been erroneously suggested that O_2^- is capable of oxidizing Mn^{2+} to Mn^{3+}, we investigated the system using the stopped-flow radiolysis technique[5] by which reactions 1 and 2 can be studied separately and in the absence of interfering reactions.

Reaction 1. The superoxide radical was generated at 23.5 °C by a 2-MeV electron beam impinging on an air-saturated 1.0 mM sodium formate solution pH 10.0:[5]

$$H_2O \xrightarrow{O_2, \, HCOO^-} O_2^-, H_2O_2, H_2 \qquad (3)$$
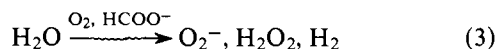
The O_2^- solution (6 μM) was rapidly mixed with a 5 mM $MnSO_4$ solution of such acidity (H_2SO_4) that the final mixture was at pH 6.0. Effective scavenging of O_2^- was monitored at 270 nm; it was found to be independent of Mn^{2+} concentration in the range studied (0.5–50 mM). With the stopped-flow technique one can use relatively low formate concentrations for the conversion of the primary radicals into O_2^-, because the Mn^{2+} cation is added ~15 ms (dead time between radiation

zone and mixer) after irradiation and does not enter into competition reactions with the primary radicals. Also, since in the final solution-mixture the total amount of formate is only 0.5 mM, effects due to Mn^{2+}-$HCOO^-$ complex formation are minimized. All chemicals and the water were of highest purity;[5] manganese(II) sulfate (99.999% purity) was an Apache Chemical Inc. product. The upper limit for scattered light was of the order of 3% at 210 nm.

The absorption spectrum of MnO_2^+ (Figure 1) was obtained by monitoring the absorbance at various wavelengths under conditions of constant energy input. The spectrum has been corrected for fluctuations in the beam current which were of the order of 5%. The corresponding molar extinction coefficients are normalized values based upon experiments in which the absorbance of MnO_2^+ at 270 nm gave a linear plot as a function of beam current (which is proportional to the energy input) and was compared with a similar plot for O_2^- at 245 nm. Hence the molar extinction $\epsilon_{MnO_2^+}^{270nm} = 3000 \pm 150$ M⁻¹ cm⁻¹ is based upon the molar absorbance of superoxide radical,[6] $\epsilon_{O_2^-}^{245nm} = 2350 \pm 120$ M⁻¹ cm⁻¹ at 23.5 °C. Control experiments carried out in presence of a wide concentration range of $MnSO_4$ (2.5–100 mM) suggest that neither Mn^{2+} nor SO_4^{2-} affects the molar absorbance of MnO_2^+. Absence of absorbance above 480 nm in the system indicates the absence of reaction 2.

Reaction 2. The spectrum of the reaction product of OH with Mn^{2+} was determined in the same apparatus as the spectrum of MnO_2^+. A 1 mM $MnSO_4$ solution, pH 6.3, saturated with N_2O was irradiated, mixed with nonirradiated solution, and monitored for absorbance at the various wavelengths:

$$H_2O \xrightarrow{N_2O} OH, H_2O_2, H_2 \qquad (4a)$$

$$Mn^{2+} + OH \rightarrow Mn(OH)^{2+} \qquad (4b)$$
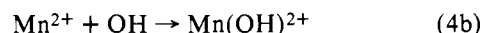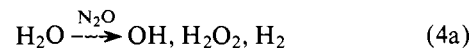
The molar absorbance of $Mn(OH)^{2+}$ was determined from a linear plot of the absorbance at 225 nm as a function of energy input and compared with an O_2^- absorbance vs. energy input curve at 245 nm. All other points in the spectrum were normalized in terms of the molar absorbance $\epsilon_{Mn(OH)^{2+}}^{225nm} = 1640 \pm 80$ M⁻¹ cm⁻¹ at 23.5 °C. The numerical values of the extinction coefficients of $Mn(OH)^{2+}$ reported here are based upon the assumption that $G(OH)_{N_2O} = G(O_2^-)_{O_2,HCOO^-} = 6.05$, where G is the number of primary radicals formed per 100-eV energy dissipated. Since the fate of the H atom is unknown in this system, $G_H = 0.55$, the values of $\epsilon_{Mn(OH)^{2+}}$ given in Figure

1 could be low by as much as 17%. In general the spectrum of $Mn(OH)^{2+}$ determined in this study is in good agreement with an earlier published spectrum of manganic pyrophosphate of pH 6.0.[7]

As is apparent from Figure 1, the spectrum of MnO_2^+ is quite different from the spectrum of $Mn(OH)^{2+}$. With the exception of the small absorbance at 420 nm, it resembles the spectrum of O_2^- which has undergone a red shift due to complexing. Since in the present study MnO_2^+ was formed directly from O_2^- and Mn^{2+} and in absence of other oxidizing chemicals, we conclude that the superoxide radical is not capable of oxidizing Mn^{2+} to Mn^{3+}.

Preliminary kinetic studies of the MnO_2^+ and $MnOH^{2+}$ species indicate that their decay mechanisms are very complex. For similar initial concentrations the observed ratio of overall half-lives of MnO_2^+/O_2^- at pH 6.0 is 10. The decay of $MnOH^{2+}$ which can be observed for up to 1 s under present experimental conditions is complicated by the formation of a precipitate.

References and Notes

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Benon H. J. Bielski*

*Department of Chemistry, Brookhaven National Laboratory
Upton, New York 11973*

Phillip C. Chan

*Department of Biochemistry, State University of New York
Downstate Medical Center, Brooklyn, New York 11203*

**Novel Bonding Mode of Diphenylketene to a
Transition Metal: a Metal Anchored Olefin System**

Sir:

Diphenylketene has been regarded as an activated olefin in its interaction mode with a transition metal.[1,2] Nevertheless,
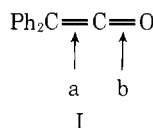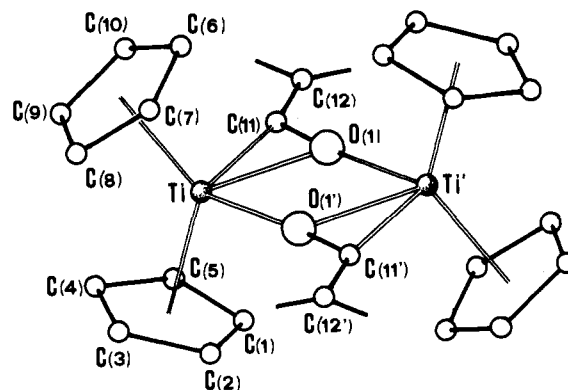
$$Ph_2C = C = O$$

a   b

I

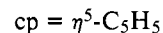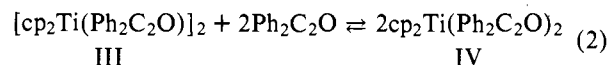**Figure 1.** A view of the molecular structure of the dimer $[cp_2Ti(Ph_2C_2O)]_2$, showing the atomic numbering scheme. The phenyl rings have been omitted for clarity.

two potential coordination sites (a and b) are, a priori, susceptible to the metal's attack. The a-bonding attachment of I to a Mn(I) complex[2] was recently confirmed by x-ray analysis, while interaction with C=O moiety is invoked as an intermediate in the metal-induced deoxygenation or decarbonylation of ketenes.[3-6] The structure here reported shows that diphenylketene is η^2-C,O bonded to the bis(η-cyclopentadienyl)titanium, $Ticp_2$, unit. This mode of attachment gives an anchored free C=C bond, highly affected by the metal. Until now, the π interaction of a ketonic C=O group was restricted to the complexes of hexafluoroacetone with d^{10} metals.[7]

It was reported that the reaction of $cp_2Ti(CO)_2$ (II) with diphenylketene gives an orange-yellow monomeric complex, which was formulated as an olefin-like compound.[8] Reaction between I and II must be, however, described by the following steps,[9]

$$2cp_2Ti(CO)_2 + 2Ph_2C_2O$$

II   I

$$\xrightarrow{60\ °C} [cp_2Ti(Ph_2C_2O)]_2 + 4CO \quad (1)$$

III

$$[cp_2Ti(Ph_2C_2O)]_2 + 2Ph_2C_2O \rightleftharpoons 2cp_2Ti(Ph_2C_2O)_2 \quad (2)$$

III   IV

$$cp = \eta^5\text{-}C_5H_5$$

giving III, orange-yellow,[10] and IV,[11] black, crystalline solids, respectively. Regarding complex III, the dramatic absence of any C=O band above 1600 cm^{-1} (C=O is at 2093 cm^{-1} in free Ph_2C_2O), together with the observed C=O stretching in the range 1700–1800 cm^{-1} for M(C=C) coordinated diphenylketene,[1,2] suggests that CO is involved in the metal-ketene interaction. An x-ray crystallographic study was required to prove the nature of the product. This was performed on $[cp_2Ti(Ph_2C_2O)]_2$·2THF (THF = tetrahydrofuran). Crystal data: $C_{48}H_{40}O_2Ti_2$·2C_4H_8O; M = 889; triclinic; a = 9.990 (1), b = 11.058 (2), c = 10.820 (2) Å; α = 73.86 (2), β = 94.98 (2), γ = 98.85 (1)°; Z = 1; d_{calcd} = 1.302 g/cm^3; space group $P\bar{1}$. Intensity data were collected on an "on-line" single-crystal automated Siemens AED diffractometer using nickel-filtered Cu Kα radiation (λ = 1.54178 Å, 6 < 2θ <

Table I. Bond Distances (Angstroms) and Bond Angles (Degrees)

Ti–C (cp)	2.410 (2)^a	2.403 (2)^a	O(1)–Ti–O(1')	67.7 (1)	Ti–O(1)	2.037 (2)
Ti–(cp)⊥	2.095 (4)^a	2.088 (4)^a	C(11)–Ti–O(1)	36.9 (1)	Ti–C(11)	2.099 (3)
C–C (cp)	1.401 (3)^a	1.394 (3)^a	Ti–O(1)–Ti'	116.0 (1)	Ti–O(1')	2.250 (3)
C–C (Ph)	1.393 (2)^a	1.386 (2)^a	Ti–O(1)–C(11)	74.1 (2)	O(1)–C(11)	1.311 (4)
cp(1)–Ti–cp(2)	131.2 (2)		O(1)–C(11)–C(12)	128.8 (3)	C(11)–C(12)	1.357 (4)
					C(12)–C(21)	1.460 (6)
					C(12)–C(31)	1.505 (6)

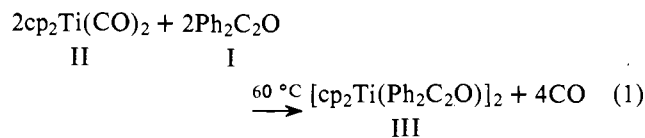^{a} Values related to crystallographically nonequivalent cyclopentadienyl and phenyl groups.