$$\mathrm{PtAu_8(PPh_3)_8^{2+} + e^- \rightleftharpoons PtAu_8(PPh_3)_8^{+} + e^- \rightleftharpoons PtAu_8(PPh_3)_8} \tag{1}$$

$$\mathrm{Au_9[P(\mathit{p}\text{-}MeOC_6H_4)_3]_8^{3+} + e^- \rightleftharpoons Au_9[P(\mathit{p}\text{-}MeOC_6H_4)_3]_8^{2+} + e^- \rightleftharpoons Au_9[P(\mathit{p}\text{-}MeOC_6H_4)_3]_8^{+}} \tag{2}$$

the parameters calculated for this mechanism and the measured data, both voltage and current functions (Table II), makes the occurrence of another mechanism very unlikely. An intermediate chemical step caused by structural changes is not likely because of the fluxionality in solution shown by these clusters.

The redox potentials for these clusters are almost solvent independent as shown by their nearly constant values vs the Fc/Fc$^+$ reference (Table III). As this Fc/Fc$^+$ redox couple is generally believed to be without specific solute-solvent interactions,[14] the same is true for the cluster ions.

The occurrence of the comproportionation equilibrium of eq 3 was demonstrated by the ESR experiment, and we assume that the comproportionation of eq 4 also occurs.

$$\mathrm{PtAu_8(PPh_3)_8^{2+} + PtAu_8(PPh_3)_8^{0} \rightleftharpoons 2PtAu_8(PPh_3)_8^{+}} \tag{3}$$

$$\mathrm{Au_9[P(\mathit{p}\text{-}MeOC_6H_4)_3]_8^{3+} + Au_9[P(\mathit{p}\text{-}MeOC_6H_4)_3]_8^{+} \rightleftharpoons 2Au_9[P(\mathit{p}\text{-}MeOC_6H_4)_3]_8^{2+}} \tag{4}$$

The comproportionation constants, K_c calculated with eq 5 for the equilibria of

$$K_c = \exp[n_1 n_2 F(\Delta E_{1/2})/RT] = \exp[\Delta E_{1/2}/25.69] \quad \text{(at 298 K and with } n_1 = n_2 = 1\text{)} \tag{5}$$

eq 3 and 4, are clearly solvent dependent (Table III). Their values increase with decreasing dielectric constants, while no dependence on acceptor or donor numbers was observed. Thus K_c is like the $E_{1/2}$'s predominantly determined by the solvent polarization, and contributions from specific solute–solvent interactions are of minor or no importance. This is not an unexpected result. Earlier we reached the same conclusion for the reaction entropies of the redox reactions for the $Au_9(PPh_3)_8^{3+/2+/+}$ couples. Only Coulombic interactions between the cluster ions and the solvent determine these ΔS_{rc} values as shown by the agreement between the Born prediction and the experimental result for the ratio of there successive values.[15]

One of the striking results of this study is the rather large difference of about 0.5 V between the redox potentials of $Au_9(PPh_3)_8^{3+}$ and $PtAu_8(PPh_3)_8^{2+}$. The difference in positive charges between the two cluster ions leads to a difference of only 0.14 V between the redox potentials ($E°(3+/2+) - E°(2+/+)$) as can be estimated from the differences in the free enthalpy changes by using the Born model.[16] SCC-EHMO calculations made clear that this difference can be ascribed for the larger part to a shift to a higher energy level of the LUMO in $PtAu_8(PPh_3)_8^{2+}$ as compared with that for $Au_9(PPh_3)_8^{3+}$ and a concomitant increase of the electron density on the platinum atom.[17]

This electronic effect is also the reason for the differences in chemical reactivity of these clusters toward small molecules.[11] In CH_2Cl_2 solutions $Au_9(PPh_3)_8^{3+}$ does not react with CO, whereas $PtAu_8(PPh_3)_8^{2+}$ reacts with CO and delivers pure samples of $(CO)PtAu_8(PPh_3)_8^{2+}$.

The difference in redox potentials of 0.15 V between $Au_9(PPh_3)_8^{3+}$ and $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+}$, can also be ascribed to the somewhat increased electron density on the latter cluster. The electron-releasing effect of the methoxy groups increases the electron density on the Au_9 core and $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+}$ is indeed reduced at a lower potential. This electronic factor seems important for the stability of the Au_9 clusters. The electronic charge is influenced by the substituents on the aryl groups of the phosphines. With phosphines like $P(p\text{-}ClC_6H_4)_3$ and also $P(p\text{-}BrC_6H_4)(C_6H_4)_2$ the preparation of a cluster with nine gold atoms failed thus far and only samples containing mainly Au_8P_8 clusters were obtained.[18]

Experimental Section

Measurements. Electrochemical measurements were made as described previously[7] by using a PAR Model 173 potentiostat equipped with a PAR Model 176 I/E converter coupled to a PAR Model 175 universal programmer. Platinum working and auxiliary electrodes were used. In dichloromethane solutions a SSCE reference electrode was used, in acetone solutions a Ag/AgCl(0.1 M LiCl in acetone) reference electrode was used, and in acetonitrile and benzonitrile a Ag/Ag$^+$ (0.1 M $AgNO_3$) reference electrode was used. The half-wave potentials for 10^{-3} M solutions of the ferrocene/ferrocenium redox couple were measured under identical experimental conditions: $E_{1/2}$ = 0.62 V (acetone) vs Ag/AgCl; $E_{1/2}$ = 0.43 V (CH_2Cl_2) vs SSCE; $E_{1/2}$ = 0.04 V (CH_3CN, C_6H_5CN) vs Ag/Ag$^+$. Coulometric measurements were made at a potential 0.1 V more negative than the second CV reduction peak with a precision for n of ±5%. Electron spin resonance experiments were carried out on a Bruker ESP 300 spectrometer. All measurements were carried out under a nitrogen atmosphere.

Materials. The cluster compounds $PtAu_8(PPh_3)_8(NO_3)_2$[8], $Au_9(PPh_3)_8(NO_3)_3$[11] were prepared as described.

$Au_9[P(p\text{-}MeOC_6H_4)_3]_8(NO_3)_3$ was prepared by following an analogous procedure as described.[9,10] $(p\text{-}MeOC_6H_4)_3PAuNO_3$ suspended in ethanol was reduced with an equivalent amount of $NaBH_4$ dissolved in ethanol.

Anal. Calcd for $C_{168}H_{168}N_3O_{33}P_8Au_9$: C, 42.4; H, 3.5; N, 0.9. Found: C, 41.5; H, 3.4; N, 0.9.

$Au_9[P(p\text{-}MeOC_6H_4)_3]_8(PF_6)_3$ was obtained from the metathesis reaction of the analogous nitrate cluster with NH_4PF_6 in ethanol. This product was used for the measurements to avoid solubility problems.

$(p\text{-}MeOC_6H_4)_3PAuCl$ was prepared as described.[19,20] $^{31}P\{^1H\}$ NMR data (in ppm with respect to trimethyl phosphate) measured in CH_2Cl_2): $(p\text{-}MeOC_6H_4)_3P$, 12.46; $(p\text{-}MeOC_6H_4)_3PAuCl$, –26.9; $Au_9[P(p\text{-}MeOC_6H_4)_3]_8(PF_6)_3$, –52.0.

Acknowledgment. We thank A. A. K. Klaassen for the recording of the ESR spectra and Professor J. J. Steggerda for his interest in this work. This investigation was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure and Applied Research (NWO).

---

(14) (a) Ennix, K. S.; McMahon, P. T.; de la Rosa, R.; Curtis, J. C. *Inorg. Chem.* **1987**, *26*, 2660. (b) Chang, P.; Fung, E. Y.; Curtis, J. F. *Inorg. Chem.* **1986**, *25*, 4233.

(15) Schmitz, J. E. J.; van der Linden, J. G. M. *Inorg. Chem.* **1984**, *23*, 117.

(16) Kassner, R. J.; Yang, W. *J. Am. Chem. Soc.* **1977**, *99*, 4351.

(17) Kanters, R. P. F. Personal communication.

(18) de Croon, M. H. J. M. Personal communication.

(19) Berner-Price, S. J.; Mazid, M. A.; Sadler, P. J. *J. Chem. Soc., Dalton Trans.* **1984**, 969.

(20) Al-Sa'aqu A. K.; McAuliffe, C. A.; Parish, R. V.; Sandbank, J. A. *Inorg. Synth.* **1985**, *23*, 191.

Contribution from the Department of Chemistry,
Faculty of Science, Tohoku University,
Sendai 980, Japan, and Department of Chemistry
and Ames Laboratory, Iowa State University,
Ames, Iowa 50011

Kinetics of the Reduction of Cobalt(III) Amine Complexes by 1-Hydroxy-1-methylethyl Radicals

Keiji Kusaba,[1a] Hiroshi Ogino,*,[1a] Andreja Bakac,[1b] and James H. Espenson[1b]

Received July 9, 1988

The pentaaquoorganochromium complexes $(H_2O)_5CrR^{2+}$ can serve as storage depots for aliphatic free radicals.[2-4] The controlled homolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ has been used as a source of 1-hydroxy-1-methylethyl radicals in our previous work,[5] including the study of the reduction of several Co(III) amine

---

(1) (a) Tohoku University. (b) Iowa State University.

(2) Kirker, G. W.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.

(3) Espenson, J. H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 1.

(4) Espenson, J. H. *Prog. Inorg. Chem.* **1983**, *30*, 189.

(5) See for example: (a) Espenson, J. H.; Shimura, M.; Bakac, A. *Inorg. Chem.* **1982**, *21*, 2537. (b) Bakac, A.; Butkovic, V.; Espenson, J. H.; Marcec, R.; Orhanovic, M. *Inorg. Chem.* **1986**, *25*, 341.

complexes.[5a,6] The reduction of $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, $Co(tn)_3^{3+}$, and $Co(chxn)_3^{3+}$ by $^{\bullet}C(CH_3)_2OH$ takes place by an outer-sphere mechanism with the radicals possibly approaching the complexes at a trigonal face.[5a] The rate constants for three of the complexes correlate well with the kinetic data for other outer-sphere reductions, as well as with the positions of the first d–d band maxima of the cobalt complexes, whereas $Co(chxn)_3^{3+}$ reacts much more slowly than expected. We suggested that the inability of the chelate ligands to undergo conformational changes might be responsible.[5a]

In order to understand better the factors controlling these rates, we carried out reactions of the 1-hydroxy-1-methylethyl radical with several additional cobalt(III) complexes of bidentate amines. The larger number of complexes examined increases the credibility of the correlation of the spectral and kinetic data. Also, the range of the absorption maxima and (presumably) of the reduction potentials has increased in the process. The reduction of $Co(sep)^{3+}$ by $^{\bullet}C(CH_3)_2OH$ has also been studied. This should be an especially instructive case owing to the potential operation of two opposing effects. The C_3 axis in this complex is blocked by the $N(CH_2)_3$ groups, which should make the approach by $^{\bullet}C(CH_3)_2OH$ more difficult and thus *retard* the rate. On the other hand, the self-exchange rate constant for the $Co(sep)^{3+/2+}$ couple, 5.1 M^{-1} s^{-1},[7] is much higher than those for the Co(III) complexes of monodentate and bidentate amines. This should result in an *increase* in the rate constant relative to those of the other Co(III) amines. The final outcome should allow us to estimate the relative importance of the two factors.

Experimental Section

The cobalt(III) complexes $[Co(en)_2(tn)](ClO_4)_3$,[8] $[Co(en)_2(tmd)](ClO_4)_3$,[8] $[Co(en)(tn)_2](ClO_4)_3$,[8] $[Co(tmd)_3](ClO_4)_3$,[9] and $[Co(sep)](ClO_4)_3$[7] were prepared by the literature methods. Solutions of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ were prepared under a nitrogen atmosphere from H_2O_2 and an excess of Cr^{2+} in the presence of 0.3–0.4 M 2-propanol as previously described.[5a]

The kinetics of the disappearance of $CrC(CH_3)_2OH^{2+}$ at 25 °C were monitored at 407 nm (ϵ 700 M^{-1} cm^{-1}). The ionic strength was controlled by addition of $NaClO_4$ at 1.0 or 0.20 M. The experimental conditions were quite similar to those described previously.[5a]

Results

The chemical competition used in this work requires that the reduction of the Co(III) complexes by Cr^{2+} be slow on the time scale of the overall reaction. This is well established for the complexes used in the previous study[5a] and has been confirmed in this work for $Co(tmd)_3^{3+}$. The rate constant was determined from the initial 2 half-lives of the reaction by use of the Kezdy–Swinbourne method[10] and has a value of $(1.4 \pm 0.3) \times 10^{-3}$ M^{-1} s^{-1} at 25 °C and 1.0 M ionic strength. Other complexes are expected to have similarly low rate constants for the reduction by Cr^{2+}.

The reduction of the cobalt(III) complexes by $^{\bullet}C(CH_3)_2OH$ followed cleanly the chemical competition pattern (eq 1 and 2) in parallel with the background acidolysis of the organochromium cation (eq 3). The rate constants for this last process were

$$CrC(CH_3)_2OH^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr^{2+} + {}^{\bullet}C(CH_3)_2OH \qquad (1)$$

$$^{\bullet}C(CH_3)_2OH + Co(III) \xrightarrow{k_{Co}} Co(II) + (CH_3)_2CO + H^+ \qquad (2)$$

$$CrC(CH_3)_2OH^{2+} \xrightarrow[H^+]{k_a} Cr^{3+} + CH(CH_3)_2OH \qquad (3)$$

determined earlier[2,11,12] and are confirmed in this work. The values of k_a used (s^{-1}) were $3.32 \times 10^{-3} + (5.31 \times 10^{-3})[H^+]$ and $(4.37 \times 10^{-3})[H^+]$ at 1.0 and 0.20 M ionic strength, respectively. The steady-state approximation for $[^{\bullet}C(CH_3)_2OH]$ yields an expression[5a] that can be rearranged to eq 4. The plots suggested

$$\frac{1}{k_{obsd} - k_a} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_{Co}} \frac{[Cr^{2+}]}{[Co(III)]} \qquad (4)$$

by eq 4 are shown for three of the complexes in Figure 1. From the slopes of the lines and the known values of k_1 (0.127 s^{-1})[2] and k_{-1} (5.1×10^7 M^{-1} s^{-1})[11] one calculates the values of k_{Co} for reaction 2. All the data are summarized in Table I.

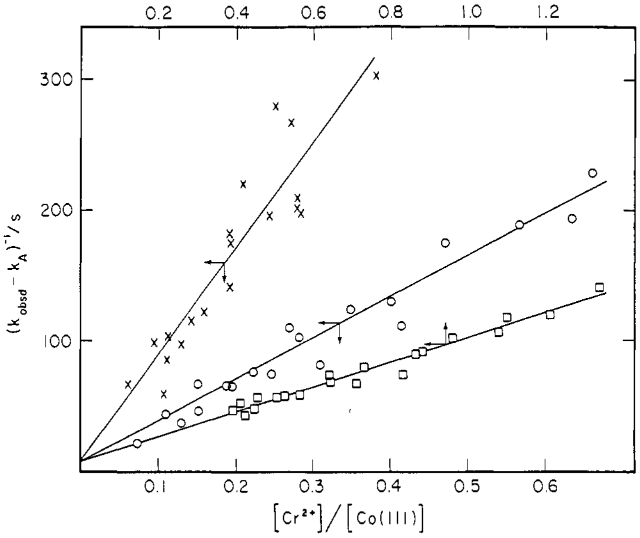

Figure 1. Plots of $(k_{obsd} - k_a)^{-1}$ vs $[Cr^{2+}]/[Co(III)]$ for the reduction of $Co(tmd)_3^{3+}$ (squares), $Co(en)(tn)_2^{3+}$ (circles), and $Co(en)_2(tn)^{3+}$ (crosses) by $^{\bullet}C(CH_3)_2OH$. Conditions: 25 °C, 1.0 M ionic strength, $[CrC(CH_3)_2OH^{2+}]_0 = (1–5) \times 10^{-4}$ M, $[H^+]$ = 0.03–0.35 M.

Table I. Summary of the Kinetic Data for the Reduction of Cobalt(III) Amine Complexes by $^{\bullet}C(CH_3)_2OH$[a]

Co(III) complex	k_{Co},[b] M^{-1} s^{-1}	$\tilde{\nu}$,[c] 10^3 cm^{-1}	ref
$[Co(tmd)_3]^{3+}$ (**1**)	4.3×10^6 [d]	19.9	this work
$[Co(tn)_3]^{3+}$ (**2**)	1.8×10^6	20.3	5a
$[Co(en)(tn)_2]^{3+}$ (**3**)	1.3×10^6	20.7	this work
$[Co(en)_2(tmd)]^{3+}$ (**4**)	1.0×10^6	20.9	this work
$[Co(en)_2(tn)]^{3+}$ (**5**)	5.0×10^5	21.0	this work
$[Co(NH_3)_6]^{3+}$ (**6**)	4.1×10^5 [e]	21.1	5a
$[Co(en)_3]^{3+}$ (**7**)	1.7×10^5	21.3	5a
$[Co(chxn)_3]^{3+}$ (**8**)	$<5 \times 10^3$	20.3	5a
$[Co(sep)]^{3+}$ (**9**)	4.6×10^6	21.2	this work

[a] 25.0 °C; μ = 1.0 M unless otherwise indicated. [b] Values of k_{Co} were calculated with $k_1 = 0.127$ s^{-1} (25.0 °C) and $k_{-1} = 5.1 \times 10^7$ M^{-1} s^{-1} (22 ± 2 °C).[11] The uncertainty in k_{Co} is thus ±10–15%. [c] The frequency of the lowest energy d–d band. [d] μ = 0.20 M. [e] μ = 0.10 M.

Discussion

The most appropriate analysis of the kinetic data for the reactions listed in Table I would be that based on the Marcus–Hush theory.[13] All the cobalt amines listed are substitutionally inert, and any mechanism other than outer-sphere electron transfer seems highly improbable. The self-exchange rate constants and standard reduction potentials needed for the Marcus cross relation are, however, unavailable for a number of complexes listed in Table I, as well as for the radical itself, although a value of $E° = -1.2$ V has been estimated for the oxidation of the radical.[14]

---

(6) Abbreviations: en = 1,2-diaminoethane; tn = 1,3-diaminopropane; chxn = *trans*-1,2-diaminocyclohexane; tmd = 1,4-diaminobutane; sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane.

(7) Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.

(8) Ogino, H.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1836.

(9) Fujita, J.; Ogino, H. *Chem. Lett.* **1974**, 57.

(10) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 24–30.

(11) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(12) Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117.

(13) (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679, 2654. (b) Marcus, R. A.; Sutin, N. *Biochem. Biophys. Acta* **1985**, *811*, 265. (c) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557. (d) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(14) Endicott, J. F. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; Chapter 3.

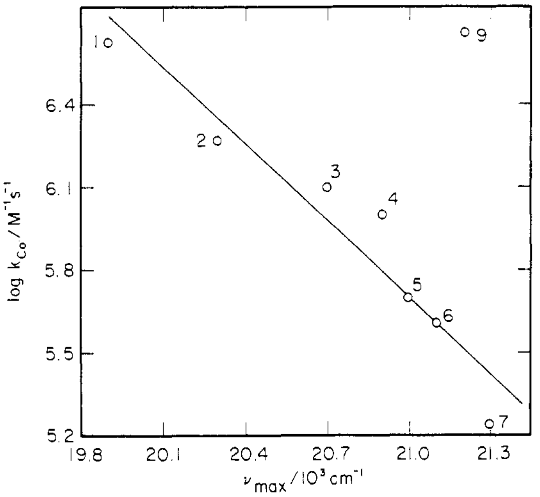

Figure 2. Illustration of the near-linear dependence of log k_{Co} on the position of the lowest energy d–d band for all the Co(III) amine complexes except $Co(sep)^{3+}$ (**9**) and $Co(chxn)_3^{3+}$ (not shown). The numbering scheme is the same as in Table I.

A readily available parameter that should be related to the oxidizing power is the energy of the lowest excited state of these complexes.[15] A plot depicting the relationship between the kinetics of the reduction of the Co(III) amines by $^\bullet C(CH_3)_2OH$ and the position of the first d–d band for the Co(III) complexes is shown in Figure 2. If we ignore for the moment the point for $Co(sep)^{3+}$, the plot indicates a good correlation between the two parameters for $Co(NH_3)_6^{3+}$ and all the complexes with the bidentate amines except $Co(chxn)_3^{3+}$. Since the self-exchange rate constants and the reduction potentials are unknown for most of the complexes, it is difficult to analyze the data in much more detail. We would like to point out, however, that two of the complexes for which the data are available, namely $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$, differ substantially in their reduction potentials and self-exchange rate constants,[16–18] yet both complexes fit the correlation in Figure 2 quite well. The position of a complex in the plot thus seems to be determined by its overall kinetic reducibility and not the reduction potential alone, at least for this series of closely related complexes of monodentate and bidentate amines.

$Co(sep)^{3+}$ reacts by over 1 order of magnitude more rapidly than predicted on the basis of its visible spectrum. This seems to be the result of the exceptionally high self-exchange rate constant, which generally causes the redox reactivity of $Co(sep)^{3+}$ to exceed significantly[19] that of $Co(en)_3^{3+}$, despite the close similarity in the visible spectra of the two complexes.

The "normal" behavior of $Co(sep)^{3+}$ in terms of its redox reactivity toward $^\bullet C(CH_3)_2OH$ strongly suggests that this is a purely outer-sphere reaction and that there are no special requirements as to the site of the radical attack at the complex as compared to the case for other reductants. This being true for this encapsulated complex, we infer that the reduction of other Co(III) amine complexes by carbon-centered radicals should also be free of any special steric or geometric requirements. Indeed, the rate constant for the reduction of $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$ and $Co(tn)_3^{3+}$ by $^\bullet C(CH_3)_2OH$ follows the same reactivity pattern as the reduction by an outer-sphere transition-metal reductant, $Cr(bpy)_3^{2+}$.[5a] Thus, the attack of the radical at a trigonal face of the Co(III) complexes seems to be ruled out by the high reactivity of $Co(sep)^{3+}$ (trigonal faces blocked) relative to that of the other Co(III) amines (trigonal faces accessible). Similarly, the extremely low reactivity of $Co(chxn)_3^{3+}$ toward $^\bullet C(CH_3)_2OH$ cannot be explained by the inability of $Co(chxn)_3^{3+}$ to undergo conformational changes, since the rigid and bulky $Co(sep)^{3+}$ reacts readily. At the present time we are unable to offer a good explanation for the low reactivity of $Co(chxn)_3^{3+}$.

The application of the Marcus cross relation to the reductions of $Co(en)_3^{3+}$ and $Co(sep)^{3+}$ by $^\bullet C(CH_3)_2OH$ may yield an estimate of the self-exchange rate constant for the couple $^\bullet C(CH_3)_2OH/C(CH_3)_2OH^+$. The standard reduction potential for the couple $(CH_3)_2CO/^\bullet C(CH_3)_2OH$ (eq 5) is related to the potential of the desired couple (eq 6) by the acidity constant of protonated acetone (eq 7). Although the value of the last value

$$(CH_3)_2CO + e^- + H^+ \rightarrow {}^\bullet C(CH_3)_2OH \qquad E^\circ = -1.2\ \mathrm{V} \tag{5}$$

$$C(CH_3)_2OH^+ + e^- \rightarrow {}^\bullet C(CH_3)_2OH \tag{6}$$

$$C(CH_3)_2OH^+ \rightleftarrows (CH_3)_2CO + H^+ \qquad K_a \tag{7}$$

is somewhat uncertain, $pK_a = -4 \pm 1$,[20] it still yields a useful estimate of E° for the $C(CH_3)_2OH^{+/0}$ couple, -0.97 ± 0.07 V. The use of this value in the equation for the electrostatics-corrected Marcus cross relation[13,21] yields a self-exchange rate constant for the $C(CH_3)_2OH^{+/0}$ couple of $10^{4\pm1}$ M^{-1} s^{-1} from the data on $Co(en)_3^{3+}$ and $10^{2\pm1}$ M^{-1} s^{-1} from the data on $Co(sep)^{3+}$. The agreement is almost acceptable within the framework of Marcus theory. We want to emphasize, however, that this treatment is justified only if the proton is bound in the transition state, a point that will have to be addressed independently.

Acknowledgment. This research was supported by Nippon Sheet Glass Foundation for Material Science and the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

---

(15) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 2092. (b) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; pp 513–515.

(16) (a) Hammershoi, A.; Geselowitz, D.; Taube, H. *Inorg. Chem.* **1984**, *23*, 979. (b) Geselowitz, D.; Taube, H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 391.

(17) Dwyer, F. P.; Sargeson, A. M. *J. Phys. Chem.* **1961**, *65*, 1892.

(18) Bartelt, H.; Skilandat, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1969**, *23*, 407.

(19) Creaser, I. I.; Sargeson, A. M.; Zanella, A. W. *Inorg. Chem.* **1983**, *22*, 4022.

(20) (a) Arnett, E. M.; Quirk, R. P.; Larsen, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 3977. (b) Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983.

(21) The equations used are those given in: (a) Howes, K. R.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 791. (b) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

Contribution from the Department of Chemistry,
University of Victoria, Victoria, BC, Canada V8W 2Y2

Singlet Oxygen Production by Energy Transfer from the Chromium Complex Cr(tacn)(NCS)₃ (tacn = 1,4,7-Triazacyclononane)

Alexander David Kirk,* C. Namasivayam,† William Riske, and Dusan Ristic-Petrovic

Received June 27, 1988

Quenching of the phosphorescence of chromium(III) complexes by molecular oxygen was first reported and systematically studied by Pfeil.[1] He found that complexes with "conducting" ligands such as isothiocyanate and cyanide were subject to quenching to an extent that increased at lower temperatures as the doublet state lifetime increased. The activation energy for the quenching rate constant was about the same as that for diffusion (6 kcal mol^{-1}), and there was no quenching at lower temperatures where the medium was rigid. He suggested that the quenching mechanism was collisional and suggested energy transfer to produce $O_2(^1\Delta_g)$ on the basis of its energetic feasibility. In contrast to this behavior,

---

* To whom correspondence should be addressed.
† Visiting Research Associate from CBM College, Coimbatore 641.042, India.

0020-1669/89/1328-0972$01.50/0 © 1989 American Chemical Society