the reaction mixture of 1 and $Fe_2(CO)_9$ showed that small quantities of 3 were already formed during the preparation of 2. Irradiation is therefore only necessary to accelerate the overall reaction.

The oxidative addition product 3 was obtained in higher yield (71%) by a modification of the preparation procedure, by which workup after the first step is unnecessary: To avoid the presence of unreacted 1, which has to be separated, a 2-fold excess of $Fe_2(CO)_9$ was used. A toluene solution of 1 and $Fe_2(CO)_9$ was heated to 60 °C for 15 min and then irradiated at −10 °C for 24 h without isolation of 2. Although $(CO)_3Fe[PPh_2(CH_2)_2SnPh_3]_2$ was also present after the thermal reaction step, only 3 (and some unreacted 2) was isolated after irradiation. Obviously $(CO)_3Fe[PPh_2(CH_2)_2SnPh_3]_2$ was also converted to 3 by loss of a phosphine ligand.

The ν_{CO} pattern in the IR spectra of 3 is consistent with a meridional $Fe(CO)_3$ moiety. In the ^1H-NMR spectrum one phenyl group shows a high-field shift relative to 2. The ^{119}Sn NMR signal is shifted from 4.0 ppm in 1 to 137.5 ppm in 3, and the SnP coupling constant decreases from 172 Hz in 1 to 75 Hz in 3 (due to the mixing of $^2J_{SnFeP}$ and $^3J_{SnCCP}$). In the ^{13}C NMR spectrum two signals are observed for the chemically nonequivalent CO ligands; therefore, the molecule is rigid at room temperature. While the spectra clearly prove the occurrence of a Fe–Sn bond and a Fe–Ph group in 3, the spectra give no unequivocal information on the stereochemical outcome of the oxidative addition reaction. The X-ray structure analysis of 3[8] (Figure 1) shows that the phenyl group is cis to the tin atom and therefore trans to the phosphorus atom. In toluene solution there is no isomerization up to 85 °C according to high-temperature ^{31}P NMR spectra. The octahedral coordination of the iron atom is slightly distorted, the biggest deviation being the bending of two CO ligands toward the tin atom (C(1)–Fe–C(2) = 160.1 (5)°, Sn–Fe–C(1) = 83.0 (4)°, Sn–Fe–C(2) = 81.3 (4)°).

Octahedral hydrido stannyl complexes of iron, $(CO)_2(dppe)Fe(H)SnR_3$ or *mer*-$(CO)_3(PPh_3)Fe(H)SnR_3$ (R = Me, Ph), were previously prepared by us by reacting the silyl complexes $(CO)_3(PPh_3)Fe(H)SiMe_3$ or $(CO)_2(dppe)Fe(H)SiMe_3$ with $HSnR_3$.[9] The driving force for this reaction is both the higher stability of Fe–Sn bonds and the volatility of $HSiMe_3$, which prevents readdition of the silane. We used a similar approach to develop an alternative method for the preparation of 3 (Scheme I). The hydrido silyl complex $(CO)_4Fe(H)SiMePh_2$ (4) in toluene was reacted with 1 at room temperature (18 h) and then at 70 °C (4 h). Complex 3 was obtained by this procedure 3 in 83% yield. As an intermediate, the phosphine-substituted hydrido silyl complex 5 was spectroscopically identified. When the reaction was carried out at −50 to −30 °C, complex 5 was the sole product,[10] which was then converted to 3 at higher temperatures by silane elimination. The alternate mechanistic possibility, replacement of $H{-}SiMePh_2$ by $R_3Sn{-}Ph$ and subsequent addition of the phosphorus atom to the metal, was not observed.

Although complexes of the type $(CO)_3(PR'_3)Fe(H)SiR_3$ were prepared by thermal CO/PR'_3 exchange,[11] it is rather surprising that reaction of 4 with 1 proceeds at such low temperatures. Formation of 3 from 5 shows that addition of the Sn–C bond is favored over the readdition of $HSiMePh_2$. This is probably due to both the chelate effect and the higher strength of the Fe–Sn compared with Fe–Si bond.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supplementary Material Available: Tables of the positional parameters, anisotropic thermal parameters, and all bond distances and angles for 3 (11 pages). Ordering information is given on any current masthead page.

OM920411R

---

(8) Crystals were obtained from toluene/hexane (1:1). Crystallographic data for 3: orthorhombic, space group $P2_12_12_1$; a = 1353.8 (3), b = 1391.7 (5), c = 1653.7 (4) pm; V = 3116 (3) pm^3; Z = 4; d_{calcd} = 1.49 g cm^{-3}. A total of 3818 reflections were measured at 293 K ($2° \leq 2\theta \leq 54°$, Mo Kα radiation, λ = 71.069 pm) on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods (SHELXS) using 2619 decay and absorption corrected reflections ($I \geq \sigma(I)$); R = 0.061, R_w = 0.063.

(9) Knorr, M.; Piana, H.; Gilbert, S.; Schubert, U. *J. Organomet. Chem.* **1990**, *388*, 327.

(10) Spectroscopic data for 5 (−40 °C): ^{31}P NMR ($C_6D_5CD_3$) δ 59.1 ($^3J_{SnP}$ = 251 Hz); ^1H NMR ($C_6D_5CD_3$) δ 2.71 (m, 2 H, PCH_2), 1.55 (m, 2 H, $SnCH_2$), 1.24 (s, 3 H, Si*Me*), −9.04 (d, 1 H, Fe*H*, $^2J_{PFeH}$ = 27.7 Hz).

(11) Bellachioma, G.; Cardaci, G.; Colomer, E.; Corriu, R. J. P.; Vioux, A. *Inorg. Chem.* **1989**, *28*, 519.

β-Hydrogen Abstraction by Thiyl Radicals

P. Huston, J. H. Espenson,* and A. Bakac*

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received May 21, 1992

Summary: Alkanethiyl radicals, typified by $C_2H_5S^•$, react rapidly in aqueous solution with $C_2H_5ML(H_2O)^{2+}$, where ML = Co([14]aneN$_4$), $k = 1.15 \times 10^8$ L mol^{-1} s^{-1}, and Cr([15]aneN$_4$), $k = 5.9 \times 10^7$ L mol^{-1} s^{-1}. The use of $C_2D_5ML(H_2O)^{2+}$ leads to $k_H/k_D = 2.6$ (Co) and 3.3 (Cr), consistent with β-hydrogen abstraction and formation of ethylene. The methylcobalt complex forms $C_2H_5SCH_3$, with $k = 2.4 \times 10^7$ L mol^{-1} s^{-1} and $k_H/k_D \sim 1$.

Since C–H bonds are in general stronger than S–H bonds, the position of equilibrium lies to the left in reactions such as

$$RS^• + R'H \rightleftarrows RSH + R'^• \qquad (1)$$

Indeed, alkanethiyl radicals can be prepared by the reverse of (1), as we have done in this study. Alkyl radicals were generated by photohomolysis[1] of $R'Co([14]aneN_4)H_2O^{2+}$ ($R' = CH_3, C_2H_5$) in aqueous solution in the presence of a thiol such as cysteine or ethanethiol, thus yielding $RS^•$.[2]

What is new and unexpected, however, is the observation of a reaction between $C_2H_5S^•$ and organometallic com-

---

(1) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 3901.

(2) Huston, P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1992**, *31*, 720.

plexes of cobalt and chromium. Examples are represented by the equation

$$C_2H_5S^\bullet + C_2H_5ML(H_2O)^{2+} + H_2O \rightarrow C_2H_5SH + C_2H_4 + (H_2O)_2ML^{2+} \quad (2)$$

in which ML = Co([14]aneN$_4$) and Cr([15]aneN$_4$). The gas chromatographic determinations of ethylene yielded the ratio C_2H_4:ML^{2+} (M = Co) of 0.8:2. This is acceptably close to the expected ratio of 1:2 for the overall reaction (photohomolysis and reaction 2). Kinetic simulations by use of the program KINSIM[3] showed that dimerization of thiyl radicals was not important during steady-state photolysis conditions used in product studies.

The kinetics of reaction 2 were studied at pH 1.0 by laser flash photolysis.[4] For such experiments this reaction was coupled to a probe reaction based on $ABTS^{2-}$ (2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate) ion):

$$C_2H_5S^\bullet + ABTS^{2-} \xrightarrow{H^+} C_2H_5SH + ABTS^{\bullet -} \quad (3)$$

With both probe and alkylmetal complexes present in concentrations much higher than that of $C_2H_5S^\bullet$, the buildup of the highly colored[5] and persistent $ABTS^{\bullet -}$ radical follows first-order kinetics (after a minor correction for the dimerization of $C_2H_5S^\bullet$) with a rate constant given by

$$k = k_2[C_2H_5ML(H_2O)^{2+}] + k_3[ABTS^{2-}] \quad (4)$$

Since the second term is known from metal-free reactions,[2] $k_3 = (5.6 \pm 0.2) \times 10^7$ L mol^{-1} s^{-1} in 0.10 M HClO$_4$, the desired values of k_2 can be determined. If, as we claim, the reaction proceeds by abstraction of a hydrogen atom from a saturated C–H bond, one would expect an appreciable kinetic isotope effect. Thus, experiments with $C_2D_5ML(H_2O)^{2+}$ were also carried out. The rate constants (in 0.10 M HClO$_4$) are as follows (given as $k_2/10^7$ L mol^{-1} s^{-1}):

RCo([14]aneN$_4$)H$_2$O^{2+}	C_2H_5: 11.5	C_2D_5: 4.5
RCr([15]aneN$_4$)H$_2$O^{2+}	C_2H_5: 5.9	C_2D_5: 1.8

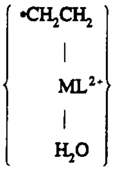
There is indeed a substantial isotope effect amounting to $k_H/k_D = 2.6$ for Co and 3.3 for Cr.

The rate constants show that the metal itself plays a small role in the rate-controlling process, possibly because the thermodynamics of the reactions of $C_2H_5CoL^{2+}$ and $C_2H_5CrL^{2+}$ with $C_2H_5S^\bullet$ are comparable. The only difference would come from a difference in metal–ethyl bond energies. Previous studies[6] have shown that Co–C bonds are often stronger than Cr–C bonds, as manifested by the values of equilibrium constants being greater than 1 for the alkyl exchange reactions:

$$RCr^{2+} + Co(dmgBF_2)_2 \rightleftharpoons Cr^{2+} + RCo(dmgBF_2)_2 \quad (5)$$

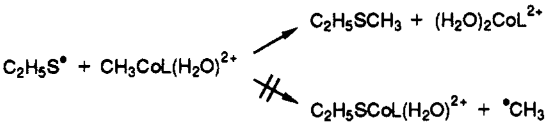
However, the saturated macrocyclic complexes studied here apparently have comparable M–C bond energies. The rate of homolysis[7] of RCo([14]aneN$_4$](H$_2$O)$^{2+}$ is similar to that of RCr([15]aneN$_4$)(H$_2$O)$^{2+}$, and the reverse reaction, capture of radicals, is expected not to be very different for the two metal complexes.[8,9]

The significant deuterium isotope effect and the minor effect of the metal, taken together, suggest an intermediate resulting from hydrogen atom abstraction, in which the metal–carbon bond has not broken and the metal center not reduced. We picture it as



$$\left\{ \begin{array}{c} {}^\bullet CH_2CH_2 \\ | \\ ML^{2+} \\ | \\ H_2O \end{array} \right\}$$

Quite interestingly, the methyl complexes $CH_3CoL(H_2O)^{2+}$ and $CD_3CoL(H_2O)^{2+}$ also react with $C_2H_5S^\bullet$. The rate constants are $k_6 = 2.4 \times 10^7$ and 2.7×10^7 L mol^{-1} s^{-1}. The only major product found in addition to methane (formed in reaction 1) was $CH_3SC_2H_5$. The ratio of $CH_3SC_2H_5$ to CoL^{2+} was determined to be 0.9:2, which agrees with the expected yield of 1:2 from photohomolysis and reaction 6. In the case of $(H_2O)_5CrCH_3^{2+}$, $k_6 = 3.4 \times 10^8$ L mol^{-1} s^{-1}. Clearly, $C_2H_5S^\bullet$ reacts with methyl complexes by an S$_H$2 attack at carbon, displacing metal (eq 6). S$_H$2 attack at cobalt (eq 7) is ruled out not only by the formation of $CH_3SC_2H_5$ as the only product but also on kinetic grounds. If reaction 7 were important, then a chain reaction would set in with reactions 7 and 1 as chain-propagating steps. This was not observed.



$$C_2H_5S^\bullet + CH_3CoL(H_2O)^{2+} \rightarrow C_2H_5SCH_3 + (H_2O)_2CoL^{2+} \quad (6)$$

$$C_2H_5S^\bullet + CH_3CoL(H_2O)^{2+} \not\rightarrow C_2H_5SCoL(H_2O)^{2+} + {}^\bullet CH_3 \quad (7)$$

Two observations in this work are significant and quite unexpected. First, the C–H bonds in $C_2H_5ML^{2+}$ complexes are much more reactive toward RS$^\bullet$ than are C–H bonds in alkanes and alcohols. (Note also, $K_1 \ll 1$.) Coordination to the metal may weaken the β-C–H bond in $C_2H_5ML^{2+}$ and stabilize the radical center. Second, thiyl radicals are much more reactive than $CH_3^\bullet$[10] toward C–H bonds in $C_2H_5ML^{2+}$, despite the C–H bond energy in CH$_4$ being ~16 kcal/mol larger than the S–H bond energy in RSH.[11] The reactivity order is thus exactly opposite from what would be predicted on thermodynamic grounds. The extraordinary kinetic advantage of the thiyl radicals may be related to the polarizability of sulfur.[12]

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Research, Chemical Sciences Division, under Contract W-7405-Eng-82.

OM920284Z

---

[3] Barshop, B. A.; Wrenn, C. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134. We are grateful to Professor Frieden for a copy of this program.

[4] The excitation wavelength was 490 nm, and typical reagent concentrations were as follows: (1-4) × 10^{-4} M C$_2$H$_5$Co([14]aneN$_4$)$^{2+}$, 0.10 M C$_2$H$_5$SH, and 6 × 10^{-4} M ABTS^{2-}.

[5] Hünig, S.; Balli, H.; Conrad, H.; Schott, A. *Leibigs Ann. Chem.* **1964**, *676*, 36.

[6] Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5197.

[7] (a) Shi, S.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1990**, *29*, 4318. (b) Bakac, A. Unpublished observations.

[8] Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 3901, 4319.

[9] Huston, P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1991**, *30*, 4826.

[10] No reaction between CH$_3^\bullet$ and C$_2$H$_5$Cr^{2+} was observed, which allows us to put an upper limit of <10^6 L mol^{-1} s^{-1} on the rate constant for H-atom abstraction. Similarly, CH$_3^\bullet$ reacts with ethylcobaloxime by S$_H$2 displacement at carbon with an estimated rate constant of 10^6–10^7 M^{-1} s^{-1} (McHatton, R. C.; Espenson, J. H.; Bakac, A. *J. Am. Chem. Soc.* **1986**, *108*, 5885). Under the assumption that hydrogen abstraction would have been observed had it comprised >10% of the total reaction, an upper limit of $k < 10^6$ L mol^{-1} s^{-1} is obtained for this reaction as well.

[11] Griller, D.; Simões, J. A. M.; Wayner, D. D. M. In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Asmus, K.-D., Eds.; Plenum: New York, 1990; p 359.

[12] Pryor, W. A.; Gojon, G.; Church, D. F. *J. Org. Chem.* **1978**, *43*, 793.