Mechanistic Study of the Reaction of $^{\bullet}Cr(CO)_3C_5Me_5$ with H_2S Yielding $HCr(CO)_3C_5Me_5$, $HSCr(CO)_3C_5Me_5$, and $C_5Me_5(CO)_2Cr{=}S{=}Cr(CO)_2C_5Me_5$. Kinetic Evidence for Formation of the Substituted Radical Complex $^{\bullet}Cr(CO)_2(H_2S)C_5Me_5$[†]

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Reaction of a large excess of H_2S with 2 mol of $^{\bullet}Cr(CO)_3C_5Me_5$ yields $HCr(CO)_3C_5Me_5$ and $HSCr(CO)_3C_5Me_5$. Kinetic studies of this reaction show two reaction pathways are followed. At pressures of CO above 10−15 atm and temperatures ≤10 °C, a third-order rate law $d[P]/dt = k^{3rd\ order}[^{\bullet}Cr(CO)_3C_5Me_5]^2[H_2S]$ is followed. The value of the third-order rate constant $70 \pm 5\ M^{-2}\ s^{-1}$ is essentially independent of temperature in the range −30 to +10 °C. As the pressure of CO is reduced, mixed-order kinetics is followed, and under argon atmosphere the reaction obeys the following second-order rate law: $d[P]/dt = k^{2nd\ order}[^{\bullet}Cr(CO)_3C_5Me_5][H_2S]$. The value of $k^{2nd\ order}$ was found to be $0.20 \pm 0.05\ M^{-1}\ s^{-1}$ at 1 °C and $0.30 \pm 0.05\ M^{-1}\ s^{-1}$ at 10 °C. This reaction channel is proposed to proceed by rate-determining ligand substitution and formation of the hydrogen sulfide substituted radical complex $^{\bullet}Cr(H_2S)(CO)_2C_5Me_5$. The rate of ligand substitution of $^{\bullet}Cr(CO)_3C_5Me_5$ by PMe_2Ph yielding the phosphine-substituted radical $^{\bullet}Cr(PMe_2Ph)(CO)_2C_5Me_5$ has been reinvestigated and shown to have rate constants and activation parameters similar to those proposed for rate-determining formation of $^{\bullet}Cr(H_2S)(CO)_2C_5Me_5$. A reasonable fit to data at intermediate pressures of CO is obtained at $T \leq 10$ °C by combining the $17e^-$ second order and $19e^-$ third-order mechanisms for oxidative addition. The complex $HSCr(CO)_3C_5Me_5$ can react with an additional 2 mol of $^{\bullet}Cr(CO)_3C_5Me_5$ yielding $HCr(CO)_3C_5Me_5 + C_5Me_5(CO)_2Cr{=}S{=}Cr(CO)_2C_5Me_5 + 2CO$. At a temperature of 50 °C under 1 atm of CO the net reaction $4^{\bullet}Cr(CO)_3C_5Me_5 + H_2S \rightarrow 2HCr(CO)_3C_5Me_5 + C_5Me_5(CO)_2Cr{=}S{=}Cr(CO)_2C_5Me_5 + 2CO$ occurs within minutes without formation of detectable amounts of $HSCr(CO)_3C_5Me_5$.

Introduction

The apparent simplicity of H_2S masks the complex and difficult chemistry of its interaction with metals. There are only a few examples of molecular hydrogen sulfide complexes stable enough to be characterized. Photochemically generated $W(CO)_5(SH_2)$ has been detected in solution,[1] but it has not been isolated. The Kubas complex, $W(CO)_3(PCy_3)_2$, was shown to undergo reversible oxidative addition of hydrogen sulfide,[2] presumably through initial formation of a molecular hydrogen sulfide complex (eq 1).

$$W(CO)_3(PCy_3)_2 + H_2S \rightleftharpoons W(CO)_3(PCy_3)_2(H_2S) \rightleftharpoons W(CO)_3(PCy_3)_2(H)(SH) \quad (1)$$

Oxidative addition in $W(CO)_3(PCy_3)_2(H_2S)$, compared to simple complex formation in $W(CO)_5(H_2S)$, is probably controlled by thermodynamic factors—the more electron donating phosphine ligands stabilizing the higher oxidation state.[3] Sellmann and co-workers[4] reported the first crystallographically characterized hydrogen sulfide complex $Ru(PPh_3)(\text{"}S_4\text{"})(SH_2)$. More recently, James and co-workers have also determined the structure of a stable hydrogen sulfide complex.[5] The high reactivity of hydrogen sulfide complexes is illustrated by this scarcity of structural data. Due to its toxicity and difficulty in handling, there are also relatively few reports on the kinetics and mechanisms of reactions of hydrogen sulfide with metal complexes in solution.[6] This paper presents results on the rate and mechanism of reaction of hydrogen sulfide with the stable 17-electron chromium-centered radical $^{\bullet}Cr(CO)_3C_5Me_5$ and allows comparison to earlier reports on the reactivity of the chromium radical with disulfides,[7] thiols,[8] and hydrogen.[9]

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or in a Vacuum Atmospheres glovebox. Toluene was distilled from sodium/benzophenone under argon into flame-dried glassware. Carbon monoxide (99.99%) and hydrogen sulfide (99.5%) were obtained from Matheson gas and used as received. $[C_5Me_5(CO)_3Cr]_2$ was prepared and purified by literature procedures.[10] Kinetic studies were performed on a Perkin-Elmer Spectrum 2000 FT-IR equipped with an i-series

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[†] This paper is dedicated to Professor John W. Connolly on the occasion of his retirement from the University of Missouri at Kansas City.

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microscope described in detail elsewhere.[11] ^1H NMR data were recorded on a Varian VXR 400 spectrometer. Concentrations of H_2S and CO were calculated using literature data on solubilities.[12]

Qualitative Studies of Reaction of H_2S and $^{\bullet}Cr(CO)_3C_5Me_5$. (a) Room Temperature under CO Atmosphere. A 0.019 M solution of $^{\bullet}Cr(CO)_3C_5Me_5$ in toluene was prepared under a CO atmosphere. An aliquot of this solution was withdrawn, and its FT-IR spectrum showed the characteristic peaks in the carbonyl region at 1994 and 1886 cm^{-1}. The atmosphere was then changed to H_2S (about 5 psi), with the solution rapidly turning yellow-brown. The FT-IR spectrum, taken about 5 min after addition of H_2S, showed clean conversion to $H{-}Cr(CO)_3C_5Me_5$ (1995 and 1929 cm^{-1}) and $HS{-}Cr(CO)_3C_5Me_5$ (2008 and 1949 cm^{-1}). ^1H NMR also confirmed the clean nature of this reaction with $HSCr(CO)_3C_5Me_5$ peaks at 1.37 ($C_5\mathit{Me}_5$) and −3.23 ppm ($S\mathit{H}$) and $HCr(CO)_3C_5Me_5$ peaks at 1.54 ($C_5\mathit{Me}_5$) and −5.54 ppm (H) in C_6D_6.

(b) Evacuation of H_2S and Reaction with Additional $^{\bullet}Cr(CO)_3C_5Me_5$. The above solution was evacuated to remove excess H_2S and then syringed on top of $^{\bullet}Cr(CO)_3C_5Me_5$ (0.1031 g, 0.380 mmol) in 8 mL of toluene, yielding a ratio of 2:1:1 $^{\bullet}Cr/HS{-}Cr/H{-}Cr$. FT-IR spectroscopy showed conversion to give an additional 1 mol of $H{-}Cr(CO)_3C_5Me_5$ as well as $C_5Me_5(CO)_2Cr{=}S{=}Cr(CO)_2C_5Me_5$ (1974, 1931, 1899, and 1891 cm^{-1}).

(c) High Temperature under CO Atmosphere. Under an atmosphere of CO, 30 mL of a 0.0020 M toluene solution of $^{\bullet}Cr(CO)_3C_5Me_5$ was allowed to equilibrate to 50 °C in a thermostated glass reactor (about 60 min). Two milliliters of this solution were removed to purge the syringe lines and obtain a spectrum of the stock solution prior to beginning the reaction. A dilute solution of hydrogen sulfide (0.175 M) was prepared in 5 mL of toluene. A 150 μL volume of the hydrogen sulfide solution was then added to initiate the reaction, yielding a ratio of 2:1 $^{\bullet}Cr$ to H_2S. At this temperature and under these conditions, the only detectable organometallic products are $HCr(CO)_3C_5Me_5$ and $C_5Me_5(CO)_2Cr{=}S{=}Cr(CO)_2C_5Me_5$ and reaction is complete within minutes of mixing the reagents. No sign of buildup of the expected intermediate product $HS{-}Cr(CO)_3C_5Me_5$ was observed at this temperature and Cr/H_2S ratio.

Kinetic Studies of Reaction of H_2S and $^{\bullet}Cr(CO)_3C_5Me_5$. A typical kinetic run is described: Under 1.5 atm of CO, 20 mL of freshly distilled toluene was added to $[Cr(CO)_3C_5Me_5]_2$ (103 mg, 0.190 mmol) and allowed to stir for 30 min until all the dimer dissolved to give a solution of the radical. To a thermostated reactor, 20 mL of toluene and 5 mL of the chromium solution were added under a CO pressure of 189 psi and allowed to equilibrate to 1 °C with saturation of the gas. The pressure of CO was determined from a pressure transducer obtained from Omega Instruments. The temperature of the solution was measured by a calibrated precision resistance thermistor in direct thermal contact with the solution. Three milliliters of this solution were removed to purge the syringe lines and obtain a spectrum of the stock solution prior to beginning the reaction. A saturated solution of hydrogen sulfide (0.70 M)[12] was prepared in 5 mL of toluene. Two milliliters of the hydrogen sulfide solution were added to initiate the reaction, yielding a solution with $[^{\bullet}Cr(CO)_3C_5Me_5] = 3.47 \times 10^{-3}$ M and $[H_2S] = 0.0583$ M, a $Cr{:}H_2S$ ratio of 1:16. The first spectrum and subsequent spectra were obtained at approximately 15 s intervals by withdrawing an aliquot under pressure to a high-pressure cell. The lines to the cell were also thermostated. Between measurements, the entire apparatus was vigorously shaken to ensure gas saturation was maintained. Pressure and temperature of the solution were monitored continuously during the experiment. Hydrogen sulfide and carbon monoxide were vented to a hood through a sodium hydroxide trap. **Caution!** *Both hydrogen sulfide and carbon monoxide are highly toxic and should be handled with appropriate safety devices.*

Kinetic Studies of Reaction of PMe_2Ph and $^{\bullet}Cr(CO)_3C_5Me_5$. This reaction was performed in analogous fashion to the reaction described above, with addition of 0.85 mL of a 0.639 M PMe_2Ph solution in toluene, yielding a solution with $[^{\bullet}Cr(CO)_3C_5Me_5] = 1.38 \times 10^{-3}$ M and $[PMe_2Ph] = 0.0228$ M, a $Cr{:}PMe_2Ph$ ratio of 1:17. The reaction is conveniently monitored by FT-IR spectroscopy by following either decay of bands due to $^{\bullet}Cr(CO)_3C_5Me_5$ or buildup of bands due to formation of product $^{\bullet}Cr(PMe_2Ph)(CO)_2C_5Me_5$ at 1900 and 1780 cm^{-1}. Solutions of the phosphine-substituted radical slowly decompose. Decomposition is slow, and rate and equilibrium data are readily calculated directly from the FT-IR data using standard techniques.

Calorimetric Measurement of the Enthalpy of Reaction of PMe_2Ph and $^{\bullet}Cr(CO)_3C_5Me_5$. Solutions of $^{\bullet}Cr(CO)_3C_5Me_5$ and of PMe_2Ph (≈10-fold excess) in toluene were prepared in the glovebox, filtered, and loaded into the solution mixing cells of a Setaram C-80 Calvet microcalorimeter. Following temperature equilibration, reaction was initiated by rotation of the calorimeter. Analysis of the thermograms through the first 10 min of reaction yielded an average value of $\Delta E_o = -0.6 \pm 0.5$ kcal/mol for the closed system calorimeter. Since 1 mol of CO(g) is given off in this reaction, this corresponds to $\Delta H^\circ = 0.0 \pm 0.5$ kcal/mol. Analysis of the reaction mixtures by FT-IR spectroscopy confirmed conversion of $^{\bullet}Cr(CO)_3C_5Me_5$ to $^{\bullet}Cr(PMe_2Ph)(CO)_2C_5Me_5$ in yields ≥90%. Due to the fact that the vessel is sealed, CO pressure builds up and a small amount of unreacted $^{\bullet}Cr(CO)_3C_5Me_5$ remains at the end of reaction. No other reaction products were detected.

Results and Discussion

The goal of this work was to investigate the rate of reaction of the stable $17e^-$ chromium-centered radical $^{\bullet}Cr(CO)_3C_5Me_5$ with H_2S. Reactions of this radical with PhSH and BuSH[8] were shown earlier to follow the third-order mechanism shown in eq 2 [$^{\bullet}Cr = {}^{\bullet}Cr(CO)_3C_5Me_5$]. The rate law for eq 2, obtained by

$$^{\bullet}Cr + RSH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RSH\cdots Cr + {}^{\bullet}Cr \xrightarrow{k_2} RS{-}Cr + H{-}Cr \qquad (2)$$

applying the steady-state approximation in $[RSH\cdots Cr]$, is $-d[^{\bullet}Cr]/dt = 2k_1k_2[^{\bullet}Cr]^2\,[RSH]/\{k_{-1} + k_2[^{\bullet}Cr]\}$. Provided $k_{-1} \gg k_2[^{\bullet}Cr]$ the third-order rate law reduces to $-d[^{\bullet}Cr]/dt = 2k_1k_2/k_{-1}[^{\bullet}Cr]^2\,[RSH]$.

The first step of eq 2 is proposed formation of a $19e^-$ adduct in which the $17e^-$ radical coordinates the thiol. The second step is attack of a second 1 mol amount of the metal radical on this activated complex forming the proposed termolecular transition state which leads to products.

The third-order mechanism shown in eq 2 is followed because thermochemical factors limit direct H atom transfer such as shown in eq 3.

$$^{\bullet}Cr(CO)_3C_5Me_5 + H{-}SR \rightarrow H{-}Cr(CO)_3C_5Me_5 + {}^{\bullet}SR \qquad (3)$$

The sulfur−hydrogen bond ($PhS{-}H = 79$, $BuS{-}H = 89$, $HS{-}H = 91$ kcal/mol)[13] is sufficiently strong compared to the chromium−hydrogen bond ($H{-}Cr(CO)_3C_5Me_5 = 62$ kcal/mol)[14] to make reaction 3 endothermic by 17 (PhSH) to 29 (HSH) kcal/mol. The third-order reactions in eq 2 were shown to have $\Delta H^\ddagger = 0 \pm 1$ kcal/mol and $\Delta S^\ddagger = -50 \pm 5$ cal/(mol deg).[8] Third-order reactions of MeSSMe,[7] H_2,[9] and D_2[9] also have comparable activation parameters. The rates of all of these reactions were shown to be essentially independent of temperature. Solutions of the chromium radical are readily generated by dissolution of the metal−metal-bonded dimer.[10] The equilibrium shown in eq 4 is rapidly established[15] and lies to the

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$$C_5Me_5(CO)_3Cr{-}Cr(CO)_3C_5Me_5 \rightleftharpoons 2{}^{\bullet}Cr(CO)_3C_5Me_5 \tag{4}$$

right for dilute solutions above $T \approx -10$ °C. The rates of the third-order oxidative addition reactions such as shown in eq 2 were all found to be independent of carbon monoxide pressure. Solutions of the radical are stabilized when under an atmosphere of CO, which serves to inhibit formation of the triple bonded dimeric complex (eq 5).

$$2{}^{\bullet}Cr(CO)_3C_5Me_5 \rightarrow 2CO + C_5Me_5(CO)_2Cr{\equiv}Cr(CO)_2C_5Me_5 \tag{5}$$

Qualitative Observations on Reaction of H_2S and $\cdot Cr(CO)_3C_5Me_5$. Reaction of hydrogen sulfide with the chromium radical proceeds in two stages. The initial products are the metal−hydride and metal−sulfhydride obtained by oxidative addition of one of the S−H bonds of H_2S (eq 6).

$$H_2S + 2{}^{\bullet}Cr(CO)_3C_5Me_5 \rightarrow H{-}Cr(CO)_3C_5Me_5 + HS{-}Cr(CO)_3C_5Me_5 \tag{6}$$

In the presence of excess hydrogen sulfide, reaction of the radical normally stops at this point. Evacuation of excess hydrogen sulfide and addition of 2 mol of metal radical results in attack on the remaining S−H bond (eq 7).

$$HS{-}Cr(CO)_3C_5Me_5 + 2{}^{\bullet}Cr(CO)_3C_5Me_5 \rightarrow H{-}Cr(CO)_3C_5Me_5 + 2CO + C_5Me_5(CO)_2Cr{=}S{=}Cr(CO)_2C_5Me_5 \tag{7}$$

The complexes $HS{-}Cr(CO)_3C_5Me_5$ and $C_5Me_5(CO)_2Cr{=}S{=}Cr(CO)_2C_5Me_5$, which have been previously prepared by other methods,[16,17] account for all organometallic products provided oxygen and other contaminants are rigorously excluded.

In kinetic studies described below, use of pseudo-first-order conditions of a large excess of H_2S results in observation of only reaction 6, with no contribution of reaction 7. As the reaction temperature is increased, however, suppression of the rate of formation of $C_5Me_5(CO)_2Cr{=}S{=}Cr(CO)_2C_5Me_5$ becomes increasingly difficult. At 50 °C under 1.3 atm CO and a $[{}^{\bullet}Cr(CO)_3C_5Me_5]:[H_2S]$ ratio of 2:1 reaction occurs according to the net stoichiometry of eq 8.

$$4{}^{\bullet}Cr(CO)_3C_5Me_5 + H_2S \rightarrow 2HCr(CO)_3C_5Me_5 + 2CO + C_5Me_5(CO)_2Cr{=}S{=}Cr(CO)_2C_5Me_5 \tag{8}$$

At this temperature and $[{}^{\bullet}Cr(CO)_3C_5Me_5]:[H_2S]$ ratio, attack of 4 mol of chromium radical on H_2S occurs within minutes at millimolar concentrations and occurs without buildup of detectable quantities of $HS{-}Cr(CO)_3C_5Me_5$.

Rate of Reaction of H_2S and ${}^{\bullet}Cr(CO)_3C_5Me_5$ under 1.2−1.4 atm of CO with $T = 20{-}40$ °C. The rate of oxidative addition of hydrogen sulfide was initially investigated under conditions such as were used to study the analogous reaction of thiols. Reaction 6 proceeds quantitatively in toluene solution under slight positive pressure of carbon monoxide and provided $[H_2S]/[{}^{\bullet}Cr(CO)_3C_5Me_5] \geq 15$ and $T \leq 40$ °C. The concentration of all species in solution is readily calculated from FT-IR spectroscopic data. As shown in Supporting Information Figure 1, these data show the clear presence of isosbestic points maintained throughout the entire course of the reaction. As shown in Supporting Information Figure 2 attempts to fit experimental data to a rate law second order in metal radical concentration were curved. As shown in Supporting Information Figure 3, attempts to fit experimental data to a rate law first order in metal radical, while not giving a good fit, were close to being linear. Variation of the pseudo-first-order $[H_2S]$ from 0.014 to 0.081 M showed that dependence on hydrogen sulfide concentration was first order. Calculated values of the approximate second-order rate constants obtained from plots such as those shown in Supporting Information Figure 3 were 0.19, 0.29, and 0.46 $M^{-1}\ s^{-1}$ at 20, 30, and 40 °C.

A reasonable mechanism for oxidative addition of hydrogen sulfide, which is first order in both hydrogen sulfide and chromium radical, could be proposed on the basis of eqs 9 and 10.

$${}^{\bullet}Cr(CO)_3C_5Me_5 + H_2S \xrightleftharpoons{\text{rds}} H{-}Cr(CO)_3C_5Me_5 + {}^{\bullet}SH \tag{9}$$

$${}^{\bullet}Cr(CO)_3C_5Me_5 + {}^{\bullet}SH \xrightarrow{\text{fast}} HS{-}Cr(CO)_3C_5Me_5 \tag{10}$$

Hydrogen atom transfer reactions to the chromium radical have been shown[14] to be rapid when thermodynamically allowed (eq 11).

$${}^{\bullet}Cr(CO)_3C_5Me_5 + H{-}Cr(CO)_2(PPh_3)C_5H_5 \rightarrow H{-}Cr(CO)_3C_5Me_5 + {}^{\bullet}Cr(CO)_2(PPh_3)C_5H_5 \tag{11}$$

However, as discussed earlier, thermochemical arguments imply $\Delta H^{\ddagger} \geq 29$ kcal/mol for eq 9. The temperature dependence of our data yielded an estimated value of $\Delta H^{\ddagger} \approx 8$ kcal/mol and ruled out this possibility.

Dependence of Rate of Reaction of H_2S and $\cdot Cr(CO)_3C_5Me_5$ on [CO]. A key to understanding the mechanism of oxidative addition of hydrogen sulfide to the chromium radical was discovery that the rate of reaction was much faster when studied under argon rather than carbon monoxide atmosphere. This experiment was performed only to complete this work. No effect was expected since, to the authors' knowledge, none of the oxidative addition reactions studied to date for ${}^{\bullet}Cr(CO)_3C_5Me_5$ have shown any dependence on CO pressure. The very first reaction at 20 °C under argon atmosphere proved to be much faster than one under identical conditions but under carbon monoxide. This led to investigation of the rate of oxidative addition as a function of carbon monoxide pressure.

Rate of Reaction of H_2S and ${}^{\bullet}Cr(CO)_3C_5Me_5$ under 0−15 atm CO with $T = -30$ to 10 °C. The mechanism of oxidative addition of hydrogen sulfide to the chromium radical could be resolved into two pathways at low temperatures and moderate pressures of CO. As was found at higher temperatures, under pseudo-first-order conditions of excess hydrogen sulfide, the rate of reaction was found to be first order in $[H_2S]$. Representative data as a function of gas pressure are shown in Figure 1 for attempted fit to a first-order dependence on metal radical and in Figure 2 for attempted fit to a second-order dependence on metal radical.

As shown in Figure 1, data under argon show a good fit to a first-order plot with deviation as the pressure of carbon monoxide is increased. (The observed influence of CO pressure on the rate of reaction was not due to volume of activation or pressure effects. Reactions done under 10 atm argon pressure

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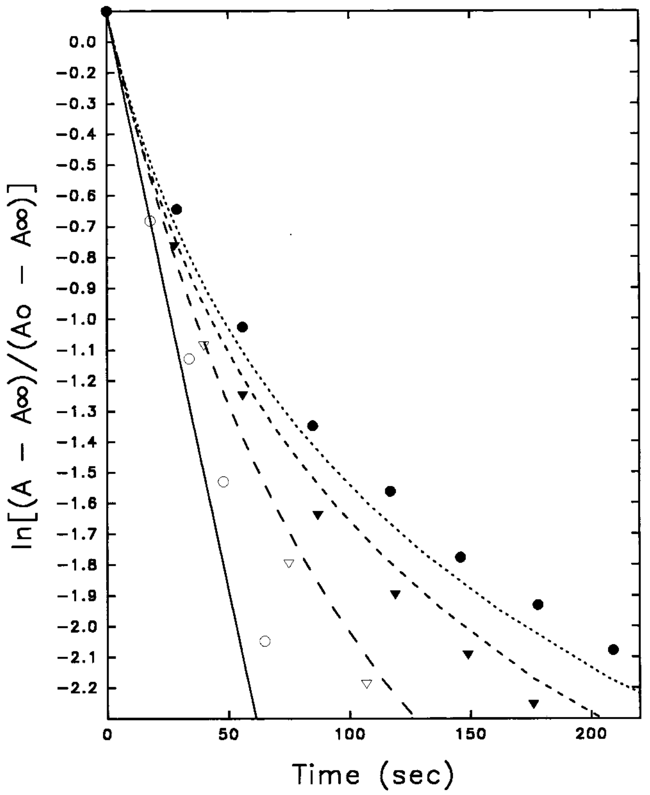


Figure 1. Plot of ln[($A - A_\infty$)/($A_0 - A_\infty$)] versus time (s) for reaction of $^{\bullet}Cr(CO)_3C_5Me_5$ with H_2S at 1 °C under argon (○), CO at 1.5 atm (▽), CO at 6.4 atm (▼), and CO at 11.5 atm (●) as described in the text. Lines are calculated on the basis of the reaction model described in the text. Concentrations of H_2S were 0.058 M except for reaction under argon, which was 0.081 M.

occurred at rates identical to those done under 1 atm argon pressure.) As shown in Figure 2, attempts to fit the same data to a rate law second order in chromium show the opposite trend—as the pressure of CO is increased, the "goodness of fit" increases. At pressures above 10 atm, the rate of reaction was found to level off. The highest pressure studied was ≈15 atm, and the rate was found to be the same as at 10 atm within experimental error.

The value of the limiting high-pressure third-order rate constant was found to be $k^{\text{3rd order}} = 70 \pm 5$ M^{-2} s^{-1} and identical within experimental error at −10, 1, and 10 °C. Several experiments were performed at −30 °C and 10 atm of CO. These data were also consistent with the same rate of reaction as found at the higher temperatures when correction was made for the reduced radical concentrations present in solution due to dimer formation according to eq 4. These data yield calculated activation parameters for the third-order reaction pathway $\Delta H^{\ddagger} = 0 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -49 \pm 5$ cal/(mol deg).

Data for the second-order pathway under an argon atmosphere could only be obtained at 1 and 10 °C. At higher temperatures as discussed above the products are not stable in the absence of CO. At lower temperatures the third-order reaction pathway becomes dominant even under argon. Values of $k^{\text{2nd order}} = 0.20 \pm 0.05$ and 0.30 ± 0.05 M^{-1} s^{-1} were derived from these data at 1 and 10 °C, respectively, and can be used to estimate $\Delta H^{\ddagger} \approx 6.5$ kcal/mol and $\Delta S^{\ddagger} \approx -38$ cal/(mol deg).

The physical resolution of these two pathways by study as a function of temperature, pressure, and radical concentration could only be achieved over a relatively narrow set of conditions.

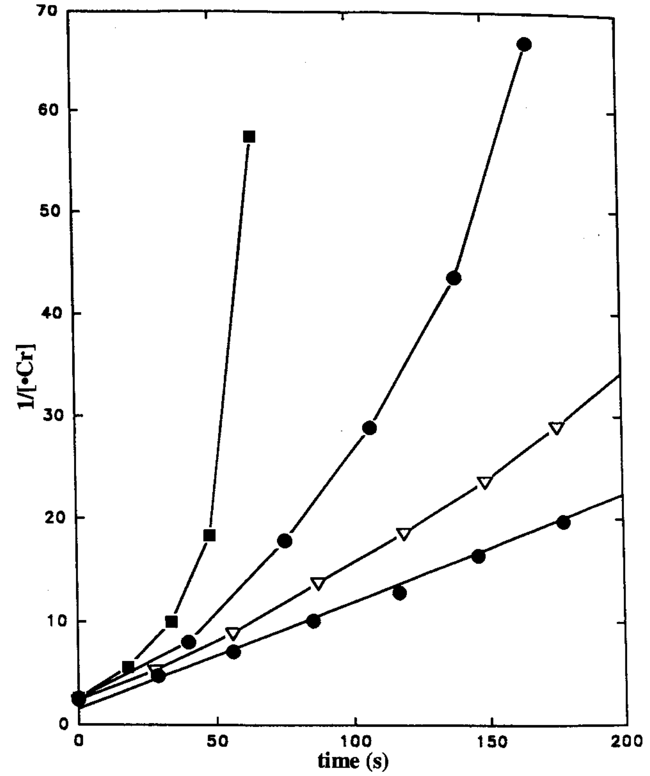
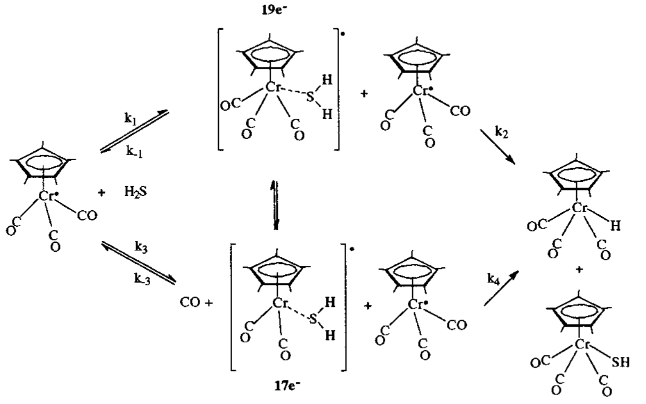


Figure 2. Plots of 1/[Cr] (M^{-1}) versus time (s) for reaction of $^{\bullet}Cr(CO)_3C_5Me_5$ with H_2S at 1 °C under argon (■), CO at 1.5 atm (●), CO at 6.4 atm (▽), and CO at 11.5 atm (●) as described in the text. Concentrations of H_2S were 0.058 M except for reaction under argon, which was 0.081 M.

Under most circumstances both pathways are followed as shown in the combined mechanism in eq 12.



(12)

The top line of eq 12 involves formation of a 19e⁻ hydrogen sulfide adduct in the reversible k_1/k_{-1} step. This intermediate is attacked by a second 1 mol of radical in step k_2 which leads directly to products. This is identical to the reaction mechanism proposed for thiols.

The significant difference in observed reactivity of hydrogen sulfide compared to thiols is attributed to the lower pathway in reaction 12. The key step in the lower pathway is the k_3/k_{-3} step in which hydrogen sulfide undergoes a reversible ligand substitution of carbon monoxide producing the substituted radical complex $^{\bullet}Cr(H_2S)(CO)_2C_5Me_5$.

The derived rate law for the combined mechanism in eq 12 is shown in eq 13.

$$\mathrm{d}[P]/\mathrm{d}t = -{}^1/_2\mathrm{d}[{}^\bullet\mathrm{Cr}]/\mathrm{d}t = \{k_1k_2/[k_{-1} + k_2[{}^\bullet\mathrm{Cr}]] + k_3k_4/[k_{-3}[\mathrm{CO}] + k_4[{}^\bullet\mathrm{Cr}]]\}[{}^\bullet\mathrm{Cr}]^2[\mathrm{H_2S}] \quad (13)$$

Assuming $k_{-1} \gg k_2[\mathrm{Cr}]$, eq 13 can be solved using time as the dependent variable[18] as a function of three rate constants k_1k_2/k_{-1}, k_3, and k_{-3}/k_4. A calculated fit based on this analysis is shown in Figure 1 obtained using the following values: $k_1k_2/k_{-1} = 65$ M^{-2} s^{-1}; $k_3 = 0.23$ M^{-1} s^{-1}; $k_{-4}/k_{-3} = 12$. This is an acceptable fit to the experimental data, and the rate constants used are close to those experimentally observed at the two extreme conditions of 0 and 15 atm CO pressure. Consideration of all data sets yielded average estimated values at 1 °C of these quantities: $k_1k_2/k_{-1} = 70 \pm 5$ M^{-2} s^{-1}, $k_3 = 0.2 \pm 0.05$ M^{-1} s^{-1}; $k_{-4}/k_{-3} = 10 \pm 5$.

Rate of Ligand Substitution Reaction of $^\bullet$Cr(CO)$_3$C$_5$Me$_5$ with PMe$_2$Ph: Comparison to Rate of Second-Order Reaction with H$_2$S. The key step in the proposed second-order mechanism in eq 12 involved ligand substitution of the chromium radical by hydrogen sulfide. Baird and co-workers[19] have reported UV−vis stopped-flow kinetic study of the kinetics of reaction 14 under CO. The literature study was completed in the range 25−40 °C. The rate of approach to equilibrium under pseudo-first-order conditions investigated in this study (variable [PMe$_2$Ph] and fixed [CO] both in large excess) yielded $k_{\mathrm{obs}} = k_1[\mathrm{PMe_2Ph}] + k_{-1}[\mathrm{CO}]$ from which Baird and co-workers derived at 24.8 °C the following: $k_1 = 0.957 \pm 0.004$ M^{-1} s^{-1} , $\Delta H^\ddagger = 2.7 \pm 0.45$ kcal/mol and $\Delta S^\ddagger = -49.7 \pm 1.4$ cal/(mol deg); $k_{-1} = 1.61 \pm 0.03$ M^{-1} s^{-1} , $\Delta H^\ddagger = 16.7 \pm 1.0$ kcal/mol and $\Delta S^\ddagger = -1.7 \pm 3.1$ cal/(mol deg). Calculation of thermodynamic parameters for reaction 14 yields the following at 24.8 °C: $K_{\mathrm{eq}} = 0.59$, $\Delta H^\circ = -14.0 \pm 1.5$ kcal/mol, and $\Delta S^\circ = -48.0 \pm 4.5$ cal/mol deg). Large negative enthalpies and entropies of reaction for reaction 14 would not be expected[20] and argued against use of these activation parameters to extrapolate to lower temperatures for comparison to the rate of reaction of hydrogen sulfide.

$$\mathrm{C_5Me_5Cr(CO)_3} + \mathrm{PMe_2Ph} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C_5Me_5Cr(CO)_2(PMe_2Ph)} + \mathrm{CO} \quad (14)$$

The rate of reaction 14 was reinvestigated in the temperature range 1−30 °C. As shown in Supporting Information Figure 4, FT-IR spectroscopic data for this reaction showed clean and quantitative production of the phosphine substituted radical under argon atmosphere. Plots of ln [$^\bullet$Cr] versus time were linear through 3−4 half-lives as shown in Supporting Information Figure 5 allowing direct measurement of k_1. The rates of reaction were also studied under 1.0−1.3 atm of CO allowing calculation of k_{-1} as summarized in Supporting Information Table 1. Of particular relevance to this work are the values of k_1 at 1.0 and 10.1 °C of 0.19 and 0.33 M^{-1} s^{-1}, which are quite close to those measured for the rate of oxidative addition of H$_2$S discussed above. Rate constants for reaction 14 measured in this work are roughly similar to those reported by Baird and co-workers.[19] Activation parameters calculated for reaction 14 in this work are in disagreement outside experimental error with those in the literature and discussed above. The reported data (for k_1, $\Delta H^\ddagger = 8.2 \pm 1.0$ kcal/mol and $\Delta S^\ddagger = -31.4 \pm 4.0$ cal/(mol deg); for k_{-1}, $\Delta H^\ddagger = 7.5 \pm 1.5$ kcal/mol and $\Delta S^\ddagger = -32.9 \pm 6.0$ cal/(mol deg)) yield the calculated thermodynamic parameters $\Delta H^\circ = +\ 0.7 \pm 2.5$ kcal/mol and $\Delta S^\circ = +\ 1.5 \pm 10.0$ cal/(mol deg) for reaction 14. In keeping with these data, our average value for $K_{\mathrm{eq}} = 0.53 \pm 0.05$ (in approximate agreement with that reported by Baird and co-workers[19]) was found to show no significant temperature dependence, implying a low value for ΔH° .

Direct calorimetric measurement of the enthalpy of reaction 14 yielded a value $\Delta H^\circ = 0.0 \pm 0.5$ kcal/mol at 30 °C , in agreement with the value $\Delta H^\circ = +\ 0.7 \pm 2.5$ kcal/mol derived from the kinetic studies describe above. This provides additional support for the derived activation parameters. In addition, it shows that for the 17e$^-$ chromium radical the Cr−CO and Cr−PMe$_2$Ph bond strengths are essentially identical. This order resembles what has been found for saturated 18e$^-$ complexes such as L−M(CO)$_5$ (M = Cr, Mo, W)[20] and may imply that no fundamental difference in relative bond strengths exist for the 17- and 18e$^-$ species.

The derived enthalpy of activation for substitution by PMe$_2$Ph reported here ($\Delta H^\ddagger = 8.2 \pm 1.0$ kcal/mol) is quite close to that estimated for the second-order pathway under argon atmosphere at 1 and 10 °C ($\Delta H^\ddagger \approx 6.5$ kcal/mol) and also the overall temperature dependence under an atmosphere of CO in the range 20−40 °C ($\Delta H^\ddagger \approx 8$ kcal/mol) discussed earlier. While the retarding influence of CO slows the rate of oxidative addition in keeping with the mechanism in eq 12, its temperature dependence would be dominated by the lower mechanism. The authors tentatively assign an enthalpy of activation for this process of $\Delta H^\ddagger = 9 \pm 4$ kcal/mol to the second-order pathway. Experimental difficulties inherent in this system limit more accurate resolution.

Possible Transition-State Structures for the Oxidative Addition. These data provide convincing evidence that oxidative addition of hydrogen sulfide proceeds when a second 1 mol amount of metal radical attacks either the 19 ($x = 3$) or 17 ($x = 2$) electron adducts "$^\bullet$Cr(SH$_2$)(CO)$_x$C$_5$Me$_5$". While no mechanism can ever be considered proven, the evidence for these two pathways is strong. Little is known about the detailed structure of the 19e$^-$ termolecular transition state, but two rational pathways can be considered for oxidative addition in the 17e$^-$ pathway in eq 12 as shown in Scheme 1.

The first possibility is that intramolecular oxidative addition occurs forming a Cr(III) complex prior to reaction with a second 1 mol amount of radical. Atom transfer reaction with the Cr(I) radical leads to the Cr(II) products. The first products are formulated as HCr(CO)$_3$C$_5$Me$_5$ and HSCr(CO)$_2$C$_5$Me$_5$, since it is expected that additional donation of electron density from sulfur will stabilize the initial dicarbonyl adduct. Rapid combination with CO yields HSCr(CO)$_3$C$_5$Me$_5$. Wegman and Brown[21] have proposed that photochemically generated $^\bullet$Co(CO)$_3$(PBu$_3$) radicals can lose CO and undergo oxidative addition of the Sn−H bond.

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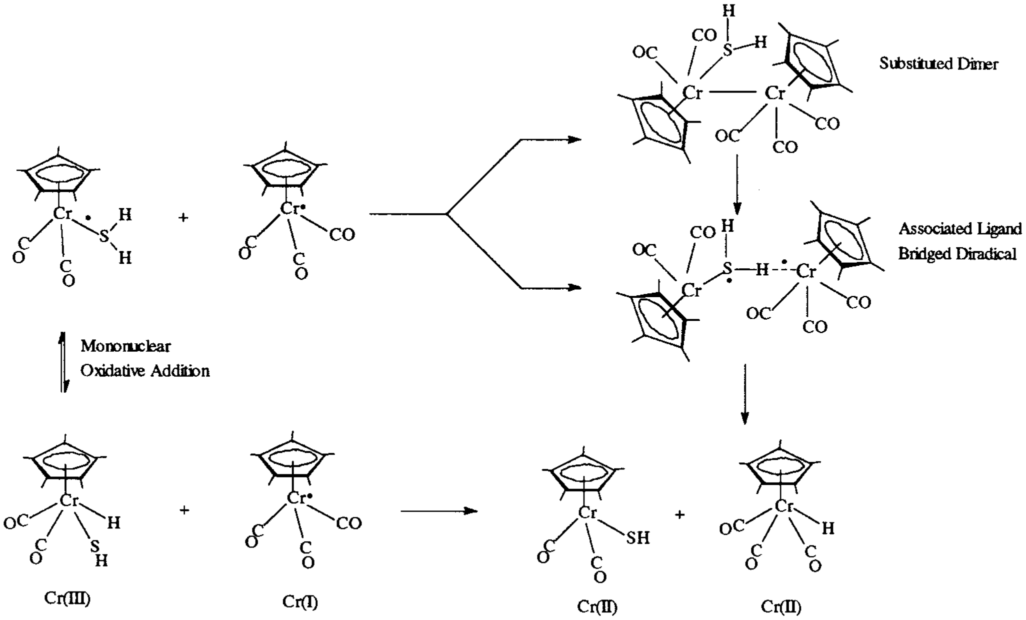
[18] Provided $k_{-1} \gg k_2[\mathrm{Cr}]$, eq 13 can be rearranged letting $x = 1/[\mathrm{Cr}]$: $\mathrm{d}x/\mathrm{d}t = 2[\mathrm{H_2S}]\{k_1k_2/k_{-1} + k_3x/\{1 + (k_{-3}[\mathrm{CO}]/k_4)x\}$. This can be solved in terms of time and the constants $a = k_1k_2/k_{-1}$, $b = k_3$, and $c = k_{-3}/k_4$ and [Cr], [CO], and [H$_2$S]: $t = 2[\mathrm{H_2S}]\{c[\mathrm{CO}]/(b + ac[\mathrm{CO}])(1/[\mathrm{Cr}]) + (b/(b + ac[\mathrm{CO}])^2)\ln(1 + (b + ac[\mathrm{CO}])(1/[\mathrm{Cr}])\}$. Subtraction of the integration constant in the equation above allows calculation of time as a function of the three relevant concentrations. Systematic analysis of the data led to the final estimates at 1 °C: $k_1k_2/k_{-1} = 70 \pm 5$ M^{-2} s^{-1}, $k_3 = 0.20 \pm 0.05$ M^{-1} s^{-1}; $k_{-3}/k_4 = 10 \pm 5$.

[19] Watkins, W. C.; Hensel, K.; Fortier, S.; Maccartney, D. H.; Baird, M. C.; McLain, S. J. *Organometallics* **1992**, *11*, 2418.

[20] The enthalpies of ligand substitution for the series of phosphine ligands PMe$_3$, PMe$_2$Ph, PMePh$_2$, and PPh$_3$ have been investigated for a number of metal complexes.[3] For most low-valent metal complexes, the M−CO bond strength is somewhere in the middle of this series of donors.

[21] Wegman, R. W.; Brown, T. L. *Organometallics* **1982**, *1*, 47.

Scheme 1



The alternate pathway to initial oxidative addition at one metal site is that prior to oxidative addition, a second 1 mol amount of radical interacts either with the chromium atom or with the bound hydrogen sulfide. In the top path in Scheme 1, a hydrogen sulfide-substituted metal−metal-bonded dimer is drawn as being formed by radical coupling. The lower pathway shows the incoming radical attacking the bound hydrogen sulfide to give a ligand-bridged spin-paired diradical complex. Since it is the S−H bond that is broken if the substituted metal−metal-bonded dimer is formed initially, it probably must ultimately rearrange with loss of the metal−metal bond and reorientation of the radical to the sulfur−hydrogen bond. For metals with stronger metal−metal bonds, and for which such a dimer might be formed by direct ligand substitution, the same ligand bridged diradical species is a reasonable transition state. Thus the transition states arrived at by reaction of 2 mol of the radical may bear some resemblance to those derived from initial ligand substitution of a more strongly bound metal−metal-bonded dimer.

Conclusion

The small size of hydrogen sulfide allows its facile oxidative addition to the chromium radical to occur by mechanisms following either first- or second-order dependence on the radical concentration. The reaction mechanism first order in metal radical is inhibited by added CO pressure and has rate and activation parameters similar to ligand substitution by PMe_2Ph. Formation of the substituted radical complex $^{\bullet}Cr(H_2S)(CO)_2C_5Me_5$ is the key step in this reaction channel as shown in the bottom line of eq 12. Under moderate pressures of CO, particularly at low temperatures, this reaction pathway is inhibited and a mechanism second order in metal complex is followed as shown in the top line of eq 12. This net third-order pathway is similar to what has been observed previously for reactions of thiols and other substrates and may be considered a "fallback" mechanism for this weak radical. Values for the third-order rate constants measured to date for $^{\bullet}Cr(CO)_3C_5Me_5$ are the following: MeSSMe $(400)^7 < H_2(350)^9 < D_2(280)^9 < H_2S$ (70) (this work) $<$ PhSH $(25)^8 <$ BuSH $(5)^8$ M^{-2} s^{-1}. For all these third-order reactions $\Delta H^{\ddagger} = 0 \pm 1$ kcal/mol and $\Delta S^{\ddagger} \approx 50$ cal/(mol deg). The differences in observed third-order rate constants are due primarily to differences in entropies of activation. No correlation between the rate constants and the strengths of the bonds broken or formed is apparent.

The key intermediates proposed in eq 12, the $17e^-$-substituted radical complex $^{\bullet}Cr(H_2S)(CO)_2C_5Me_5$ and the $19e^-$ adduct $H_2S\cdots{}^{\bullet}Cr(CO)_3C_5Me_5$, can be viewed as radical analogues of the classic inner- and outer-sphere complexes in coordination chemistry. In the absence of inhibiting CO the fastest reaction pathway involves formation and reaction of $^{\bullet}Cr(H_2S)(CO)_2C_5Me_5$ which would appear to imply that this complex is more active toward attack by a second 1 mol amount of radical than is $H_2S\cdots{}^{\bullet}Cr(CO)_3C_5Me_5$. Additional work on the kinetics and thermodynamics of these and other related radical systems is in progress.

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Supporting Information Available: A table and figures providing kinetics data. This material is available free of charge via the Internet at http://pubs.acs.org.

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