Reaction of Phenyl and Methyl Disulfide with $\cdot Cr(CO)_3C_5Me_5$ and $HCr(CO)_3C_5Me_5$. Metal Radical and Metal Hydride Reactivity at the Sulfur−Sulfur Bond. Different Mechanisms for Oxidative Addition of Alkyl and Aryl Disulfides

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Received March 14, 1996[⊗]

The enthalpies of reaction of the $\cdot Cr(CO)_3C_5Me_5$ and disulfides (RSSR) forming $RS{-}Cr(CO)_3C_5Me_5$ have been measured by solution calorimetry, $\Delta H = -13.3 + 1.5$ kcal/mol (R = Ph) and $-11.2 + 1.2$ kcal/mol (R = Me). These data lead to Cr−SR bond strength estimates of 35 and 43 kcal/mol, respectively. The rates of oxidative addition have been investigated by FTIR spectroscopy. Phenyl disulfide reacts by a second-order mechanism whose rate-determining step is the attack of the chromium radical on the sulfur−sulfur bond, yielding chromium thiolate and a thiyl radical [k(298 K) = 1.3 $M^{-1}\ s^{-1}$, $\Delta H^{\Phi} = +10.2$ kcal/mol, $\Delta S^{\Phi} = -24.4$ cal/(mol deg)]. Methyl disulfide reacts by a third-order mechanism going through a termolecular transition state in which the stronger sulfur−sulfur bond in the alkyl disulfide is attacked simultaneously by two chromium radicals [k(298 K = 393 $M^{-2}\ s^{-1}$, $\Delta H^{\Phi} = -0.2$ kcal/mol, $\Delta S^{\Phi} = -47$ cal/(mol deg)]. The rates of reaction of MeSSMe and PhSSPh with the hydride $H{-}Cr(CO)_3C_5Me_5$ have also been investigated in the presence of varying amounts of added $\cdot Cr(CO)_3C_5Me_5$ radical. MeSSMe shows no apparent reaction with $HCr(CO)_3C_5Me_5$, even in the presence of added $\cdot Cr(CO)_3C_5Me_5$. PhSSPh reacts with $HCr(CO)_3C_5Me_5$ primarily by a radical chain process involving $\cdot Cr(CO)_3C_5Me_5$ and PhS· radicals. The upper limit to the rate of reaction by nonradical concerted addition is $k_{obs} < 4 \times 10^{-4}\ M^{-1}\ s^{-1}$.

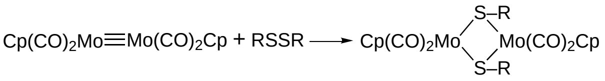
Introduction

Oxidative addition of sulfur−hydrogen and sulfur−sulfur bonds are fundamental reactions in metal sulfur chemistry. Physical studies of the transition metal−sulfur bond for complexes in solution are rare.[1] The "soft" nature of the metal−sulfur bond, its ability to coordinate to metals in a number of ways, and the "noninnocent" nature of many of its reactions contribute to the extensive chemistry of metal thiolates, but also make physical studies difficult. An understanding of relatively simple systems is the first step in establishing a basis for understanding the thermochemistry of metal/sulfur complexes.

Disulfides can react with metal complexes in different ways. Simple complex formation[2] has been observed as shown in eq 1:

$$W(CO)_5(THF) + PhSSPh \rightarrow W(CO)_5(PhSSPh) + THF \quad (1)$$

Addition to metal−metal multiple bonds to form clusters[3] has been observed:



$$Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp + RSSR \longrightarrow Cp(CO)_2Mo(\mu\text{-}S{-}R)_2Mo(CO)_2Cp \quad (2)$$

Single-electron as well as two-electron oxidations commonly occur as shown in eqs 3 and 4, respectively[4,5] (R = Ph; R′ = ^tBu, Ph, and Me):

$$2W(P(i\text{-}Pr)_3)_2(CO)_3 + RSSR \rightarrow 2W(P(i\text{-}Pr)_3)_2(CO)_3\text{-}SR\cdot \quad (3)$$

$$W(phen)(CO)_3(NCEt) + RSSR \rightarrow W(phen)(CO)_2(SR)_2 + CO + NCEt \quad (4)$$

Disulfides conventionally function as oxidizing agents; however, Stieffel and co-workers[6] have reported unusual internal redox reactions in which phenyl disulfide reduces the metal, while oxidizing coordinated sulfide:

$$MoS_4^{2-} + PhSSPh \rightarrow [Mo_2S_2(\mu\text{-}S)_2(S_2)_2]^{2-} + 2PhS^- \quad (5)$$

Disulfides are also known to react with metal hydrides yielding thiols and metal thiolates as shown in eq 6:

$$H{-}Mo(CO)_3C_5H_5 + RS{-}SR \rightarrow RS{-}H + RS{-}Mo(CO)_3C_5H_5 \quad (6)$$

The enthalpy of eq 6 as well as subsequent reactions of $RSMo(CO)_3C_5H_5$ yielding Mo/S dimers has been reported recently,[7] but to our knowledge the mechanisms of these reactions are unknown.

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.

(1) (a) For thermochemical data on metal−sulfur single bond strength estimates see: Simoes, J. A. M.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90,* 629 and references therein. (b) For thermochemical data on metal−sulfur coordinate bonds see: Hoff, C. D. *Prog. Inorg. Chem.* **1992**, *40,* 503−561 and references therein.

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S0020-1669(96)00294-7 CCC: $14.00

The relative ease of generation and the stability of thiyl radicals,[8] while not often explicitly seen in metal chemistry, is a recurrent theme in organic sulfur chemistry. Since the sulfur−hydrogen bond is weaker than almost all carbon−hydrogen bonds, carbon-centered radicals are rapidly trapped by thiols, yielding the weaker thiyl radical.

$$\mathrm{R\cdot + H{-}SR \rightarrow R{-}H + \cdot SR \rightarrow {}^{1}/_{2}RS{-}SR} \qquad (7)$$

In the absence of other reaction pathways the thiyl radicals readily recombine to form disulfide.[8]

Since the metal−hydrogen bond is weaker than the sulfur−hydrogen bond for almost all metals,[9] attack of thiyl radicals on the metal−hydrogen bond generating metal radicals should be thermodynamically favorable:

$$\mathrm{RS\cdot + H{-}M \rightarrow RSH + \cdot M} \qquad (8)$$

Kinetic studies on related systems indicate that such a radical process should have low enthalpies of activation and occur near the diffusion-controlled rate.[10]

Even with a strong precedent for thiyl radicals as reactive intermediates in organic reactions, the question of whether reactions occur by radical or concerted processes is always present. For example, we recently investigated[11] the kinetics and thermodynamics of oxidative addition of thiols to the $17e^-$ chromium radical $\cdot Cr(CO)_3C_5Me_5$. The reaction was expected to proceed by the thermodynamically uphill H atom transfer in reaction 9 followed by a radical combination step in eq 10:

$$\mathrm{PhSH + \cdot Cr(CO)_3C_5Me_5 \rightleftharpoons PhS\cdot + H{-}Cr(O)_3C_5Me_5} \qquad (9)$$

$$\mathrm{PhS\cdot + \cdot Cr(CO)_3C_5Me_5 \rightarrow PhS{-}Cr(CO)_3C_5Me_5} \qquad (10)$$

Since the PhS−H bond strength is 79 kcal/mol[12] and the $H-Cr(CO)_3C_5Me_5$ bond strength is 62 kcal/mol,[13] the first step in reaction 9, generation of a thiyl radical, is endothermic by 17 kcal/mol [reaction 9 is the reverse of the general reaction 8]. This barrier proved to be high enough that the reaction followed instead the third-order mechanism shown in eq 11:

$$\mathrm{\cdot Cr + RSH \rightleftharpoons RSH\cdots Cr + \cdot Cr \rightarrow RS{-}Cr + H\text{-}Cr} \qquad (11)$$

This paper extends our earlier work on reactions of thiols and the chromium radical to disulfides. Study of the reaction of disulfides with the hydride $HCr(CO)_3C_5Me_5$ is also reported.

Experimental Section

General Procedures. All manipulations were carried out with rigorous exclusion of oxygen using standard inert atmosphere techniques. The complexes $\cdot Cr(CO)_3C_5Me_5$ and $H-Cr(CO)_3C_5Me_5$ were prepared by literature methods or with minor variations.[14] Organosulfur derivatives were obtained from Aldrich Chemical. Phenyl disulfide was recrystallized from a methylene chloride/heptane mixture prior to use. Liquid disulfides and thiols were degassed prior to use. Toluene was distilled from sodium benzophenone ketyl under argon atmosphere into flame-dried glassware. Carbon monoxide and hydrogen gas were obtained from Matheson scientific and were of research purity. FTIR measurements were made on a Perkin-Elmer Spectrum 2000 FTIR equipped with an i-series microscope. Calorimetric measurements were made on a Setaram C-80 Calvet calorimeter using procedures strictly analogous to those described earlier.[13]

Qualitative Study of Reaction of $\cdot Cr(CO)_3C_5Me_5$ and Disulfides. Initial study of the reaction of $\cdot Cr(CO)_3C_5Me_5$ with phenyl and methyl disulfide was done in Schlenk tubes under an argon atmosphere. A 6×10^{-3} M solution of $\cdot Cr(CO)_3C_5Me_5$ in 25 mL of toluene was prepared under a CO atmosphere. An aliquot of this solution was withdrawn, and its FTIR showed the characteristic peaks in the carbonyl region at 1994 (s) and 1886 (s, br) cm^{-1}. To this solution was added neat MeSSMe or a small volume of a concentrated PhSSPh solution in toluene such that the disulfide was present in a 10-fold excess. A rapid bleaching of the purple color of the $\cdot Cr(CO)_3C_5Me_5$ solution to a yellow-orange occurred for both disulfides. The FTIR spectrum showed clean conversion to the product, which is formulated as $RS-Cr(CO)_3C_5Me_5$. The bands in the FTIR spectrum occur at 1996 (m), 1932 (s), and 1915 (m) cm^{-1} for $MeS-Cr(CO)_3C_5Me_5$ and at 2008 (m), 1952 (s), and 1925 (m) cm^{-1} for $PhS-Cr(CO)_3C_5Me_5$. The position and shape of these bands are in agreement with data for analogous Mo and W derivatives.[15] Addition of thiophenol to a solution of $MeS-Cr(CO)_3C_5Me_5$ results in liberation of methanethiol (detected by its characteristic odor) and complete conversion to $PhS-Cr(CO)_3C_5Me_5$. The same peaks at 2008, 1952, and 1925 cm^{-1} from reaction of PhSSPh and $\cdot Cr(CO)_3C_5Me_5$ are also obtained in reaction of PhSH with $\cdot Cr(CO)_3C_5Me_5$, which also produces $H-Cr(CO)_3C_5Me_5$ with bands at 1995 and 1912 cm^{-1}. The clean nature of these reactions is demonstrated by the sharp isosbestic points obtained in the kinetic studies described below. The reaction stoichiometry was confirmed in titrimetric procedures. Elemental analysis of the products was not performed since the FTIR data, stoichiometry of reaction, and chemical evidence provided sufficient proof that the complexes were $RS-Cr(CO)_3C_5Me_5$ as formulated.

Calorimetric Measurements. Calorimetric measurements were made as described in earlier publications[13] with minor modification to allow performance of the addition of the disulfide solution to the solution of $\cdot Cr(CO)_3C_5Me_5$ under an atmosphere of carbon monoxide. The use of mercury mixing cells in the Setaram calorimeter is not advisable with organosulfur compounds since side reaction of the sulfur complex with elemental mercury is a complicating factor. Addition of the organosulfur ligand was effected by use of thermostated Hamilton microliter syringes directly into the septum-sealed solution cells. The concentration of $\cdot Cr(CO)_3C_5Me_5$ at the beginning of the experiment and $RS-Cr(CO)_3C_5Me_5$ at the end of the experiment was made by quantitative FTIR spectroscopy. There was excellent agreement between separate experiments in which disulfide or chromium radical was the limiting reagent. The experimental values of $-12.9 + 1.5$ kcal/mol (PhSSPh) and $-10.8 + 1.2$ kcal/mol (MeSSMe) are the averages of five to eight separate determinations. Due to the fact that about 3% of the complex exists as metal−metal bonded dimer,[16] a correction factor of an additional -0.4 kcal/mol must be added to correct for the endothermic dissociation of this material.

Kinetic Studies. Kinetic studies were performed using the FTIR microscope/reactor system which will be described in detail elsewhere.[17] The majority of studies were performed under a slight overpressure of CO (1.1 atm) to avoid complications due to decarbonylation and

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[8] Brauman, J. I. In *Frontiers in Free Radical Chemistry*; Pryor, W. A., Ed.; Academic Press: New York, NY, 1980; pp 23−30.

[9] See, for example, Kristjansdottir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; p 309.

[10] (a) Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S.; Watkins, W. C.; Jaeger, T. *J. Am. Chem. Soc.* **1989**, *111*, 268. (b) Alnajjar, M. S.; Garrossian, S. T.; Autrey, S. T.; Ferris, K. F.; Franz, J. A. *J. Phys. Chem.* **1992**, *96*, 7037.

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[14] (a) Watkins, W. C.; Jaeger, T.; Kidd, C. E.; Fortier, S.; Baird, M. C.; Kiss, G.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 907. (b) Kiss, G. Doctoral Dissertation, University of Miami, 1993.

[15] Analogous $RS-M(CO)_3C_5H_5$ have been reported, see for example: (a) Weinmann, D. J.; Abrahamson, H. B. *Inorg. Chem.* **1987**, *26*, 3034. (b) Treichel, P. M.; Wilkes, G. R. *Inorg. Chem.* **1966**, *5*, 1182.

[16] This calculation is made from equilibrium data from ref 14. It does not significantly influence the kinetics of the reaction. At the start of the reaction the dimer may be present in 3−4%; however, this value decreases progressively as the reaction goes on. The monomer/dimer equilibrium is rapidly established (see ref 24).

[17] Ju, T. D.; Hoff, C. D. Manuscript in preparation.

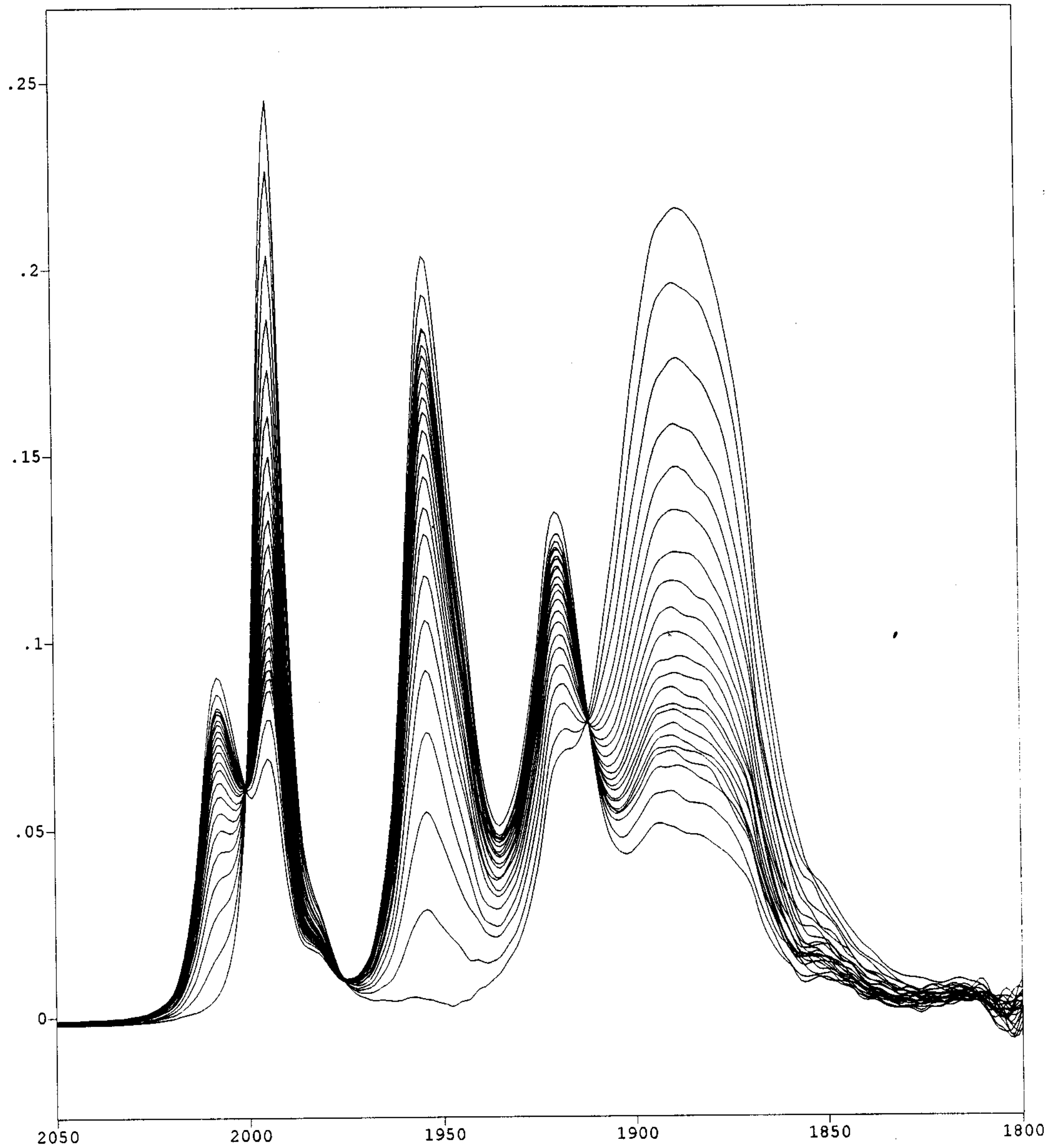

Figure 1. FTIR (absorbance versus wavenumber) plots for kinetic study of reaction of PhSSPh (3 mM) and $\cdot Cr(CO)_3C_5Me_5$ (6 mM), in toluene solution, at 45 °C under 1 atm of CO. The bands at 1994 and 1886 cm^{-1} due to the radical decrease while the bands at 2008, 1954, and 1925 cm^{-1} increase. The isosbestic points, for example, at 1912 and 2001 cm^{-1} at the 1/1 Cr/SPh ratio, provide good evidence of the clean nature of the reaction. Spectra were collected at approximately 20 s intervals.

formation of dimeric complexes.[18] Reactions performed under an argon atmosphere showed similar rate behavior, and no influence of CO was found in these radical reactions. Representative procedures are described below.

Reactions of $\cdot Cr(CO)_3C_5Me_5$ with PhSSPh. (a) Pseudo-First-Order Conditions. Under an atmosphere of CO, 30 mL of a 0.006 17 M toluene solution of $\cdot Cr(CO)_3C_5Me_5$ was allowed to equilibrate to a temperature of 25.2 °C. Three milliliters of this solution was removed to purge the syringe lines and obtain a spectrum of the stock solution prior to beginning the reaction. To this solution was added 2.0 mL of a 0.4587 M PhSSPh solution, yielding a final solution with $[\cdot Cr(CO)_3C_5Me_5] = 0.005\ 74$ M and $[PhSSPh] = 0.0316$ M, a Cr/S ratio of 1/11. The reaction followed first-order kinetics with a half-life of 14 + 3 s. Doubling the concentration of PhSSPh doubled the rate of reaction. The average value of $k_{obs}/(2[PhSSPh])$ (which corresponds to k_1 in eq 14, see Discussion) was determined to be $1 \pm 0.5\ M^{-1}\ s^{-1}$ under pseudo-first-order conditions at disulfide concentrations between 30 and 60 mM, in reasonable agreement with the value determined as described below of 1.3 $M^{-1}\ s^{-1}$ for 3 mM disulfide.

(b) Stoichiometric Ratio of Cr/S. These reactions were performed in strictly analogous fashion to the pseudo-first-order reactions described above. Stock solutions of accurately known $[\cdot Cr(CO)_3C_5Me_5\ ]$ in the range 3−6 mM were reacted with exactly mass balanced solutions containing $[PhSSPh] = 0.5[\cdot Cr(CO)_3C_5Me_5]$. Due to the lower [PhSSPh], the reaction is slower under these conditions, and data could be conveniently collected about every 20 s. Typical spectroscopic data under these conditions are shown in Figure 1, showing the decrease in bands at 1994 and 1886 cm^{-1} due to $\cdot Cr(CO)_3C_5Me_5$ and the increase in bands at 2008, 1954, and 1925 cm^{-1} due to $PhS{-}Cr(CO)_3C_5Me_5$. Kinetic analysis done on both the decrease in $[\cdot Cr(CO)_3C_5Me_5]$ based on the band at 1886 cm^{-1} and the increase in $[PhS{-}Cr(CO)_3C_5Me_5]$ based on the band at 1952 cm^{-1} gave an identical rate constant. The isosbestic point at 1912 cm^{-1} was maintained throughout the entire reaction, giving clear evidence of the clean nature of the reaction. A plot of $1/\{[\cdot Cr(CO)_3C_5Me_5]_{t=0} - [\cdot Cr(CO)_3C_5Me_5\}_{t=t}\}$ for decay of the 1886 cm^{-1} peak of $\cdot Cr(CO)_3C_5Me_5$ was linear through 3−4 half-lives. Experimental values for k_1 were obtained in the temperature range 25.2−55.0 °C, were the average of 3−5 individual measurements, and are summarized in Table 1. Kinetic data for the third order reaction

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(18) The radical $\cdot Cr(CO)_3C_5Me_5$ slowly loses CO to form the stable triple-bonded complex $[Cr(CO)_2C_5Me_5]_2$. So far as we can tell, this complex is inert to reaction with thiols and disulfides under these conditions, unlike the triple-bonded molybdenum complex which reacts with disulfides, see ref 7.

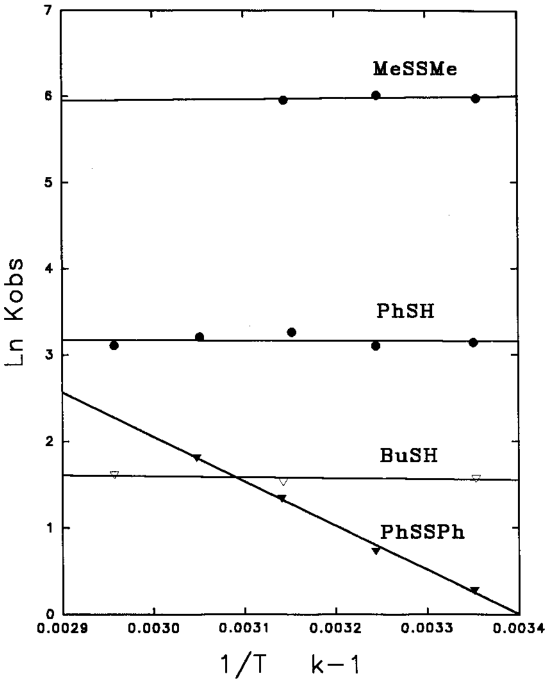

Figure 2. Plot of ln k_{obs} versus $1/T$ for reaction of disulfides and thiols with $\cdot Cr(CO)_3C_5Me_5$ showing the near zero slope for the rate of third-order oxidative addition of thiols and methyl disulfide and the stronger temperature dependence of the second-order oxidative addition of PhSSPh.

Table 1. Rate Constants and Derived Activation Parameters for Reactions of $\cdot Cr(CO)_3C_5Me_5$ with Disulfides and Thiols[a]

	PhSSPh[b]	MeSSMe[c]	PhSH[c]	BuSH[c]
25 °C	1.3	393	23.1	4.9
35 °C	2.1	408	22.2	
45 °C	3.9	385	26.0	4.7
55 °C	6.2		24.7	
65 °C			22.4	5.1
ΔH[d]	+10.2	−0.2	+0.1	+0.2
ΔS[e]	−24	−47	−52	−55

[a] Rate constants are in toluene solution and are considered accurate to within 10%. [b] Second-order rate constant in M^{-1} s^{-1}, corresponding to the value for k_1 in eq 14. [c] Third-order rate constant in M^{-2} s^{-1}, corresponding to $k_{obs} = 2k_1k_2/k_{-1}$ in a third-order mechanism of the general form in eq 27. [d] Enthalpy of activation in kcal/mol. [e] Entropy of activation in cal/(mol deg).

of $\cdot Cr(CO)_3C_5Me_5$ and MeSSMe was obtained using strictly analogous techniques. Rate constants and activation parameters are summarized in Table 1.

Reaction of $H-Cr(CO)_3C_5Me_5$ and PhSSPh in the Presence of Varying Amounts of $\cdot Cr(CO)_3C_5Me_5$. (a) Atmospheric Pressure Reaction in a Glass Reactor in the Absence of Added $\cdot Cr(CO)_3C_5Me_5$. A 50 mL Schlenk tube was loaded with 0.029 g of $\cdot Cr(CO)_3C_5Me_5$ in the glovebox. It was taken from the glovebox to a Schlenk line where the atmosphere was changed from argon to carbon monoxide. Toluene (35.0 mL) was added to prepare a solution of $\cdot Cr(CO)_3C_5Me_5$ of 3.05 × 10^{-3} M. The slurry was stirred for approximately a half-hour until it had dissolved completely. At that time, 30.0 mL of this solution was transferred via syringe to a thermostated glass reactor, which was under a slight positive pressure of 4−6 psi of H_2. It was stirred for 3−4 h until it was nearly colorless, and the FTIR spectrum showed no significant absorbance at 1886 cm^{-1}, only bands at 1995 and 1912 cm^{-1}, characteristic of $HCr(CO)_3C_5Me_5$. The reaction atmosphere was changed from H_2 to CO. A 3.44 M solution of phenyl disulfide (7.5 g) in toluene (10 mL) was prepared in the glovebox. Prior to beginning the reaction, 3.0 mL of the $HCr(CO)_3C_5Me_5$ solution was removed for spectroscopic analysis. The reaction was initiated by adding 0.5 mL of this solution to the reactor, yielding a final [PhSSPh] = 0.062 M. The FTIR spectra were collected by periodically removing 0.5−1.0 mL aliquots. A typical plot of the decrease in absorbance due to $HCr(CO)_3C_5Me_5$ under these conditions is shown in Figure 3. The slope of this curve was found to depend on the amount of time the $\cdot Cr(CO)_3C_5Me_5$ had been left under a H_2 atmosphere in its conversion to $HCr(CO)_3C_5Me_5$.

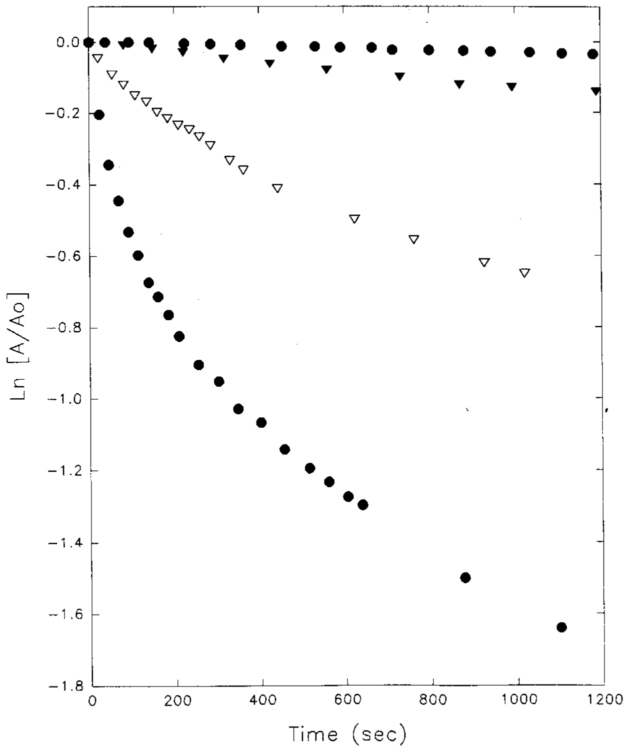

Figure 3. Plot of ln $[A/A_0]$ versus time (s) for absorbance at 1912 cm^{-1} for $H-Cr(CO)_3C_5Me_5$ under various conditions. All reactions are at 25 °C and at initial hydride concentrations of 4−6 mM. The top trace (●), which shows a very slow reaction, is for the purest sample of hydride prepared by hydrogenation of $\cdot Cr(CO)_3C_5Me_5$ at 42 atm of H_2 for over 3 days as described in the experimental section and with a high initial [PhSSPh] of 164 mM. All other reactions were done at [PhSSPh] = 62 mM. The second (▼) and third (▽) traces are for preparation of the hydride by reaction of the radical with 1−3 atm of hydrogen for approximately 6 and 1 h, respectively. The bottom trace (●) is for the reaction in which, to the approximately 6 mM hydride solution, 1.8 mM of $\cdot Cr(CO)_3C_5Me_5$ was deliberately added.

(b) Atmospheric Pressure Reaction in a Glass Reactor in the Presence of Added $\cdot Cr(CO)_3C_5Me_5$. This reaction was performed in strictly analogous fashion to that described in part a, and the spectra were generated using the same procedure. The excess concentration of $\cdot Cr(CO)_3C_5Me_5$ was added as a solution to the reactor under a CO atmosphere and before the reaction was initiated. The solution was prepared in such a way that the initial concentration of $H-Cr(CO)_3C_5Me_5$ was the same as that of part a, but with an addition of about 0.30 mole fraction of $\cdot Cr(CO)_3C_5Me_5$ present. Iterative computer subtraction and simulation of the spectra allowed determination of the concentration of all species present in solution as a function of time. These data are shown in Figure 4. During the rapid decay of $\cdot Cr(CO)_3C_5Me_5$, $H-Cr(CO)_3C_5Me_5$ also underwent a much faster reaction than in the absence of added radical.

(c) Medium Pressure Reaction in a Stainless Steel Reactor in the Absence of Added $\cdot Cr(CO)_3C_5Me_5$. In order to minimize the amount of $\cdot Cr(CO)_3C_5Me_5$ present in solution, this reaction was studied in a high-pressure stainless steel autoclave/FTIR cell equipped with germanium windows that has been described previously.[19] A solution of 0.0124 g of $\cdot Cr(CO)_3C_5Me_5$ was prepared in 15 mL of toluene and stirred under CO until it had completely dissolved. This solution (10 mL) was transferred via syringe to the apparatus which was under an overpressure of 9 psi of H_2. The entire assembly was then filled with H_2 gas to a 624 psi pressure for 3−4 days. A spectrum taken of the sample under these conditions showed no trace of radical present. The

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(19) Gonzalez, A. A.; Hoff, C. D. *Inorg. Chem.* **1989**, *28*, 4295.

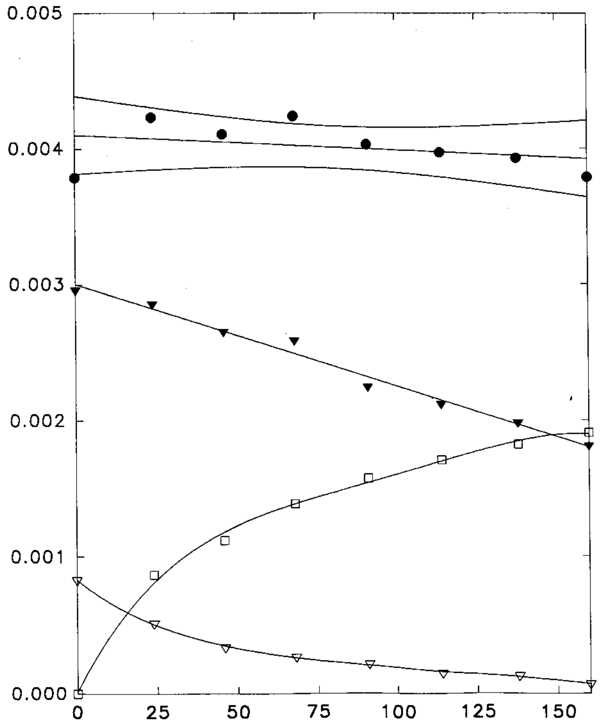

Figure 4. Concentrations in M for $\cdot Cr(CO)_3C_5Me_5$ (▽), $HCr(CO)_3C_5Me_5$ (▼), $PhS-Cr(CO)_3C_5Me_5$ (□), and total chromium (● shown with 99% confidence interval lines) versus time (s) for reaction of PhSSPh (0.062 M) in toluene at 25 °C with $[Cr(CO)_3C_5Me_5]/[H-Cr(CO)_3C_5Me_5]_{t=0}$ of approximately 0.3.

pressure was released to 50 psi, and a 0.5 mL solution of 3.44 M PhSSPh was added through a septum port fitted to a high-pressure ball valve, yielding a final solution with $[HCr(CO)_3C_5Me_5] = 0.004\,35$ M and [PhSSPh] = 0.164 M. During this time, H_2 escaped from around the septum and the pressure inside due to H_2 dropped to 22 psi. High-purity CO from a manifold was added to yield a total pressure gas pressure of 220 psi. The first spectrum was run approximately 3 min after addition of the disulfide to the solution. The cell was periodically shaken so that the bulk of the solution could replace the material between the windows. No difference was observed in the rate of reaction between the bulk solution and that in the windows. After about 25 min, during which very little reaction had occurred, gas pressure was reduced to 25 psi to see if there was a retarding influence of CO on the rate of reaction. No acceleration in rate was observed. The reaction was followed for a period of several hours and occurred at a negligible rate as shown in the top curve of Figure 3.

(d) Reaction of MeSSMe and $H-Cr(CO)_3C_5Me_5/\cdot Cr(CO)_3C_5Me_5$ Mixtures. In experiments done in strictly analogous fashion to those described above for PhSSPh, MeSSMe was investigated. In reactions in which MeSSMe was added to mixtures of $\cdot Cr(CO)_3C_5Me_5$ and $H-Cr(CO)_3C_5Me_5$, it was observed that $\cdot Cr(CO)_3C_5Me_5$ reacted with MeSSMe, yielding $MeS-Cr(CO)_3C_5Me_5$ at essentially the same rate as in the absence of $H-Cr(CO)_3C_5Me_5$. No concurrent reaction of $H-Cr(CO)_3C_5Me_5$ was observed in these reactions.

Results and Discussion

The goal of this work was to investigate the energetics and mechanism of reaction of disulfides with the stable 17-electron chromium radical $\cdot Cr(CO)_3C_5Me_5$. Solution calorimetric measurements of the enthalpies of reaction 12 were made in toluene solution at 30 °C under a CO atmosphere.

$$\cdot Cr(CO)_3C_5Me_5 + {}^1/_2RSSR \rightarrow RS-Cr(CO)_3C_5Me_5 \qquad (12)$$

$$R = Ph, \Delta H = -13.3 + 1.5 \text{ kcal/mol}$$

$$R = Me, \Delta H = -11.2 + 1.2 \text{ kcal/mol}$$

The enthalpies of reaction are similar in spite of the much greater sulfur−sulfur bond strength in MeSSMe (63 kcal/mol) compared to PhSSPh (43 kcal/mol),[20] which leads to the bond strength estimates $D_{PhS-Cr} = 34.8$ kcal/mol and $D_{MeS-Cr} = 42.7$ kcal/mol. These values are in agreement with independent bond strength estimates[11] made earlier based on heats of reaction of PhSH and BuSH: $D_{PhS-Cr} = 35.3$ kcal/mol and $D_{BuS-Cr} = 43$ kcal/mol (it is reasonable to expect that $D_{BuS-Cr} = D_{MeS-Cr}$). Average values for D_{RS-Cr} of 35 (R = aryl) and 43 (R = alkyl) are assigned an error of ±3 kcal/mol for typical alkyl and aryl groups. In comparison D_{PhS-Mo} for the corresponding molybdenum complex shows the expected increase in bond strength in going from Cr (35 kcal/mol) to Mo (41 kcal/mol).[7]

The Cr−SR bond strength values derived above allow calculation of the energetics of radical cleavage of the sulfur−sulfur bond: It is important to note that reaction 13 is

$$\cdot Cr(CO)_3C_5Me_5 + RS-SR \rightarrow \cdot SR + RS-Cr(CO)_3C_5Me_5 \qquad (13)$$

$$R = Ph, \Delta H = +8 \text{ kcal/mol}$$

$$R = Me, \Delta H = +20 \text{ kcal/mol}$$

endothermic for both disulfides. The reverse of reaction 13, attack of a thiyl radical on the chromium thiolate, producing a disulfide and a chromium radical, is calculated to be thermodynamically favorable.

In spite of the endothermic nature of reaction 13, the barriers are not prohibitive for oxidative addition of disulfide to occur by the mechanism below:

$$\cdot Cr(CO)_3C_5Me_5 + RSSR \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RS-Cr(CO)_3C_5Me_5 + RS\cdot \qquad (14)$$

$$RS\cdot + \cdot Cr(CO)_3C_5Me_5 \rightarrow RS-Cr(CO)_3C_5Me_5 \qquad (15)$$

Applying steady state treatment in [RS•] leads to the rate equation shown in eq 16:

$$\frac{d[Cr\cdot]}{dt} = \frac{-2k_1k_2[Cr\cdot]^2[RSSR]}{k_{-1}[CrSR] + k_2[Cr\cdot]} \qquad (16)$$

Under the conditions that $k_2[Cr\cdot] \gg k_{-1}[Cr-SR]$ (see later discussion), this reduces to $d[Cr\cdot]/dt = -2k_1[Cr\cdot][RSSR]$.

Kinetic studies of the reaction of $\cdot Cr(CO)_3C_5Me_5$ and PhSSPh were initially done under pseudo-first-order conditions at chromium/sulfur ratios of 1/10 and 1/20. These established that the reaction was first-order in both Cr and PhSSPh and had a second-order rate constant of approximately 1 $M^{-1}\,s^{-1}$ at 25 °C. The most accurate data was obtained using the special condition that $[PhSSPh] = [\cdot Cr(CO)_3C_5Me_5]/2$. Under these conditions the reaction follows the apparent second-order rate law $-d[\cdot Cr(CO)_3C_5Me_5]/dt = k_1[\cdot Cr(CO)_3C_5Me_5]^2$. The reactions are slower when the decay in disulfide concentration parallels that in metal concentration, which allows the generation of spectral data with a high signal/noise ratio. The high quality of the spectroscopic data obtained using the flow-through reactor/FTIR microscope system is shown in Figure 1. Decrease

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[20] The value of 43 kcal/mol for the sulfur−sulfur bond strength in phenyl disulfide is obtained from literature data on the enthalpy of formation of phenyl disulfide and thiophenol (see, for example: Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969; p 36) as well as enthalpies of solution as discussed in ref 7, and the PhS−H bond strength as determined in ref 19.

in the radical peaks and increase in thiolate peaks occurred with clear and sharp isosbestic points. Excellent fits were obtained through 3−4 half-lives. The quality of the data was needed since in practice it can be difficult to distinguish reaction order in the metal complex when dealing with air sensitive systems such as these. Experimental values of k_1 are collected in Table 1. A plot of ln k_1 versus $1/T$ is shown in Figure 2. Activation parameters derived from this plot are $\Delta H^{\Phi} = +10.2 + 1.5$ kcal/mol and $\Delta S^{\Phi} = -24.4 + 3.5$ cal/(mol deg).

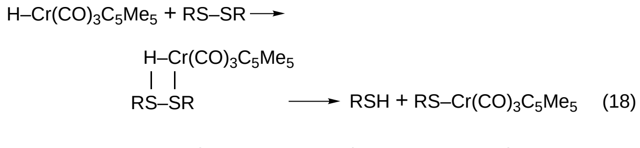
The majority of kinetic experiments were studied under a slight positive pressure of carbon monoxide. This serves to stabilize the chromium radical.[18] In order to rule out mechanisms which involved dissociation of CO as a first step, reactions were also performed under an argon atmosphere. Identical reaction rates were observed, and mechanisms such as that shown in eq 17, while reasonable, were ruled out on the basis of the lack of influence of CO concentration on reaction rate.

$$\begin{array}{c}\cdot\mathrm{Cr(CO)_3C_5Me_5} \rightleftharpoons \cdot\mathrm{Cr(CO)_2C_5Me_5} + \mathrm{CO} \\ \downarrow + \mathrm{RSSR} \\ \text{products}\end{array} \tag{17}$$

The activation parameters as well as chemical reactions discussed later all support the mechanism proposed in eqs 14 and 15. The enthalpy of activation derived for k_1 of 10.2 kcal/mol is close to the thermochemical barrier of 8 kcal/mol calculated in eq 13. The negative entropy of activation is in keeping with an associative transition state. The low overbarrier for k_1 (10.2 − 8 = 2.2 kcal/mol) implied a low value of ΔH^{Φ} for the k_{-1} step. Examination of eq 16 implies that the reaction should deviate from first-order dependence on the chromium radical as the concentration of thiolate builds up and the term $k_{-1}[\mathrm{PhS{-}Cr(CO)_3C_5Me_5}]$ becomes significant relative to $k_2[\cdot\mathrm{Cr(CO)_3C_5Me_5}]$.

No kinetic evidence for this appeared in the data through 3 half-lives in the absence of additional added $\mathrm{PhS{-}Cr(CO)_3C_5Me_5}$. Experiments where the thiolate product was added at the beginning of the experiment did show this effect. Reactions with initial $[\mathrm{PhS{-}Cr(CO)_3C_5Me_5}]/[\cdot\mathrm{Cr(CO)_3C_5Me_5}]$ ratios of 2−4 showed curvatures in the second and third half-lives of the reaction when the $\mathrm{PhS{-}Cr(CO)_3C_5Me_5}]/[\cdot\mathrm{Cr(CO)_3C_5Me_5}]$ ratio began to exceed about 15/1. We estimate a k_2/k_{-1} ratio on the order of 30 from these studies. This implies an activation energy difference between the k_2 and k_{-1} steps on the order of 2 kcal/mol at room temperature. The inhibitory effect of added thiolate is best attributed to the reversible nature of reaction 14.

Investigation of the reaction of disulfides with the metal hydride $\mathrm{H{-}Cr(CO)_3C_5Me_5}$ also provided (by accident) support for a mechanism which generates free phenyl thiyl radicals. This work was begun independently of the work on reaction of $\cdot\mathrm{Cr(CO)_3C_5Me_5}$ and PhSSPh. The initial goal was to measure the rate of addition of the sulfur−sulfur bond to the chromium−hydrogen bond, which was expected to occur by a concerted reaction as shown in eq 18. The concerted mechanism shown in eq 18 is similar to mechanisms for thiol/thiolate exchange.[21]



$$\mathrm{H{-}Cr(CO)_3C_5Me_5} + \mathrm{RS{-}SR} \longrightarrow \begin{array}{c}\mathrm{H{-}Cr(CO)_3C_5Me_5}\\ |\quad|\\ \mathrm{RS{-}SR}\end{array} \longrightarrow \mathrm{RSH} + \mathrm{RS{-}Cr(CO)_3C_5Me_5} \tag{18}$$

Kinetic results for reaction of phenyl disulfide and the chromium hydride were difficult to reproduce. The rate of reaction depended strongly on the history of the specific sample used. This can be indicative of radical chain reactions. Due to its air sensitivity, solutions of $\mathrm{H{-}Cr(CO)_3C_5Me_5}$ were prepared *in situ* from solutions of $\cdot\mathrm{Cr(CO)_3C_5Me_5}$, according to eq 19:

$$\cdot\mathrm{Cr(CO)_3C_5Me_5} \xrightarrow{\mathrm{CO/H_2}} \mathrm{H{-}Cr(CO)_3C_5Me_5} \tag{19}$$

Preparation of the hydride under $\mathrm{CO/H_2}$ at pressures of 1−3 atm (this reaction occurs by a third-order mechanism[22]) leads to a product that is colorless and "spectroscopically pure" in about 30 min. Peaks in the infrared spectrum due to the $\cdot\mathrm{Cr(CO)_3C_5Me_5}$ are barely discernible above baseline noise. Differing residual levels of $\cdot\mathrm{Cr(CO)_3C_5Me_5}$ are believed to be present in the solutions. That would account for the difficulty in reproducing the results. Deliberate addition of $\cdot\mathrm{Cr(CO)_3C_5Me_5}$ confirmed this. Reactions in which the $[\cdot\mathrm{Cr(CO)_3C_5Me_5}]/[\mathrm{H{-}Cr(CO)_3C_5Me_5}]$ ratio was controlled were studied, and the initial rate of decay of the hydride under various conditions is shown in Figure 3.

The top curve in Figure 3 represents the slowest rate of reaction achieved and is for the purest sample of $\mathrm{HCr(CO)_3C_5Me_5}$ that we were able to prepare. This sample was prepared by hydrogenation of a solution of $\cdot\mathrm{Cr(CO)_3C_5Me_5}$ for 3 days under 1 atm of CO and 41 atm of $\mathrm{H_2}$. The reaction itself was performed under approximately 3 atm of $\mathrm{CO/H_2}$ to minimize the presence of $\cdot\mathrm{Cr(CO)_3C_5Me_5}$. It was clear that oxidative addition of disulfide was extremely slow for this reaction. It can be concluded from this data that the second-order rate constant (if the reaction is occurring by this mechanism at all) at 25 °C must be $<4 \times 10^{-4}\ \mathrm{M^{-1}\ s^{-1}}$.

The fastest reaction rate shown in Figure 3 occurred when excess radical was deliberately added to the hydride solution with an initial ratio of $[\cdot\mathrm{Cr(CO)_3C_5Me_5}]/[\mathrm{H{-}Cr(CO)_3C_5Me_5}] = 0.30$ and [PhSSPh] = 20-fold excess. Iterative computer subtractions yielded the time dependence of $[\cdot\mathrm{Cr(CO)_3C_5Me_5}]$, $[\mathrm{H{-}Cr(CO)_3C_5Me_5}]$, and $[\mathrm{PhS{-}Cr(CO)_3C_5Me_5}]$ shown in Figure 4 for this reaction. This data was fit to the following mechanism:

$$\cdot\mathrm{Cr(CO)_3C_5Me_5} + \mathrm{RSSR} \overset{k_1}{\rightleftharpoons} \mathrm{RS{-}Cr(CO)_3C_5Me_5} + \cdot\mathrm{SR} \tag{20}$$

$$\cdot\mathrm{SR} + \cdot\mathrm{Cr(CO)_3C_5Me_5} \xrightarrow{k_2} \mathrm{RS{-}Cr(CO)_3C_5Me_5} \tag{21}$$

$$\cdot\mathrm{SR} + \mathrm{H{-}Cr(CO)_3C_5Me_5} \xrightarrow{k_3} \mathrm{RSH} + \cdot\mathrm{Cr(CO)_3C_5Me_5} \tag{22}$$

Reactions 20 and 21 are identical to those in the mechanism of reaction of $\cdot\mathrm{Cr(CO)_3C_5Me_5}$ and disulfide discussed above. Reaction 22 provides the basis for the catalytic role of $\cdot\mathrm{Cr(CO)_3C_5Me_5}$ in oxidative addition of disulfides to $\mathrm{H{-}Cr(CO)_3C_5Me_5}$. The thiyl radical generated from a chromium radical in reaction 20 can react with the chromium hydride (if it is present in high enough concentration) to regenerate the chromium radical. Reactions 20 and 22 represent the radical-catalyzed mechanism for oxidative addition of disulfide to the chromium hydride.

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(21) (a) There is support for thiol exchange proceeding through initial H-bonded adducts such as $\mathrm{PhSH\cdots[RS{-}M]} \rightarrow \mathrm{RS{-}H} + \mathrm{PhS{-}M}$ (see, for example, ref 21b). Such a transition state bears some resemblance to concerted addition in eq 18. Initial H-bonding would come from the metal hydride to the disulfide. If such a reaction pathway exists in toluene solution, it is prohibitively slow, as mentioned in the Discussion. (b) Darensbourg, M. Y.; Longridge, E. M.; Payne, V.; Reibenspies, J.; Riordan, C. G.; Springs, J. J.; Calabrese, J. C. *Inorg. Chem.* **1990**, *29*, 2721.

(22) Capps, K. B., Ju, T. D., Hoff, C. D. Unpublished results.

Steady state treatment of eqs 20−22 in thiyl radical yields equations for the rate of decay of the radical and hydride. Division of these equations to eliminate the time variable[23] yields eq 23:

$$\frac{d \ln [\mathrm{Cr}\bullet]}{d \ln [\mathrm{HCr}]} = 2k_2/k_3 \qquad (23)$$

A plot of ln [Cr] versus ln [HCr] for the data in Figure 4 yielded a k_2/k_3 ratio of 2.2 + 0.5. Using this k_2/k_3 value allowed calculation of $k_1 = 1.1 + 0.5\ \mathrm{M^{-1}\ s^{-1}}$, in agreement with the value calculated independently from a study of reaction 14 of $1.3\ \mathrm{M^{-1}\ s^{-1}}$. These results, taken together, provide strong support for the mechanism in reaction 13.

The phenyl thiyl radical ejected in the mechanism for reaction of phenyl disulfide can react with organometallic species in solution as summarized in eq 24:

	k_{rel}	ΔH	
$\mathrm{PhS\bullet + PhS{-}Cr \rightarrow PhSSPh + \bullet Cr}$	0.03	−8	(24)
$\mathrm{PhS\bullet + H{-}Cr \rightarrow PhSH + \bullet Cr}$	0.5	−17	
$\mathrm{PhS\bullet + \bullet Cr \rightarrow PhS{-}Cr}$	1.0	−35	

In addition to determination of the relative rates of reaction, an estimate of the absolute values of radical reactions can be made by combining the calorimetric and kinetic data. Assuming that the entropy change in reaction 14 is near zero and using the enthalpy change of +8 kcal/mol allows the calculation of $K_{eq} = k_1/k_{-1} = 1.3 \times 10^{-6}$. Using the value of $k_1 = 1.3\ \mathrm{M^{-1}\ s^{-1}}$ yields a value of k_{-1} of $10^6\ \mathrm{M^{-1}\ s^{-1}}$. Using the data in eq 24 leads to an estimation for the rate constant for second-order combination of the PhS• and $\bullet\mathrm{Cr(CO)_3C_5Me_5}$ radicals of $3 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$. This value is close to that reported recently by Geiger and co-workers[24] for dimerization of the $\bullet\mathrm{Cr(CO)_3C_5Me_5}$ radical, $k = 1.7 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$. Rates of group transfer in photogenerated $\bullet\mathrm{M(CO)_3C_5H_5}$ radicals have also been shown to occur with a range of rate constants, but in this order of magnitude.[25]

The above arguments all provided strong support for the radical mechanism proposed in eqs 14 and 15. Surprisingly, examination of plots of ln k_{obs} versus $1/T$ in Figure 2 showed that the second-order reaction of phenyl disulfide has a lower value than does the third-order reaction of thiophenol, implying a lower free energy of activation for the third-order reaction of thiophenol. This did not seem consistent with our observation of a second-order reaction of the disulfide when the corresponding third-order reaction would have a lower activation energy. It seemed possible that for bonding reasons the sulfur−hydrogen bond could be attacked in a termolecular transition state but not the sulfur−sulfur bond. It should be kept in mind, however, that the observed reaction pathway depends not only on the free energy but also on concentration. For parallel reaction pathways, first- and second-order in $\bullet\mathrm{Cr(CO)_3C_5Me_5}$, the observed rate of reaction obeys the equation

$$-d[\bullet\mathrm{Cr}]/dt = k^{2nd}[\bullet\mathrm{Cr}][\mathrm{RSSR}] + k^{3rd}[\bullet\mathrm{Cr}]^2[\mathrm{RSSR}] \qquad (25)$$
$$= \{k^{2nd} + k^{3rd}[\bullet\mathrm{Cr}]\}\{[\bullet\mathrm{Cr}][\mathrm{RSSR}]\}$$

The concentration of $\bullet\mathrm{Cr(CO)_3C_5Me_5}$ is typically $<5 \times 10^{-3}$ M, which will favor the second-order reaction. For the third-order rate to constitute 10% of the total reaction pathway at this concentration, its rate constant must have a numerical value of 20 times greater than the competing second-order reaction. That corresponds to 3 ln units in Figure 2. Thus, if third-order reaction of PhSSPh had activation parameters identical to those of PhSH, it would still not be observed.

The difference of 12 kcal/mol in eq 13 (originally estimated assuming $D_{\mathrm{BuS-Cr}}{}^{11} = D_{\mathrm{MeS-Cr}}$) implied that the rate of reaction by a free radical pathway should be approximately 8 orders of magnitude slower for MeSSMe. Test reactions showed that oxidative addition of methyl disulfide and phenyl disulfide under comparable conditions at room temperature occurred at similar rates! This implicated immediately a third-order reaction such as that shown in eq 26:

$$\begin{array}{l} \bullet\mathrm{Cr(CO)_3C_5Me_5} + \mathrm{RSSR} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RSSR}{\cdots}\mathrm{Cr(CO)_3C_5Me_5} \qquad (26) \\ \qquad\qquad\qquad\qquad\qquad k_2\big\downarrow \bullet\mathrm{Cr(CO)_3C_5Me_5} \\ \qquad\qquad\qquad\qquad\qquad 2\mathrm{RS{-}Cr(CO)_3C_5Me_5} \end{array}$$

The rate law for eq 26, obtained by applying the steady state approximation in $[\mathrm{RSSR}{\cdots}\mathrm{Cr(CO)_3C_5Me_5}]$, is $-d[\bullet\mathrm{Cr(CO)_3C_5Me_5}]/dt = 2k_1k_2\,[\bullet\mathrm{Cr(CO)_3C_5Me_5}]^2[\mathrm{MeSSMe}]/k_{-1} + k_2[\bullet\mathrm{Cr(CO)_3C_5Me_5}]$. Provided $k_{-1} \gg k_2[\bullet\mathrm{Cr(CO)_3C_5Me_5}]$ the third-order rate law $-d[\bullet\mathrm{Cr(CO)_3C_5Me_5}]/dt = k_{obs}\,[\bullet\mathrm{Cr(CO)_3C_5Me_5}]^2[\mathrm{MeSSMe}]$ will be obeyed where k_{obs} corresponds to $2k_1k_2/k_{-1}$ in the mechanism shown. It is this value that is reported in Table 1. As shown by this data, and also by the plot in Figure 2, the rate of reaction was essentially unchanged at 25, 35, and 45 °C. Temperature independence of reaction rate was also observed for the two thiols studied in this system,[11] data for which is also shown in Table 1 and Figure 2. The enthalpies of activation for all three third-order reactions are essentially zero and the entropies of activation near −50 cal/(mol deg). The rate constant for reaction of MeSSMe is nearly 2 orders of magnitude larger than for BuSH. As shown by the activation parameters in Table 1, this appears to be due primarily to a lower entropy of activation for the disulfide compared to the thiol. Cleavage of both sulfur−sulfur and sulfur−hydrogen bonds by termolecular processes appear to occur with roughly equal facility.

Radical species are not predicted to be formed in the third-order reaction sequence. This was tested by using $\mathrm{H{-}Cr(CO)_3C_5Me_5}$ as a thiyl radical trap as described above for PhSSPh. Methyl disulfide reacted with $\bullet\mathrm{Cr(CO)_3C_5Me_5}/\mathrm{H{-}Cr(CO)_3C_5Me_5}$ mixtures, but only with $\bullet\mathrm{Cr(CO)_3C_5Me_5}$. The rate of reaction was the same as that observed in the absence of $\mathrm{H{-}Cr(CO)_3C_5Me_5}$. $\mathrm{H{-}Cr(CO)_3C_5Me_5}$ was not consumed during reaction of $\bullet\mathrm{Cr(CO)_3C_5Me_5}$ and MeSSMe. That is in contrast to the behavior of PhSSPh discussed above and the clear evidence that the reaction is not proceeding by generation of free methyl thiyl radicals. Additional investigations are in progress for cleavage of other bonds by $\bullet\mathrm{Cr(CO)_3C_5Me_5}$ by third-order processes.

Conclusion

The major conclusions from this work are (i) disulfides can react by both second- and third-order pathways depending primarily on the strength of the sulfur-sulfur bond cleaved; (ii) concerted reaction of disulfides and metal hydrides is prohibitively slow compared to radical process; and (iii) phenyl thiyl radicals generated from interaction of metal radicals and phenyl disulfides can undergo secondary reactions with organometallic complexes, the scope of which are under continued investigation.

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(23) Elimination of time as an independent variable is a standard technique in this type of analysis, see for example: Benson, S. W. *The Foundations of Chemical Kinetics*; McGraw Hill: New York, 1960; p 43.

(24) Richards, T. C.; Geiger, W. E.; Baird, M. C. *Organometallics* **1994**, *13*, 4494.

(25) Song, J. S.; Bullock, R. M.; Creutz, C. *J. Am. Chem. Soc.* **1991**, *113*, 9862.

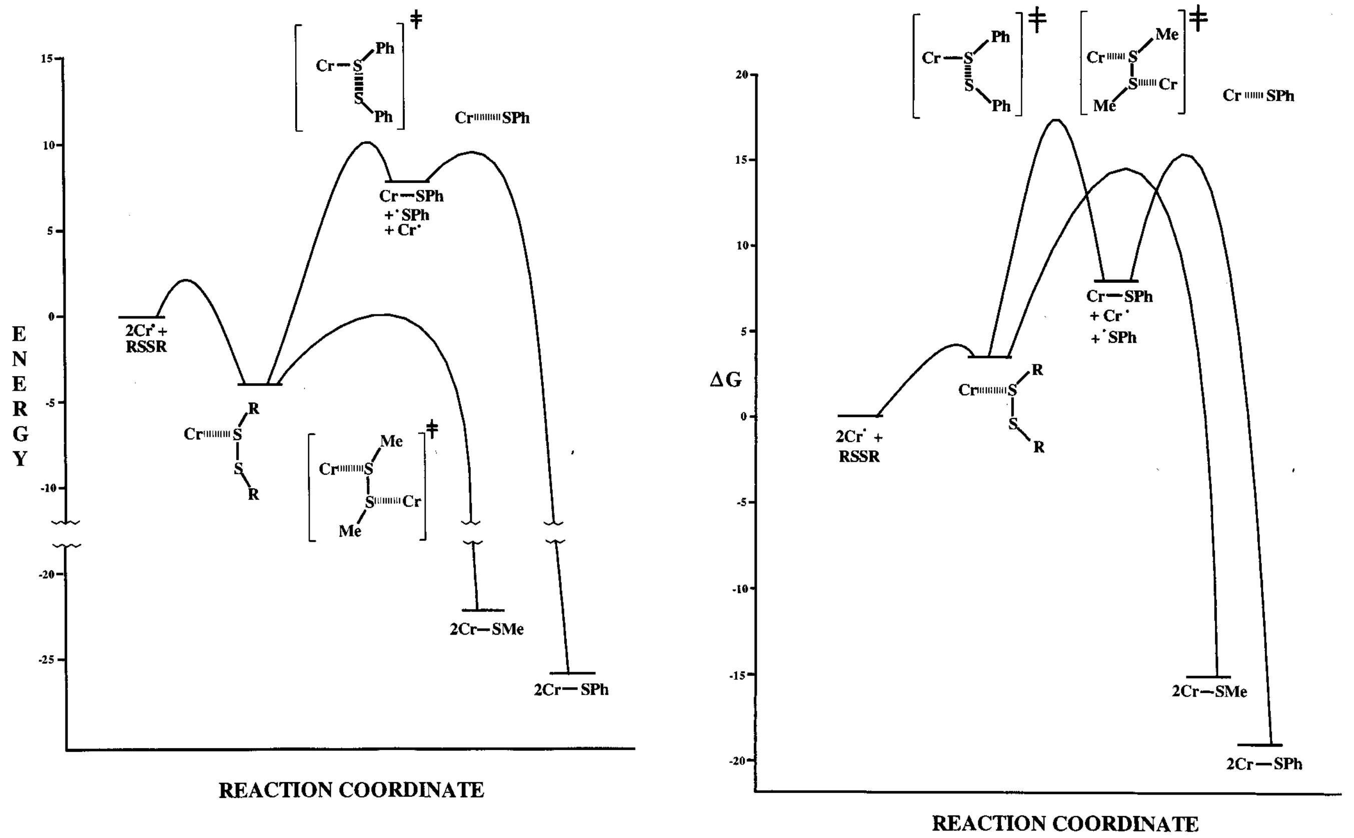

Figure 5. Potential energy diagram for reaction of RSSR and $\cdot Cr(CO)_3C_5Me_5$ by the overall second-order and third-order pathways described in the text: (a) ΔH in kcal/mol and (b) ΔG in kcal/mol. See text for additional discussion.

The potential energy diagram summarizing the second- and third-order pathways is shown in Figure 5a (ΔH) and b (ΔG). As is the case for all proposed mechanisms, this represents the simplest model that explains the measurements and observations made in this study. The reaction is presumed to proceed through initial formation of the 19-electron adduct $(RSSR)\cdots Cr(CO)_3C_5Me_5$. That is in keeping with extensive literature evidence for similar adducts.[26] All attempts to spectroscopically detect this proposed intermediate failed, even for nonreactive relatively strong sulfur donors such as tetrahydrothiophene. Estimated values are used for $\Delta H = -4$ kcal/mol and $\Delta S = -25$ cal/(mol deg).[27] The reactions are assumed to pass through this point, but other values are derived totally from the kinetic and thermodynamic values discussed above and are referenced to the starting materials.

The proposed 19-electron complex is the branching point in the mechanism. For phenyl disulfide the radical path is followed. The enthalpy and entropy of activation measured for this reaction, +10.2 kcal/mol and −24 cal/(mol deg), support a transition state that occurs just prior to breaking the sulfur−sulfur bond. Release of the chromium thiolate and a free thiyl radical from the transition state concludes the first part of the reaction. The net entropy change from the starting material is taken to be zero, and hence $\Delta G = \Delta H = +8$ kcal/mol. Combination of the phenyl thiyl radical and a second chromium radical occurs in the last step. The presence of the metal hydride presents another reaction channel.

For methyl disulfide the sulfur−sulfur bond is too strong to be readily broken by a single chromium radical. The energy required to "spit out" a methyl radical would be 12 kcal/mol higher, as seen in Figure 5a. The termolecular transition state occurs when a second chromium radical attacks $[MeSSMe]\cdots Cr(CO)_3C_5Me_5$. Efficient "molecular disassembly" occurs from there since two chromium thiolate bonds are formed concurrently with cleavage of the strong sulfur−sulfur bond. As was the case for thiols,[11] it is only the high entropic barrier that causes this reaction to be slow. That bodes well for design of complexes where two weak radicals in the correct geometry simultaneously attack a strong bond.

Acknowledgment. Support of this work by the National Science Foundation (Grant CHE9221265) is gratefully acknowledged.

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(26) (a) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325. (b) Geiger, W. E. *Acc. Chem. Res.* **1995**, *28*, 351.

(27) The entropy of ligand binding of −25 cal/(mol deg) is in keeping with the observed entropy of activation and also with literature estimates for the loss (mainly translational entropy) in ligand binding. See for example: Page, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 449. The moderately exothermic value for ligand binding in the 19-electron complexes is in keeping with other data (see ref 26) and the fact that, if the enthalpy of binding were greater than −7.5 kcal/mol, there would be a favorable free energy of binding. The relatively strong sulfur donor tetrahydrothiophene, which does not have the S−S or S−H functionalities, was not observed to form an adduct with $\cdot Cr(CO)_3C_5Me_5$, even at 1 M concentrations.