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# Oxidative Addition of Butanethiol and Thiophenol to the $^{\bullet}\mathrm{Cr(CO)_3C_5Me_5}$ Radical. Kinetic and Thermodynamic Study of a Third-Order Reaction and Its Catalysis

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Cleavage of the sulfur−hydrogen bond at metal centers is a key reaction in many biochemical[1] as well as industrial catalytic processes.[2] In spite of the importance of thiol activation by metals there are few thermodynamic or kinetic studies of these reactions. Radical processes have a long history in thiol chemistry,[3] and we wish to report reaction of a stable chromium-centered radical[4] with thiols as shown in eq 1:

$$2^{\bullet}\mathrm{Cr(CO)_3C_5Me_5} + \mathrm{RSH} \rightarrow \mathrm{RS{-}Cr(CO)_3C_5Me_5} + \mathrm{H{-}Cr(CO)_3C_5Me_5} \qquad \mathrm{R = Ph},\ n\text{-}\mathrm{Bu} \quad (1)$$

Calorimetric measurements of reaction 1 yield absolute RS−Cr(CO)$_3$C$_5$Me$_5$ bond strengths of 35 ± 3 (R = Ph) and 43 ± 3 (R = *n*-Bu) kcal/mol.[5] These values are the first direct calorimetric measurement of a transition metal−sulfur bond strength in solution.[6] They provide a basis for determining other metal−thiolate bond stengths by measurement of enthalpies of transfer of the $^{\bullet}$SR fragment.[7] Two possible second-order mechanisms for reaction 1 are shown in eqs 2 and 3:

$$\mathrm{Cr}^{\bullet} + \mathrm{RSH} \rightleftharpoons \mathrm{RS{-}Cr} + \mathrm{H}^{\bullet} + \mathrm{Cr}^{\bullet} \rightarrow \mathrm{H{-}Cr} \qquad (2)$$

$$\mathrm{Cr}^{\bullet} + \mathrm{RSH} \rightleftharpoons \mathrm{H{-}Cr} + {}^{\bullet}\mathrm{SR} + \mathrm{Cr}^{\bullet} \rightarrow \mathrm{RS{-}Cr} \qquad (3)$$

The Cr−SR bond strength estimates derived above can be used to rule out mechanism 2. The RS−H bond strengths of 79 (R = Ph) and 89 (R = Bu) kcal/mol[5] would make the first step in eq 2 endothermic by +44 (R = Ph) and +46 (R = Bu) kcal/mol. The Cr−H bond strengh of 62 kcal/mol[4b] can be used to calculate that generation of free thiyl radicals as shown in eq 3 is only endothermic by +17 (R = Ph) or +27 (R = Bu) kcal/mol. The low nature of the Cr−SR bond strength makes 3 the preferred second-order path.

Kinetic data for reaction 1 were obtained in toluene solution using a specially constructed flow cell mounted on an FTIR microscope.[8] The simple third-order equation, rate = $k_{\mathrm{obs}}[^{\bullet}\mathrm{Cr(CO)_3C_5Me_5}]^2[\mathrm{RSH}]$, was found true over the entire range of available concentrations for the chromium radical and thiophenol concentrations out to 1 M. The values of the rate contstants at room temperature [$k_{\mathrm{obs}} = 23 \pm 3\ \mathrm{M^{-2}\ s^{-1}}$ (R = Ph) and $5.0 \pm 1\ \mathrm{M^{-2}\ s^{-1}}$ (R = *n*-Bu)] showed no significant change over a 40 °C range [calculated activation parameters in the temperature range 25−65 °C: $\Delta H^{\ddagger} = +0.1 \pm 1$ kcal/mol, $\Delta S^{\ddagger} = -52 \pm 5$ cal/mol deg for PhSH, and $\Delta H^{\ddagger} = +0.2 \pm 1$ kcal/mol, $\Delta S^{\ddagger} = -55 \pm 6$ cal/mol deg for R = BuSH]. The near zero enthalpies of activation and high negative entropies of activation are consistent with other reports for third-order reactions.[9] The fact that thiophenol only reacts 5 times faster than butanethiol is also surprising in view of a 10 kcal/mol difference in bond strength. All of these observations point to a termolecular transition state in which 2 mole of the chromium radical attack the sulfur hydrogen bond.

The proposed third-order mechanism for reaction 1 is shown in the potential energy diagram in Figure 1. The first step is binding of thiol to the 17-e$^-$ radical forming a proposed 19-e$^-$ adduct.[10] This pre-equilibrium is probably rapidly established but thermodynamically disfavored. The second step is attack of the second mole of radical on the sulfur−hydrogen bond of the adduct leading to the termolecular transition state. The near zero observed enthalpy of activation implies that enthalpy of binding in the first step cancels the barrier to H atom transfer in the second step.

Additional support for the mechanism shown in Figure 1 was gained from study of reactions of stable 18-e$^-$ complexes of thiols. We have recently studied reaction of W(CO)$_3$(phen)(EtCN) with disulfides[11] and thiophenol,[12] both of which undergo oxidative addition. In the case of butanethiol, however, equilibrium amounts of a thiol complex[12,13] are formed as shown in eq 4:

$$\mathrm{W(CO)_3(phen)(EtCN)} + \mathrm{BuSH} \rightleftharpoons \mathrm{W(CO)_3(phen)(BuSH)} + \mathrm{EtCN} \quad (4)$$

Addition of 2 equiv of $^{\bullet}\mathrm{Cr(CO)_3C_5Me_5}$ to solutions of W(CO)$_3$(phen)(BuSH)/BuSH results in rapid consumption of 2 mol of the radical on the millisecond time scale[14] and produces 1 mol of H−Cr(CO)$_3$C$_5$Me$_5$ and 1 mol of W(CO)$_3$(phen)[BuS−

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(5) (a) For reaction 1, the enthalpy of reaction in toluene solution is −18.6 ± 1.8 kcal/mol for R = Ph. Using the value of 79 kcal/mol for the PhS−H bond strength[5b] and 62.3[4b] for H−Cr(CO)$_3$C$_5$Me$_5$ leads to the value of 35.3 kcal/mol. The BuS−Cr bond strength was determined from the enthalpy of thiol/thiolate exchange: BuS−Cr + PhSH → PhS−Cr + BuSH, $\Delta H = -2.5 \pm 0.2$ kcal/mol. The BuS−H bond is 89 kcal/mol.[5c] Using values for PhSH of 79[5b] and PhS−Cr of 35.3 (see above) leads directly to the value of 42.8 kcal/mol. The estimates of 35 and 43 kcal/mol are considered accurate to ±3 kcal/mol. (b) Bordwell, F. G.; Zhang, X. M.; Satish, A. V.; Cheng, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 6605. (c) Brauman, J. I. In *Frontiers in Free Radical Chemistry*; Pryor, W. A., Ed.; Academic Press: New York, NY, 1980; pp 23−30.

(6) We have recently reported measurement of the W(CO)$_3$(PCy$_3$)$_2$−SR bond strength in solution; however this was relative to an agostic bond whose exact strength is not known: Lang, R. F.; Ju, T. D.; Kiss, G.; Hoff, C. D.; Bryan, J. C.; Kubas, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 7917.

(7) RS−Cr(CO)$_3$C$_5$Me$_5$ and RS−Cr(CO)$_2$(PPh$_3$)Cp undergo rapid thiolate exchange with other metal radicals, and some coordinatively unsaturated metals as well: Ju, T. D.; Hoff, C. D. Unpublished results.

(8) Details of construction of the FTIR microscope reaction system will be published later.

(9) (a) Halpern, J. *Inorg. Chim. Acta.* **1982**, *62*, 31 and references therein. (b) The original proposal by Bodenstein of third-order reactions occurring by an initial "sticky collison" between two of the reactants which then collides with the third applies. See: Bodenstein, M. *Z. Phys. Chem.* **1922**, *100*, 118.

(10) (a) Two reasonable alternative mechanisms, both suggested by the referees, would be to view the initial adduct between the chromium radical and the thiol as a hypervalent sulfur radical rather than a 19-electron organometallic complex and that the order of assembly of the transition state could go through initial formation of a metal−metal dimer which then reacts with thiol. The authors considered these alternatives also and give preference to the 19-electron adduct on the basis of the literature data (ref 10b,c). In addition, failure to deviate from third-order kinetics at high thiophenol concentration provides some argument that in steady state treatment of the kinetics it is the thiol adduct that is formed first. The related radical/dimer system [Cr(CO)$_3$C$_5$H$_5$]$_2$ reacts more slowly with thiols than does $^{\bullet}\mathrm{Cr(CO)_3C_5Me_5}$. Since the former exists primarily as a dimer in solution and the later primarily as a radical, it seems more likely that it is the initial interaction with thiol that is important. (b) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325. (c) Geiger, W. E. *Acc. Chem. Res.* **1995**, *28*, 351.

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(13) The crystal structure of $\mathrm{Cr(CO)_5(^{\mathit{t}}BuSH)}$ has been reported recently: Darensbourg, M. Y.; Longridge, E. M.; Payne, V.; Reibenspies, J. R.; Riordan, C. G.; Springs, J. J.; Calabrese, J. C. *Inorg. Chem.* **1990**, *29*, 2721.

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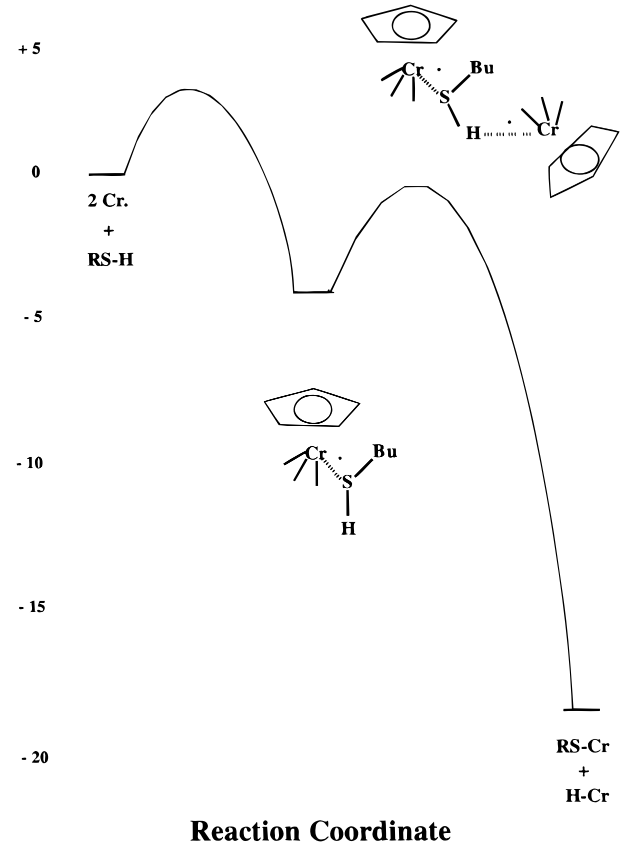
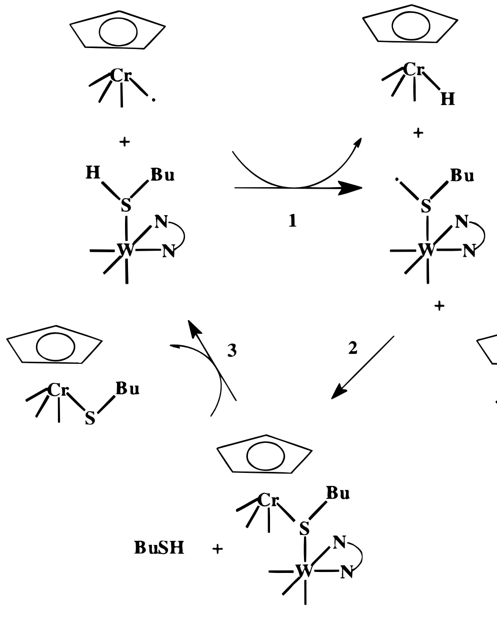


**Figure 1.** Reaction profile (kcal/mol) for $2^{\bullet}Cr(CO)_3C_5Me_5 + PhSH \rightarrow H-Cr(CO)_3C_5Me_5 + PhS-Cr(CO)_3C_5Me_5$.

**Scheme 1**



$Cr(CO)_3C_5Me_5$]. The W(O) complex of the chromium thiolate[14c] can be detected in solution, but we have not been able to isolate it.[14d] It is labile to ligand exchange with free butanethiol. This provides the basis for the catalytic cycle in Scheme 1.

The first step in Scheme 1 is H atom transfer to generate 1 mol of $HCr(CO)_3C_5Me_5$ and the proposed radical complex $W(CO)_3(phen)(SBu^{\bullet})$. This complex is not detected spectroscopically since it undergoes rapid radical combination with a second mol of the chromium radical to form $W(CO)_3(phen)$-[$BuS-Cr(CO)_3C_5Me_5$] in the second step. This proposal is reasonable since we have recently prepared analogous W(I) thiolate radical complexes[6] stabilized by the presence of bulky phosphine ligands:

$$W(CO)_3(PCy_3)_2(H)(SR) + Cr'' \rightarrow W(CO)_3(PCy_3)_2(SR)^{\bullet} + H-Cr'' \qquad Cr'' = Cr(CO)_2(PPh_3)C_5H_5 \quad (5)$$

The first two steps in Scheme 1 correspond to "dissection" of the sulfur−hydrogen bond as in eq 3 for free butanethiol, but with the difference that the sulfur remains bound to tungsten. The stable 18-$e^-$ complex in Scheme 1 thus serves as a model for the proposed unstable 19-$e^-$ complex in Figure 1. Kinetic studies show a dramatic influence of metal coordination on the rate of H atom transfer from sulfur to metal. The first two steps in Scheme 1 obey the second-order equation: rate = $k_{obs}[W(CO)_3(phen)(BuSH)][^{\bullet}Cr(CO)_3C_5Me_5]$. The value of $k_{obs}$ at 25 °C , $5 \times 10^4$ $M^{-1}$ $s^{-1}$, is in the range of those reported for similar H atom transfer to metal radicals.[15] The 27 kcal/mol thermodynamic barrier to cleavage of the sulfur hydrogen bond in eq 3 has been reduced to near zero[14b] for the bound thiol. This is attributed to the increase in the metal−sulfur bond strength that occurs concomitantly with H atom abstraction as the weak metal−thiol bond is converted to the stronger metal−thiolate bond. Increase in the acidity of thiols upon coordination has been demonstrated;[16] however this work demonstrates that the sulfur−hydrogen bond of thiols is effectively reduced some 25−30 kcal/mol upon coordination.

Few metals have strong enough bonds to hydrogen[17] to "single-handedly" cleave the sulfur−hydrogen bond and generate a free thiyl radical as shown in eq 3. Prior coordination to a metal changes that picture. The large reduction in the sulfur−hydrogen bond strength observed in the stable 18-$e^-$ complex $W(CO)_3(phen)(BuSH)$ is proposed to be similar to that in the postulated 19-$e^-$ complex $RSH\cdots Cr(CO)_3C_5Me_5$. Independent of its exact order of assembly, reaction 1 requires the presence of all three reactants in the transition state. The weak nature of the Cr−SR and Cr−H bonds relative to the H−SR bond is why the termolecular mechanism is the lowest free energy pathway in spite of a large entropic barrier: which might be reduced in properly designed complexes. Dinuclear oxidative addition of thiols to 2 mol of the weak chromium radical has been shown to be catalyzed by presence of a third mol of metal complex, ($W(CO)_3(phen)(EtCN)$), which can be viewed as a more efficient thiol receptor. The mechanisms proposed here may be relevant to enzymatic and surface reactions in which simultaneous (or near simultaneous) attack of the sulfur hydrogen bond by two or more metals occurs.

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(14) (a) For solubility reasons, this reaction was studied in methylene chloride solution. The rate of reaction 1 was also studied in methylene chloride, and its rate is essentially the same as it is in toluene. Due to the rapid nature of this reaction the high-pressure continuous flow reactor system was used. (b) Preliminary estimates of the activation parameters for the first two reactions in Scheme 1 are $\Delta H^{\ddagger} = +3 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = -25 \pm 5$ cal/mol deg. The low enthalpy of activation is consistent with a rate-determining first step which has $\Delta H^{\circ} < 0$. (c) The complex $W(CO)_3(phen)[BuS-Cr(CO)_3C_5Me_5]$ is assigned on the basis of its infrared spectrum which resembles that of the seperate components: $BuS-Cr(CO)_3C_5Me_5$ [1998, 1937, and 1916(sh) $cm^{-1}$] and $W(CO)_3(phen)[BuS-H]$ [1901 and 1785 $cm^{-1}$] with the difference that the bands of the chromium thiolate are shifted to higher wavenumber by about 4 $cm^{-1}$ whereas the W complex bands are shifted a comparable amount to lower wavenumber. These are the shifts expected on the basis of simple complex formation and quite different from those that would occur if oxidative addition occurred. The same peaks are observed by mixing preformed $RS-Cr(CO)_3C_5Me_5$ and $W(CO)_3(phen)(EtCN)$. (d) In addition to its lability, the complex $W(CO)_3(phen)[BuS-Cr(CO)_3C_5Me_5]$ undergoes a slow but clean reaction with free thiol to produce $H-Cr(CO)_3C_5Me_5$, CO, and $W(CO)_2(phen)(SR)_2$ (previously characterized[11]). This happens in the stoichiometric and toward the end of the catalytic cycles.

(15) The second-order rate constant[4b] for the H atom transfer reaction, $H-Cr(CO)_2(PPh_3)Cp + {}^{\bullet}Cr(CO)_3C_5Me_5 \rightarrow Cr(CO)_2(PPh_3)Cp + H-Cr(CO)_3C_5Me_5$ of $10^3$ $M^{-1}$ $s^{-1}$, is actually slower than that observed for eq 6.

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