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Mass Spectra of Organometallic Compounds. V. Electron-Impact Study of the Cyclopentadienylmanganese Thiocarbonyl and Carbonyl Complexes $RC_5H_4Mn(CO)_2CX$ [$R = H, CH_3$; $X = S, O$]

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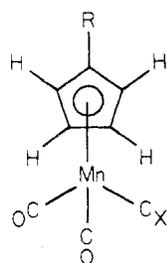
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The mass spectra of the related manganese complexes $RC_5H_4Mn(CO)_2CX$ ($X = S, O$; $R = H, CH_3$) have been examined and the appearance potentials of most of the metallic fragment ions determined. The manganese to carbonyl and thiocarbonyl ionic bond dissociation energies have been estimated from the energetics of the relevant fragmentations. These bond dissociation energies have revealed considerably stronger Mn-CS than Mn-CO bonds. The Mn-CO bonds in the thiocarbonyl complexes ($X = S$) appear to be stronger than those of the carbonyl analogs ($X = O$) and this is taken to suggest that coordinated thiocarbonyl is primarily a σ -donor ligand.

Introduction

Despite the growing interest in metal thiocarbonyl complexes, relatively few such compounds have been prepared and studied.¹ Furthermore, except for speculation based on limited experimental data, little is currently known about the bonding properties of the thiocarbonyl ligand.¹ In view of the resemblance between the ligands CS and CO, of special interest are the comparative studies on the coordinated thiocarbonyl and carbonyl ligands. The results of several such studies, including X-ray structure analysis of $[Ir(CO)_2(CS)(PPh_3)_2]^+PF_6^- \cdot Me_2CO_2$ and $RhCl(CX)(PPh_3)_2$ [$X = S$ and O]³ and mass spectral data on $C_5H_5Mn(CO)_2CS$,¹ have been taken to suggest a stronger M-CX bond for coordinated thiocarbonyl ($X = S$) than for carbonyl ($X = O$). According to SCF-MO calculations for CX [$X = S^4$ and O^5], this was attributed to the greater σ -donor and π -acceptor abilities of the thiocarbonyl ligand compared with those of carbonyl. Insofar as the π -acceptor property of the ligands is concerned, plausible evidence in support of the relative π -acidity order $CS > CO$ has been obtained from some spectral data.⁶⁻⁸

In order to gain further knowledge on the bonding of coordinated thiocarbonyl in relationship with carbonyl, a comprehensive electron-impact study of the isoelectronic and structurally related manganese complexes $RC_5H_4Mn(CO)_2CX$ [$R = H, CH_3$; $X = S, O$] has been undertaken. Bond dissociation energies determined from energetics of fragmentations may not be accurate in an absolute sense because of indeterminate errors due to the kinetic and excitation energies of the participants in these processes. Nonetheless, in analogous complexes, whose mass spectra consist of similar fragmentation steps, indeterminate errors should be about equal in magnitude, and, thus, it may be inferred that the relative scale of ionic bond dissociation energies is expected to be meaningful and reflect the relative order of metal-to-ligand bond strengths in the parent molecules.



- 1a, $R = H, X = S$
 b, $R = CH_3, X = S$
 2a, $R = H, X = O$
 b, $R = CH_3, X = O$

Experimental Section

The thiocarbonyl complex $C_5H_5Mn(CO)_2CS$ (**1a**) and its methyl analog $CH_3C_5H_4Mn(CO)_2CS$ (**1b**) were prepared and purified according to known procedures.⁹ Gift samples of the carbonyl complexes $C_5H_5Mn(CO)_3$ (**2a**) and $CH_3C_5H_4Mn(CO)_3$ (**2b**), received from Ethyl Corp., Ferndale, Mich., were purified by sublimation and distillation, respectively. The mass spectra of these compounds were measured at 80-eV on a Hitachi RMU-7E mass spectrometer which has been modified with a Keithley 427 current amplifier. The samples were introduced into the spectrometer under a low pressure of $\sim 10^{-6}$ Torr through a reservoir system with a small molecular leak into the ionization chamber. The sample heater temperature was kept at $100 \pm 2^\circ C$ and the ionization chamber temperature was maintained at $200 \pm 2^\circ C$. Intensities, corrected for background, of the molecular and most of the metallic fragment ions (Table I) are given relative to an arbitrary value of 100.0 chosen for $RC_5H_4Mn^+$ ($R = H, CH_3$) which is the base peak in all four spectra. Metastable ions, observed in the mass spectra of these complexes, are given in Table II.

The ionization potentials of the complexes and the appearance potential of the metallic ions reported in Table I were determined by a modified Honig method according to the procedure of Lossing, Tickner, and Bryce¹⁰ and by using benzene ($i = 9.24$ eV) as a calibrant. The appearance potential of each ion was measured several times independently and the precision of the mean result is indicated by the quoted standard deviation. The accuracy of the results is probably an order of magnitude greater than the indicated precision.

Results and Discussion

The manganese complexes, studied in this work, were found to exhibit sufficient thermal stability under the specified conditions used in obtaining their mass spectra. This has been inferred by examining the intensity ratio of the ions in the spectra as a function of the inlet and chamber temperatures. Further support of this comes from the appearance potential data (Table I) which are consistent with fragmentations initiated from the molecular ions, rather than through thermally produced radicals. The latter process involving the ionization of radical fragments would have been expected to afford potentials of lower value than those actually found.

The absence of the ions $RC_5H_4Mn(CO)_2^+$ and $RC_5H_4MnCO^+$ from the mass spectra of the manganese thiocarbonyl complexes $RC_5H_4Mn(CO)_2CS$ [**1a**, $R = H$; **1b**, $R = CH_3$] indicates that the dissociation of the CS ligand occurs after rather than simultaneously with or before that of the carbonyl groups. However, despite this observation, the complexes $RC_5H_4Mn(CO)_2CS$ (**1**) and $RC_5H_4Mn(CO)_3$ (**2**) appear to undergo similar fragmentations, Scheme I. Starting with the molecular ions both systems first undergo a two-step, unimolecular carbonyl dissociation, sequence I, II. The resulting ions $RC_5H_4MnCX^+$ ($R = H, CH_3$; $X = S, O$) fragment further by losing either CX (III) and RC_5H_4 (IV) to give $RC_5H_4Mn^+$ and Mn^+ or RC_5H_4 (III') and CX (IV') to give $MnCS^+$ and Mn^+ , respectively. The large relative intensity ratios $RC_5H_4Mn^+ : MnCX^+$ in each of the four

Table I. Relative Intensities (RI) (at 80 eV) and Appearance Potentials (AP) of the Major Metal-Containing Ions in the Mass Spectra of $RC_5H_4Mn(CO)_2CS$ and $RC_5H_4Mn(CO)_3$ [R = H, CH_3]

Ion	R = H		R = CH_3		
	RI	AP, eV	RI	AP, eV	
		$RC_5H_4Mn(CO)_2CS$			
$RC_5H_4Mn(CO)_2CS^+$	42.1	7.78 ± 0.01	31.4	7.72 ± 0.02	
$RC_5H_4Mn(CO)CS^+$	2.6	8.18 ± 0.01	1.5	7.95 ± 0.02	
$RC_5H_4MnCS^+$	68.8	9.25 ± 0.01	63.6	9.15 ± 0.01	
$RC_5H_4Mn^+$	100.0	12.25 ± 0.03	100.0	12.20 ± 0.01	
$MnCS^+$	5.7	16.91 ± 0.02	7.0	17.97 ± 0.01	
Mn^+	12.3	16.51 ± 0.04	43.2	16.22 ± 0.02	
		$RC_5H_4Mn(CO)_3^a$			
$RC_5H_4Mn(CO)_3^+$	36.4 (25.7)	8.06 ± 0.01 (8.3 ± 0.4)	24.8	7.86 ± 0.01	
$RC_5H_4Mn(CO)_2^+$	3.6 (0.2)	8.37 ± 0.01	1.9	8.13 ± 0.01	
$RC_5H_4Mn(CO)^+$	30.0 (22.7)	9.28 ± 0.01 (9.8 ± 0.3)	25.3	9.01 ± 0.03	
$RC_5H_4Mn^+$	100.0 (100.0)	11.67 ± 0.04 (12.0 ± 0.3)	100.0	11.21 ± 0.03	
$MnCO^+$	0.7 (0.2)		0.8		
Mn^+	52.7 (63.1)	15.32 ± 0.02 (15.9 ± 0.3)	57.9	16.33 ± 0.02	

^a The data indicated in parentheses have previously been reported by Winters and Kiser;¹² relative intensities were measured at 70 eV. Other values of the ionization potential of $C_5H_5Mn(CO)_3$ include 8.12 eV [mass spectrometry: J. Müller and F. Fenderl, *J. Organomet. Chem.*, 19, 123 (1969)] and 8.0–8.5 eV [photoelectron spectroscopy: T. H. Whiteside, D. L. Lichtenberger, and R. A. Rudnik, *Inorg. Chem.*, 14, 68 (1975)].

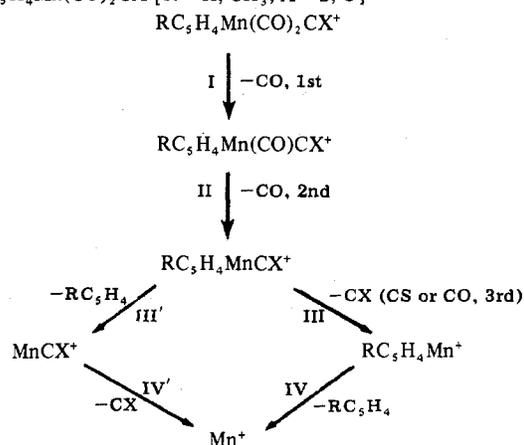
Table II. Metastable Ions (M^*) in the Mass Spectra of $RC_5H_4Mn(CO)_2CS$ and $RC_5H_4Mn(CO)_3$ [R = H, CH_3]

$M^* = M_2^2/M_1^a$	M_1	M_2	$M_1 - M_2$	
	$RC_5H_4Mn(CO)_2CS$			
167.6 (s); R = H	$RC_5H_4Mn(CO)_2CS^+$	$RC_5H_4Mn(CO)CS^+$	CO	
181.3 (s); R = CH_3				
87.8 (vs); R = H	$RC_5H_4MnCS^+$	$RC_5H_4Mn^+$	CS	
100.9 (vs); R = CH_3				
25.2 (vw); R = H	$RC_5H_4Mn^+$	Mn^+	RC_5H_4	
22.6 (vw); R = CH_3				
	$RC_5H_4Mn(CO)_3$			
151.8 (vw); R = H	$RC_5H_4Mn(CO)_3^+$	$RC_5H_4Mn(CO)_2^+$	CO	
165.6 (s); R = CH_3				
110.8 (w)	$CH_3C_5H_4Mn(CO)^+$	$CH_3C_5H_4Mn^+$	CO	
25.2 (vw); R = H	$RC_5H_4Mn^+$	Mn^+	RC_5H_4	
22.6 (vw); R = CH_3				

^a Relative intensities are given in parentheses: s, strong; vs, very strong; vw, very weak; w, weak.

spectra (**1a**, **1b**, **2a**, and **2b**) and the higher appearance potential of $MnCS^+$ than that of Mn^+ in the case of the thio-carbonyl complexes (**1a** and **1b**) suggest that the major route of fragmentation of these complexes involves steps III and IV rather than steps III' and IV'. The appearance potentials of the ions, given in Table I, clearly demonstrate that the major fragmentation pattern, described in Scheme I, is essentially correct since subsequent ions, in each spectrum, are formed with higher appearance potentials as expected. Some of the fragmentation steps in Scheme I are also supported by the presence of appropriate metastable ions, Table II.

The approximate heat of reaction (ΔH) of the major fragmentation steps in Scheme I can be calculated from the difference between the appearance potential of the product ion and that of the presumed reactant ion. In the spectra of the manganese complexes **1** and **2**, ΔH of the individual fragmentation steps I, II, and III provide a direct estimate of the metal-to-CX ionic bond dissociation energy [$D(Mn^+-CX)$; X = O, S]. The values of $D(Mn^+-CO)$ in **2a** (**2b**), obtained from the appearance potential data provided in Table I, are; 0.31 (0.27), 0.91 (0.88), and 2.39 eV (2.20 eV) for the first, second, and third carbonyl group, respectively. The trend of higher bond dissociation energy for subsequent carbonyl groups, observed for **2**, appears to be common for most other complexes of the type $QM(CO)_n$ [e.g., $QMn(CO)_3$ (Q = indenyl,¹¹ fluorenyl,¹¹ pyrrolyl¹¹), $C_5H_5Co(CO)_2$,¹² $C_5H_5V(CO)_4$,¹² $C_4H_4Fe(CO)_3$,¹¹ etc.] as well as for the thio-carbonyl complexes **1a** and **1b**. Therefore, in the related

Scheme I. Main Fragmentation Steps in the Mass Spectra of $RC_5H_4Mn(CO)_2CX$ [R = H, CH_3 ; X = S, O]

thiocarbonyl (**1**) and carbonyl (**2**) complexes, the energetics of parallel fragmentation steps should provide a meaningful comparison of bond dissociation energies. Relevant comparison between **1** and **2**, according to Scheme I, may include the mean heat of reaction per carbonyl of the two-step (I and II), unimolecular carbonyl dissociation sequence [$D(Mn^+-CO)$] and the heat of reaction of the third step (III) which provides estimates of $D(Mn^+-CS)$ and $D(Mn^+-CO, 3rd)$, respectively. The results of this comparative study, summarized in Table

Table III. Mn-CO and Mn-CS Bond Dissociation Energies of Ions in the Mass Spectra of $RC_5H_4Mn(CO)_2CX$ (R = H, CH₃; X = S, O)

Assumed process	Type	Ionic bond dissociation	
		Energy, eV	
		R = H	R = CH ₃
$RC_5H_4Mn(CO)_2CS^+ \rightarrow RC_5H_4MnCS^+ + 2CO$ $RC_5H_4MnCS^+ \rightarrow RC_5H_4Mn^+ + CS$	$RC_5H_4Mn(CO)_2CS$		
	$\bar{D}(Mn^+-CO)$	0.73 ± 0.01	0.71 ± 0.02
	$D(Mn^+-CS)$	3.0 ± 0.03	3.05 ± 0.01
$RC_5H_4Mn(CO)_3^+ \rightarrow RC_5H_4MnCO^+ + 2CO$ $RC_5H_4MnCO^+ \rightarrow RC_5H_4Mn^+ + CO$	$RC_5H_4Mn(CO)_3^a$		
	$\bar{D}(Mn^+-CO)$	0.61 ± 0.01	0.57 ± 0.03
	$D(Mn^+-CO, 3rd)$	2.39 ± 0.04	2.20 ± 0.04

^a The ionic bond dissociation energies of $C_5H_4Mn(CO)_3$ were determined from appearance potential data given in this work.

III, have revealed that $D(Mn^+-CS)$ of complexes **1a** and **1b** are ~25% and ~39% larger than $D(Mn^+-CO, 3rd)$ of complexes **2a** and **2b**, respectively. Moreover, the $\bar{D}(Mn^+-CO)$ of the thiocarbonyl complexes **1a** and **1b** are ~20% and ~24% larger than those of **2a** and **2b**, respectively. The small standard deviation of the appearance potentials, obtained during the course of this investigation, combined with the consistent bond dissociation energy trends established from two related systems, suggest that the above results are real and not coincidental.

The results of the current study concerning the strength of the Mn-CS bond appear to be consistent with the interpretation of the crystallographic data of the iridium² and rhodium³ complexes as well as with the theoretical prediction by Richards,⁴ which have been mentioned earlier. However, of special interest is the observation that the metal-to-carbonyl bond is strengthened in the presence of a coordinated thiocarbonyl. According to the synergic-bonding mechanism, this might suggest that coordinated thiocarbonyl has lower π acidity than that of carbonyl. This π -acidity order, taken in the context of the considerably stronger metal to thiocarbonyl than to carbonyl bonds, would imply that coordinated thiocarbonyl is primarily a σ -donor ligand. In the model system $RC_5H_4Mn(CO)_2CX$ [X = S, O], the ionization potentials of the analogs should depend on the relative σ basicity: π acidity ratio of the CX ligand; an increase in the ratio is concomitant with a decrease in the ionization potential.¹³ The higher ionization potential of **2** compared with that of **1**, in the two series R = H and CH₃, is therefore consistent with the proposed primarily σ -donor character of coordinated thiocarbonyl. The new bonding model, proposed for coordinated thiocarbonyl, is also supported by the infrared spectra of **1** and **2**, since the former complexes show lower $\nu(CO)_{max}$. Despite views to the contrary,¹ the π -acidity order CO > CS may be generally true since in related cationic and neutral metal complexes of the types $C_5H_5Fe(CO)_2CX^+$ (X = S,¹⁴ O¹⁵), $C_5H_5Mn(CO)(NO)CX^+$ (X = S,¹⁶ O¹⁷), $C_5H_5Mn(CO)_2CX$ (X = S,⁹ O¹⁸), and $C_5H_5Mn(CO)(CX)L$ (X = S,¹⁹ O²⁰; L = phosphines and related σ -donor ligands) the infrared $\nu(CO)_{max}$ of the thiocarbonyl (X = S) complex is invariably lower than that of its carbonyl (X = O) analog. Infrared criterion of the π acidity of ligands, although tentative by itself,²¹ may be reliable when supported by other independent experimental data such as from electron-impact studies in the case of complexes **1** and **2**.

Specially important in the evaluation of the metal-to-thiocarbonyl bond character are the C-S stretching frequencies observed in the infrared spectra of thiocarbonyl complexes.¹ Except for some 20 neutral manganese complexes of the types $C_5H_5Mn(CO)_2CS^9$, $C_5H_5Mn(CO)(CS)L$,¹⁹ and $C_5H_5Mn(CS)L_2$ (L = phosphines, phosphites, Ph₃As, Ph₃Sb, and other related σ -donor ligands),¹⁹ all other metal thiocarbonyl complexes,¹ including the cationic manganese complexes $C_5H_5Mn(CO)(NO)CS^+$ and $C_5H_5Mn(NO)(CS)L^+$ (L = Ph₃P, Ph₃As, and Ph₃Sb),¹⁶ display infrared $\nu(CS)$ higher than

that of "free" CS (1274 cm⁻¹ when trapped in a CS₂ matrix).²² Moreover, the $\nu(CS)$ values of many of the above-mentioned neutral manganese complexes¹⁹ differ relatively little from that of "free" CS. This behavior of $\nu(CS)$ is taken to indicate that in most cases the C-S bond order either increases, or decreases by only a little, on complexation compared with that of "free" CS. By comparison, with "free" and coordinated CS, the C-O bond order of coordinated carbonyl is invariably lower than that of free CO. In general, extensive M-CX $d\pi \rightarrow p\pi^*$ back-bonding interaction is expected to lower the C-X (X = O, S) bond order. Therefore, the observed $\nu(CX)$ differences in behavior between the coordinated and "free" thiocarbonyl (X = S) and carbonyl (X = O) ligands are, rather strongly, in favor of limited back-bonding interaction in case of complexed thiocarbonyl and this conclusion supports the relative π -acidity order CO > CS set forth before.

Recently, Show et al.²³ have postulated that the CS bond in metal thiocarbonyls is more ionic (C^{+ δ} -S^{- δ}) than that of CO in metal carbonyls. This postulated bonding model was said to explain the low Raman and high infrared $\nu(CS)$ intensities⁸ and to be consistent with the high electrophilic character of the carbon atom in coordinated thiocarbonyl which has been determined chemically.²⁴ However, contrary to the claim that this model is compatible with the strong π -acceptor ability of coordinated thiocarbonyl,²³ the opposite might apparently be true. Clearly, the model pertains to coordinated ligand and therefore describes the results rather than the causes of bonding interactions. In short, the higher electrophilicity of the carbon atom in coordinated thiocarbonyl compared with that in coordinated carbonyl is probably the result of weaker $d\pi \rightarrow p\pi^*$ back-bonding and/or stronger σ -donor interactions. This interpretation of the "more ionic than carbonyl" model for coordinated thiocarbonyl appears to be consistent with the primarily σ -donor character assignment, set forth above.

Further studies on the chemical, spectroscopic, and physical properties of various metal thiocarbonyl complexes are currently in progress and will be reported in due course.

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Reduction of an Organic Disulfide by a One-Equivalent Reagent. Kinetics and Mechanism of the Reaction of Chromium(II) with *p*-Aminophenyl Disulfide in Aqueous Perchloric Acid

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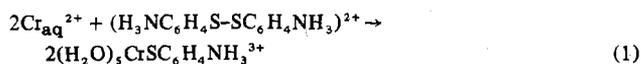
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The rate of the title reaction has been measured under concentration conditions ranging from pseudo-first-order excess chromium(II) to pseudo-first-order excess disulfide (diS), the maximum concentrations of chromium(II) and disulfide being 0.409 and 0.307 *F*, respectively. Under all conditions the observed rate law is $d[\text{[(H}_2\text{O)}_5\text{CrSC}_6\text{H}_4\text{NH}_3]^{3+}]/dt = a \cdot [\text{Cr(II)}][\text{diS}]/(1 + b[\text{diS}])$ where at 25.0°, $[\text{H}^+] = 1.00 \text{ F}$, $\mu = 2.00 \text{ F}$ ($\text{Zn}(\text{ClO}_4)_2$), $a = 0.103 \pm 0.004 \text{ F}^{-1} \text{ sec}^{-1}$, $b = 14.5 \pm 0.9 \text{ F}^{-1}$, $\Delta H_{a/2}^* = 9.4 \pm 0.4 \text{ kcal/mol}$, and $\Delta S_{a/2}^* = -33 \pm 1 \text{ eu}$. The observed rate is predominantly independent of $[\text{H}^+]$ but does decrease with increasing μ as well as decrease with increasing $[\text{ClO}_4^-]_{\text{total}}$. These marked and unusual medium effects are taken to indicate the existence of a perchlorate-disulfide ion pair. With excess chromium(II) the title reaction proceeds stoichiometrically to yield 2.0 mol of $[(\text{H}_2\text{O})_5\text{CrSC}_6\text{H}_4\text{NH}_3]^{3+}$ product for every mole of disulfide present. Under conditions of excess disulfide, where the $b[\text{diS}]$ term in the denominator of the rate law becomes important, the title reaction yields less than 90% of the primary product ion. These stoichiometric and kinetic effects are accounted for by a mechanism which features the radical ion dimer RSSR^- coordinated to chromium(III); this species may react further with chromium(II) to yield the primary product ion but may also undergo oxidation by free disulfide (RSSR) to yield other products.

Introduction

The reduction of organic disulfides by 1-equiv reagents plays a key role in the metal ion promoted thiol-disulfide interconversions which are the basis of many biological energy-transfer cycles.² Reaction of complexes of the 1-equiv reductants chromium(II),^{3,4} cobalt(II),⁵⁻⁷ and iron(II)⁸ with organic disulfides has also recently been shown to be a viable synthetic route to the corresponding metal(III) complexes containing coordinated thiols. These resultant thiolato complexes are useful models for biologically important metal-thiol species,⁷⁻¹⁰ and they also demonstrate some very unusual chemical^{5,9-12} and physical¹³ properties that are not yet understood. Therefore, because of the chemical and biological importance of both metal(II)-disulfide reactions and the resulting metal(III)-thiol products, we thought it worthwhile to investigate in detail the kinetics of one specific metal(II)-disulfide electron-transfer process with the goals of delineating the mechanism and limitations of this type of reaction. To this end we have chosen to examine the title reaction (eq 1) since the thiolatochromium(III) product of this



reaction has been characterized³ and the kinetics of aquation of this product in aqueous perchloric acid media have previously been investigated.³ To our knowledge this is the first detailed kinetic study of a 1-equiv metal ion reduction of an organic disulfide to be reported.

Experimental Section

Materials. Common laboratory chemicals, doubly distilled water, doubly distilled perchloric acid, and purified Dowex 50W-X2 ion-exchange resin were obtained as previously described.^{3,4,6} Hexaquo-chromium(III) perchlorate was prepared and purified by reported procedures;¹⁴ solutions of chromium(II) perchlorate were prepared by reduction over zinc amalgam as previously described.¹⁴ Zinc perchlorate was prepared by neutralization of zinc oxide and then purified by two recrystallizations from water. Lithium perchlorate was prepared by two procedures; the first was as previously reported,¹⁴ whereas the second consisted of neutralization of a weighed amount of Baker "Ultrex" lithium carbonate with standardized perchloric acid, heating to effect complete reaction, filtration, and finally dilution to a known volume.¹⁵ Kinetic experiments using either source of lithium perchlorate gave identical results, to within experimental error, for (a) chromium(III) aquation reactions, (b) electron-transfer reactions involving the strong reductant chromium(II), and (c) electron-transfer reactions involving the strong oxidant neptunium(VII),¹⁵ and in this work the two sources were used interchangeably.

p-Aminophenyl disulfide, purified as previously described,³ was further purified by neutralization with sulfuric acid, two crystallizations from water as the sulfate salt, reconversion to the free base by addition of ammonium hydroxide, and, after removal of ammonium sulfate by filtration, crystallization of the free base from aqueous ethanol. This product was washed with copious amounts of water to remove traces of sulfate and then recrystallized from aqueous ethanol. The final crystals were rinsed with water, dried, and stored at room temperature under vacuum over P_2O_5 ; a qualitative test with barium(II) indicated no detectable sulfate in this product. One batch of disulfide was purified as above, except all hot solutions were deoxygenated with an argon stream and continuously kept under an