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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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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 $d[[(H_2O)_5CrSC_6H_4NH_3]^{3+}]/dt = a\cdot[Cr(II)][diS]/(1 + b[diS])$ where at 25.0°, $[H^+] = 1.00\ F$, $\mu = 2.00\ F\ (Zn(ClO_4)_2)$, $a = 0.103 \pm 0.004\ F^{-1}\ sec^{-1}$, $b = 14.5 \pm 0.9\ F^{-1}$, $\Delta H^*_{a/2} = 9.4 \pm 0.4$ kcal/mol, and $\Delta S^*_{a/2} = -33 \pm 1$ eu. The observed rate is predominantly independent of $[H^+]$ but does decrease with increasing μ as well as decrease with increasing $[ClO_4^-]_{total}$. 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 $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ product for every mole of disulfide present. Under conditions of excess disulfide, where the b[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 physical[13] 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

$$2Cr_{aq}^{2+} + (H_3NC_6H_4S\text{-}SC_6H_4NH_3)^{2+} \rightarrow 2(H_2O)_5CrSC_6H_4NH_3^{3+} \qquad (1)$$

reaction has been characterized[3] 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] Hexaaquochromium(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 argon atmosphere; kinetic experiments employing the two sources of disulfide gave identical results within experimental error.

Analyses. The total solution concentrations of chromium and perchlorate were determined as previously described.[3,14] The concentration of zinc in zinc perchlorate stock solutions was determined by titration with commercially standardized Na_2EDTA solutions using Eriochrome Black T indicator.

Equipment. The instrumentation used to obtain visible–ultraviolet spectra and kinetic data was the same as previously described.[3,4] Computer calculations were also performed as previously described,[3,4] the LASL least-squares program[16] again being used for all nonlinear analyses.

Kinetic Measurements. Unless specified otherwise, kinetic experiments were performed in aqueous perchloric acid solutions that were maintained at constant ionic strength 1.00 ± 0.01 or 2.00 ± 0.02 *F* with either $LiClO_4$ or $Zn(ClO_4)_2$. Reactions were carried out under a nitrogen atmosphere using syringe techniques that have been previously described.[14] In a typical experiment, a sample of *p*-aminophenyl disulfide was weighed as the free base, dissolved in perchloric acid solution, and diluted if necessary; after addition of zinc or lithium perchlorate and additional acid, the resultant solution was diluted to a known volume and deoxygenated with a nitrogen stream. The reaction was then initiated by injection of an aliquot of a chromium(II) stock solution. Since perchloric acid solutions of *p*-aminophenyl disulfide slowly turn pink over the course of several days, they were freshly prepared each working day. Reaction rates were monitored spectrophotometrically at either of the absorption maxima (595 and 295 nm; ϵ 52 and 8250 F^{-1} cm^{-1}, respectively[3]) of the pentaaquo(4-thioanilinium-*S*)chromium(III) product; observed reaction parameters were independent, within experimental error, of the wavelength used to monitor the reaction. All reactions were monitored for at least 4 half-lives.

Calculations. As described later, subsequent aquation of the initial reaction product, $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$, prevents the experimental determination of A_∞, the absorbance at infinite time. Therefore standard nonlinear least-squares data analysis[16] was used to calculate the rate parameters k'_{obsd} and k''_{obsd} (obtained under pseudo-first-order and second-order concentration conditions, respectively) as well as σ_k the standard deviation of each calculated rate parameter. The details of these calculations, as well as evidence indicating that the standard first-order and second-order rate equations adequately describe the observed A_t–t data, are presented in the Appendix.[17] In subsequent calculations, each rate parameter is weighted as $1/\sigma_k^2$. Unless otherwise noted, all reported errors are standard deviations.

Results

Stoichiometry. As previously reported,[3] we have isolated, characterized, and determined the kinetics of acid-catalyzed aquation of $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$, the primary product of the title reaction.

When chromium(II) is present in pseudo-first-order excess and the initial concentration of *p*-aminophenyl disulfide is less than 0.01 *F*, spectrophotometric analysis of the initial product solution shows that $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ is stoichiometrically produced according to eq 1 (i.e., 2.0 mol of product result from every mole of $[(H_3NC_6H_4S-)_2]^{2+}$ originally present). This analysis is based on extinction coefficients (see Experimental Section) previously determined[3] for the isolated product complex. The absorbance due to $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ subsequently decreases due to acid-catalyzed[3] and chromium(II)-catalyzed[18] aquation of this species.

When *p*-aminophenyl disulfide is present in pseudo-first-order excess, spectrophotometric analysis of the initial product solution at 595 nm[19] shows that while $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ is still the predominant product, the yield of this species is less than ca. 90% of that predicted from the stoichiometry of eq 1. This yield, calculated as above, is only an upper limit since other possible chromium products are also expected to absorb at 595 nm. The absorbance of the product solution again subsequently decreases, presumably due to acid-catalyzed[3] aquation of $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ (chromium(II)-catalyzed aquation is ineffective under conditions of excess disulfide). Ion-exchange separations of product mixtures obtained under conditions of excess disulfide show that the combined fraction of 3+ formal charge contains 85–90% of the total chromium present (this fraction includes any $[(H_2O)_6Cr]^{3+}$ formed from aquation of $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ or from a competing reaction). In some separations a band of higher charged chromium species eluted after the 3+ fraction, but the quantity of material present in this band was insufficient to allow its characterization.

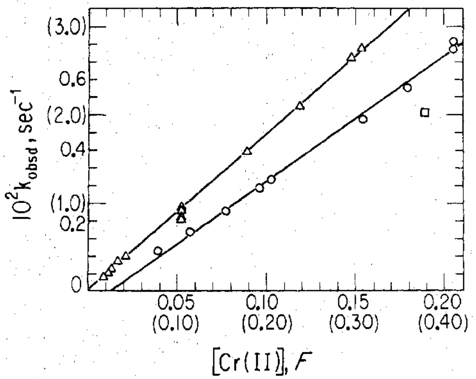

Figure 1. Plot of k'_{obsd} vs. $[Cr(II)]_0$ for the title reaction under conditions of pseudo-first-order excess of chromium(II), 25.0°, μ = 2.00 *F* ($Zn(ClO_4)_2$). Data were taken from Table I.[17] Triangles represent experiments performed at $[HClO_4]$ = 1.00 *F*, and the corresponding axes labels are unparenthesized. Circles represent experiments performed at $[HClO_4]$ = 0.100 *F* and $[(H_3NC_6H_4S-)_2{}^{2+}]_0 < 0.002$ *F*, and the corresponding axes labels are in parentheses. The single square represents an experiment performed at $[HClO_4]$ = 0.100 *F* and $[(H_3NC_6H_4S-)_2{}^{2+}]_0 = 0.174$ *F*. The indicated lines are those determined by an unweighted least-squares treatment of each data set (square not included).

Kinetics in the Presence of Excess Chromium(II). When the title reaction is conducted with chromium(II) in pseudo-first-order excess, $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ appears in a first-order fashion. Table I[17] gives the first-order rate parameters, k'_{obsd}, observed for these conditions as a function of temperature and [Cr(II)] at $[H^+]$ = 1.00 *F* and as a function of [Cr(II)] at $[H^+]$ = 0.100 *F* (all data at μ = 2.00 *F* maintained with $Zn(ClO_4)_2$). Figure 1 shows a plot of k'_{obsd} vs. [Cr(II)] for the 25.0°, $[H^+]$ = 1.00 *F* data; a weighted linear least-squares analysis of these data yields a slope of (4.36 ± 0.06) × 10^{-2} F^{-1} sec^{-1} and an intercept of (3.6 ± 1.6) × 10^{-5} sec^{-1} (these least-squares parameters reproduce the k'_{obsd} values to an average deviation of 4.2% with a maximum deviation of 11.4%) clearly indicating that under these conditions the reaction is simply first-order in chromium(II). Therefore, under conditions of excess chromium(II) and constant $[H^+]$ the observed rate law for the title reaction may be expressed as

$$d[[(H_2O)_5CrSC_6H_4NH_3]^{3+}]/dt = (a/2)[Cr(II)][(H_3NC_6H_4S-)_2{}^{2+}] \qquad (2)$$

where $(a/2)^{20} = k'_{obsd}/[Cr(II)]$. All 26 k'_{obsd} values ($[H^+]$ = 1.00 *F*) of Table I[17] were analyzed simultaneously by the nonlinear least-squares procedure[16] for all chromium(II) concentrations and temperatures according to the standard Eyring expression

$$k'_{obsd} = \frac{kT}{h}[Cr(II)]e^{\Delta S^*_{a/2}/R}e^{-\Delta H^*_{a/2}/RT} \qquad (3)$$

The resulting activation parameters are $\Delta H^*_{a/2}$ = 9.4 ± 0.4 kcal/mol and $\Delta S^*_{a/2}$ = −33 ± 1 eu. Individual rate parameters calculated from these optimized activation parameters according to eq 3 are listed in Table I[17] as k_{calcd}; the average deviation between k'_{obsd} and k_{calcd} is 3.8% and the maximum

Table II. Observed Rate Constants for Chromium(II) Reduction of *p*-Aminophenyl Disulfide as a Function of $[H^+]$ and μ under Conditions of Pseudo-First-Order Excess Chromium(II)[a]

$[H^+]$, F	μ, F	$10^2k'_{obsd}$, sec^{-1}	$10^2k'_{obsd}/[Cr(II)]_0$, F^{-1} sec^{-1}
0.050	2.00[b]	0.271 ± 0.002	5.26
0.100	2.00[b]	0.248 ± 0.001	4.82
0.300	2.00[b]	0.230 ± 0.001	4.46
1.00	2.00[b]	0.200 ± 0.001	3.89
1.00	2.00[b]	0.203 ± 0.001	3.94
1.00	2.00[b]	0.207 ± 0.001	4.02
0.100	0.32[b]	0.207 ± 0.001	4.02
0.100	1.00[b]	0.271 ± 0.001	5.25
0.100	1.49[b]	0.265 ± 0.001	5.14
0.100	2.00[b]		4.82[c]
0.100	2.49[b]	0.227 ± 0.001	4.41
0.100	2.66[b]	0.207 ± 0.001	4.02
1.00	1.23[d]	0.214 ± 0.001	4.14
1.00	2.00[d]		4.43 ± 0.06[e]
1.00	3.79[d]	0.187 ± 0.002	3.62

[a] $[Cr(II)]_0 = 0.0516$ F; $[(H_3NC_6H_4S-)_2{}^{2+}]_0 = 5.3 \times 10^{-5}$ F; kinetics monitored at 295 nm, 25.0°. [b] $LiClO_4$ medium. [c] Entry identical with second entry of this table. [d] $Zn(ClO_4)_2$ medium. [e] Average of first 18 entries of Table I.

deviation is 11.2%. Figure 1 also shows a plot of k'_{obsd} vs. [Cr(II)] at the lower acid concentration of $[H^+] = 0.100$ F. It is again seen that k'_{obsd} depends linearly upon [Cr(II)] (omitting the point determined at 0.017 F disulfide as will be discussed later), but the extrapolated intercept is negative; a weighted linear least-squares treatment of these data yields a slope of $(6.52 \pm 0.13) \times 10^{-2}$ F^{-1} sec^{-1} and an intercept of $(-6.8 \pm 1.4) \times 10^{-4}$ sec^{-1} (these least-squares parameters reproduce the k'_{obsd} values to an average deviation of 2.3% with a maximum deviation of 8.1%). The negative intercept value is presumed to be due to a medium effect[21] arising from the replacement of $Cr_{aq}{}^{2+}$ by $Zn_{aq}{}^{2+}$ in order to maintain constant ionic strength and constant total perchlorate concentration. This medium effect is not manifested in the studies at $[H^+] = 1.00$ F presumably because in these experiments there is less variation in the concentrations of the 2+ metal ions (i.e., a significant, constant portion of the ionic strength is provided by $HClO_4$ over the entire range of chromium(II) concentrations).

The fact that the two lines of Figure 1 have different slopes indicates that the title reaction may have a small inverse acid dependence. Therefore a series of experiments was conducted wherein $[H^+]$ ranged from 0.050 to 1.00 F and ionic strength was maintained at 2.00 F with $LiClO_4$ to minimize medium effects.[21] The results of these experiments are given in Table II and it is seen that k'_{obsd} does decrease slightly with increasing $[H^+]$. Since it is difficult to distinguish between minor rate terms and activity effects,[21] these k'_{obsd}–$[H^+]$ data were treated within each hypothesis. A weighted linear least-squares analysis of a plot of $k'_{obsd}/[Cr(II)]$ vs. $1/[H^+]$ yields a slope of $(7.9 \pm 1.5) \times 10^{-4}$ sec^{-1} and an intercept of $(3.95 \pm 0.10) \times 10^{-2}$ F^{-1} sec^{-1} (these least-squares parameters reproduce the $k'_{obsd}/[Cr(II)]$ data to an average deviation of 3.2% with a maximum deviation of 5.6%). A weighted linear least-squares analysis according to the Harned formulation[21]

$$\ln k = \ln k_0 + \alpha[H^+] \tag{4}$$

yields a slope of $\alpha = -0.23 \pm 0.03$ F^{-1} and an intercept of -3.010 ± 0.022 which corresponds to a $k_0 = (a/2)_0$ value of 0.049 F^{-1} sec^{-1} (these least-squares parameters reproduce the $\ln(k'_{obsd}/[Cr(II)])$ data to an average deviation of 0.8% with a maximum deviation of 2.5%). It should be noted that neither formulation alone yields a satisfactorily linear plot and the total observed acid dependence may in fact result from a combination of the two effects; however, the data are too limited and too imprecise to allow analysis in terms of a combined acid path and medium effect.

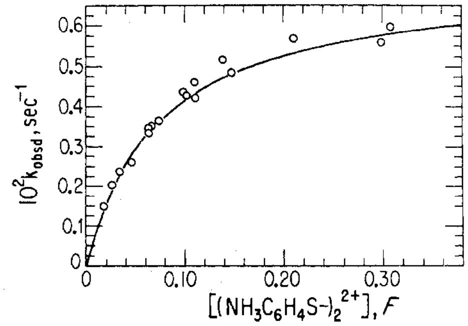

Figure 2. Plot of k'_{obsd} vs. $[(H_3NC_6H_4S-)_2{}^{2+}]_0$ for the title reaction under conditions of pseudo-first-order excess of *p*-aminophenyl disulfide, 25.0°, $\mu = 2.00$ F $(Zn(ClO_4)_2)$. Data were taken from Table III.[17] The indicated line is that calculated from the expression $k'_{obsd} = a[diS]_0/(1 + b[diS]_0)$ where $[diS]_0 = [(H_3NC_6H_4S-)_2{}^{2+}]_0$ and a and b have their least-squares optimized values $a = 0.1034$ F^{-1} sec^{-1} and $b = 14.5$ F^{-1}.

Table II also delineates the dependence of k'_{obsd} on ionic strength in both $LiClO_4$ and $Zn(ClO_4)_2$ media. In both media this dependence is very unusual; the observed rate increases with increasing ionic strength until it reaches a maximum at $\mu \simeq 1.5$ F and then decreases as ionic strength is further increased. In this connection it should be noted that the value of $a/2 = 0.0394 \pm 0.004$ F^{-1} sec^{-1} ($[H^+] = 1.00$ F, 25.0°, $\mu = 2.00$ F), determined in lithium perchlorate medium where $[ClO_4^-]_{total} = 1.92$ F, is *smaller* than the value of $a/2 = 0.0436 \pm 0.006$ F^{-1} sec^{-1} (same conditions) determined in zinc perchlorate medium where $[ClO_4^-]_{total}$ is only 1.67 F.

Two experiments were conducted under second-order concentration conditions and the resulting data were analyzed as described in the Experimental Section. The rate constants, k''_{obsd}, so obtained for initial concentrations of *p*-aminophenyl disulfide of 0.0295 and 0.0315 F (other conditions: $[Cr(II)]_0 = 0.110$ F, $[H^+] = 1.00$ F, $\mu = 2.00$ F $(Zn(ClO_4)_2)$, 25.0°) are 0.0371 ± 0.003 and 0.0358 ± 0.0002 F^{-1} sec^{-1} respectively. These directly observed second-order rate parameters are significantly smaller than the slope of the upper line of Figure 1 (0.0436 ± 0.003 F^{-1} sec^{-1}) which was obtained using much smaller initial disulfide concentrations (all other conditions identical). In this connection it should be noted that the one significantly deviant point of Figure 1 (indicated by a square) arises from an experiment in which the initial concentration of disulfide is much higher (0.0174 F) than in the other experiments (less than 0.004 F; see Table I[17]). These observations indicate that, even in the presence of excess chromium(II), the calculated second-order rate constants resulting from experiments employing initial disulfide concentrations greater than ca. 0.01 F are significantly smaller than expected on the basis of experiments employing lower disulfide concentrations (0.00005–0.004 F; see Table I[17]).

Kinetics in the Presence of Excess *p*-Aminophenyl Disulfide. When the title reaction is conducted with *p*-aminophenyl in pseudo-first-order excess, $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ appears in a first-order fashion[19] for at least the first 80% of the reaction. Table III[17] lists values of the observed first-order rate parameters, k'_{obsd}, which were obtained as described in the Experimental Section, and Figure 2 shows a plot of k'_{obsd} vs. $[diS]_0$[22] which is seen to be a curve of continuously decreasing slope. A plot of $1/k'_{obsd}$ vs. $1/[diS]_0$ is a straight line and therefore the nonlinear least-squares technique was used to analyze the k'_{obsd}–$[diS]_0$ data according to the function

$$k'_{obsd} = \frac{a[diS]_0}{1 + b[diS]_0} \tag{5}$$

Table IV. Observed Second-Order Rate Constants for Chromium(II) Reduction of *p*-Aminophenyl Disulfide under Second-Order Conditions[a]

10^2 $[\mathrm{Cr(II)}]_0$, F	$10^2[\mathrm{diS}]_0$, F	$10^2k''_{\mathrm{obsd}}$, F^{-1} sec^{-1}	10^2k_{cor},[b] F^{-1} sec^{-1}
0.882	0.915	9.46 ± 0.09	10.7
0.882	1.68	8.70 ± 0.08	10.8
0.882	1.68	8.40 ± 0.03	10.4
0.882	1.68	8.51 ± 0.03	10.6
0.882	1.68	8.79 ± 0.08	10.9
0.882	1.68	8.60 ± 0.06	10.7
0.882	2.09	8.02 ± 0.07	10.5
0.882	2.61	7.63 ± 0.07	10.5

[a] $[\mathrm{HClO_4}] = 1.00\ F$, $\mu = 2.00\ F$ ($\mathrm{Zn(ClO_4)_2}$), 25.0°, $[\mathrm{diS}] = [(\mathrm{H_3NC_6H_4S-})_2{}^{2+}]$. [b] $k_{\mathrm{cor}} = k''_{\mathrm{obsd}}(1.0 + 14.5[\mathrm{diS}]_0)$.

Table V. Observed Rate Constants for Chromium(II) Reduction of *p*-Aminophenyl Disulfide as a Function of $[\mathrm{H^+}]$ and μ under Conditions of Pseudo-First-Order Excess Disulfide[a]

10^2 $[\mathrm{Cr(II)}]_0$, F	10^2 $[\mathrm{diS}]_0$, F	$[\mathrm{H^+}]$, F	μ, F	$10^2k'_{\mathrm{obsd}}$, sec^{-1}	10^2 $k'_{\mathrm{obsd}}/[\mathrm{diS}]_0$, F^{-1} sec^{-1}
0.733	9.76	0.100	2.00[b]	0.312 ± 0.001	3.19
0.733	9.78	0.500	2.00[b]	0.316 ± 0.001	3.23
0.733	9.64	1.00	2.00[b]	0.329 ± 0.002	3.41
0.733	9.69	1.00	2.00[b]	0.327 ± 0.002	3.37
0.92	2.99	0.10	0.314[c]	0.231 ± 0.002	7.73
0.92	6.04	0.10	0.316[c]	0.396 ± 0.005	6.56
0.92	5.91	0.10	1.22[c]	0.370 ± 0.007	6.26

[a] Kinetics monitored at 595 nm, 25.0°, $[\mathrm{diS}] = [(\mathrm{H_3NC_6H_4S-})_2{}^{2+}]$. [b] $\mathrm{LiClO_4}$ medium. [c] $\mathrm{Zn(ClO_4)_2}$ medium.

The resulting optimized parameters are $a = 0.1034 \pm 0.0036$ F^{-1} sec^{-1} and $b = 14.5 \pm 0.9$ F^{-1} (25.0°, $\mu = 2.00\ F$ ($\mathrm{Zn(ClO_4)_2}$), $[\mathrm{H^+}] = 1.00\ F$). Individual rate constants calculated from these parameters according to eq 5 are listed in Table III[17] as k_{calcd}; the average deviation between k'_{obsd} and k_{calcd} is 3.0% and the maximum deviation is 7.4%. The smooth curve of Figure 2 is calculated from the optimized values of a and b according to eq 5.

Table IV lists the values of k''_{obsd} directly obtained from experiments conducted under second-order concentration conditions. These data show that, just as in the experiments with excess chromium(II), as the initial disulfide concentration is increased over ca. 0.01 F, the calculated value of k''_{obsd} decreases significantly.

Several checks were conducted in order to determine if an impurity in the *p*-aminophenyl disulfide starting material could be responsible for the above effects: (1) the rate constants of Table III[17] were reproducible within experimental error independent of the preparation of disulfide used (see Experimental Section) and independent of the age of the disulfide stock solutions (over several hours); (2) the rate constants of Table III[17] were reproducible within experimental error when all procedures were carried out under conditions of reduced light; (3) the data of Table III[17] show no significant trend as a function of initial chromium(II) concentration—such a trend might be expected if an impurity were reacting with chromium(II) in a competing reaction. Hence, there is no experimental evidence for a disulfide impurity.

Data listed in Table V show that in the presence of pseudo-first-order excess disulfide, the rate of the title reaction is not detectably dependent upon $[\mathrm{H^+}]$. As in the experiments with excess chromium(II), the data of Table V also show that the rate decreases with increasing ionic strength, and at constant ionic strength the rate decreases with increasing $[\mathrm{ClO_4^-}]_{\mathrm{total}}$ (compare to data of Table III,[17] $\mu = 2.00\ F$, $[\mathrm{H^+}] = 1.00\ F$, 25.0°; $k'_{\mathrm{obsd}}/[\mathrm{diS}]_0$[22] $= 0.034$ F^{-1} sec^{-1} in $\mathrm{LiClO_4}$ medium when $[\mathrm{ClO_4^-}]_{\mathrm{total}} = 1.89\ F$ but is 0.045 F^{-1} sec^{-1} in $\mathrm{Zn(ClO_4)_2}$ medium where $[\mathrm{ClO_4^-}]_{\mathrm{total}}$ is only 1.66 F).

Discussion

The demonstrated kinetic effects of varying [diS][22] may be taken as true rate phenomena since all experiments designed to detect a disulfide impurity were negative. This conclusion is bolstered by the fact that, even in pseudo-first-order excess Cr(II), observed rates are slower at high $[\mathrm{diS}]_0$ than would be predicted from data collected at lower initial disulfide concentrations—this observation would be difficult to reconcile with the hypothesis that the effect of [diS] in excess disulfide is due to an impurity.

For all concentration conditions investigated the observed effect of varying [Cr(II)] and [diS] may be expressed by the rate law

$$\text{rate} = \frac{d[(\mathrm{H_2O})_5\mathrm{CrSC_6H_4NH_3}^{3+}]}{dt} = \frac{a[\mathrm{Cr(II)}][\mathrm{diS}]}{1 + b[\mathrm{diS}]} \qquad (6)$$

where b is determined (under conditions of pseudo-first-order excess disulfide) to be 14.5 ± 0.9 F^{-1} and therefore the term b[diS] is negligible with respect to 1.0 at disulfide concentrations less than about 0.005 F. The applicability of this rate law to all concentration conditions investigated is supported by the fact that the following determinations of a (F^{-1} sec^{-1}) within the formalism of eq 8 are in good agreement (common conditions are 25.0°, $[\mathrm{H^+}] = 1.00\ F$, $\mu = 2.00\ F$ maintained with $\mathrm{Zn(ClO_4)_2}$): (1) with disulfide in pseudo-first-order excess, the data of Table III[17] (see also Figure 2) give $a = 0.1034 \pm 0.0036$; (2) with disulfide in excess, but otherwise second-order concentration conditions, the mean value of a calculated from the observed second-order rate parameters of Table IV by correcting for the effect of the b[diS] term ($a = k_{\mathrm{cor}} = k''_{\mathrm{obsd}}(1 + b[\mathrm{diS}])$ where b is taken as 14.5 F^{-1}) is 0.106 ± 0.001; (3) with chromium(II) in excess, but otherwise second-order concentration conditions ($[\mathrm{diS}]_0 = 0.03\ F$), values of $a/2$[20] calculated as in (2) from the two reported values of k''_{obsd} (see Results) are 0.053 and 0.052; (4) with chromium(II) in pseudo-first-order excess and $[\mathrm{diS}]_0$ always less than 0.004 F, the data of Table I[17] give $a/2$[20] $= 0.0436 \pm 0.006$ (slope of upper line of Figure 1).

The 16% difference in values of a as determined in (4) and (1) above may reasonably be ascribed to a medium effect. As indicated several times in the Results, the rate of the title reaction is very sensitive to the nature of the medium; in the above comparison the medium varies from mostly inorganic 2+ species ($\mathrm{Zn_{aq}}^{2+}$ and $\mathrm{Cr_{aq}}^{2+}$) with only traces of organic 2+ disulfide for (4) to one where the organic disulfide comprises up to 92% of the 2+ species for (1). A significant portion of this medium sensitivity appears to arise from a specific interaction between the disulfide cation and the perchlorate anion used to maintain the ionic medium. Contrary to what is normally expected[23] for a reaction between two 2+ species, the rate of the title reaction decreases with increasing ionic strength (after an initial increase when chromium(II) is present in excess—see Tables II and V) and at constant μ decreases with increasing total perchlorate ion concentration. These effects can be explained by postulating the existence of a disulfide–perchlorate ion pair which reacts with chromium(II) at a slower rate than does the free disulfide. This hypothesis is consistent with the limited water solubility of $(\mathrm{NH_3C_6H_4S-})_2(\mathrm{ClO_4})_2$, but the kinetic data are not extensive enough to warrant analysis within this formulation. The large medium effects observed in this system also preclude an unequivocal analysis of the $[\mathrm{H^+}]$ dependency data of Table II. While there is some indication of the existence of a minor inverse acid path when chromium(II) is present in excess (possibly reaction via a deprotonated $(\mathrm{H_3NC_6H_4S-})_2{}^{2+}$ ion), it is clear that the bulk of the title reaction proceeds by an acid-independent path (see Tables II and V).

A mechanism which is consistent with all the details[24] of the stoichiometric and kinetic observations may be constructed about a steady-state intermediate which can either decompose directly to give the primary $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ product or react with free disulfide to give products other than $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$. Within this scheme the observed rate law demands that the steady-state intermediate be composed of the elements of one chromium(II) and one *p*-aminophenyl disulfide, and in the following discussion we have formulated it as a chromium(III) complex containing a coordinated radical ion dimer, $RSSR^-$. While not necessary to the scheme, this formulation is chosen because of the results of recent pulse radiolysis work which show that free $RSSR^-$ species, produced either by reduction of RSSR with e_{aq}^-

$$RSSR + e_{aq}^- \rightarrow RSSR^- \tag{7}$$

or by oxidation of RSH with OH·

$$RSH + OH\cdot \rightarrow RS\cdot \tag{8a}$$

$$RS\cdot + RSH = RSSR^- + H^+ \tag{8b}$$

are relatively stable[25] and because of recent results on the oxidation of a thiolatocobalt(III) complex which demonstrate that a coordinated $RSSR^-$ species can function as a long-lived reaction intermediate.[11] In reactions 9-1 to 9-3a ASH^+

$$Cr_{aq}^{2+} + ASSA^{2+} \xrightarrow{k_1} (H_2O)_5Cr(ASSA)^{4+} \tag{9-1}$$

$$(H_2O)_5Cr(ASSA)^{4+} \xrightarrow{k_2} (H_2O)_5CrSA^{3+} + AS\cdot^+ \tag{9-2}$$

$$Cr_{aq}^{2+} + AS\cdot^+ \xrightarrow{fast} (H_2O)_5CrSA^{3+} \tag{9-2a}$$

$$(H_2O)_5Cr(ASSA)^{4+} + ASSA^{2+} \xrightarrow{k_3} (H_2O)_5Cr(ASSA)^{5+} + ASSA^+ \tag{9-3}$$

$$2ASSA^+ + 2H^+ \xrightarrow{fast} ASSA^{2+} + 2ASH^+ \tag{9-3a}$$

represents $[H_3NC_6H_4SH]^+$ and therefore the radical ion dimer, $RSSR^-$, corresponds to $ASSA^+$. Assuming that the steady-state assumption holds for the intermediate $[(H_2O)_5Cr(ASSA)]^{4+}$, this mechanism leads to the rate law of eq 10 where diS[22] represents $ASSA^{2+}$. This is of the same

$$\text{rate} = \frac{d[(H_2O)_5CrSA^{3+}]}{dt} = \frac{2k_1[Cr(II)][diS]}{1 + (k_3/k_2)[diS]} \tag{10}$$

functional form as the observed rate law given by eq 6 with $a = 2k_1$ and $b = k_3/k_2$. Step 9-3 is the crucial reaction in this sequence since it is responsible for the b[diS] denominator term observed only at high concentrations of disulfide. While the actual chemistry of this step is of course unknown, the above formulation as a simple electron transfer converting a coordinated $RSSR^-$ to a coordinated RSSR (concomitantly converting a free RSSR to a free $RSSR^-$) is not unreasonable. The product of eq 9-3 is therefore formulated as a chromium(III)–disulfide complex which is expected to undergo aquation fairly rapidly

$$H_2O + (H_2O)_5Cr(ASSA)^{5+} \xrightarrow{k_4} (H_2O)_6Cr^{3+} + ASSA^{2+} \tag{9-4}$$

Step 9-4, combined with the effects of steps 9-3 and 9-3a, accounts for the nonstoichiometric yields of $[(H_2O)_5CrSA]^{3+}$ observed in the presence of excess disulfide, and the $[(H_2O)_5Cr(ASSA)]^{5+}$ ion may be the transient highly charged chromium(III) product sometimes observed in the ion-exchange separations of reaction mixtures containing excess disulfide. In this context it should be noted that a simple cobalt(III) complex containing a coordinated organic disulfide has been shown to be a stable species.[11] In the presence of excess chromium(II) step 9-3 will be ineffective, and other steps such as

$$Cr_{aq}^{2+} + (H_2O)_5Cr(ASSA)^{4+} \xrightarrow{fast} 2(H_2O)_5CrSA^{3+} \tag{11}$$

are likely to become important, leading to the observed simple bimolecular rate law and stoichiometric yields of $[(H_2O)_5CrSA]^{3+}$.

In summary, the results of this specific study (1) imply that in order to optimize yields when synthesizing thiolatometal(III) complexes via the metal(II) reduction of organic disulfides, the reaction should *not* be conducted in the presence of excess disulfide, (2) indicate that both free and coordinated radical ion dimers, $RSSR^-$, likely play an important role in the 1-equiv reductions of organic disulfides, and (3) reaffirm the necessity of employing the greatest possible extremes of reactant concentrations in determining experimental rate laws. The applicability of conclusions (1) and (2) to other systems is currently under investigation.

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Supplementary Material Available. Following these pages in the microfilm edition of this volume of the journal will appear (1) Tables I and III, giving observed first-order rate parameters for the title reaction under conditions of pseudo-first-order excess chromium(II) and pseudo-first-order excess disulfide as a function of [Cr(II)], [diS],[22] and temperature, and (2) the Appendix, giving the details of the data analyses used in this study. Photocopies of the supplementary material from this paper only or microfiche (105 × 148), 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50316+-11-75.

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(18) Chromium(II)-catalyzed aquation has been observed for most $[(H_2O)_5CrX]^{n+}$ species and presumably involves electron transfer through a water (or hydroxide) bridge (ref 14 and citations therein). Specific rate constants observed for the chromium(II)-catalyzed aquation of $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ are (after correction for acid-catalyzed aquation) 4×10^{-4} and 2×10^{-4} F^{-1} sec^{-1} at $[HClO_4] = 0.100$ and 1.00 F, respectively (25.0°, $\mu = 2.00$ F $(Zn(ClO_4)_2)$.

(19) In these experiments the appearance of $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ can only be monitored at 595 nm since the free disulfide absorbs strongly at 295 nm.

(20) The stoichiometry of reaction 1 demands that the second-order rate parameter observed in excess chromium(II) be half the second-order rate parameter observed in excess disulfide.

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(22) $[\text{diS}] = [(\text{H}_3\text{NC}_6\text{H}_4\text{S}-)_2{}^{2+}]$.

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(24) The data of Figure 2 suggest two mechanisms which, although plausible, are not consistent with the details of the observed data. (1) A mechanism involving a rapid prior equilibrium between chromium(II) and *p*-aminophenyl disulfide demands that in the presence of high concentrations of chromium(II) the observed rate law be rate = $(a/2)[\text{Cr(II)}][\text{diS}]/(1 + b[\text{Cr(II)}])$ where b has the same value as is effective in eq 8 (i.e., 14.5 F^{-1}); this is not the case. (2) A mechanism involving a rapid prior association of two disulfide molecules to form an unreactive dimer leads to a rate law which does not satisfy the data of Table III over the entire range of disulfide concentrations investigated.

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Trends in the Acidities of the Zinc Family Elements

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Quantitative data are presented which provide a thermodynamic basis for trends in the acidities of the zinc family elements and for the reluctance of many two-coordinate mercury compounds to expand their coordination number. A model is presented which accounts for the high preference of mercuric ion or RHg^+ for covalent ligands in acquiring coordination number 2. The ability of the two-coordinate mercury complex to expand its coordination number is also predictable with this model in terms of the properties of the two ligands attached. The bis(hexamethyldisilylamino) compounds of zinc, cadmium, and mercury all undergo extensive reorganization upon adduct formation. They provide a basis for further examination of the concept of reorganization energy in acid–base chemistry. We illustrate how these effects could be incorporated into the E and C parameters. Some recent proposals on this topic which are at variance with the E and C formulation are also discussed.

Introduction

The observed fact that mercury tends to form two-coordinate compounds while zinc and cadmium usually have higher coordination numbers has been of considerable interest for some time.[1,2] Theoretical rationalizations[1,2] have been offered to account for these very complicated (in a thermodynamic sense) observations of reactivity. Accordingly, it was of interest to obtain solvation-minimized enthalpies of adduct formation to ascertain if the proposed explanations were correct. The reduced tendency of mercury to have high coordination numbers should be observed in the bond strengths of coordinated ligands. Since the bis(hexamethyldisilylamino) compounds[3] of zinc, cadmium, and mercury all contain a linear N–M–N system, they are ideally suited to obtaining quantitative data relating to the ability of this family of metals to expand their coordination shell and form coordination number 3. These data can provide a quantitative test of the rationalizations which have been applied to the chemistry of this family of elements.

It is important to the understanding of inorganic chemistry to have quantitative data relating to the strength of bonding of a family of elements of the periodic table. Although much of the descriptive chemistry of the compounds of the elements is presented from the view of chemical periodicity, there is very little quantitative information to support the proposed explanations which are often based upon guesses of bond strengths. Too many important concepts in inorganic chemistry have as their basis qualitative observations about chemical reactivity—an exceedingly complex phenomenon.

The compounds studied here all are soluble in benzene or cyclohexane and are monomeric. They form adducts with a variety of bases. Studies of the zinc and analogous cobalt compounds with pyridine and substituted pyridines have led to the isolation of stable 1:1 adducts[4] which are soluble in nonpolar solvents.

In the course of investigating the trends in the thermodynamics of adduct formation of compounds of the elements of the zinc family, it was also of interest to attempt to incorporate these acids into the E and C approach[5] to chemical reactivity. A very large fraction of the acid–base systems presently contained in the E and C correlation involve hydrogen-bonding interactions, and it is desirable to extend the types of acids which are included in order to establish more adequately the generality of the correlation.

These acids are also of significance to the general area of acid–base chemistry, for they constitute additional examples of systems in which the acid (or base) geometry is extensively distorted in the course of forming an adduct. These linearly coordinated free acids form trigonal-planar adducts. Early workers[6,7] in the field, viewed such geometry changes as an independent, endothermic energy contribution required to get the acid or base ready to form an adduct. According to this view, a very strong donor atom–acceptor atom bond could form, but a small $-\Delta H$ of adduct formation might result because of the large amount of energy required to rearrange the acid or base. In the boron trifluoride–ethyl acetate adduct, for example, a very strong boron–oxygen atom bond might form, but the net $-\Delta H$ of adduct formation would be small because of the energy spent to break the B–F π bonds.

There are important practical consequences associated with the role of reorganization energy. For example, if complexation is assumed to be complete and BF_3 made a larger perturbation on the base coordinated to it than BCl_3, BF_3 would be a better Lewis acid catalyst for an acid-catalyzed reaction of the base than BCl_3 in contrast to the predicted enthalpy of adduct formation. There is considerable evidence to suggest that the above view is not generally correct in acid–base chemistry although it is conceivable that such an efffect could be found in isolated systems. For example, it is found that, in general, not only is BF_3 a poorer acid than BCl_3 but it is also a poorer Lewis acid catalyst.[8] There is even more convincing evidence. We had shown previously[9] that the