204 ($M^+ - C_4F_6O_4$) 1%, 127 ($NPOC_5H_6^+$) 5.4%, 113 ($CF_3CO_2^+$) 35.4%, 99 ($NPC_4H_6^+$) 12.8%, 69 (CF_3^+) 37.7%, and 57 ($C_4H_9^+$) 100%.

Anal. Calcd for $C_{12}H_{18}F_6P_2N_2O_4$: P, 14.41; C, 33.49; H, 4.19. Found: P, 13.51; C, 33.08; H, 4.34.

(7) [$(Me_3Si)_2NPN$-*t*-Bu]$_2$ (X). The lithium salt of $(Me_3Si)_2NH$ was preformed in a manner similar to that described for the polyfluorinated alcohols. The large clear crystals were recrystallized by using diethyl ether (30% yield) in which it is only slightly soluble. Deuteriated acetone was used as the solvent for NMR. The $^{31}P\{H\}$ NMR spectrum had a peak at δ 211.8. The CI mass spectrum at 6.0 V gave an intense molecular ion (M + 1) of *m/e* 525 (50%). Other major fragments observed at *m/e* 467 ($M^+ - C_4H_9$) 8.8%, 451 ($M^+ - SiC_3H_9$) 5%, 364 ($M^+ - NSi_2C_6H_{18}$) 83%, 204 ($PN_2Si_2C_6H_{17}^+$) 12.2%, 191 ($PNSi_2C_6H_{18}^+$) 24.5%, and 73 ($SiC_3H_9^+$) 52%.

Anal. Calcd for $C_{20}H_{54}Si_4P_2N_4$: P, 11.83; C, 45.80; H, 10.31. Found: P, 11.20; C, 44.95; H, 10.10.

(8) [*t*-BuNPOCH$_2$(CF$_2$)$_n$CH$_2$OPN-*t*-Bu] (XI) (*n* = 2, 3). The lithium salt of each diol was preformed in a manner similar to the other polyfluorinated alcohols. After addition of *n*-BuLi at −78 °C, the solution was allowed to warm to 25 °C to ensure completion in the reaction. II was introduced slowly at −78 °C and the mixture was warmed slowly to 25 °C.

(a) For *n* = 2. After the precipitate was removed by filtration, the solvent was evaporated from the filtrate and a slightly brown sticky substance was obtained. The $^{31}P\{H\}$ NMR spectrum consisted of a peak at δ 221.5, and the ^{19}F NMR spectrum had a resonance at ϕ −121.4 mult. In the ^1H NMR spectrum a multiplet was centered at δ 4.41. The CI mass spectrum at 3.1 V gave a molecular ion (M + 1) at *m/e* 365 (14.9%). Other fragments observed were at *m/e* 349 ($M^+ - CH_3$) 4.7%, 307 ($M^+ - C_4H_9$) 6%, 292 ($M^+ - C_5H_{12}$) 7.1%, 277 ($M^+ - PC_4H_8$) 69.5%, 220 ($M^+ - OC_9H_{20}$) 31.7%, 204 ($N_2P_2C_8H_{18}^+$) 22.3%, 160 ($C_4H_4F_4O_2^+$) 14.3%, and 57 ($C_4H_9^+$) 100%.

Anal. Calcd for $C_{12}H_{22}F_4P_2N_2O_2$: C, 39.56; H, 6.04; N, 7.69. Found: C, 38.86; H, 6.01; N, 6.98.

(b) For *n* = 3. As for the *n* = 2 compound, upon evaporation of the solvent from the filtrate, a sticky light brown liquid was obtained. The $^{31}P\{H\}$ NMR spectrum consisted of a peak at δ 222.3, and in the ^{19}F NMR spectrum peaks at ϕ −119.9 and −126.0 were observed. The FAB mass spectrum at 10 V had molecular ions (M + 1, M + 2) at *m/e* 415, 9.1%, and 416, 14.2%, respectively. Other fragments found were at *m/e* 357 ($M^+ - C_4H_9$) 3%, 300 ($M^+ - C_8H_{18}$) 1%, 241 ($C_5H_4F_6O_2P^+$) 2.5%, 210 ($C_5H_4F_6O_2^+$) 8.9%, 204 ($M^+ - C_5H_4F_6O_2$) 2.3%, 182 ($C_6H_{11}F_2NOP^+$) 13.2%, 106 ($P_2N_2O^+$) 2.8%, 75 (PN_2O^+) 100%, and 57 ($C_4H_9^+$) 95%.

Anal. Calcd for $C_{13}H_{22}F_6P_2O_2N_2$: C, 37.68; H, 5.31; N, 6.76. Found: C, 37.77; H, 5.34; N, 5.92.

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Kinetics and Products of the Complexation of $(H_2O)_5CrCH_2CN^{2+}$ by Carboxylic Acids

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The kinetics and products of the reaction of $(H_2O)_5CrCH_2CN^{2+}$ with glycine, *N,N,N*-trimethylglycine, chloroacetate, trifluoroacetate, oxalate, and monomethyl oxalate have been studied. The systems show an initial reaction on the stopped-flow time scale that gives the mono-ligand product. For oxalate and methyl oxalate, subsequent reactions produce *cis*-$(C_2O_4)_2Cr(OH_2)_2^-$ as the dominant product in a more complex reaction sequence. Hydrolysis of the methyl ester is greatly accelerated by complexation.

Introduction

The anation reactions of pentaaquachromium(III) alkyl complexes are unusually rapid compared to substitution on most chromium(III) complexes.[1-6] The lability is attributed to the trans-labilizing influence of the alkyl group.

In this study the reaction of $(H_2O)_5CrCH_2CN^{2+}$ with several carboxylate ligands has been examined. The results provide information on the products, equilibrium constants, and kinetics for the general reaction

$$(H_2O)_5CrCH_2CN^{2+} + O_2CR^{n-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (H_2O)_4(RCO_2)CrCH_2CN^{2-n} + H_2O \quad (1)$$

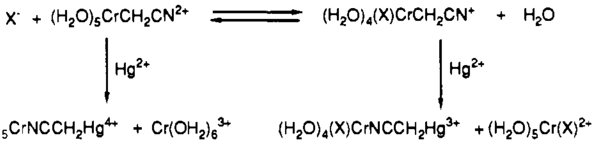
Variations of k_1 and K_1 ($=k_1/k_{-1}$) with the nature and basicity of the carboxylate reactant have been determined.

The observations with oxalate and monomethyl oxalate show several reactions subsequent to (1). The products and kinetics of these processes have been studied and explained by isomerization and substitution reactions analogous to those proposed recently for hypophosphite.[6]

Results and Discussion

The details of the individual systems will be discussed in subsequent sections. However some of the common features will be noted here to avoid repetition. When a potential carboxylate ligand RCO_2^- and $(H_2O)_5CrCH_2CN^{2+}$ are mixed in dilute aqueous acid, there is an initial rapid reaction that is complete in at most a few minutes at normal reagent concentrations. This reaction causes a general increase in absorbance in the regions of the maxima of $(H_2O)_5CrCH_2CN^{2+}$ (525 and 408 nm).

Scheme I



In the case of oxalate and methyl oxalate, there are further slower changes that occur on the tens of minutes to hours time scale. There are at least two kinetically separable slower processes. These produce larger absorbance changes than the first stage.

Finally, there are much slower changes requiring many hours or days which are associated with loss of the alkyl group. These processes have not been studied in detail here, but have been reported for the acetate system.[7]

Because the reaction products are so labile it is generally necessary to remove the $-CH_2CN$ group by reaction with Hg(II) before separation by chromatography. The results of the Hg(II) reaction are described in Scheme I. The product distribution from $(H_2O)_5CrCH_2CN^{2+}$ + Hg^{2+} has been shown to be 52%

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Table I. Electronic Spectra of Chromium(III) Complexes and Reaction Products

species	λ_1 (ϵ_1)[a]	λ_2 (ϵ_2)[a]
$(H_2O)_5CrCH_2CN^{2+}$	525 (40.1)	408 (102)
$CrCH_2CN^{2+} + {}^-O_2CCH_2N(CH_3)_3{}^{+}$[b]	574 (22.6)	410 (22.0)
$CrCH_2CN^{2+} + {}^-O_2CCH_2NH_3{}^{+}$[b]	573 (21.8)	409 (22.2)
$((H_2O)_5CrO_2CCH_2NH_3)^{3+}$[c,d]	574 (20.6)	410 (20.6)
$(H_2O)_4Cr(O_2CCH_2NH_2)^{2+}$[d]	555 (38.0)	420 (41.0)
$CrCH_2CN^{2+} + {}^-O_2CCF_3$[e]	575 (20.0)	408 (21.6)
$(H_2O)_5CrO_2CCF_3{}^{2+}$[f]	576 (19.7)	409 (20.9)
$CrCH_2CN^{2+} + {}^-O_2CCH_2Cl$[e]	572 (23.3)	410 (22.8)
$CrCH_2CN^{2+} + HC_2O_4{}^-$	533 (80.1)	409 (152)
$CrCH_2CN^{2+} + HC_2O_4{}^- + Hg^{2+}$	562 (45.2)	415 (60.1)
cis-$(C_2O_4)_2Cr(OH_2)_2{}^-$	563 (52.8)	415 (68.3)
$(C_2O_4)Cr(OH_2)_4{}^+$	555 (34.5)	417 (39.4)
$Cr(C_2O_4)_3{}^{3-}$[g]	468 (76.9)	418 (96.3)
$CrCH_2CN^{2+} + CH_3O_2C_2O_2{}^-$	533 (80.3)	410 (153)
$CrCH_2CN^{2+} + CH_3O_2C_2O_2{}^- + Hg^{2+}$	562 (45.8)	414 (62.9)

[a] λ in nm; ϵ in M^{-1} cm^{-1}. [b] Initial 3+ fraction after reaction with Hg(II). [c] Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 3469. [d] Lane, R. H.; et al. *Inorg. Chem.* **1977**, *16*, 102. [e] The 2+ product after reaction with Hg(II). [f] Prepared from $(NH_3)_5CoO_2CCF_3{}^{2+}$ + Cr^{2+} and separated by ion exchange. [g] Krishnamurty, K. V.; Harris, G. M. *Chem. Rev.* **1961**, *61*, 213.

$(H_2O)_5CrNCCH_2Hg^{4+}$ and 48% $Cr(OH_2)_6{}^{3+}$.[8] In some cases the product distribution after reaction with Hg(II) can be used to estimate the equilibrium constant (K_1) for eq 1. In some cases K_1 has been determined from absorbance changes at 525 nm. The rate law for the fastest step also can be used sometimes to calculate K_1.

Glycine and *N,N,N*-Trimethylglycine: These ligands are present as the zwitterion $^-O_2CCH_2NY_3{}^+$ or cation $HO_2CCH_2NY_3{}^+$ (Y ≡ H or CH_3) under the dilute acidic conditions of these studies. The complexes formed after reaction with Hg(II), $(H_2O)_4(Y_3NCH_2CO_2)CrNCCH_2Hg^{4+}$ and $(H_2O)_5CrO_2CCH_2NY_3{}^{3+}$, have the same charges as their parent chromium(III) complexes. As a result ion-exchange chromatography did not completely separate the products. However, the electronic spectra of the initial 3+ eluates are clearly not $Cr(OH_2)_6{}^{3+}$, but are similar to $(H_2O)_5CrO_2CCH_2NH_3{}^{3+}$ (see Table I) and quite different from the chelate $(H_2O)_4Cr(O_2CCH_2NH_2)^{2+}$. Therefore, the initial reaction for these two ligands is represented by

$$(H_2O)_5CrCH_2CN^{2+} + {}^-O_2CCH_2NY_3{}^+ \overset{K_1}{\rightleftharpoons} (H_2O)_4(Y_3NCH_2CO_2)CrCH_2CN^{2+} + H_2O \qquad (2)$$

The equilibrium constant for this reaction has been determined by spectrophotometry at 525 nm. For glycine, the zwitterion concentration was varied from 0.05 to 0.20 M, and the variation of absorbance was analyzed to give K_1 = 9.1 ± 1.0 M^{-1} and ϵ (525 nm) = 49.7 M^{-1} cm^{-1} for the product. The *N,N,N*-trimethylglycine zwitterion was varied between 0.10 and 0.40 M to give K_1 = 5.6 ± 0.6 M^{-1} and ϵ (525 nm) = 50.9 M^{-1} cm^{-1}.

The kinetics of the reaction were studied at 525 nm by standard methods under pseudo-first-order conditions with $[Y_3NCH_2CO_2{}^\pm]_{tot} \gg [(H_2O)_5CrCH_2CN^{2+}]$. The results are shown in Figure 1 and are consistent with the rate law expected from eq 2 and given by eq 3. For concentrations of $Y_3NCH_2CO_2{}^\pm$

$$k_{obsd} = k_1([Y_3NCH_2CO_2{}^\pm] + 1/K_1) \qquad (3)$$

$\gtrsim$ 0.2 M the k_{obsd} values show a small saturation effect, which could be due to ion pairing or ionic medium effects due to the nonequivalence of Li^+ and $Y_3NCH_2CO_2H^+$. Ion pairing seems unlikely because this saturation effect is not observed with $H_2PO_2{}^-$[6] or the carboxylate anions discussed later.

For *N,N,N*-trimethylglycine, a least-squares fit of the data below 0.25 M to eq 3 gives k_1 = (1.3 ± 0.06) × 10^{-2} M^{-1} s^{-1} and K_1 = 5.42 ± 0.43 M^{-1}. The latter value is in excellent agreement with that determined spectrophotometrically. For glycine, the least-squares analysis gives k_1 = (1.18 ± 0.05) × 10^{-2} M^{-1} s^{-1} and K_1 = 5.7 ± 0.4 M^{-1}. The latter value does not agree with that from the spectrophotometric measurements. However, if K_1 is fixed at 9.1 M^{-1}, the fit of the kinetic data gives k_1 = (1.52 ± 0.03) × 10^{-2} M^{-1} s^{-1} and all the calculated values are within 10% of the observed values. This fit is shown in Figure 1.

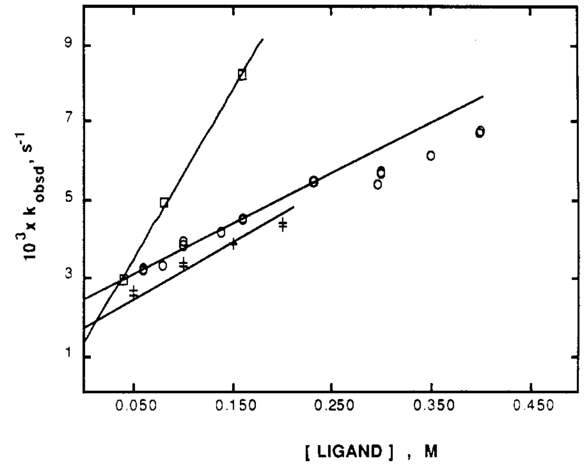

Figure 1. Variation of k_{obsd} with ligand concentration for the first reaction: (○) $^+N(CH_3)_3CH_2CO_2{}^-$; (+) $^+NH_3CH_2CO_2{}^-$; (□) $ClCH_2CO_2{}^-$ (ordinate scale ×2).

Trifluoroacetate and Chloroacetate. Since these ligands will complex as anions, the product should be more easily separated than was the case with the zwitterions described above.

A solution containing 1.0 M $CF_3CO_2{}^-$ and 9.0 × 10^{-3} M $(H_2O)_5CrCH_2CN^{2+}$ in 0.03 M $HClO_4$ was allowed to react for 5 min before $Hg(ClO_4)_2$ was added (3.6 × 10^{-2} M final concentration). The solution was subjected to cation-exchange chromatography (Dowex 50W-X2 (H^+)), which indicated product distribution and charges as follows: 17%, 2+; 50%, 3+; 33%, 4+. If the system is described by Scheme I, then the 2+ product should be $(H_2O)_5CrO_2CCF_3{}^{2+}$. This was confirmed by comparison of the electronic spectrum to that of an authentic sample prepared from $(NH_3)_5CoO_2CCF_3{}^{2+}$ and chromium(II). The spectral results are given in Table I.

The product distribution can be analyzed in terms of Scheme I. The 33% of $(H_2O)_5CrNCCH_2Hg^{4+}$ indicates that the 3+ fraction is 30.5% $Cr(OH_2)_6{}^{3+}$ and 19.5% $(H_2O)_4(CF_3CO_2)CrNCCH_2Hg^{3+}$. The results indicate that the solution before addition of Hg(II) contains 63.5% $(H_2O)_5CrCH_2CN^{2+}$ and 19.5% + 17% or 36.5% $(H_2O)_4(CF_3CO_2)CrCH_2CN^{2+}$. Then the equilibrium constant K_1 = (36.5)/(63.5)(1) = 0.57 M^{-1}. Previous work[6] with $H_2PO_2{}^-$ has shown that this type of analysis yields an equilibrium constant in satisfactory agreement with other methods of determination. However the results with $ClCH_2CO_2{}^-$ discussed below show that complications can arise, and the value for $CF_3CO_2{}^-$ may be best regarded as a lower limit on K_1.

Attempts to measure the rate of anation with $F_3CCO_2{}^-$ have not been successful because a useful absorbance change could not be detected. This is probably because the small value of K_1 causes limited amounts of product to form at reasonable anion concentrations and because the absorbancies of reactant and product are not greatly different. These factors also prevented an independent spectrophotometric determination of K_1.

Chloroacetate obviously differs from trifluoroacetate in the basicity of the anion since their conjugate acids have pK_a's of 2.64 and 0.3, respectively. When chloroacetate and $(H_2O)_5CrCH_2CN^{2+}$ are allowed to react for a few minutes, then treated with Hg(II), and ion exchanged, one obtains the usual 2+-, 3+-, and 4+-charged products. In addition, there is a small amount ($\lesssim$5%) of product with charge <2+. The electronic spectrum of the 2+ product (Table I) is similar to that with $CF_3CO_2{}^-$, and the product is assigned to $(H_2O)_5CrO_2CCH_2Cl^{2+}$. The 4+ species has the properties expected for $(H_2O)_5CrNCCH_2Hg^{4+}$.

A problem arose with the product distributions in that an analysis to calculate K_1, as described for $CF_3CO_2{}^-$, did not give

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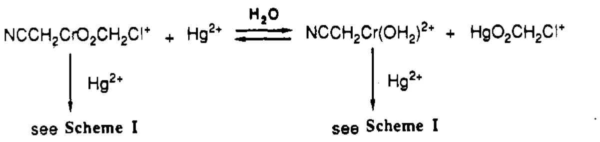
(8) Sisley, M. J.; Jordan, R. B. *Inorg. Chem.* **1986**, *25*, 3547.

Scheme II



a value in satisfactory agreement with spectrophotometric and kinetic results described below. Further experiment showed that the major product distribution was affected by the total Hg(II) concentration. For example, if a solution with 0.125 M $ClCH_2CO_2^-$, 0.120 M total H^+ and 1.2×10^{-3} M $CrCH_2CN^{2+}$ is made 0.05 M in $Hg(ClO_4)_2$ after 6 min, the products are 5.4% <2+, 46.1% 2+, 27.2% 3+, and 20.4% 4+. However, when the initial concentrations were 0.118 M, 0.127 M, and 1.31×10^{-2} M, respectively, and the $[Hg(ClO_4)_2]$ was 0.208 M, then the products are 3.8% <2+, 41.0% 2+, 27.0% 3+, and 26.4% 4+. There is an increase in the 4+ product, which is balanced by a loss in the 2+ product at the higher [Hg(II)]. The product distribution gives values for K_1 of 11.6 and 7.3 M^{-1} at the lower and higher [Hg(II)], respectively.

It has not been possible to prove the source of the variation in the product distribution: however, we suspect that it is related to the complexing affinity of Hg(II) and chloroacetate. Rossotti and Whewell[9] have obtained the complex formation constants in this system as $K_{1f} = 890$ M^{-1} and $K_{2f} = 457$ M^{-1} (25 °C, 3.0 M $NaClO_4$). For the experiment with $[Hg(II)]_{tot} = 0.05$ M, the Hg(II) is actually present as 87% $Hg(O_2CCH_2Cl)_2$ and 12% $Hg(O_2CCH_2Cl)^+$, so that there is a very small amount of the most effective electrophile Hg^{2+}. When $[Hg(II)]_{tot} = 0.208$, there is 0.102 M Hg^{2+}, but a larger amount of the 4+ product is formed, which would imply a larger amount of $(H_2O)_5CrCH_2CN^{2+}$ present at equilibrium. This cannot be true because the concentration of $ClCH_2CO_2^-$, which is in excess, is almost the same in the two experiments.

The implication of these observations is that Hg^{2+} is removing chloroacetate from $(H_2O)_4(ClCH_2CO_2)CrCH_2CN^+$. This might happen by Hg^{2+}-assisted aquation as shown in Scheme II. This would have to be fast enough to be competitive with alkyl transfer to Hg(II).

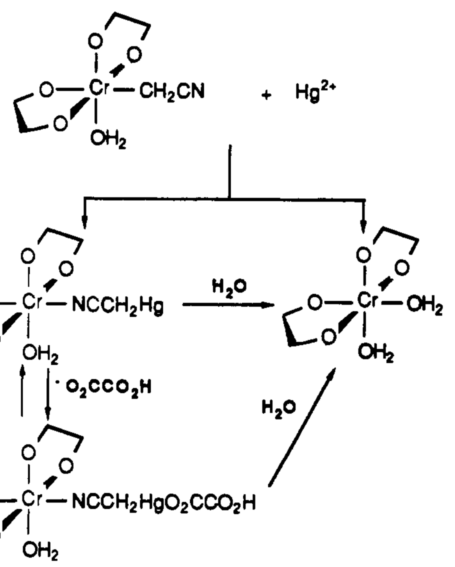
The equilibrium constant for the chloroacetate system has been determined spectrophotometrically at 525 nm between 0.069 and 0.207 M chloroacetate ion concentration. The results give $K_1 = 20.5 \pm 0.7$ M^{-1} (25 °C, 1 M $LiClO_4/HClO_4$) and ϵ (525 nm) = 50.9 M^{-1} cm^{-1}.

The kinetics of chloroacetate complexation have been studied between 0.08 and 0.32 M chloroacetate ion concentrations on diode-array and stopped-flow systems at 525 nm. The results are shown in Figure 1 and give $k_1 = (4.35 \pm 0.22) \times 10^{-2}$ M^{-1} s^{-1} and $k_{-1} = (2.58 \pm 0.46) \times 10^{-3}$ s^{-1}. The ratio k_1/k_{-1} gives $K_1 = 16.9$ M^{-1}, in reasonable agreement with the spectrophotometric value.

Thiocyanate. This system has been studied by Bakac et al.,[10] but recent work with $(NH_3)_5CoOH_2^{3+}$ [11] indicates that linkage isomers might form if anation of $(H_2O)_5CrCH_2CN^{2+}$ has a dissociative mechanism. Our observations at 290 nm confirm those of Bakac et al. Studies on a diode-array spectrophotometer between 350 and 500 nm failed to reveal any significant wavelength dependence of k_{obsd} or any non-first-order behavior of the absorbance–time data. These observations could mean that only one linkage isomer forms, that the two isomers have very similar electronic spectra, or that the isomers are formed in relative amounts very similar to those of the equilibrium mixture.

Hydrogen Oxalate. The final spectrum in the kinetic runs with oxalate and $CrCH_2CN^{2+}$ was always the same, and the details are given in Table I. The product was sufficiently stable that it could be chromatographed directly without treatment with Hg(II). Anion-exchange chromatography on Amberlite IRA-400 or Dowex 2-X8 (Cl^- form) gave a tightly held orange band, and some chromium (5–6%) passed directly through the resin. On continued elution, the orange band gradually became less intensely colored and 0.25 M $HClO_4$ eventually eluted all of the chromium after 15 h. The final fraction gave an oxalate to chromium ratio of 1.84:1 and contained no chloride ion. The orange species is tentatively identified as $(C_2O_4)_2(H_2O)_nCrCH_2CN^{2-}$. Slow dissociation of an oxalate ligand to produce $(C_2O_4)(H_2O)_mCrCH_2CN$ would account for the elution characteristics.

Scheme III



The reaction of the $CrCH_2CN^{2+}$ + oxalate product solution with Hg^{2+} yielded a violet-blue solution. The HgC_2O_4 precipitate was removed by filtration and the product spectrum recorded. This spectrum was found to decrease in absorbance with time, and the rate decreased with increasing total oxalate in the solution. When the $[oxalate]_{tot}$ was ~0, 0.01, and 0.027 M, the transformation was commplete in ~50, 240, and 480 min, respectively. This kinetic behavior is not consistent with a system coming to equilibrium through dissociation of oxalate. Past experience with these systems, and estimates of the formation constants[9,12] for mercury(II) oxalate complexes suggest that the observed spectrophotometric changes could be explained by Scheme III.

Complexation of the alkylmercury functions by oxalate would reduce the rate of aquation of the Cr–N bond because of the greater negative charge on the leaving group. This could explain the slower rate of transformation at higher total oxalate concentrations.

The final spectrum of the solution after treatment with Hg(II) is given in Table I. The spectrum corresponds to a mixture of ~70% *cis*-$(C_2O_4)_2Cr(OH_2)_2^-$ and ~30% $(C_2O_4)Cr(OH_2)_4^+$. Anion-exchange chromatography confirmed that the solution contains substantial amounts of at least two complexes. One fraction of the chromium does not bind to the anion resin and has an electronic spectrum similar to that of $(C_2O_4)Cr(OH_2)_4^+$ (555 (34.9), 414 nm (42.0)). The second fraction is weakly bound to the anion resin and has an electronic spectrum identical with that of $(C_2O_4)_2Cr(OH_2)_2^-$ (562 (51.6), 414 nm (68.6)).

The overall analysis of these product results reveals an anomaly in that the spectrum of the alkylchromium product is independent of the total oxalate concentration. This indicates that the overall reaction proceeds as follows:

$$(H_2O)_5CrCH_2CN^{2+} + 2O_2CCO_2H^- \rightarrow (C_2O_4)_2Cr(OH_2)CH_2CN^{2-} \quad (4)$$

However, after reaction with Hg(II), there are two products present in significant amounts. One of these is clearly the expected

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(9) Rossotti, F. J. C.; Whewell, R. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1223.

(10) Bakac, A.; Espenson, J. H.; Miller, L. P. *Inorg. Chem.* **1982**, *21*, 1557.

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Scheme IV

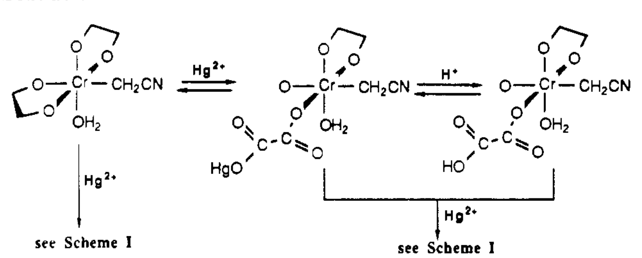


Table II. Kinetic Data for the Slower Stages of the Reaction of $(H_2O)_5CrCH_2CN^{2+}$ and $HC_2O_4^-$ (25 °C, 1 M $HClO_4/LiClO_4/LiHC_2O_4$)

$10^2[HC_2O_4^-]$, M	$10^4k_2'$, s^{-1} obsd[a]	$10^4k_2'$, s^{-1} calcd[b]	10^4k_3, s^{-1}
0.10	0.722 ± 0.12	0.684	
0.20	1.32 ± 0.03	1.37	
0.30	1.82 ± 0.03	2.04	
0.50	3.82 ± 0.11	3.39	
0.76			7.13 ± 0.10
1.00	6.80 ± 0.10	6.69	7.80 ± 0.05
2.00	13.0 ± 0.1	13.1	7.19 ± 0.05
3.00	18.9 ± 0.1	19.2	7.84 ± 0.11
4.00	26.0 ± 0.1	25.0	6.83 ± 0.17
6.00	36.8 ± 0.2	35.8	6.24 ± 0.07
8.00	48.1 ± 0.4	45.8	8.06 ± 0.12
12.0	61.8 ± 0.3	63.4	7.13 ± 0.10
18.0	85.5 ± 0.4	85.3	5.09 ± 0.14

[a] Data obtained at 257 nm for $[HC_2O_4^-]$ from 1×10^{-3} to 5×10^{-3} M and at 403 nm otherwise.

$(C_2O_4)_2Cr(OH_2)_2^-$, the other is neutral or cationic and has a spectrum similar to that of the monooxalato complex. It is possible that Hg(II) is having an effect similar to that suggested with chloroacetate; i.e., it tends to complex and remove coordinated oxalate. Blank experiments have shown that Hg(II) does not remove oxalate from $(C_2O_4)_2Cr(OH_2)_2^-$ under the conditions of our experiments. However, in the alkyl oxalate complex, the more weakly held end of the oxalate chelate trans to the $-CH_2CN$ may be more susceptible to attack by Hg(II) and may undergo ring opening as shown in Scheme IV. Dealkylation of the monodentate species could produce the bis chelate by ring closure as the Cr–C bond is broken as well as $(C_2O_4)(HC_2O_4)Cr(OH_2)_3$. The latter complex may be the nonanion, which has a spectrum quite similar to that of $(C_2O_4)Cr(OH_2)_4^+$.

The time course of the complexation in the oxalate system showed three stages. There is an initial stage on the stopped-flow time scale that produces a relatively small absorbance change. Two slower stages are complete in 1–2 h, with the second stage having an isosbestic point at 403 nm.

The fastest reaction was followed at 355 nm, but the small absorbance change and limited solubility of lithium oxalate confined the study to two values of $[HC_2O_4^-] = 0.10$ and 0.15 M. Even then, the large absorbance change of the second reaction required the data to be fitted as two first-order processes. Fortunately, the larger rate constant was quite insensitive to the value of the rate constant for the second reaction, and the results gave $k_1 = 1.6$ M^{-1} s^{-1} and $k_{-1} = 0.64$ s^{-1}. Therefore $K_1 = 2.5$ M^{-1}.

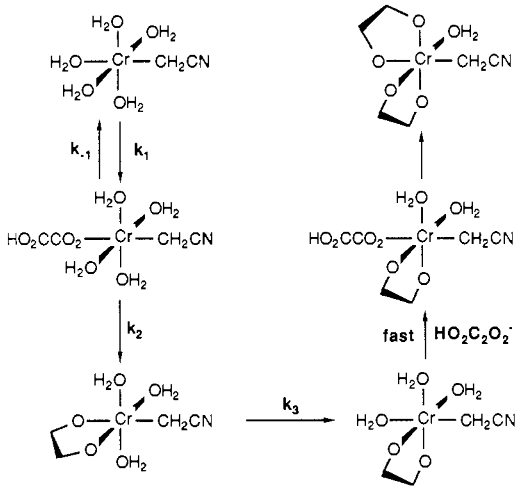
The second reaction was monitored at 257 and 403 nm, and the results are given in Table II. The dependence of the observed rate constant on $[HC_2O_4^-]$ is given by eq 5, with $a = (6.86 \pm 0.17)$

$$k_2' = \frac{a[HC_2O_4^-]}{1 + b[HC_2O_4^-]} \qquad (5)$$

$\times 10^{-2}$ M^{-1} s^{-1} and $b = (2.49 \pm 0.45)$ M^{-1}. The observed and calculated values are compared in Table II. The significance of the fact that numerically $b = K_1$ will be discussed below with regard to the overall reaction scheme.

The slowest reaction was studied at 525 nm, and the absorbance time data were analyzed by a double-exponential fit, keeping k_2' constant at the value indicated by eq 5 while determining k_3. The results are given in Table II and show that k_3 is independent of $[HC_2O_4^-]$ with an average value of 7.0×10^{-4} s^{-1}.

Scheme V



The kinetic and product observations can be understood in terms of Scheme V. The fastest reaction is associated with substitution of $HC_2O_4^-$ for the H_2O trans to $-CH_2CN$. This step is followed by ring closing. Kinetically the anation reaction is a rapid preequilibrium to the ring-closing step so that the rate constant is given by eq 6. This equation has the same form as that observed

$$k_2' = \frac{k_2K_1[HC_2O_4^-]}{1 + K_1[HC_2O_4^-]} \qquad (6)$$

experimentally (eq 5), so that $b = K_1$, $a = k_2K_1$, and $k_2 = 2.75 \times 10^{-2}$ s^{-1}. As noted above, the value of b agrees with the value of K_1 determined from the kinetics of the first reaction.

The slowest kinetic step is independent of $[HC_2O_4^-]$ and is assigned to an isomerization that moves one end of the oxalate chelate from a trans to a cis position relative to the $-CH_2CN$ ligand. Then a relatively rapid anation and ring closing give the final product. These steps are analogous to k_1 and k_2 and are assumed to occur at similar rates to that they will be much faster than k_3.

An isomerization step analogous to k_3 was assigned in the $H_2PO_2^-$–$(H_2O)_5Cr$–CH_2CN^{2+} system[6] with a rate constant of 2.5×10^{-4} s^{-1}. Isomerization of $(C_2O_4)_2Cr(OH_2)_2^-$ has a rate constant of 6.4×10^{-4} s^{-1}.[13] These values simply show that a $k_3 = 7 \times 10^{-4}$ value is not unreasonable for isomerization on chromium(III).

Methyl Oxalate. The products at the end of this reaction both with or without treatment with Hg(II) are the same as for the oxalate system. The electronic spectra are given in Table I.

These observations imply relatively rapid hydrolysis of the ester. The early studies[14] of the hydrolysis of methyl oxalate have been extended to correspond to our experimental conditions. The reaction was monitored at 248 nm in 2.5×10^{-2} M $HClO_4$ at 25 °C and gave a rate constant of $(3.77 \pm 0.03) \times 10^{-6}$ s^{-1} for hydrolysis of methyl oxalate. Therefore the half-time for hydrolysis of the free ester is about 50 h compared to 1–2 h in the presence of $(H_2O)_5CrCH_2CN^{2+}$.

On the stopped-flow system the reaction was monitored at 355 nm for five values of $[CH_3O_2CO_2^-]$ between 0.10 and 0.50 M. The qualitative observations were different than those with oxalate in that the next reaction stage did not interfere and the stopped-flow traces were single exponential curves. The results give $k_1 = 1.48 \pm 0.14$ M^{-1} s^{-1} and $k_{-1} = 0.67 \pm 0.05$ s^{-1} so that $K_1 = 2.2 \pm 0.4$ M^{-1}. These parameters are similar to those for oxalate.

In the subsequent stages, the absorbance changes are somewhat different from those for oxalate. With methyl oxalate, the ab-

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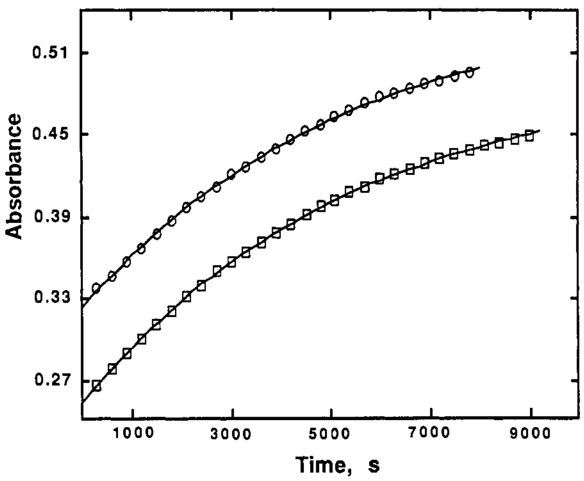

Figure 2. Variation of absorbance (525 nm) with time for the slower reaction of $CH_3O_2C_2O_2^-$ with $(H_2O)_5CrCH_2CN^{2+}$: (□) 0.05 M $CH_3O_2C_2O_2^-$; (○) 0.40 M $CH_3O_2C_2O_2^-$ (time ×5). Curves are calculated with k_2' values in Table III.

Table III. Kinetic Data for the Reaction of $(H_2O)_5CrCH_2CN^{2+}$ with $CH_3O_2CCO_2^-$ (1 M $HClO_4/LiClO_4/NaO_2C_2O_2CH_3$)

$[CH_3O_2C_2O_2^-]$, M	k_1', s^{-1}		$10^4k_2'$, s^{-1}	
	obsd[a]	calcd	obsd[b]	calcd
0.010			0.467 ± 0.01	0.415
0.050			1.84 ± 0.02	1.91
0.10	0.79 ± 0.06	0.82	3.39 ± 0.06	3.48
0.20	1.02 ± 0.06	0.97	5.23 ± 0.08	5.89
0.30	1.08 ± 0.07	1.11	7.36 ± 0.13	7.68
0.40	1.26 ± 0.05	1.26	9.39 ± 0.17	9.03
0.50	1.41 ± 0.10	1.41	11.7 ± 0.23	10.1

[a] Each rate constant is the average of at least 10 runs, and errors are the standard deviation. [b] Errors are one standard deviation from the least-squares fit of the absorbance–time data.

sorbance rises in the region of the visible maxima throughout a given run with no isosbestic points between 350 and 650 nm. With oxalate, the absorbance around 530 nm also rises, but around 405 nm there is an initial increase followed by a decrease with an isosbestic point near 403 nm for the last stage. This qualitative difference could be caused by a different reaction sequence or by a change in relative rates of the two processes. The increasing absorbance stage with oxalate has been attributed to chelate ring closing (Scheme V). If this step is slower with methyl oxalate, then it might not manifest itself so clearly.

The absorbance–time data for the slower stage with methyl oxalate do not show any significant deviation from simple exponential behavior. Results at two concentrations of $CH_3O_2C_2O_2^-$ are shown in Figure 2. The observed rate constants are consistent with the rate law given by eq 7 with $K_1 = 2.2$ M^{-1} and $k_2 = 1.93 \times 10^{-3}$ s^{-1}. The observed and calculated values are compared in Table III.

$$k_2' = \frac{k_2K_1[CH_3O_2C_2O_2^-]}{1 + K_1[CH_3O_2C_2O_2^-]} \qquad (7)$$

It seems almost certain that this simple behavior is not a true reflection of the reaction because ester hydrolysis, isomerization, and further anation to give $(C_2O_4)_2Cr(OH_2)_2^-$ must be occurring. Therefore k_2 must be a composite rate constant. The value of k_2 is ~15 times smaller than that with $HO_2C_2O_2^-$, which is consistent with the qualitative observations about the asorbance–time behavior noted above. This difference in k_2 values could be accounted for by the reactions in Scheme VI, in which case $k_2 = k_ck_h/(k_{-c} + k_h)$. The chelate ring opening rate constant k_{-c} may be significant in this case because the ester function would be expected to complex less strongly than the carboxylate in oxalate.

Scheme VI

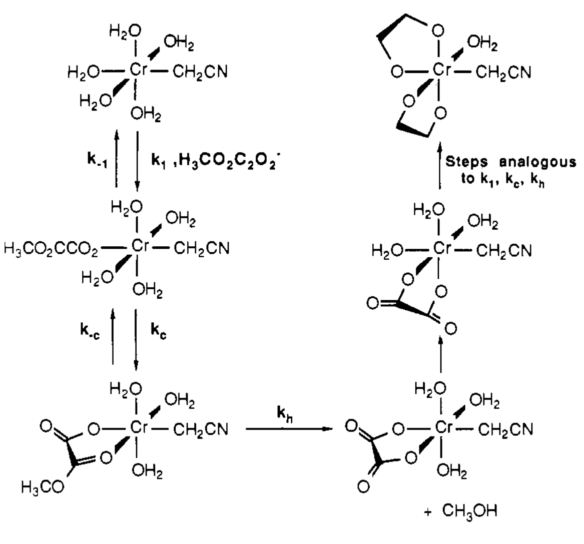

Table IV. Summary of Results for the Initial Reaction with $(H_2O)_5CrCH_2CN^{2+}$ (25 °C, 1 M $HClO_4/LiClO_4$)

ligand	pK_a	K_1,[a] M^{-1}	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}
$ClCH_2CO_2^-$	2.64	20.5	0.044	0.0026
$^+NH_3CH_2CO_2^-$	2.35	9.1	0.012	0.0021
$^+N(CH_3)_3CH_2CO_2^-$	1.83	5.6	0.013	0.0024
$H_2PO_2^-$ [c]	1.30	6.1[b]	0.23	0.038
$HO_2CCO_2^-$	1.20	2.5[b]	1.6	0.64
$H_3CO_2CCO_2^-$	1.15	2.2[b]	1.5	0.67
$F_3CCO_2^-$	0.3	0.57		
NCS^- [d]	−1.1	3.5	0.091	0.027

[a] Determined by spectrophotometry unless otherwise noted. [b] Determined from k_1/k_{-1}. [c] Results from ref 6. [d] Results from ref 5.

Cr–C Bond Cleavage in the Presence of Oxalate. Anion acceleration of the hydrolysis of the Cr–C bond in the complexes has been known for some time.[7,15,16] Oxalate also promotes this reaction but on a much slower time scale than any of the other reactions reported here. The process was studied in solutions containing 9×10^{-4} M $(H_2O)_5CrCH_2CN^{2+}$, 2×10^{-2} M H^+, and binoxalate concentrations in the range 0–2.0 × 10^{-2} M. Solutions were allowed to stand at ambient temperature, and the electronic spectra were monitored periodically. After 20 days the solution with the highest oxalate concentration appeared to have lost the Cr–C bond, and the spectrum was similar to that of *cis*-$(C_2O_4)_2Cr(OH_2)_2^-$ (562 (51.5), 416 nm (66.6)). The half-time for hydrolysis of the Cr–C bond is estimated to be ~6 days in the presence of 2.0 × 10^{-2} M oxalate compared to ≥190 days in the absence of oxalate.

Conclusions

The kinetic and equilibrium constant results for the first anation step (eq 1) are summarized in Table IV. There is a good linear free energy correlation of pK_a and log K_1 for the carboxylate ligands, which is given by eq 8. However, this correlation does not hold for the hypophosphite and thiocyanate systems.

$$\log K_1 = 0.62(pK_a) - 0.39 \qquad (8)$$

The values of k_1 are several orders of magnitude larger than "normal" anation rates for chromium(III) complexes. This has been attributed to the trans-labilizing influence of the alkyl ligand.[1] If anything, k_1 shows an inverse relationship with the proton basicity of the ligand and therefore does not show the variation expected for an associative mechanism. However the k_1 values do vary by over a factor of 100 for these systems and therefore do not show the level of constancy that might be expected for a purely dissociative mode of activation. At least part of the variation in k_1 may be due to differences in ion pair precursor complex formation. This could account for the lower reactivity of the amino

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acid zwitterions, but it seems unlikely that this factor would explain the 35-fold difference in k_1 for methyl oxalate and chloroacetate.

The slower reactions observed with oxalate and methyl oxalate are clearly related to further anation, because the product is the bis(oxalato) complex. However, the kinetics reveal that these are not just simple complexation reactions, and they have been assigned to chelate ring closing and isomerization. Similar bis-complex formation was observed in the hypophosphite system,[6] which also required an isomerization step.

It is noteworthy that complexing of methyl oxalate to $(H_2O)_5CrCH_2CN^{2+}$ results in ester hydrolysis at a rate much greater than that of the free ester. This type of intramolecular rate acceleration could be an important property of these alkylchromium complexes and is being investigated further.

Experimental Section

Solutions of $(H_2O)_5CrCH_2CN^{2+}$ and standard reagents were prepared as described previously.[6,17] The low solubility of zinc(II) oxalate required the use of zinc-free chromium solutions that were prepared from chromium metal (99.999% United Mineral & Chemical Corp.) and perchloric acid. Ionic strength was maintained with $LiClO_4$.

Lithium oxalate was made by treating a saturated solution of oxalic acid at 65 °C with Li_2CO_3. The warm solution was filtered, reduced to one third of its volume, and cooled in ice. The white solid was collected and dried in vacuum over silica gel. Anal. Calcd for $Li_2C_2O_4$: C, 23.57; H, O. Found: C, 23.32; H, 0.04.

Sodium methyl oxalate was prepared by hydrolysis of dimethyloxalate[18] following the method of Skrabal[14] for the potassium salt. The sodium salt is much less soluble than the potassium salt in methanol, and it was not recrystallized. The product was identified as >99.6% $NaO_2C_2O_2CH_3$ by both saponification and permanganate analyses. The ^1H NMR spectrum in D_2O shows a singlet at 3.90 ppm vs. external Me_4Si.

Solutions of $(C_2O_4)Cr(OH_2)_4^+$ and *cis*-$(C_2O_4)_2Cr(OH_2)_2^-$ were prepared as described by Schenck et al.[19] Solid *cis*-$Na[(C_2O_4)_2Cr(OH_2)_2]$ was prepared by the method of Werner.[20]

Sodium trifluoroacetate was prepared by adding Na_2CO_3 to aqueous CF_3CO_2H and then evaporating the solution on a steam bath until white solid began to appear. Then 2-butanol was added until the solution became cloudy, and the mixture was cooled in ice. The white solid was collected by filtration, washed with ether, and dried over silica gel. Anal. Calcd for $NaO_2C_2F_3$: C, 17.66, H, O. Found: C, 17.59; H, 0.09.

Acid Dissociation Constant of $CH_3O_2C_2O_2H$. The absorbance of solutions of $NaO_2C_2O_2CH_3$ was monitored at 240 nm as a function of added $HClO_4$. The results were analyzed by an iterative least-squares method, which corrected for the amount of bound H^+ and gave K_a = (7.04 ± 0.24) × 10^{-2} M at 25 °C.

Product Analysis. In the study with oxalate, the Cr:oxalate ratio was determined in the product after ion-exchange separation. Chromium was determined spectrophotometrically as chromate after oxidation with alkaline hydrogen peroxide. The oxalate was liberated from the chromium(III) by treatment with solid NaOH followed by acidification with glacial acetic acid. However blank experiments with known amounts of chromium(III) and oxalate revealed that one oxalate per chromium was always held back, and results were corrected for this fact. The oxalate was too dilute to determine by standard permanganate titration, so that the spectrophotometric method described by Burriel-Marti et al.[21] was used.

Instrumentation. The stopped-flow system is described elsewhere.[6,22] Spectrophotometric measurements were done on a Cary 219 spectrophotometer except for a few kinetic studies on a Hewlett-Packard 8451 diode-array system.

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Registry No. $(H_2O)_5CrCH_2CN^{2+}$, 76068-68-3; $NH_3CH_2CO_2^-$, 56-40-6; $^+N(CH_3)_3CH_2CO_2^-$, 107-43-7; $ClCH_2CO_2^-$, 14526-03-5; $CF_3CO_2^-$, 14477-72-6; $HO_2C_2O_2^-$, 920-52-5; $CH_3O_2C_2O_2^-$, 44546-01-2.

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Formation and Reactivity of Palladium(II) Sulfito Complexes in Aqueous Solution. 2. Kinetics and Mechanisms

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The kinetics of the formation of $Pd(Et_4dien)SO_3$ (Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine) via the reaction of $Pd(Et_4dien)OH_2^{2+}$ with HSO_3^-/SO_3^{2-} was studied in detail as a function of pH, [total S], temperature, and pressure. The observed rate law excludes the possibility of SO_2 uptake by $Pd(Et_4dien)OH^+$ and favors an anation mechanism that involves a rapid encounter complex formation preequilibrium. The rate law and activation parameters support an associative reaction mode. On acidification to pH <6, the $Pd(Et_4dien)SO_3$ species undergoes complete loss of the Et_4dien ligand, and the reaction is characterized by a typical two-term rate law, $k_{obsd} = k_a + k_b[\text{total S}]$. The k_a path exhibits a characteristic pH dependence and reaches a limiting value of 5 × 10^{-3} s^{-1} at 25 °C and 0.5 M ionic strength with $\Delta H^* = 78 \pm 5$ kJ mol^{-1}, $\Delta S^* = -26 \pm 17$ J K^{-1} mol^{-1}, and $\Delta V^* \approx 0$. These data are discussed in terms of a rate-determining ring-opening reaction of the Et_4dien ligand. In strongly acidic medium, partial loss of the sulfite ligand occurs to produce the corresponding aquo complex, and the observed rate constant exhibits a linear dependence on $[H^+]$. Kinetic data for the dechelation reaction measured under conditions where the $Pd(Et_4dien)SO_3$ complex is produced in acidic medium via anation of the aquo complex are in good agreement with those measured with the pH-jump method described before. The results of this study are discussed in terms of the general substitution behavior of Pd(II) complexes and the labilization effect of coordinated sulfite.

Introduction

In part 1 of this study[1] a detailed spectroscopic (UV-vis, IR, and NMR) investigation of the overall reactions was performed. The results enabled a qualitative description of the formation and decomposition processes in terms of characterized intermediate and product species. In this study we have performed a detailed kinetic analysis of the system and can now present a quantitative description of the reactions. Similar mechanistic studies[2-12] have

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