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Substitution Reactions of Metallic Complexes of β, β', β'' -Triaminotriethylamine. 12. Kinetics of the Hydrolysis of the (Oxalato)(β, β', β'' -triaminotriethylamine)chromium(III) Cation in Dilute and Concentrated Acid¹

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In studies of the reactions of Cr(III) complexes of the type $\text{CrN}_x\text{L}_{6-x}^{n+}$, where N is an amine donor or ammonia and L is an anionic ligand, aquation with loss of L is the commonly encountered reaction.² When L is fluoride,³ acetate,⁴ or oxalate,⁵⁻⁷ however, aquation of a chromium-nitrogen bond is the major reaction pathway. Much effort has focused upon the kinetic and mechanistic behavior of such Cr-N bond-rupture reactions, and comparisons have been made between species differentiated only by the complexity of the amine, as in the series $[\text{Cr}(\text{NH}_3)_4\text{ox}]^+$,⁵ $[\text{Cr}(\text{en})_2\text{ox}]^+$,⁶ and α - $[\text{Cr}(\text{trien})\text{ox}]^+$.⁷ All of these complexes, however, undergo Cr-N bond rupture until the amine is completely released. Chromium(III)-tren complexes, (tren = β, β', β'' -triaminotriethylamine), on the other hand, are reported to undergo only a single Cr-N aquation when fluoride⁸ and chloride⁹ are present as ligands, and F^- and Cl^- are also released. We were interested, therefore, in studying the Cr-N bond-rupture reactions of tren complex in which the aquation of an acido ligand would not be a complicating factor. It was thought that $[\text{Cr}(\text{tren})\text{ox}]^+$ would afford such an opportunity; the Cr-O bond is inert, and significant aquation of the oxalate group is not expected in solutions of $\sim\text{pH}$ 1.0. Furthermore, recent work^{10,11} with $[\text{Rh}(\text{tren})\text{Cl}_2]^+$ has shown that the two non-amine coordination sites are nonequivalent. The effect of this nonequivalency on the usually inert Cr-O bond is unknown.

This note describes the study of the kinetics of the stepwise reactions of $[\text{Cr}(\text{tren})\text{ox}]^+$ in both dilute and concentrated acid, as well as the characterization in solution of some new Cr(III)-tren complexes in which the amine is less than a quadridentate ligand.

Experimental Section

Complexes and Procedures. (Oxalato)(triaminotriethylamine)chromium(III) Perchlorate Hydrate, $[\text{Cr}(\text{tren})\text{ox}]\text{ClO}_4 \cdot \text{H}_2\text{O}$. This complex was synthesized by the method of Zipp and Madan.⁹ Anal. Calcd for $[\text{Cr}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_2\text{O}_4)]\text{ClO}_4 \cdot \text{H}_2\text{O}$: C, 23.79; H, 4.96; N, 13.88; Cr, 12.89; ClO_4^- , 24.66. Found: C, 24.39; H, 4.89; N, 14.12; Cr, 12.85; ClO_4^- , 24.50.

(Oxalato)quo(ammoniodiaminotriethylamine)chromium(III), (Oxalato)diaquo(diammonioaminotriethylamine)chromium(III),

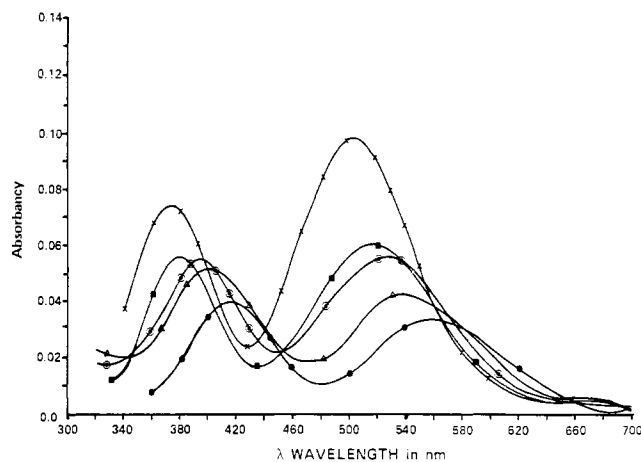


Figure 1. Visible spectra of products of aquation of $[\text{Cr}(\text{tren})\text{ox}]^+$ in 0.1 M HClO_4 : x, $[\text{Cr}(\text{tren})\text{ox}]^+$; ■, $[\text{Cr}(\text{trenH})\text{ox}(\text{H}_2\text{O})]^{2+}$; ●, $[\text{Cr}(\text{H}_2\text{O})_4\text{ox}]^+$; Δ, $[\text{Cr}(\text{trenH}_3)\text{ox}(\text{H}_2\text{O})_3]^{4+}$; ○, $[\text{Cr}(\text{trenH}_2)\text{ox}(\text{H}_2\text{O})_2]^{3+}$.

(Oxalato)triaquo(triammoniotriethylamine)chromium(III), and (Oxalato)tetraquo chromium(III) Cations. These were generated in acidic solution by the aquation of $[\text{Cr}(\text{tren})\text{ox}]^+$ at 60 °C for various reaction times. Appropriately aged solutions were charged onto a 15×1 cm column of H^+ Dowex AG50W-X8 cation-exchange resin (100-200 mesh). Separation of the complexes occurred upon washing of the column with increasing concentrations of HClO_4 . Elution was accomplished with the following concentrations of HClO_4 : for $[\text{Cr}(\text{trenH})\text{ox}(\text{H}_2\text{O})]^{2+}$, 2 M; for $[\text{Cr}(\text{trenH}_2)\text{ox}(\text{H}_2\text{O})_2]^{3+}$, 3.5 M; for $[\text{Cr}(\text{trenH}_3)\text{ox}(\text{H}_2\text{O})_3]^{4+}$, ≥ 5 M; for $[\text{Cr}(\text{H}_2\text{O})_4\text{ox}]^+$, 0.5 M. In all chromatography experiments, recovery of Cr-containing species was at least 98%. The products were characterized on the basis of visible spectra, charge per Cr atom, and aquation behavior.

Other Chemicals. All inorganic salts, acids, etc. were reagent grade quality.

Analytical Methods. Chromium was determined spectrophotometrically as chromate at 372 nm after oxidation of the Cr(III) in alkaline peroxide.¹² Oxalate determinations were carried out by charging solutions of the appropriate complex onto an ion-exchange column, washing with 0.1 M HClO_4 to remove all free oxalate, and titrating the eluate with standardized KMnO_4 .¹³ Carbon, hydrogen, and nitrogen analyses were performed by Strauss, Oxford, England. Perchlorate was determined by precipitation with nitron.¹⁴

Visible Spectra. Spectra were recorded on a Beckman Acta MIV recording spectrophotometer.

Kinetic Methods. The kinetics of aquation of $[\text{Cr}(\text{tren})\text{ox}]^+$, $[\text{Cr}(\text{trenH})\text{ox}(\text{H}_2\text{O})]^{2+}$, $[\text{Cr}(\text{trenH}_2)\text{ox}(\text{H}_2\text{O})_2]^{3+}$, and $[\text{Cr}(\text{trenH}_3)\text{ox}(\text{H}_2\text{O})_3]^{4+}$ were measured in HClO_4 at a variety of temperatures, acid and complex concentrations, and ionic strengths. Chromatographically isolated solutions of the appropriate complex at the desired conditions were monitored spectrophotometrically. For each reaction, isosbestic points, whose wavelengths agreed with the predicted values, were maintained through at least 50-60% reaction, and infinite time absorbances were determined as described elsewhere¹⁵ and were linear for at least 3 half-lives. Consecutive kinetic runs always agreed to better than 5%.

Results and Discussion

Aquation of $[\text{Cr}(\text{tren})\text{ox}]^+$ to $[\text{Cr}(\text{H}_2\text{O})_4\text{ox}]^+$ in Dilute Acid. When $[\text{Cr}(\text{tren})\text{ox}]\text{ClO}_4 \cdot \text{H}_2\text{O}$ is dissolved in 0.1 M HClO_4 at 15 °C, the spectrum of the original red solution rapidly changes to that of $[\text{Cr}(\text{trenH})\text{ox}(\text{H}_2\text{O})]^{2+}$. Heating acidic solutions of $[\text{Cr}(\text{trenH})\text{ox}(\text{H}_2\text{O})]^{2+}$ to 60 °C causes a red shift in the d-d maxima, consistent with the replacement of amine

(1) Work done by M.J.S. in partial fulfillment of the Ph.D Degree submitted at SUNY, Binghamton, NY, 1980. M.J.S. now at the Department of Chemistry, University of New Haven, West Haven, CT 06516.
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Table I. Values of k_1 for the First Aquation of $[\text{Cr}(\text{tren})\text{ox}]^+{}^a$

$T, ^\circ\text{C}$	$[\text{H}^+], \text{M}$	$\mu, {}^b \text{M}$	$10^3 k_1, \text{s}^{-1}$
20.2	0.101	0.102	3.26 ± 0.03
25.0	0.101	0.102	5.96 ± 0.24
30.0	0.101	0.102	10.8 ± 0.7
30.0	0.101	1.00	8.62 ± 0.02
30.0	0.101	2.00	6.79 ± 0.06
30.0	0.051	2.00	6.98 ± 0.06
30.0	2.00	2.00	6.79 ± 0.09
35.0	0.101	0.102	17.7 ± 1.6
35.0 ^c	0.101	0.102	17.9 ± 1.3
35.0 ^d	0.101	0.102	17.6 ± 1.1

^a $\lambda = 500 \text{ nm}$; $[\text{complex}] = 1.0 \times 10^{-3} \text{ M}$. ^b Adjusted with NaClO_4 . ^c $\lambda = 480 \text{ nm}$. ^d $[\text{complex}] = 3.0 \times 10^{-3} \text{ M}$.

groups by water molecules. Spectral changes continue until the formation of $[\text{Cr}(\text{H}_2\text{O})_4\text{ox}]^+$ is complete; continued heating induces no further observable reaction. The visible spectra of these complexes are shown in Figure 1.

Each complex was isolated in solution via ion-exchange chromatography (see Experimental Section). Charge per chromium atom determinations performed on the chromatographically isolated product solutions were $+2.19 \pm 0.14$ for $[\text{Cr}(\text{trenH})\text{ox}(\text{H}_2\text{O})]^{2+}$, $+3.32 \pm 0.21$ for $[\text{Cr}(\text{trenH}_2)\text{ox}(\text{H}_2\text{O})_2]^{3+}$, $+4.21 \pm 0.34$ for $[\text{Cr}(\text{trenH}_3)\text{ox}(\text{H}_2\text{O})_3]^{4+}$, and $+1.06 \pm 0.14$ for $[\text{Cr}(\text{H}_2\text{O})_4\text{ox}]^+$. The magnitudes of these numbers are well within those reported for complexes of similar charge.^{7,8,16,17} Additional evidence for the presence of uncoordinated amine groups in the first three complexes comes from the fact that when solutions of these complexes were adjusted to pH 8–11 with NaOH at 5°C and reacidified, the spectrum of $[\text{Cr}(\text{tren})\text{ox}]^+$ was regenerated. This indicates that deprotonation and rechelation of the free amino groups had occurred.

Furthermore, tests for released oxalate showed that less than 4% of the coordinated oxalate was released during the overall reaction sequence. Trials done with $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ as a standard confirmed that $\text{C}_2\text{O}_4^{2-}$ could be recovered quantitatively from the ion-exchange column.

Further evidence for complete amine aquation was obtained by allowing solutions of $[\text{Cr}(\text{tren})\text{ox}]^+$ to aquate completely to $[\text{Cr}(\text{H}_2\text{O})_4\text{ox}]^+$ and by charging the product solutions onto an ion-exchange column. The $[\text{Cr}(\text{H}_2\text{O})_4\text{ox}]^+$ was removed with 0.5 M HClO_4 , and the top third of the column was removed manually. Any $[\text{trenH}_3]^{3+}$ which was present would have remained near the top of the column because of its high positive charge. The removed resin was washed with concentrated HCl , filtered, and treated with a large excess of absolute ethanol. Upon cooling of the solution in an ice-salt bath, a small amount of white solid precipitated. The infrared spectrum of this solid was similar to that of a sample of $\text{tren} \cdot 3\text{HCl}$ that had been synthesized by an independent route.

Due to the steric properties of the tren ligand, it is extremely likely that the tertiary nitrogen is the last one to be displaced from the complex. The complex $1,2,3\text{-}[\text{Cr}(\text{trenH})\text{ox}(\text{H}_2\text{O})]^{2+}$ contains a coordinated primary amine on each side of the tertiary nitrogen. The tertiary amine also has a dangling, uncoordinated ethylamine group. It would not be expected to unhook. However, in $[\text{Cr}(\text{trenH}_3)\text{ox}(\text{H}_2\text{O})_3]^{4+}$, there are no such restrictions, and Cr–N bond rupture can occur.

Direct experimental evidence for this sequence of Cr–N bond rupture reactions is the isolation of a 4+ species by ion-exchange chromatography. The tertiary amine is not protonated even in concentrated acid. Thus, if the tertiary amine aquated before either of the primary amines, the highest

Table II. Values of k_2 for the Aquation of $[\text{Cr}(\text{trenH})\text{ox}(\text{H}_2\text{O})]^{2+}{}^a$

$T, ^\circ\text{C}$	$[\text{H}^+], \text{M}$	$\mu, {}^b \text{M}$	$10^4 k_2, \text{s}^{-1}$
59.0	0.100	0.100	6.42 ± 0.05
64.0	0.100	0.100	9.91 ± 0.12
69.0	0.100	0.100	15.2 ± 0.5
69.0	0.100	1.00	13.7 ± 0.3
69.0	0.100	2.00	13.2 ± 0.4
69.0	1.00	2.00	12.9 ± 0.5
69.0	2.00	2.00	13.5 ± 0.7
74.0	0.100	0.100	23.3 ± 0.5
74.0 ^c	0.100	0.100	23.3 ± 1.0
74.0 ^d	0.100	0.100	23.9 ± 0.6

^a $\lambda = 406 \text{ nm}$; $[\text{complex}] = 3.0 \times 10^{-3} \text{ M}$. ^b Adjusted with NaClO_4 . ^c $[\text{complex}] = 1.0 \times 10^{-3} \text{ M}$. ^d $\lambda = 572 \text{ nm}$.

Table III. Values k_3 for the Aquation of $[\text{Cr}(\text{trenH}_2)\text{ox}(\text{H}_2\text{O})_2]^{3+}{}^a$

$T, ^\circ\text{C}$	$[\text{H}^+], \text{M}$	$\mu, {}^b \text{M}$	$10^4 k_3, \text{s}^{-1}$
75.0	0.093	0.093	1.41 ± 0.06
75.0	0.093	2.00	1.24 ± 0.10
75.0	1.00	2.00	1.29 ± 0.04
80.0	0.093	0.093	2.90 ± 0.11
86.0	0.093	0.093	4.10 ± 0.04
91.0	0.093	0.093	7.56 ± 0.14
91.0	0.093	1.00	7.25 ± 0.08
91.0 ^c	0.093	0.093	7.49 ± 0.06

^a $\lambda = 587 \text{ nm}$; $[\text{complex}] = 5.0 \times 10^{-3} \text{ M}$. ^b Adjusted with NaClO_4 . ^c $[\text{complex}] = 3.0 \times 10^{-3} \text{ M}$.

Table IV. Values for k_4 for the Aquation of $[\text{Cr}(\text{trenH}_3)\text{ox}(\text{H}_2\text{O})_3]^{4+}{}^a$

$T, ^\circ\text{C}$	$[\text{H}^+], \text{M}$	$\mu, {}^b \text{M}$	$10^5 k_4, \text{s}^{-1}$
70.0	0.100	0.100	1.56 ± 0.06
80.0	0.100	0.100	4.62 ± 0.13
85.0	0.100	0.100	7.93 ± 0.08
90.0	0.100	0.100	12.6 ± 0.4
90.0	0.100	1.00	11.4 ± 0.3
90.0	0.100	2.00	10.6 ± 0.7
90.0	1.00	2.00	10.2 ± 0.4
90.0	2.00	2.00	10.0 ± 0.5
90.0 ^c	0.100	0.100	12.3 ± 0.3
90.0 ^d	0.100	0.100	12.5 ± 0.8

^a $\lambda = 540 \text{ nm}$; $[\text{complex}] = 5.0 \times 10^{-3} \text{ M}$. ^b Adjusted with NaClO_4 . ^c $\lambda = 500 \text{ nm}$. ^d $[\text{complex}] = 2.5 \times 10^{-3} \text{ M}$.

possible charge on any of the aquation products would be 3+. The appearance of a 4+ complex can only be rationalized if the tertiary nitrogen is lost in the final aquation step. A species with only the tertiary nitrogen coordinated to the metal would be stabilized by the hydrogen bonding between the amine protons and water.¹⁸

Values of the pseudo-first-order rate constants are given in Tables I–IV. The following activation parameters were calculated (complex, ΔH^\ddagger (kcal mol⁻¹), ΔS^\ddagger (cal deg⁻¹ mol⁻¹): $[\text{Cr}(\text{tren})\text{ox}]^+$, 19.0 ± 1.3 , -4.8 ± 1.9 ; $[\text{Cr}(\text{trenH})\text{ox}(\text{H}_2\text{O})]^{2+}$, 19.5 ± 1.1 , -14.7 ± 1.8 ; $[\text{Cr}(\text{trenH}_2)\text{ox}(\text{H}_2\text{O})_2]^{3+}$, 25.0 ± 1.5 , -4.3 ± 2.0 ; $[\text{Cr}(\text{trenH}_3)\text{ox}(\text{H}_2\text{O})_3]^{4+}$, 26.0 ± 1.5 , -4.7 ± 2.0 .

Comparison of the rate constant at 25°C for this reaction with that for the first aquation of $\alpha\text{-}[\text{Cr}(\text{tren})\text{ox}]^+$ ($k = 3.63 \times 10^{-4} \text{ s}^{-1}$)⁷ reveals that the tren complex reacts more rapidly by a factor of approximately 20. This is explained by the unique structure of the amine. By undergoing Cr–N bond fission, the intraligand repulsions present in this octahedral complex are reduced. Such repulsions are not present to as great an extent in the tren complex.

Subsequent Cr–N bond-breaking reactions in this complex are much slower than the primary aquation, and there is a

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decrease in the rate of each successive aquation. Two explanations can be given to account for this behavior. The first is based on simple charge arguments. As the charge on the complex increases, it becomes more difficult for Cr-N bond rupture to occur. The second is the "grease" effect of the aliphatic chains within the amine ligand.¹⁸ These hydrocarbon chains make solvation of the transition state very difficult in aqueous solution, especially since greater solvation is required by the separating charges on the protonated amine group and the Cr(III) center.

The activation parameters also provide some insight into the nature of these aquations. The activation enthalpy increases as the number of coordinated nitrogen atoms decreases. Such a trend is a reflection of the increasing difficulty of solvation of both the ground and transition states as the number of chelated groups decreases. However, there are no observable trends in activation entropies for these reactions, except for the fact that they are all negative. This is due to the hydrogen bonding between the solvent and the free, unprotonated amino group. This hinders the mobility of the free arm of the ligand and makes coordination of a water molecule easier.

The acid independence of the rates of Cr-N aquations is not an unexpected result, although acid dependence has been reported in a few cases.^{6,7} It is especially interesting that the kinetics of the aquo complexes show no acid dependence. An inverse $[H^+]$ term has been reported in the rate laws for aquation of certain Co(III)-aquo-tren complexes.^{19,20} Apparently, in the oxalato-aquo-tren species, the acid dissociation constants for the loss of a proton from the aquo ligands are too small to generate sufficient concentrations of the corresponding hydroxo species. The decrease of the rates of all these reactions with increasing ionic strength is within the normal range of salt effects at such high ionic strengths.

It is significant that $[Cr(tren)ox]^+$ undergoes complete amine aquation. In both $[Cr(tren)Cl(H_2O)]^{2+}$ ⁹ and $[Cr(tren)F(H_2O)]^{2+}$,⁸ Cr-N bond breaking stops after release of only one ethylamine group. Any mechanism invoked to explain these observations must also account for the fact that the tren does not undergo aquation in a linear fashion, as do some of the complexes of the linear polyamines.^{18,21,22}

The complex $[Cr(tren)ox]^+$ presents an ideal situation for oxyanion catalysis. Since protonation of one of the oxygen atoms occurs readily in 6 M $HClO_4$, it is reasonable to assume that some protonation occurs even in 0.1 M $HClO_4$. Broomhead et al.²³ have reported that the racemization reactions of $[Cr(phen)(ox)_2]^-$ and $[Cr(bpy)(ox)_2]^-$ proceed via a mechanism involving the breaking of a Cr-O bond. In that case, protonation of a carbonyl oxygen occurred even in solutions of <1 M $HClO_4$. Protonation of a carbonyl oxygen in $[Cr(tren)ox]^+$ would increase the lability of the Cr-O moiety and lead to a unidentate oxalate ligand. Transient rechelation of the uncoordinated oxygen could expel one of the ethylamine groups, which would then be stabilized by the uptake of a proton from solution. This process could conceivably continue until $[Cr(H_2O)_4ox]^+$ was produced.

Reaction of $[Cr(tren)ox]^+$ in Concentrated Acid. When $[Cr(tren)ox]^+$ reacts in 12 M HCl at 25 °C, within 30 s the d-d bands are shifted to lower energies. Another slower reaction follows, with further shifting of the d-d bands to longer wavelengths. The final spectrum is identical with that of $[Cr(tren)Cl_2]^+$:⁹ λ_{max} (ϵ , $M^{-1} cm^{-1}$) reported, 549 (114), 408

Table V. Values of k_6 for the Second Reaction of $[Cr(tren)ox]^+$ in Concentrated HCl at 25 °C^a

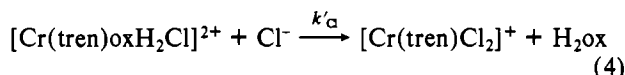
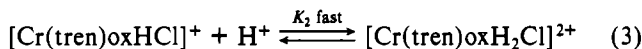
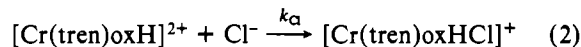
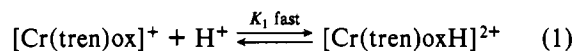
$[H^+]$, M	$[Cl^-]$, M	$10^3 k_6$, s ⁻¹
11.00	11.00	1.07 ± 0.01
11.00	11.50 ^b	1.41 ± 0.02
11.00	12.00 ^b	1.50 ± 0.05
11.25	11.25	1.12 ± 0.04
11.50	11.50	1.39 ± 0.03
11.50	12.00	1.53 ± 0.16
11.75	11.75	1.70 ± 0.04
12.00	12.00	1.98 ± 0.16

^a $\lambda = 590$ nm. ^b Adjusted with LiCl.

(95.0); found, 548 (109), 408 (89.0).

Since the first reaction occurred very quickly in 8 M HCl even at 5 °C, a kinetic study was not possible by these methods. Table V gives the kinetic data (k_6) for the second observed reaction at various HCl and chloride concentrations. Because the acid concentrations were so high, no attempt was made to determine the activation parameters for this reaction, since interpretation under such conditions would be difficult.

The kinetic data in Table V suggest that both $[H^+]$ and $[Cl^-]$ appear in the rate expression for the second reaction, and although k_5 was too large to be measured, it is reasonable to assume that both coordinated oxygens are anated by the same pathway. A mechanism consistent with the experimental observations is one which involves a rapid protonation equilibrium followed by the rate-determining entry of a chloride ion (eq 1-4). For the second reaction (eq 3 and 4) rate =



$[Cr(tren)oxHCl]^+ = k'_{cl}[[Cr(tren)oxH_2Cl]^{2+}][Cl^-]$. With the steady-state approximation, rate = $k_6[[Cr(tren)oxHCl]^+]$ = $k'_{cl}K_2[[Cr(tren)oxHCl]^+][H^+][Cl^-]$ and

$$k_6 = k'_{cl}K_2[H^+][Cl^-] \quad (5)$$

At such high acid concentrations, activities²⁴ rather than concentrations must be used, and eq 5 reduces to $k_6 = k'_{cl}K_2a_{\pm HCl}$.² Thus, a plot of $\log k_6$ vs. $\log a_{\pm HCl}$ should yield a line of slope 2. The calculated slope of this line is 1.90 ± 0.25 , in excellent agreement with that predicted from the proposed mechanism.

Comparison of the rates of these reactions shows that the entrance of the first chloride into $[Cr(tren)ox]^+$ is faster than it is into $[Cr(en)_2ox]^+$.⁶ The second reaction, however, is slower in the case of tren. These results can be rationalized in terms of the geometry of the tren complex. Work with molecular models shows that the environments around the two coordinated oxygens differ significantly. The coordination site trans to the tertiary nitrogen is located in a hydrophilic pocket, whereas the other nonamine coordination site occupies a hydrophobic area, one that is susceptible to repulsions from the aliphatic chains in the amine. It is reasonable to expect that a reaction in which both H^+ and Cl^- ions must be obtained from the solvent will occur more readily at the hydrophilic site. The presence of this pocket causes an enhancement of the rate as compared to that of the ethylenediamine complex. The

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effect of the hydrophobic pocket, however, is to hinder the entry of the H^+ and Cl^- ions, leading to a slower rate for the second reaction than in case of ethylenediamine.

Registry No. $[Cr(tren)ox]^+$, 57719-00-3; $[Cr(trenH)ox(H_2O)]^{2+}$, 75234-31-0; $[Cr(trenH_2)ox(H_2O)]^{3+}$, 75234-32-1; $[Cr(trenH_3)ox(H_2O)_3]^{4+}$, 75234-33-2; $[Cr(H_2O)_4ox]^+$, 24777-95-5.

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Difluoroborane, a Hydrogen-Deuterium Exchange Catalyst. Application to Pentaborane(9) and Methylpentaborane(9)

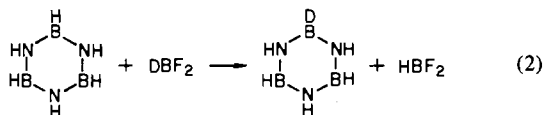
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An interesting chemical property of difluoroborane (HBF_2) is its reactivity with deuterium gas to undergo H-D exchange. The reaction



proceeds with a second-order rate constant $k_2 = (7.4 \pm 2.0) \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 25 °C. This reaction, which is quite rapid at 100 °C, has an apparent activation energy of $17.8 \pm 1.2 \text{ kcal/mol}$. Curtis and Porter¹ proposed that the process involves an activated intermediate formed by a three-center interaction of D_2 with the electron-deficient boron atom in HBF_2 . The possibility of using HBF_2 as an H-D exchange catalyst is evident in the thermodynamic investigation of DeStefano and co-workers.² Results of that study showed that mixtures of H_2 and D_2 , which do not exchange at a perceptible rate at 25 °C, reach an equilibrium mixture of H_2 , HD, and D_2 with 24 h when HBF_2 is present in the gas mixture. The rate of scrambling is increased significantly at higher temperatures. Borazine ($H_3B_3N_3H_3$) reacts with DBF_2 at ordinary temperatures by H-D exchange. The process shown in eq 2 is accelerated when borazine is present in a

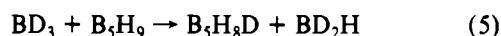


D_2 - DBF_2 mixture by the replacement of the deuterated reactant in reaction 1. The process is site selective at the B-H bonds, and consecutive H-D exchange reactions lead to tri-B-deuterioborazine as the final product. Coyle and co-workers³ found that process 3 proceeds rapidly at ordinary temperatures.



From these observations and the nature of reaction 1, it is clear that B_2D_6 could be obtained directly from a mixture of B_2H_6 , HBF_2 , and D_2 in excess. These considerations have suggested the use of HBF_2 as an H-D exchange catalyst for preparing partially or totally deuterated boron hydrides. In this paper we report experimental results for B_5H_9 , 1- $CH_3B_5H_8$, and 2- $CH_3B_5H_8$.

The exchange of hydrogens between diborane and pentaborane(9) was studied by Koski and co-workers.⁴⁻⁶ They applied infrared, mass, and NMR spectroscopy to their investigations of the reaction. The exchange was reported to occur by a bimolecular collision between borane and pentaborane (eq 4 and 5).



At 80 °C the reaction was complicated by the pyrolytic formation of pentaborane from deuterated diborane. When the B_5D_9 fraction was subtracted in the spectra of the pentaborane product, they observed that the exchange of B_2D_6 and B_5H_9 involved preferential deuteration of the terminal positions of the pentaborane.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer using 3-in. gas cells with KBr optics. The cells were thoroughly purged with dry nitrogen after cleaning, and background spectra were run before and after use. Mass spectra were obtained on a Consolidated Electroynamics Corp. Model 21-103A spectrometer at 70-eV ionizing voltage.

B_5H_9 (Callery Chemical Co.) was repurified by vacuum distillation through U-tube traps. Slow passage of the B_5H_9 through a -78 °C trap removed the higher molecular weight impurities. Pure B_5H_9 was recovered in a -98 °C trap. D_2 was obtained from Air Products and Chemicals, Inc., research grade. 1-Methylpentaborane(9) was prepared from B_5H_9 and CH_3Br under Friedel-Crafts conditions with aluminum chloride catalyst.⁷ 2-Methylpentaborane(9) was prepared from the rearrangement of 1- $CH_3B_5H_8$ by employing the base catalyst 2,6-lutidine.⁸ The product purities were confirmed by their mass, infrared, and proton NMR spectra.

Samples of DBF_2 were prepared from mixtures of B_2D_6 and BF_3 by a method similar to that of Coyle et al.³ A 3:1 mixture of $BF_3:B_2D_6$ was heated to 180 °C in $1/2$ h at a total pressure of 250 torr (1 torr = 133.3 N m^{-2}) in a 1-L stainless-steel vessel equipped with a Whitey 1KS6 valve. The products, a mixture of BF_3 and DBF_2 , were separated from small amounts of B_5D_9 by slow passage through a -98 °C trap. Quantitative determination of DBF_2 in the reagent mixture was accomplished by measuring the amount of HD and D_2 formed when the sample was exposed to an excess of H_2 . Mixtures of HBF_2 and DBF_2 may be analyzed by absorbance measurements at 924 cm^{-1} (A_H) and 787 cm^{-1} (A_D), respectively.

Results and Discussion

The DBF_2 - B_5H_9 Exchange Reaction. A mixture of reagents in the molar proportion $B_5H_9:DBF_2:BF_3 = 1:0.7:1.6$ at a total pressure of 400 torr was heated for 24 h at 98 °C in a 100-mL Pyrex vessel. The products that were recovered in a -98 °C trap indicated partial deuteration of B_5H_9 by the infrared absorption at 1950 cm^{-1} corresponding to a B-D stretching vibration. The infrared analysis of the products recovered at -198 °C indicated that nearly all of the DBF_2 had been converted to HBF_2 . Several more 24-h runs were made with the sample of pentaborane. The reaction vessel was maintained at 100 °C with approximately 100 torr of D_2 added between runs. Infrared analyses indicated progressive deuteration of the pentaborane fraction (observed in the relative intensities of the absorptions at 2600 and 1950 cm^{-1}). Due to the exchange reaction with deuterium (eq 1), the difluoroborane remained highly deuterated. A second sample with composition $B_5H_9:DBF_2:BF_3:D_2 = 1.0:0.43:1.0:2.5$ at a total pressure of 440 torr was heated for 48 h at 80 °C. The products were

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