experimental results even though the predictive tools are based primarily on one-electron-transfer reactions between dissimilar metal centers.[19] At pH 7 the reduction potential of O_2 to H_2O_2 is 0.27 V while the reduction potential of H_2O_2 to H_2O is 1.27 V. The additional driving force for the H_2O_2 reduction must compensate for the symmetry advantage of O_2 as the electron acceptor. The advantage of electron transfer between symmetry matched orbitals is ca. 10^9 between separated metal centers.[19] Only about 0.5 V of driving force in favor of H_2O_2 is needed to compensate for a 10^9 kinetic advantage. Since the electron-transfer step is a two-electron process and therefore non-Marcus in nature, the utilization of only about 50% of the overall 1.0-V advantage of the driving force for H_2O_2 relative to O_2 seems a realistic estimate to bring the observed rates for O_2 and H_2O_2 at equal concentration to within a factor of 10^2.

It is also interesting to note that although the oxidation of $Fe(CN)_6^{4-}$ by H_2O_2 is only about 0.3 V less favorable than $Ru(NH_3)_6^{2+}$ by H_2O_2, the $Fe(CN)_6^{4-}$ reductant fails to utilize the Fe(IV) pathway. Models show that the $M(CN)_6$ moiety is about equally crowded on the face as the $M(NH_3)_6$ unit. The effective availability of the t_{2g}^6 electrons is reduced both by smaller radial extension of the 3d vs. 4d level and by the CN^- ligands. The CN^- ligands compete for the t_{2g}^6 electrons much more than the saturated NH_3 ligands. Distortion to achieve a seven-coordinate structure would be much more costly for CN^- than for NH_3 ligands because of the additional change experienced for the π bonding of CN^- to the metal center. This raises the interesting possibility of finding a coordination sphere for Fe(II) strong enough to cause spin pairing but weak enough to allow for the Fe(IV) pathway in its oxidations by two-electron acceptors.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation through Grant CHE-76-21290 for these studies.

Registry No. H_2O_2, 7722-84-1; $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(NH_3)_5OH_2^{2+}$, 21393-88-4; $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$, 73697-79-7.

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(19) (a) S. S. Isied and C. G. Kuehn, *J. Am. Chem. Soc.*, **100**, 6754 (1978); (b) H. Fischer, G. M. Tom, and H. Taube, *ibid.*, **98**, 5512 (1976).

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(21) In the time interval required to publish this manuscript Taube offered an alternative explanation to his earlier data (D. M. Stanbury, O. Haas, and H. Taube, *Inorg. Chem.*, **19**, 518 (1980)). A one-electron path is suggested utilizing O_2^- as an intermediate in the oxidation of RuL_6^{2+}/O_2 and $Ru(en)_3^{2+}/O_2$ reactions reflect the primary outer-sphere electron transfer reaction forming Ru(III) and O_2^- in the first step. We have attempted to derive expressions which involve a similar one-electron transfer from $Ru(NH_3)_6^{2+}$ to H_2O_2 that would account for the saturation dependence in $[H_2O_2]$ reported here. No simple expression that utilized HO· as an intermediate, scavenged competitively by Ru(II) and H_2O_2, was obtained that predicted a rate law other than a simple power in $[H_2O_2]$. It appears that if O_2^- is the proper intermediate in the RuL_6^{2+}/O_2 reactions, as recently supported by new data, the reactivities of O_2 and H_2O_2 with these species are divergent in nature. This is consistent with strikingly different activation parameters, particularly ΔS^{*}, as reported here.

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Kinetic Studies of the Anation and Related Reactions of Aqua(nitrilotriacetato)oxovanadate(IV) in Aqueous Solution

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Received October 5, 1979

Nitrilotriacetate (nta^{3-}) gives blue complexes of composition $M[V^{IV}O(nta)H_2O]$ (M = K, Na, and $^1/_2$Ba), which seem to have the tertiary amine trans to the oxo. The aqua ligand is replaced by thiocyanate and azide.

$$[V^{IV}O(nta)H_2O]^- + X^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [V^{IV}O(nta)X]^{2-} + H_2O$$

The kinetic parameters (k_f and k_b for NCS^- and N_3^- are 0.62 and 4.1 $M^{-1}\,s^{-1}$ and 0.17 and 0.48 s^{-1} at 25 °C, respectively, and the corresponding ΔH^{*} and ΔS^{*} are 40.5, 53.5, 69.4, and 52.7 kJ mol^{-1} and −112, −52, −25, and −75 J $K^{-1}\,mol^{-1}$, respectively) are very similar to those of the corresponding substitution reactions of the complex $[V^{IV}O(pmida)H_2O]$ ($pmida^{2-}$ = (2-pyridylmethyl)iminodiacetate), and the substitution seems to correspond to the direct basal S_N2 substitution. Nitrite oxidizes the complex to $[V^VO_2(nta)]^{2-}$ through substitution at the basal site for coordinated water and subsequent electron transfer. This vanadium(V) complex replaces the aqua ligand of $[V^{IV}O(nta)H_2O]^-$ to give a deep blue binuclear complex, which has two vanadium ions in 4+ and 5+ oxidation states. Kinetic studies suggest that the same kind of S_N2 substitution with $X^{2-} = [V^VO_2(nta)]^{2-}$ is involved in the formation of the mixed-valence complex.

Introduction

Substitution reactions of oxovanadium(IV) complexes give various rates depending on the site at which the substitution takes place. We have studied the substitution for the aqua ligand in aquaoxo[(2-pyridylmethyl)iminodiacetato]vanadium(IV), $[VO(pmida)H_2O]$, in aqueous solution and found that the direct substitution at the basal site gives very small rate constants ($\simeq 10^{-1}\,s^{-1}$ at 25 °C).[1] The hitherto claimed basal substitution reactions involving unidentate ligands were considered to reflect the rate of a process involving intramolecular rearrangement of the ligand from the apical to basal site of VO^{2+} complexes. With aims of clarifying the reaction further, we have synthesized a new complex $M[V^{IV}O(nta)H_2O]$ (M = Na, K, and $^1/_2$Ba) and studied the replacement of the aqua ligand by X^- = NCS^-, N_3^-, and NO_2^-.

$$[VO(nta)H_2O]^- + X^- \rightleftharpoons [VO(nta)X]^{2-} + H_2O \quad (1)$$

Nitrite ions oxidized the vanadium(IV) to vanadium(V), and the resulting $[V^VO_2(nta)]^{2-}$ also underwent similar substitution for the aqua ligand to give a very characteristic deep blue binuclear complex of the composition $[V_2O_3(nta)_2]^{3-}$. This

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(1) Nishizawa, M.; Saito, K. *Inorg. Chem.* **1978**, *17*, 3676.

0020-1669/80/1319-2284$01.00/0

paper deals with the kinetic and mechanistic studies of these reactions in aqueous solution.

Experimental Section

Preparation of Compounds. Barium Bis[aqua(nitrilotriacetato)-oxovanadate(IV)] Tetrahydrate. Granules of barium hydroxide octahydrate were added slowly to an aqueous solution (ca. 70 mL) of nitrilotriacetic acid (3.23 g, 0.0169 mol) under stirring until the pH reached 5. Blue solution of oxovanadium(IV) sulfate (0.42 M, 40 mL) was poured into this solution and the pH was adjusted to 5 with ca. 0.1 M barium hydroxide solution (total ca. 250 mL). The suspension was centrifuged and filtered and the filtrate evaporated to 30 mL and treated with ethanol to give a light blue precipitate, which was filtered off and washed with ethanol. Recrystallization was achieved from aqueous ethanol; yield 6.35 g (50%). Analysis indicated that the isolated complex was $Ba[VO(nta)H_2O]_2{\cdot}4H_2O$. Anal. Calcd for $C_{12}H_{24}Ba_1N_2O_{20}V_2$: C, 19.07; H, 3.18; N, 3.71. Found: C, 18.98; H, 3.15; N, 3.76.

The potassium salt was prepared by passing the barium salt solution through a column of Amberlite IR-120 cation-exchange resin in the K^+ form. Blue crystals were obtained on addition of ethanol to the eluate and similarly recrystallized. Analysis indicated that the crystals were $K[VO(nta)H_2O]{\cdot}H_2O$. Anal. Calcd for $C_6H_{10}K_1O_9V_1$: C, 21.82; H, 3.03; N, 4.24. Found: C, 22.02; H, 2.99; N, 4.12.

The sodium salt was prepared by mixing the barium salt with an equimolar amount of sodium sulfate in aqueous solution, centrifuging and evaporating the mixture under a reduced pressure, and adding ethanol. The blue powder gave the composition $Na[VO(nta)H_2O]{\cdot}2.5H_2O$. Anal. Calcd for $C_6H_{13}N_1Na_1O_{10.5}V_1$: C, 21.12; H, 3.81; N, 4.11. Found: C, 21.01; H, 3.50; N, 3.89.

Potassium (Nitrilotriacetato)dioxovanadate(V) Trihydrate. An aqueous solution of $K[V^{IV}O(nta)H_2O]{\cdot}H_2O$ (0.33 g, 0.001 mol) in 10 mL of water was heated with potassium nitrite solution (0.022 M, 50 mL) at 40–50 °C for 1 h to give a yellow solution, which was condensed to oily liquid and treated with ethanol. The hygroscopic powder was washed with ethanol and dried in vacuo (yield 60%). Anal. Calcd for $C_6H_{12}N_1K_1O_{11}V_1$: C, 17.87; H, 2.98; N, 3.47. Found: C, 17.65; H, 3.38; N, 3.50. The sodium salt was prepared similarly in aqueous solution by use of the sodium salts but not in crystalline state.

Ammonium μ-Oxo-bis(nitrilotriacetato)dioxodivanadate(IV,V) Trihydrate. An aqueous solution of $Ba[V^{IV}O(nta)H_2O]$ was treated with ammonium sulfate and centrifuged to produce 100 mL of 0.2 M $(NH_4)[V^{IV}O(nta)H_2O]$ solution. This was mixed with potassium nitrite solution (1 M, 10 mL; 0.5 equiv to the vanadium(IV) complex). When gas evolution ceased, the deep blue solution was evaporated, treated with ethanol, and cooled in a refrigerator to give very dark colored crystals. The crude product was dissolved in a small amount of water, treated with ammonium perchlorate solution, filtered, and kept in a refrigerator overnight with ethanol. The deep indigo crystals gave the composition $(NH_4)_3[V_2O_3(nta)_2]{\cdot}3H_2O$, yield ca. 70%. Anal. Calcd for $C_{12}H_{30}N_5O_{18}V_2$: C, 22.71; H, 4.73; N, 11.04. Found: C, 22.63; H, 4.62; N, 10.87. The sodium salt hexahydrate was obtained from the sodium salt of the vanadium(IV) complex and sodium nitrite.

Other Materials. Sodium salts of thiocyanate, azide, and nitrite were recrystallized from aqueous ethanol. The concentrations of the aqueous solution of the thiocyanate and the azide were determined by titration with mercury(II) nitrate and cerium(IV) sulfate, respectively.

Measurement. The IR and UV absorption spectra were recorded with JASCO IR A-1 and Hitachi 323 spectrometers, respectively. The reflectance spectrum was recorded with the same spectrometer with 323-0993 integrating sphere. The equilibrium data were obtained as shown in ref 1.

Kinetic Runs. The aqueous solution of $[V^{IV}O(nta)H_2O]^-$ remained unchanged for more than 1 week in the pH range from 3.0 to 5.0. The substitution rate was measured by plotting the increase in absorbance (A_t) at 310 nm in the pH ranges 3.0–4.7 and 4.3–4.9 in the presence of 0.10–0.40 and 0.05–0.20 M NCS^- and N_3^-, respectively (complex concentration 10^{-4} M). The pH was adjusted with perchloric acid and azide–hydrazonic acid buffer, respectively, and the ionic strength at 1.0 with $NaClO_4$. The UV absorption spectra are shown in Figure 1. The absorbance increased remarkably at 310 nm within 2–50 s but not in millisecond scale. The reaction with nitrite was studied in nitrite–nitrous acid buffer of pH 4–5 and monitored by observing the increase in absorbance at 300 nm. The nitrite concentration (0.01–0.3 M) was calculated on the basis of the pK_a (3.2) of nitrous acid in the literature. The reaction between $[V^{IV}O(pmida)H_2O]$ ($pmida^{2-}$ = (2-pyridylmethyl)iminodiacetate)[2] and nitrite was also studied under similar experimental conditions. The rate of replacement of aqua ligand of $[V^{IV}O(nta)H_2O]^-$ ($\simeq 10^{-3}$ M) by $[V^VO_2(nta)]^{2-}$ ($\simeq 10^{-2}$ M) was measured at 750 nm in an acetate buffer of pH 4.9.

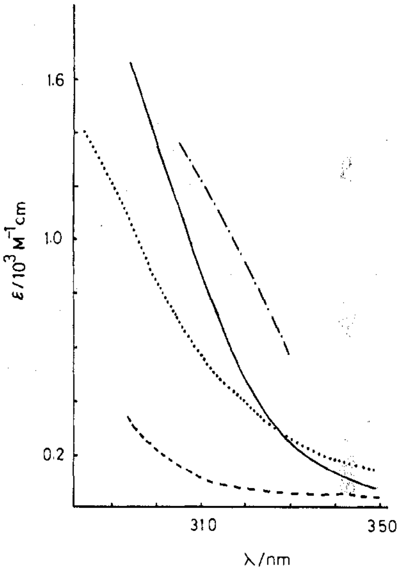

Figure 1. UV absorption spectra of $[V^{IV}O(nta)H_2O]^-$ in aqueous solution containing various reagents: (---) with no reagent added at pH 4.1; (—) after equilibration in 0.20 M NCS^- solution; (-·-) after equilibration in 0.39 M N_3^- solution; (···) with $[V^VO_2(nta)]^{2-}$ at pH 4.5 (after the NO_2^- oxidation).

All kinetic measurements were performed by the stopped-flow method with a Union Giken RA-601 spectrophotometer. The observed first-order rate constant k_o for all the reactions was calculated by the pseudo-first-order treatment with respect to the vanadium(IV) complex. The plots of log ($A_\infty - A_t$) against time gave straight lines until the change in absorbance reached 85% completion.

Results

Synthesis. Crystals of neither the barium nor the potassium salt of $[V^{IV}O(nta)H_2O]^-$ were large enough to permit X-ray diffraction studies. Their crystalline powder gave IR absorption peaks at 975 cm^{-1} in KBr disks; they must be due to the V═O stretching vibration. Their reflectance spectrum gave a broad peak around 615 nm, which must correspond to the peak at 610 nm in aqueous solution. The sodium, potassium, and barium salts are soluble in water and stable at pH 3–5. The pK_a of the aqua ligand was 6.9 at 25 °C and $I = 1.0$. The solution gave UV absorption peaks at 610 and 800 nm with ϵ values 13 and 21 $M^{-1}\ cm^{-1}$ respectively.

The binuclear complex was obtained in large crystals as ammonium salt trihydrate and sodium salt hexahydrate. Both crystals gave IR absorption at 947 cm^{-1} in KBr disks and a reflectance spectrum peak at 582 nm. The structure was determined by the X-ray diffraction method to find that the tervalent complex anion has a center of symmetry and both vanadium ions are equivalent to each other (V–O = 1.809 Å).[3] This complex is in equilibrium with the quadri- and quinquevalent vanadium complexes in aqueous solution as shown later. The absorption spectra of the aqueous solution were recorded at various concentrations and also in the presence of excessive $[V^VO_2(nta)]^{2-}$ which gives no absorption in the visible region. The molar extinction coefficients were calculated from these data, and the pattern is shown in Figure 2.

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(2) "Lange's Handbook of Chemistry", 11th ed.; McGraw-Hill: New York, 1973.

(3) Nishizawa, M.; Hirotsu, S.; Ooi, S.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1979**, 707.

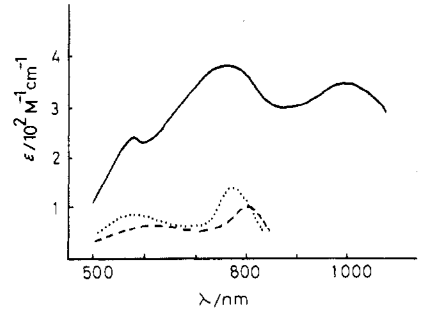

Figure 2. Visible spectra of $[V_2O_3(nta)]^{3-}$ and $[V^{IV}O(nta)H_2O]^-$: (—) $[V_2O_3(nta)]^{3-}$ (by calculation on the basis of eq 6); (---) $[V^{IV}O(nta)H_2O]^-$ (×5); (···) $[V^{IV}O(pmida)H_2O]$ (×5).

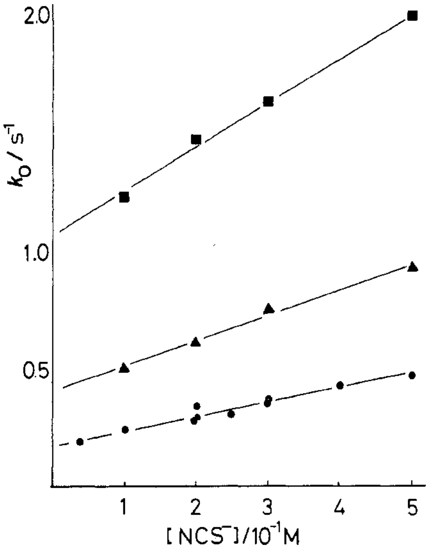

Figure 3. Dependence of the first-order rate constant k_o upon the concentration of thiocyanate ($I = 1.0$, $NaClO_4$): (●) 25 °C; (▲) 35 °C; (■) 45 °C.

A uniform electron distribution in the V–O–V core is indicated by the appearance of 15 ESR hyperfine signals[3] and by the very large ϵ values in aqueous solution which are characteristic of mixed-valence complexes.

Reactions with Thiocyanate and Azide. The formation constants of reaction 1 were determined spectrometrically at 310 nm in the pH ranges from 3.0 to 4.7 and 4.3 to 4.8, respectively, in the presence of 0.10–0.40 M NCS^- and 0.05–0.20 M N_3^-. The K values (eq 2) are 2.0 and 11 M^{-1} for NCS^- and N_3^-, respectively, at 25 °C and $I = 1.0$ ($NaClO_4$). There was no influence of pH in the given regions.

$$K = [VO(nta)X^{2-}]/[VO(nta)H_2O^-][X^-] \qquad (2)$$

The observed first-order rate constant k_o increased linearly with increase in the concentrations of NCS^- (Figure 3) and N_3^- (Figure 4) to give eq 3, in which k_f and k_b stand for the

$$d[\text{product}]/dt = k_o[VO]_t = (k_f[X^-] + k_b)[VO]_t \qquad (3)$$

forward and backward reactions of eq 1 and $[VO]_t$ represents the total concentration of the complex. The rate constants and the activation parameters are listed together with those of the related reactions in Table I.

Reaction with Nitrite. When an excess of potassium nitrite solution was added to the blue solution of $[V^{IV}O(nta)H_2O]^-$ at pH 4–5, the solution turned yellow with evolution of gas. The irreversible reaction (eq 4) was verified by comparing the

$$[VO(nta)H_2O]^- + NO_2^- \rightarrow [V^VO_2(nta)]^{2-} + NO \qquad (4)$$

UV spectra with those of authentic sample solutions and detecting nitrogen dioxide in a current of air. The first-order rate constant k_o is expressed by eq 5. The k_o increases with

$$-d[V^{IV}O]/dt = k_o[V^{IV}O(nta)H_2O^-] \qquad (5)$$

increase in nitrite concentration as shown in Figure 5; the lines have no intercept.

The reaction between $[V^{IV}O(pmida)H_2O]$ and nitrite gave a similar color change at pH 4–5. The k_o showed dependence on the nitrite concentration similar to that of the nta complex

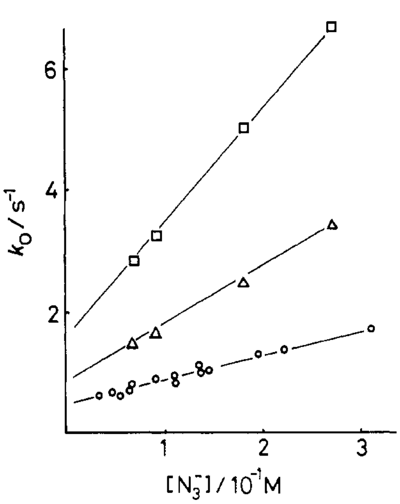

Figure 4. Dependence of the first-order rate constant k_o upon the concentration of azide ($I = 1.0$, $NaClO_4$): (○) 25 °C; (△) 35 °C; (□) 45 °C.

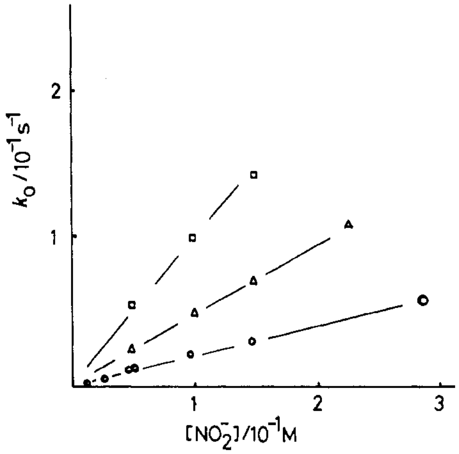

Figure 5. Dependence of the first-order rate constant k_o upon the concentration of nitrite (pH 4–5; $I = 1.0$, $NaClO_4$): (○) 45 °C; (△) 55 °C; (□) 65 °C.

Table I. Kinetic Parameters of This Work and Related Reactions

systems		$t/°C$	k/s^{-1}	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ K^{-1}\ mol^{-1}$
$[VO(nta)H_2O]^-$	anat	25	0.62 M^{-1}	41 ± 1	−112 ± 3
vs. NCS^-	aquat	25	0.17	69 ± 8	−25 ± 28
$[VO(nta)H_2O]^-$	anat	25	4.1 M^{-1}	54 ± 1	−52 ± 2
vs. N_3^-	aquat	25	0.48	53 ± 3	−75 ± 8
$[VO(pmida)H_2O]$	anat[a]	25	0.26 M^{-1}	49 ± 2	−90 ± 9
vs. NCS^-	aquat[a]	25	0.061	61 ± 3	−61 ± 10
$[VO(pmida)H_2O]$	anat[a]	25	3.7 M^{-1}	47 ± 6	−75 ± 20
vs. N_3^-	aquat[a]	25	0.13	64 ± 13	−47 ± 42
$[VO(nta)H_2O]^-$ vs. NO_2^-	redox	45	0.20 M^{-1}	66 ± 2	−48 ± 17
$[VO(pmida)H_2O]$ vs. NO_2^-	redox	45	1.0 M^{-1}	65 ± 2	−41 ± 5
$[VO(nta)H_2O]$	anat	25	1.36 M^{-1}	62 ± 13	−33 ± 41
vs. $[V^VO_2(nta)]^{2-}$	aquat	25	0.051	56 ± 22	−79 ± 70

[a] Reference 1.

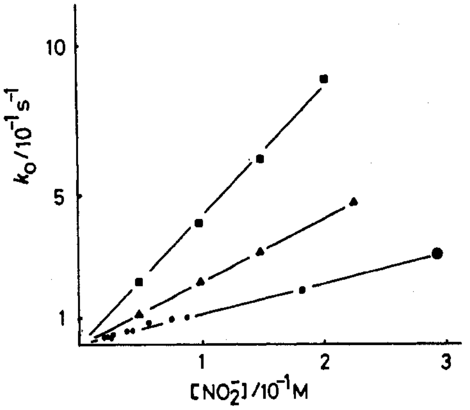

Figure 6. Dependence of the first-order rate constant k_o of the pmida complex upon the concentration of nitrite (pH 4–5): (●) 45 °C; (▲) 55 °C; (■) 65 °C.

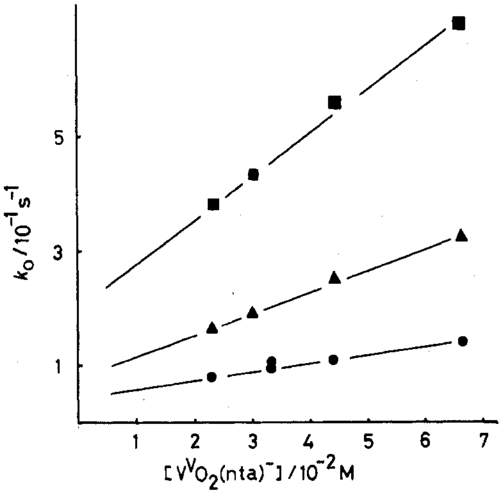

Figure 7. Dependence of the first-order rate constant k_o upon the concentration of $[V^VO_2(nta)]^{2-}$ (pH 4.9, I = 1.0, $NaClO_4$): (●) 25 °C; (▲) 35 °C; (■) 45 °C.

(Figure 6). The data are summarized in Table I.

Formation of a Mixed-Valence Complex. When equimolar solutions of $[V^{IV}O(nta)H_2O]^-$ and $[V^VO_2(nta)]^{2-}$ were mixed, a deep blue color appeared. Comparison of the absorption data of the reaction mixtures with those of the component complexes disclosed the formation of a mixed-valence complex between vanadium(IV) and vanadium(V) according to the following equilibrium:

$$[V^{IV}O(nta)H_2O]^- + [V^VO_2(nta)]^{2-} \rightleftharpoons [V_2O_3(nta)_2]^{3-} + H_2O \quad (6)$$

The equilibrium constant was measured spectrophotometrically at 750 nm to be 20 M^{-1} at 25 °C and I = 1.0. The observed rate constant k_o at pH 4.9 increased with increase in the concentration of the vanadium(V) complex (Figure 7) and is related to the rates of forward (k_f) and backward (k_b) reactions by eq 7. Concentration of acetate (~10^{-3} M) had only a

$$k_o = k_f[V^VO] + k_b \quad (7)$$

negligible effect on the rate. The k_f and k_b values are listed in Table I together with the activation parameters.

Discussion

Structure of the Complexes. So far as the nitrilotriacetate ligand coordinates as quadridentate, the three acetate oxygens should be meridional to one another. Hence the vanadium(V) complex has no geometrical isomer. The vanadium(IV) complex has two geometrical isomers, but we think that only one isomer with the tertiary nitrogen trans to the oxo ligand is present in the solution for the following reasons. This complex is very stable in aqueous solution, and the aquation is observed only at a pH less than unity, with the aid of proton catalysis.[4] Hence the isomerization which should accompany the break of metal–ligand bonds must be very slow at pH more than 3. The log $(A_\infty - A_t)$ vs. time plots of all the present substitution reactions give straight lines. Therefore, only one isomer should be present in aqueous solution. On mixing with the aqueous solution of $[V^VO_2(nta)]^{2-}$, the vanadium(IV) complex gives a binuclear complex $[V_2O_3(nta)_2]^{3-}$, in which the tertiary nitrogens are cis to the bridging oxo ligand in the crystalline state.[3] At pH 4, oxo and aqua ligands of $[V^{IV}O(nta)H_2O]^-$ are not readily interchangeable. Thus the only isomer present in the aqueous solution should have the tertiary nitrogen trans to the oxo ligand. When aqueous solutions of vanadium(IV) oxosulfate and H_3nta were mixed at pH 4–5, two absorption peaks appeared instantaneously at 611 and 800 nm with ϵ values 12 and 20 M^{-1} cm^{-1}, respectively. The UV absorption at 610 nm is sensitive to the kind of ligating atom,[5] and this particular geometrical isomer must be exclusively formed under the given condition.

The binuclear complex exhibits a characteristic electronic absorption at 750 and 1000 nm and provides an interesting example of a mixed-valence complex with d^1 configuration. Detailed studies of its electronic structure by ESR spectroscopy will be reported elsewhere.

Substitution Reaction with Thiocyanate and Azide The rate constants and activation parameters in Table I indicate that the substitution of these anions for the aqua ligand is parallel to that for the related complex $[V^{IV}O(pmida)(H_2O)]$. The change in overall electronic charge of the complex and in the coordinated atom does not seem to cause appreciable difference in the reaction rate and mechanism. The dissociation of nta^{3-} is observed in more than 0.2 M acid solution,[4] and the apical site of VO_2^{2+} is blocked under the given condition. Hence the kinetic data in Table I should reflect the direct basal substitution. The difference in rates between the substitution of azide and thiocyanate is similar to that of the pmida complex for both forward and backward reactions. These facts as well as the large negative $\Delta S^\ddagger$ values suggest that the present substitution reaction has an associative rate-determining step as in the case of the pmida complex.[1]

Reaction with Nitrite The rate was too small at 25 °C to be determined by the present stopped-flow technique with a time scale of 200 s. The $[V^{IV}O(nta)(H_2O)]^-$ was oxidized by hexachloroiridate(IV) to give the same product $[V^VO_2(nta)]^{2-}$ by the outer-sphere mechanism at a much greater rate (more than 10^3 M^{-1} s^{-1} at 25 °C).[6] The oxidation with nitrite must proceed via the inner-sphere mechanism involving the substitution of nitrite for the aqua ligand, which is followed by the electron transfer. The overall reaction path is expressed by eq 8 and 9, where k_f and k_b correspond to those in eq 1 and k_{et} is the rate of electron transfer in $[V^{IV}O(nta)ONO]^{2-}$.

$$[V^{IV}O(nta)H_2O]^- + NO_2^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [V^{IV}O(nta)ONO]^{2-} + H_2O \quad (8)$$

$$[V^{IV}O(nta)ONO]^{2-} \xrightarrow{k_{et}} [V^VO_2(nta)]^{2-} + NO \quad (9)$$

Hyde and Garner studied the oxidation of *mer*-$[Mo^VOCl_3(OPPh_3)_2]$ with nitrate and nitrite and discussed that the nitrate or nitrite first replaced the phosphine oxide at the apical site and then migrated to the basal site and drew an electron from Mo(V) to complete the oxidation. They claimed

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that the electron-transfer process coupled with the adjustment in atomic positions to produce NO_2 or NO and the *cis*-$Mo^{VI}O_2^{2+}$ moiety should be very fast because of the overlap of the d_{xy} orbital of Mo(V) with the π^* orbital of nitrate or nitrite.[7] If the same overlap were reasonably considered in the present d^1 system, the electron transfer itself and the accompanying bond break to liberate NO should be very fast as compared with the k_f process. The second-order rate constant $k_0/[NO_2^-]$ is smaller than k_f for the substitution reaction with NCS^-, despite the stronger basicity of NO_2^- than of NCS^-. The activation parameters are also different from those of the substitution reactions of eq 1. It is generally understood that the substitution reaction between aqua ligand and nitrite and vice versa involve the break of an N–O bond rather than the metal–oxygen bond accompanied by a different activation enthalpy than that for other reactions with a metal–oxygen bond break.[8]

Formation of the Binuclear Complex. The equilibrium and kinetic studies were made at pH 4.9, where a significant amount of $[V^VO_2(nta)]^{2-}$ is dissociated.[9] Hence the k_f and k_b values, the equilibrium constants, and the activation parameters in Table I should involve rather large experimental errors (e.g., the virtual concentration of $[V^VO_2(nta)]^{2-}$ in Figure 7 should be less than those expressed on the abscissa). Equilibrium studies at 25–45 °C gave $\Delta H°$ and $\Delta S°$ values ca. -20 kJ mol^{-1} and -40 J mol^{-1} K^{-1}, respectively. These values might involve large experimental errors and do not agree with those calculated kinetically. Nevertheless, the negative $\Delta H°$ value reflects the stabilization brought about by the mixed-valence state in the $V_2O_3^{3+}$ moiety. The k_f values are of the same order with those for the anation of NCS^- and N_3^- to $[V^{IV}O(nta)(H_2O)]^-$. Thus we tend to reckon the formation reaction of the binuclear complex as the replacement of the aqua ligand in $[V^{IV}O(nta)(H_2O)]^-$ by $[V^VO_2(nta)]^{2-}$. The substitution reaction must be followed by a rapid electron exchange within the $V_2O_3^{3+}$ core to give equal states of the two vanadium ions.

Registry No. $Ba[VO(nta)H_2O]_2$, 73711-57-6; $K[VO(nta)H_2O]$, 72268-05-4; $Na[VO(nta)H_2O]$, 73711-58-7; $K_2[VO_2(nta)]$, 73636-51-8; $(NH_4)_3[V_2O_3(nta)_2]$, 73728-22-0; $[VO(pmida)H_2O]$, 12348-25-3; NO_2^-, 14797-65-0; NCS^-, 302-04-5; N_3^-, 14343-69-2.

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A Cleavage Reaction of Pentaborane(9). Formation of a New Hypho Triborane Adduct

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Received January 3, 1980

The reaction of pentaborane(9) with excess trimethylphosphine proceeds to form $B_5H_9{\cdot}2P(CH_3)_3$ and then to give a mixture of $B_2H_4{\cdot}2P(CH_3)_3$ and a new hypho class compound tris(trimethylphosphine)–triborane(5), $B_3H_5{\cdot}3P(CH_3)_3$. At room temperature under vacuum, the phosphine adduct of diborane(4) sublimes out of the mixture and the triborane(5) adduct converts to $B_6H_{10}{\cdot}2P(CH_3)_3$. The yield of $B_2H_4{\cdot}2P(CH_3)_3$ based upon the pentaborane(9) used is about 110%. Reactions of $B_5H_9{\cdot}$TMED (TMED = *N,N,N′,N′*-tetramethylethylenediamine) and $B_5H_9{\cdot}$diphos (diphos = 1,2-bis(dimethylphosphino)ethane) with excess trimethylphosphine give $B_5H_9{\cdot}2P(CH_3)_3$ first and then the same cleavage reaction follows. The cleavage of pentaborane(9) is compared with that reported for the reaction of B_5H_9 with $PF_2N(CH_3)_2$. The boron-11 NMR data for the borane adducts encountered in this study are appended.

Introduction

Pentaborane(9) reacts with bases in many different ways. Certain phosphines and amines are known to form molecular addition compounds, such as $B_5H_9(\text{phosphine})_2$[2] and $B_5H_9(\text{amine})_2$,[2a,3] under appropriate conditions of the reactions. Deprotonation of pentaborane(9) by strong bases to give octahydropentaborate(1−) ion ($B_5H_8^-$) is another type of reaction that has been established.[4] The framework of B_5H_9 is cleaved by many bases as observed in the reaction of ammonia to give $B_5H_9{\cdot}2NH_3$,[5] which has been formulated as $H_2B(NH_3)_2^+B_4H_7^-$ and in the reaction of trimethylamine[3b] to give trimethylamine–borane(3) and a solid of a formula $(CH_3)_3NB_4H_6$. Many bases undergo complex reactions with B_5H_9 under various conditions to give a variety of degraded borane compounds.[6] Among these, reactions which yield diborane(4) adducts were reported by Lory and Ritter[7] and by Hertz, Denniston, and Shore.[8] The former authors presented evidence for the cleavage of B_5H_9 by (dimethylamino)difluorophosphine ($PF_2N(CH_3)_2$) to give $B_2H_4{\cdot}2PF_2N(CH_3)_2$ and $B_3H_5{\cdot}2PF_2N(CH_3)_2$, and the latter utilized the B_2H_4 adduct formation for the preparation of $B_2H_4{\cdot}2P(CH_3)_3$. In this paper we report evidence for the stoichiometric cleavage of B_5H_9 by trimethylphosphine to give $B_2H_4{\cdot}2P(CH_3)_3$ and $B_3H_5{\cdot}3P(CH_3)_3$.

Results and Discussion

A. Reaction of B_5H_9 with Excess $P(CH_3)_3$. When pentaborane(9) is treated with a large excess of trimethylphosphine

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0020-1669/80/1319-2288$01.00/0