Another interesting feature of these dimers is the lability of the acetonitrile ligands. From our qualitative results the rate of exchange is Ni $\simeq$ Pd $\gg$ Pt. This is the same order expected for ligand exchange of square-planar complexes in the +2 oxidation state.[33] Parallels between square-planar d^8 complexes and d^9–d^9 dimers have been noted previously.[29] This order also seems to coincide qualitatively with the rates of reactions of these dimers with small molecules such as hydrogen and acetylene.[30]

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Registry No. **6a**, 114718-99-9; **6b**, 114692-89-6; **7**, 109637-10-7; **8**, 114692-91-0; **9**, 114692-93-2; **10**, 114692-97-6; **11**, 114692-95-4; **12**, 114692-99-8; $[\mathrm{Ni(C_6H_5CN)_6}](\mathrm{BF_4})_2$, 114693-00-4; $[\mathrm{Pt(COD)(CH_3CN)_2}](\mathrm{BF_4})_2$, 66347-86-2; $[\mathrm{Ni(CH_3CN)_6}](\mathrm{BF_4})_2$, 15170-11-3; $\mathrm{Ni(COD)_2}$, 1295-35-8; $[\mathrm{Pd(CH_3CN)_4}](\mathrm{BF_4})_2$, 21797-13-7; $\mathrm{Pd_2(dba)_3}$, 51364-51-3; $\mathrm{Pd(COD)_2}$, 12130-66-4; Ni, 7440-02-0; Pd, 7440-05-3; Pt, 7440-06-4.

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Kinetics and Mechanism of the Outer-Sphere Electron-Transfer-Induced Formation of *cis*-Dioxovanadium(V) Species from Vanadyl(IV) Complexes. Crystal Structures of $[\mathrm{VO(TCDA)}]\cdot\mathrm{H_2O}$ and $[\mathrm{VO_2(TCDAH)}]\cdot2\mathrm{H_2O}$ (TCDA = 1,4,7-Triazacyclononane-*N*,*N'*-diacetate)

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The potentially pentadentate ligands 1,4,7-triazacyclononane-*N*,*N'*-diacetate ($\mathrm{C_{10}H_{17}N_3O_4}^{2-}$, TCDA) and 1-oxa-4,7-diazacyclononane-*N*,*N'*-diacetate ($\mathrm{C_{10}H_{16}N_2O_5}^{2-}$, DOCDA) have been synthesized, and the corresponding blue vanadyl(IV) complexes $[\mathrm{VO(TCDA)}]\cdot\mathrm{H_2O}$ (**1**) and [VO(DOCDA)] have been isolated. Oxidation of **1** in 0.1 M $\mathrm{H_2SO_4}$ with $\mathrm{PbO_2}$ or $[\mathrm{Ni([9]aneN_3)_2}]^{3+}$ ($[9]\mathrm{aneN_3}$ = 1,4,7-triazacyclononane) yields yellow $[\mathrm{VO_2(TCDAH)}]\cdot2\mathrm{H_2O}$ (**2**). The crystal structures of **1** and **2** have been determined by X-ray crystallography. Crystal data for **1**: monoclinic, space group $P2_1/c$; a = 6.679 (2), b = 10.323 (3), c = 18.701 (5) Å; β = 90.85 (2)°; V = 1289.2 (5) Å^3, Z = 4, ρ_{calcd} = 1.70 g cm^{-3}; final R = 0.036 from 3383 observed reflections. Crystal data for **2**: monoclinic, space group $P2_1/n$; a = 13.361 (8), b = 15.533 (5), c = 15.986 (8) Å; β = 111.77 (4)°; V = 3039.4 (8) Å^3; Z = 8; ρ_{calcd} = 1.59 g cm^{-3}; final R = 0.044 from 4937 observed reflections. Cyclic voltammograms of **1** and [VO(DOCDA)] in acetonitrile show one reversible one-electron-transfer process ($\mathrm{VO^{2+}} \rightleftarrows \mathrm{VO^{3+}} + \mathrm{e^-}$) at $E_{1/2}$ = +0.427 and +0.622 V vs $\mathrm{Fc^+/Fc}$, respectively. The kinetics of the acid-independent outer-sphere one-electron oxidation of **1** and [VO(DOCDA)] with $[\mathrm{Ni([9]aneN_3)_2}]^{3+}$ as one-electron oxidant has been measured in acidic aqueous solution (k_{12} = 685 M^{-1} s^{-1} for **1** and 14 M^{-1} s^{-1} for [VO(DOCDA)] at 25 °C, I = 0.56 M). This reactivity difference is discussed in the frame of the Marcus cross relation for outer-sphere electron-transfer processes.

Introduction

Oxovanadium(IV) complexes of amino polycarboxylates are readily oxidized in acidic aqueous solution by strong outer-sphere one-electron oxidants such as $[\mathrm{IrCl_6}]^{2-}$ or $[(\mathrm{en})_4\mathrm{Co^{III}}_2(\mu\text{-}\mathrm{NH_2,O_2^-})]^{4+}$ to form *cis*-dioxovanadium(V) species. Sasaki, Saito, and co-workers have in a series of elegant kinetic studies proposed that oxovanadium(V) species are probable intermediates.[2–4] They have used aquaoxo(quadridentate)vanadium(IV) complexes (quadridentate = amino polycarboxylato ligands) as starting materials, where the aqua ligand is cis with respect to the V=O group. Upon deprotonation of this aqua group ($\mathrm{OV^{IV}}$—OH), oxidation, and subsequent further deprotonation the *cis*-dioxovanadium(V) species are generated:

$$[\mathrm{OV^{IV}(OH_2)L}]^{n} \overset{K_a}{\rightleftharpoons} [\mathrm{OV^{IV}(OH)L}]^{n-1} + \mathrm{H^+} \tag{1}$$

$$[\mathrm{OV^{IV}(OH)L}]^{n-1} + \text{oxidant} \rightarrow [\mathrm{OV^{V}(OH)L}]^{n} + \text{reduced oxidant} \tag{2}$$

$$[\mathrm{OV^{V}(OH)L}]^{n} \rightarrow [\mathrm{O_2V^{V}L}]^{n-1} + \mathrm{H^+} \tag{3}$$

In the case of $\mathrm{Na[V^{IV}O(edtaH)]}$ (edtaH = monoprotonated ethylenediaminetetraacetate), a six-coordinate vanadyl(IV) complex with no aqua ligand but a pentadentate edta ligand instead, the presence of a steady-state oxovanadium(V)–edta complex has been detected.[4] The final oxidation product was again a *cis*-dioxovanadium(V)–edta complex, where the edta ligand is only tetradentate.[10]

Pseudooctahedral oxovanadium(IV)[5–7] and *cis*-dioxovanadium(V)[8–10] amino polycarboxylato complexes have been characterized by X-ray crystallography as have been a few five- and six-coordinate monooxovanadium(V) complexes with Schiff-base ligands.[11,12] Electrochemical data on $[\mathrm{VOL}]^n \rightleftarrows [\mathrm{VOL}]^{n+1} + \mathrm{e^-}$ systems are extremely rare.

At the outset of this work we hoped to be able to characterize the proposed oxovanadium(V) intermediates by oxidizing oxovanadium(IV) compounds that contain a strongly binding pentadentate chelate ligand which might inhibit the rapid formation of *cis*-dioxovanadium(V) species in aqueous solution. For this purpose we have synthesized two new, potentially pentadentate amino polycarboxylate ligands, namely 1,4,7-triazacyclononane-*N*,*N'*-diacetate (TCDA) and 1-oxa-4,7-diazacyclononane-*N*,*N'*-diacetate (DOCDA), via functionalization of the parent cyclononanes.[13] Both ligands readily form the corresponding six-co-

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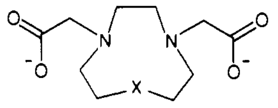

X = NH, TCDA; X = O, DOCDA

ordinate oxovanadium(IV) complexes [VO(TCDA)]·H_2O and [VO(DOCDA)]·1.5H_2O, which are oxidized by the strong outer-sphere one-electron oxidant $[Ni([9]aneN_3)_2]^{3+}$ ([9]aneN_3 = 1,4,7-triazacyclononane) in acidic aqueous solution[14,15] to yield *cis*-dioxovanadium(V) species. The electrochemistry of these vanadyl complexes in acetonitrile exhibits a reversible one-electron-transfer wave, indicating the formation of the desired oxovanadium(V) species in an aprotic solvent. The kinetics of the above reaction has been measured in aqueous solution, and the crystal structures of [VO(TCDA)]·H_2O and of [VO_2(TCDAH)]·2H_2O have been determined by X-ray crystallography (TCDAH represents the monoprotonated form of the ligand TCDA).

Experimental Section

Synthesis. The ligands 1,4,7-triazacyclononane[16] and 1-oxa-4,7-diazacyclononane[17] and the complex $[Ni([9]aneN_3)_2](ClO_4)_3 \cdot H_2O$[14] were prepared according to published procedures.

The preparation of the dilithium salts of 1,4,7-triazacyclononane-*N,N'*-diacetate (TCDA) and 1-oxa-4,7-diazacyclononane-*N,N'*-diacetate (DOCDA) was carried out in the following manner.

Li_2(TCDA). To a solution of 1,4,7-triazacyclononane (6.0 g, 46.4 mmol) in dry ethanol (160 mL) was added 2-bromoacetic acid ethyl ester (7.7 mL, 68.7 mmol) with stirring at room temperature. A solution of sodium (1.05 g, 47.4 mmol) in dry ethanol (50 mL) was added with cooling, and the mixture was stirred at 20 °C for 12 h. The precipitated NaBr was filtered off and discarded. The solvent ethanol was evaporated under reduced pressure. The resulting material was treated with dry toluene (150 mL), and solid NaBr was again removed by filtration. After removal of the solvent under reduced pressure a yellow oil of the diethyl ester of 1,4,7-triazacyclononane-*N,N'*-diacetate was obtained in 80% yield. This crude ester (7 g) was hydrolyzed in ethanol (80 mL) with LiOH·H_2O (19.5 g, 46.4 mmol). The suspension was refluxed overnight. After the suspension was cooled to 5 °C, the colorless voluminous precipitate was filtered off, washed with dry ethanol and ether, and dried in vacuo over P_2O_5 at 70 °C. This product is contaminated with small amounts of trilithium 1,4,7-triazacyclononane-*N,N',N''*-triacetate.[18] We did not attempt to further purify this material, and it was used as obtained for the synthesis of metal complexes.

Li_2(DOCDA). The same procedure as described above was employed with 1-oxa-4,7-diazacyclononane as starting material instead of 1,4,7-triazacyclononane. The colorless Li_2(DOCDA) was used as obtained without further purification for metal complex preparations.

[VO(TCDA)]·H_2O. To a solution of Li_2TCDA (1.2 g) in methanol (10 mL) was slowly added a solution of $VO(acac)_2$ (acac = acetylacetonate(1−); 1 g, 3.95 mmol) in methanol (10 mL) at 40 °C with stirring. The solution was heated to 60 °C until a blue precipitate had formed. After cooling of the solution to 15 °C, the microcrystalline precipitate was filtered off, washed with ethanol and ether, and air-dried. The compound crystallized without water molecules of crystallization. IR (KBr, cm^{-1}): ν(N—H) 3200 (m); ν(C=O) 1650, 1630 (vs); ν(C—O) 1320, 1290, 1280 (s); ν(V=O) 950 (s). Anal. Calcd for $C_{10}H_{17}N_3O_5V$: C, 38.72; H, 5.52; N, 13.54. Found: C, 38.5; H, 5.5; N, 13.6. Suitable single crystals for X-ray crystallography were obtained from recrystallization of [VO(TCDA)] dissolved in 10^{-3} M aqueous perchloric acid after standing at room temperature for 1 week. These crystals contain one water molecule of crystallization per formula unit. Anal. Calcd for $[C_{10}H_{17}N_3O_5V] \cdot H_2O$: C, 36.59; H, 5.83; N, 12.80. Found: C, 36.3; H, 6.2; N, 13.1. Two additional bands at 3400 and 3500 cm^{-1} in the infrared spectrum were found (ν(H_2O)).

Table I. Crystallographic Data of the Complexes [VO(TCDA)]·H_2O (**1**) and [VO_2(TCDAH)]·2H_2O (**2**)

	1	**2**
formula	$[C_{10}H_{17}N_3O_5V] \cdot H_2O$	$[C_{10}H_{18}N_3O_6V] \cdot 2H_2O$
fw	328.2	363.27
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
Z	4	8
a, Å	6.679 (2)	13.361 (8)
b, Å	10.323 (3)	15.533 (5)
c, Å	18.701 (5)	15.986 (8)
β, deg	90.85 (2)	111.77 (4)
V, Å^3	1289.2	3039.4
ρ_{calcd}, g cm^{-3}	1.70	1.59
cryst dimens, mm	0.26 × 0.45 × 0.71	0.15 × 0.46 × 0.48
temp. °C	22	
instrument	AED II (Siemens)	
radiation, monochromator	Mo Kα (λ = 0.71073 Å), graphite	
scan mode	ω	
scan range, deg	$3 < 2\theta < 65$	$3 < 2\theta < 66$
no. of rflns collcd	3709 (±*h*,+*k*,+*l*)	5384 (±*h*,+*k*,+*l*)
no. of rlfns used in soln	3383 ($I < 2.5\sigma(I)$)	4937 ($I > 2.25\sigma(I)$)
no. of params	187	428
abs coeff, cm^{-1}	7.73	6.7
T_{max}/T_{min}	1.0–0.82	1.0–0.85
R[a]	0.036	0.044
R_w[b]	0.034	0.037
goodness of fit[c]	2.34	1.67

[a] $R = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(I)$. [c] GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

[VO(DOCDA)]·1.5H_2O. The same procedure as described for [VO(TCDA)]·H_2O was employed. IR (KBr, cm^{-1}): ν(H_2O) 3520, 3370 (s); ν(C=O) 1670, 1650 (vs); ν(C—O) 1270 (s); ν(V=O) 950 (s). Anal. Calcd for $[C_{10}H_{16}N_2O_6V] \cdot 1.5H_2O$: C, 35.5; H, 5.7; N, 8.3. Found: C, 35.6; H, 5.7; N, 8.3.

[VO_2(TCDAH)]·2H_2O. The complex [VO(TCDA)] (0.24 g) was dissolved in 0.1 M H_2SO_4 (15 mL). To the deep blue solution was added PbO_2 (1.5 g) at room temperature with stirring. The color changed to yellow. After removal of excess PbO_2 by filtration the clear yellow solution was kept in the refrigerator for 12 h. Pale yellow crystals of [VO_2(TCDAH)]·2H_2O precipitated, which were filtered off, washed with ethanol, and air-dried. The crystals not washed and dried were suitable for X-ray crystallography and contain two H_2O molecules per formula unit. IR (KBr, cm^{-1}): ν(N—H) 3220 (m); ν(C=O) 1710 (vs), 1595 (vs); ν(C—O) 1350 (m), 1190 (m); ν(V=O) 915, 895 (s). Anal. Calcd for $C_{10}H_{18}N_3O_6V$: C, 36.70; H, 5.54; N, 12.84. Found: C, 36.6; H, 5.4; N, 13.0.

Instrumentation. The apparatus used for electrochemical measurements has been described previously.[18] Cyclic voltammograms of dried samples of complexes (~10^{-3} M) were measured in water-free acetonitrile with 0.1 M $[n\text{-}Bu_4N]PF_6$ as supporting electrolyte at scan rates of 20–200 mV s^{-1}. The ferrocenium/ferrocene couple was monitored as internal standard. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer. The magnetic susceptibility of powdered samples of the vanadyl complexes was measured by the Faraday method (Sartorius microbalance, Bruker B-E 1008 research magnet, and Bruker B-VT 1000 automatic temperature control) in the temperature range 98–293 K. Diamagnetic corrections were applied in the usual manner with use of tabulated Pascal constants.

Kinetic Measurements. The kinetics of the oxidation of [VO(TCDA)] by $[Ni([9]aneN_3)_2]^{3+}$ were measured by using stopped-flow spectrophotometry. Pseudo-first-order conditions were employed with the reductant in at least a 10-fold excess over the oxidant. The decrease in absorbance of the oxidant was followed at 365 nm as a function of time. Pseudo-first-order rate constants were calculated by use of a least-squares fitting program[19] where the absorbances at the beginning and after

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Table II. Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\times 10^3$ Å^2) of [VO(TCDA)]$\cdot$H$_2$O (**1**)

atom	*x*	*y*	*z*	U_{eq}[a]
V1	247.7 (4)	1606.0 (3)	3512.2 (2)	20.4 (1)
O1	1893 (2)	739 (2)	3928 (1)	31.6 (5)
N1	−1244 (2)	2490 (2)	4373 (1)	22.9 (4)
N2	−2065 (2)	205 (2)	3646 (1)	25.3 (5)
N3	−2448 (2)	2565 (2)	2934 (1)	23.6 (4)
C1	−1905 (3)	1373 (2)	4823 (1)	27.2 (6)
C2	−3050 (3)	399 (2)	4356 (1)	28.6 (6)
C3	−3470 (3)	248 (2)	3021 (1)	32.6 (6)
C4	−4150 (3)	1631 (2)	2890 (1)	32.4 (6)
C5	−2951 (3)	3712 (2)	3378 (1)	28.2 (6)
C6	−3018 (3)	3319 (2)	4160 (1)	28.6 (6)
C7	1594 (3)	3934 (2)	4104 (1)	30.7 (6)
C8	386 (3)	3275 (2)	4696 (1)	30.4 (6)
O2	1535 (2)	3348 (1)	3490 (1)	28.7 (4)
O3	2572 (2)	4909 (1)	4236 (1)	49.2 (6)
O4	812 (2)	1330 (1)	2486 (1)	28.2 (4)
O5	927 (2)	2365 (2)	1440 (1)	40.8 (5)
C9	148 (3)	2158 (2)	2026 (1)	27.0 (5)
C10	−1679 (3)	2935 (2)	2226 (1)	31.3 (6)
O_w	4710 (3)	2069 (2)	856 (1)	64.1 (8)

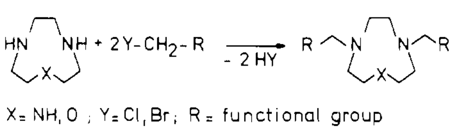
[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

completion of the reaction were treated as variables. Plots of log $(A_t - A_\infty)$ against time, where A_t and A_∞ are the absorbances at time *t* and at the end of an experiment, respectively, were linear to 4 half-lives. The ionic strength of aqueous reaction solutions was adjusted to 0.56 M by appropriate NaClO$_4$/HClO$_4$ mixtures. The kinetics of the reaction between [VO(DOCDA)] and [Ni([9]aneN$_3$)$_2$]$^{3+}$ were measured by conventional spectrophotometry with a UNICAM SP-800 spectrophotometer interfaced to a Commodore V64 computer for data acquisition. The decrease in absorbance at 360 nm was monitored as a function of time. Pseudo-first-order conditions with excess reductant were employed. Plots of log $(A_t - A_\infty)$ vs *t* were linear for at least 4 half-lives.

X-ray Crystallography. Intensities and lattice parameters of a deep blue needle-shaped crystal of **1** and of a colorless tabular-shaped crystal of **2** were measured on an AED II (Siemens) diffractometer. Crystal parameters and additional details of the data collection and reduction are given in Table I. Lattice parameters for both compounds were obtained from a least-squares fit to the setting angles of 24 reflections with $6 < 2\vartheta < 25°$. Empirical absorption corrections (ψ scans of seven reflections with $5 < 2\vartheta < 48°$ in both cases) were carried out. The structures were solved by standard Patterson and difference Fourier methods and refined[20] with anisotropic displacement parameters for all non-hydrogen atoms. Neutral atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref 21 and hydrogen atom scattering factors from ref 22. All methylene hydrogen atoms were placed at calculated positions with d(C–H) = 0.96 Å. The amine hydrogen atoms in **1** and **2** and hydrogen atoms of waters of crystallization were located in difference Fourier syntheses and were included in the final refinement cycles with isotropic thermal parameters. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(I)$. Final atom coordinates are given in Table II for **1** and Table III for **2**.

Results and Discussion

Synthesis. N-functionalized polyaza macrocycles are readily prepared from the reactions of the parent macrocycle in ethanol, e.g. 1,4,7-triazacyclononane ([9]aneN$_3$) or 1-oxa-4,7-diazacyclononane ([9]aneN$_2$O), with bromo- or chloroalkanes that contain a second functional group in stoichiometric amounts (eq 4).

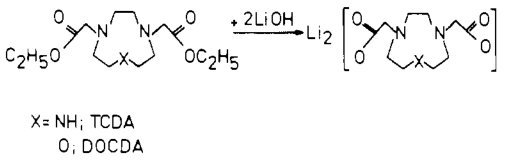


(4)

Table III. Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\times 10^3$ Å^2) of [VO$_2$(TCDAH)]$\cdot$2H$_2$O(**2**)

atom	*x*	*y*	*z*	U_{eq}
V1	1065.9 (4)	1274.2 (3)	1755.9 (3)	29.8 (2)
O1	1028 (2)	1184 (1)	722 (1)	36.5 (8)
O2	1809 (2)	470 (1)	2318 (1)	46.5 (9)
O3	2068 (2)	2246 (1)	2261 (1)	37.1 (8)
O4	3089 (2)	2924 (2)	3532 (2)	62 (1)
O5	354 (2)	5956 (1)	514 (1)	45 (1)
O6	8705 (2)	4009 (2)	365 (2)	59 (1)
N1	−401 (2)	643 (2)	1532 (2)	34 (1)
N2	669 (2)	1697 (2)	2949 (2)	32 (1)
N3	−238 (2)	2425 (2)	1214 (1)	26.3 (9)
C1	−698 (2)	568 (2)	2354 (2)	43 (1)
C2	218 (2)	888 (2)	3190 (2)	44 (1)
C3	76 (2)	2448 (2)	2799 (2)	39 (1)
C4	−102 (2)	2996 (2)	2003 (2)	34 (1)
C5	−1333 (2)	2015 (2)	848 (2)	33 (1)
C6	−1261 (2)	1035 (2)	734 (2)	38 (1)
C7	2366 (2)	2424 (2)	3124 (2)	43 (1)
C8	1746 (2)	1924 (2)	3604 (2)	45 (1)
C9	33 (2)	2896 (2)	521 (2)	31 (1)
C10	−616 (2)	3703 (2)	132 (2)	35 (1)
V2	5548.8 (4)	1146.3 (3)	1026.5 (3)	27.8 (2)
O11	5505 (2)	1397 (1)	21 (1)	39 (1)
O12	6233 (2)	233 (1)	1289 (1)	39 (1)
O13	6618 (2)	1949 (1)	1844 (1)	31.4 (8)
O14	−2373 (2)	2278 (2)	3264 (1)	49 (1)
O15	−5905 (2)	4350 (1)	−285 (2)	55 (1)
O16	3112 (2)	3944 (2)	502 (2)	53 (1)
N4	4042 (2)	498 (2)	604 (2)	33 (1)
N5	5200 (2)	1088 (2)	2311 (1)	28 (1)
N6	4276 (2)	2294 (1)	909	25 (1)
C11	3764 (2)	123 (2)	1362 (2)	40 (1)
C12	−5294 (2)	210 (2)	2262 (2)	36 (1)
C13	4504 (2)	1796 (2)	2431 (2)	32 (1)
C14	4471 (2)	2586 (2)	1847 (2)	29 (1)
C15	3161 (2)	1941 (2)	454 (2)	32 (1)
C16	3197 (2)	1082 (2)	−5 (2)	37 (1)
C17	6911 (2)	1856 (2)	2714 (2)	34 (1)
C18	6301 (2)	1156 (2)	3007 (2)	34 (1)
C19	−5501 (2)	2990 (2)	372 (2)	31 (1)
C20	−6184 (2)	3804 (2)	219 (2)	35 (1)
O_w1	7632 (2)	3934 (2)	2509 (2)	74 (1)
O_w2	−108 (2)	8842 (2)	1180 (2)	54 (1)
O_w3	6864 (2)	4174 (2)	718 (2)	53 (1)
O_w4	1656 (2)	4643 (2)	1262 (1)	43 (1)

Sodium ethanolate is used to neutralize the generated equivalents of HBr or HCl. Thus, the reaction with 2-bromoacetic acid ethyl ester yields the corresponding diesters in good yields. Hydrolysis of these esters with LiOH$\cdot$H$_2$O in ethanol affords the dilithium salts as water-soluble solid materials (eq 5). These pentadentate



(5)

ligands coordinate in methanolic solution with VO(acac)$_2$ (acac = acetylacetonate(1−)) to produce the deep blue neutral complexes [VO(TCDA)] (**1**) and [VO(DOCDA)], respectively, and uncoordinated acac. In the infrared spectrum the vanadyl group gives rise to a strong ν(V=O) band at 950 cm^{-1} in both cases. The electronic spectrum of **1** measured in aqueous solution exhibits two typical d–d transitions at 786 nm (ϵ = 20 L mol^{-1} cm^{-1}) and 571 nm (ϵ = 33 L mol^{-1} cm^{-1}). For [VO(DOCDA)] two maxima at 780 nm (ϵ = 21 L mol^{-1} cm^{-1}) and 594 nm (ϵ = 16 L mol^{-1} cm^{-1}) are observed. Both spectra do not change in 0.5 M HClO$_4$ for at least 12 h at room temperature. The same positions of the absorption maxima were found in the reflectance spectra of solid samples of both compounds. These results indicate that no ligand dissociation processes occur in water and 0.5 M perchloric acid. The stability is such that dissociation and subsequent protonation of the pendant –CH$_2$CO$_2^-$ arms of the ligands are not observed

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(20) All computations were carried out on an ECLIPSE computer using the SHELXTL program package.

(21) *International Tables of Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(22) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

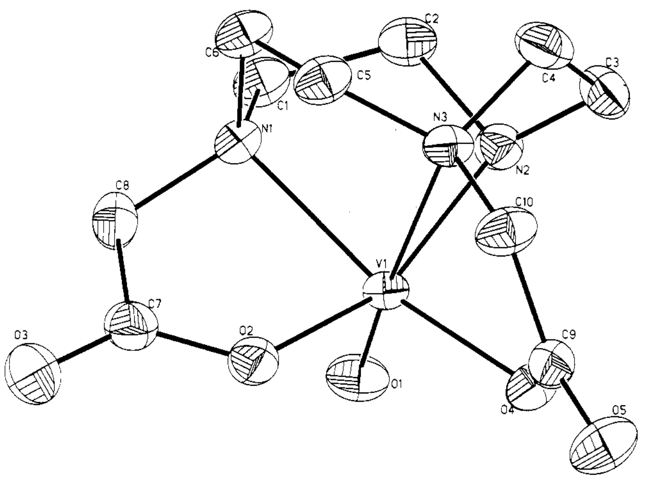

Figure 1. Perspective view of the molecule VO(TCDA) in **1** and atom-labeling scheme.

Table IV. Selected Bond Distances (Å) and Angles (deg) of $[VO(TCDA)]\cdot H_2O$ (**1**)

V1–O1	1.608 (1)	V1–N3	2.310 (2)
V1–N1	2.114 (2)	V1–O2	1.994 (1)
V1–N2	2.134 (2)	V1–O4	1.983 (1)
O1–V1–N1	101.4 (1)	N1–V1–N2	81.6 (1)
O1–V1–N2	93.3 (1)	N1–V1–N3	78.4 (1)
O1–V1–N3	170.8 (1)	N1–V1–O2	80.5 (1)
O1–V1–O2	102.7 (1)	N1–V1–O4	154.0 (1)
O1–V1–O4	104.5 (1)	N2–V1–N3	77.6 (1)
N2–V1–O2	158.0 (1)		
N2–V1–O4	99.5 (1)		
N3–V1–O2	86.4 (1)		
N3–V1–O4	76.5 (1)		
O2–V1–O4	91.2 (1)		

under these conditions. Both **1** and VO(DOCDA) have a temperature-independent magnetic moment (100–300 K) of 1.7 μ_B per vanadium(IV) center. This is also typical for vanadyl complexes.

Oxidation of **1** with PbO_2 in 0.1 M sulfuric acid leads to a yellow solution from which yellow crystals of $[VO_2(TCDAH)]\cdot 2H_2O$ (**2**) slowly precipitated at 0 °C. The infrared spectrum of **2** indicates the presence of one uncoordinated, protonated carboxylic group (ν(C═O) 1710 (s) cm^{-1}) and one coordinated carboxylate (ν(C═O) 1595 (vs) cm^{-1}); the *cis*-VO_2 group exhibits two V═O stretching frequencies at 915 cm^{-1} (ν_{as}(V═O)) and 895 cm^{-1} (ν_s(V═O)). Thus in **2** the macrocyclic ligand is only tetradentate (see below). Interestingly, the same product **2** is formed from **1** when the strong outer-sphere one-electron oxidant $[Ni([9]aneN_3)_2]^{3+}$ is used.

Description of Structures. Blue crystals of **1** consist of the neutral complex [VO(TCDA)] and a water of crystallization. Figure 1 shows such a complex and the atom-labeling scheme; Table IV summarizes important bond distances and angles. The vanadium(IV) ion is in a severely distorted octahedral environment with one secondary amine and two tertiary amine nitrogen atoms, two carboxylate oxygen atoms, and one terminal oxo ligand (*fac*-N_3O_3 donor set). The ligand 1,4,7-triazacyclononane-*N*,*N'*-diacetate is pentadentate. The V═O distance is short (1.608 (1) Å), indicating the considerable double-bond character typical of vanadyl(IV) complexes.[5-7] The V—N bond trans to the V═O group is long (V1–N3 = 2.310 (2) Å), which is characteristic for the strong trans influence of the V═O group. The other two V—N bonds of the secondary amine group (V1–N2) and the tertiary amine group (V1–N1) are shorter. The conformation of the three five-membered V-N-C-C-N chelate rings is (λλλ) or (δδδ); both enantiomers are present in the centrosymmetric unit cell. Interestingly, the two five-membered chelate rings built by the coordinated carboxylates, $\overline{\mathrm{V{-}O{-}C{-}C{-}N}}$, adopt the (λλ) conformation if the cyclononane chelate rings are (δδδ)-configured (this situation is depicted in Figure 1) and vice versa.

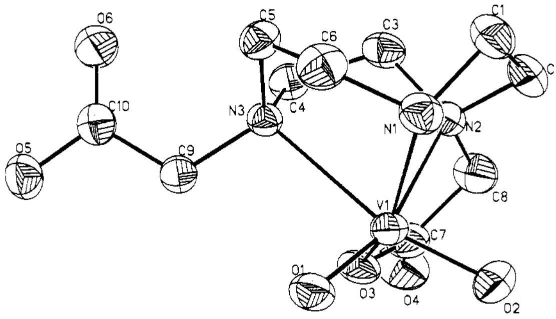

Figure 2. Perspective view of one crystallographically independent molecule of $VO_2(TCDAH)$ in **2** and atom-labeling scheme.

Table V. Selected Bond Distances (Å) and Angles (deg) of One Independent Molecule in $[VO_2(TCDAH)]\cdot 2H_2O$ (**2**)

V1–O1	1.641 (2)	V1–N1	2.094 (2)
V1–O2	1.628 (2)	V1–N2	2.255 (3)
V1–O3	1.964 (2)	V1–N3	2.403 (2)
O1–V1–O2	106.1 (1)	O2–V1–O3	99.4 (1)
O1–V1–O3	103.9 (1)	O2–V1–N1	94.9 (1)
O1–V1–N1	96.4 (1)	O2–V1–N2	92.1 (1)
O1–V1–N2	161.3 (1)	O2–V1–N3	165.2 (1)
O1–V1–N3	87.2 (1)	O3–V1–N1	150.7 (1)
O3–V1–N2	76.9 (1)		
O3–V1–N3	83.4 (1)		
N1–V1–N2	77.2 (1)		
N1–V1–N3	76.7 (1)		
N2–V1–N3	74.2 (1)		

Yellow crystals of **2** consist of the neutral species $[VO_2(TCDAH)]$ and water molecules of crystallization. Two crystallographically independent complexes are in one-fourth of the unit cell present. The dimensions of both molecules are identical within experimental error. Figure 2 shows one of these molecules and the atom-labeling scheme; Table V gives pertinent bond distances and angles. The vanadium(V) center is also in a distorted-octahedral environment comprised of three amine nitrogen atoms, two terminal oxo groups, and one coordinated carboxylato group. The ligand 1,4,7-triazacyclononane-*N*,*N'*-diacetate is only tetradentate; one pendant arm of the ligand is uncoordinated and bent away from the V(V) center and is protonated. The terminal oxo groups are cis with respect to each other as has been observed in $K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$[8] and other dioxovanadium(V) complexes.[9] The two V═O distances in **2** are equidistant but longer than the one in **1**. They are still indicative of V═O double bonds. It is interesting that the two V—N bonds trans to the VO_2 moiety (V1–N2 and V1–N3) are longer than the third V1–N1 bond (trans influence) but they are *not* equidistant, although both nitrogen atoms are tertiary amine nitrogens. This may be due to the fact that N2 carries a coordinated pendant arm whereas the arm connected to N3 is uncoordinated. Formation of the five-membered $\overline{\mathrm{V{-}O{-}C{-}C{-}N}}$ ring may induce a V—N shortening in order to reduce the strain within this chelate ring.

The C—C, C—N, and C—O bond lengths do not show any unusual features in either structure. They will not be discussed in detail here.

Electrochemistry. The cyclic voltammograms of [VO(TCDA)] and [VO(DOCDA)] ([VO] = 7.5×10^{-4} M) in dry acetonitrile that contained 0.1 M $[n\text{-}Bu_4N]PF_6$ as supporting electrolyte exhibit one reversible electron-transfer process in the potential range +0.5–1.5 V vs Ag/AgCl at 20 °C. The peak-to-peak separation of 70 mV and an i_{pc}/i_{pa} ratio of 1.0 ± 0.05, which were both found to be independent of the scan rate (20–200 mV s^{-1}), indicate the electrochemical reversibility of this one-electron transfer. Controlled-potential coulometry established a one-electron oxidation (1.0 ± 0.1 e) of both vanadyl complexes. The formal redox potentials for the couples $[VO(TCDA)]^{+/0}$ and $[VO(DOCDA)]^{+/0}$

Table VI. Summary of Kinetic Data for the Reactions between VO(TCDA), VO(DOCDA), and $[\mathrm{Ni([9]aneN_3)_2}]^{3+}$ at 25 °C

10^3[VO], M	$10^4[\mathrm{Ni^{III}}]$, M	[H$^+$], M	k_{obsd}, s^{-1} [a]
	VO(TCDA)		
0.94	1.7	*b*	0.54 (1)
1.6	2.0	*c*	0.94 (3)
1.6	3.0	0.56	1.15 (6)
1.6	1.5	0.02	1.12 (2)
1.9	2.0	0.10	1.49 (7)
3.7	3.0	0.02	2.7 (2)
4.8	3.0	0.02	3.9 (2)
9.6	3.0	0.02	6.7 (2)
	VO(DOCDA)		
0.75	1.65	0.02	0.009 (1)
1.10	1.65	0.02	0.014 (3)
1.60	1.65	0.02	0.020 (6)
3.80	1.65	0.02	0.057 (2)

[a] Ionic strength (I) 0.56 M ($\mathrm{LiClO_4/HClO_4}$). [b] I = 0.20 M (KCl/HCl buffer, pH 2). [c] I = 0.20 M (phthalate/HCl buffer, pH 3).

were determined to be 0.427 V vs Fc$^+$/Fc and 0.622 V vs Fc$^+$/Fc, respectively:

$$[\mathrm{V^VOL}]^+ + e^- \rightleftarrows [\mathrm{V^{IV}OL}]^0 \qquad (6)$$

Thus, $[\mathrm{V^VO(DOCDA)}]^+$ is a stronger oxidant than $[\mathrm{V^VO(TCDA)}]^+$ by 0.195 V. These experimental redox potentials may tentatively be referenced vs the normal hydrogen electrode (NHE) by adding 400 mV to the above values:[23] for $[\mathrm{VO(TCDA)}]^{+/0}$, $E_{1/2}$ = 0.827 V vs NHE; for $[\mathrm{VO(DOCDA)}]^{+/0}$, $E_{1/2}$ = +1.022 V vs NHE.

In aqueous solution only an irreversible oxidation peak has been observed for both complexes, indicating the instability of the oxovanadium(V) species in this medium.

Kinetics and Mechanism of the Oxidation Reactions of $[\mathrm{V^{IV}OL}]$ Complexes. Orange $[\mathrm{Ni^{III}([9]aneN_3)_2](ClO_4)_3}$ in aqueous solution is a strong one-electron oxidant;[14,15] the reduced form is blue $[\mathrm{Ni([9]aneN_3)_2}]^{2+}$, and the redox potential for the couple $\mathrm{Ni^{III}/Ni^{II}}$ has been determined to be +0.95 V vs NHE at 25 °C. McAuley and co-workers have used this complex in a series of outer-sphere electron-transfer reactions.[24,25] They have determined the self-exchange rate constant k_{11} to be 6×10^3 M^{-1} s^{-1} at 25 °C (I = 1.0 M):[25]

$$[\mathrm{Ni([9]aneN_3)_2}]^{3+} + [\mathrm{Ni([9]aneN_3)_2}]^{2+} \xrightleftharpoons{k_{11}} [\mathrm{Ni([9]aneN_3)_2}]^{2+} + [\mathrm{Ni([9]aneN_3)_2}]^{3+} \qquad (7)$$

The reaction of VO(TCDA) or VO(DOCDA) with $[\mathrm{Ni([9]aneN_3)_2}]^{3+}$ in acidic aqueous solution yields $[\mathrm{Ni([9]aneN_3)_2}]^{2+}$ and $[\mathrm{VO_2(TCDAH)}]$ or $[\mathrm{VO_2(DOCDAH)}]$. The stoichiometry of these reactions was determined spectrophotometrically to be 1:1, as in eq 8 and 9. The kinetics of eq 8 was studied at 25 °C

$$[\mathrm{VO(TCDA)}] + [\mathrm{Ni([9]aneN_3)_2}]^{3+} \xrightarrow[-\mathrm{H^+}]{+\mathrm{H_2O}} [\mathrm{VO_2(TCDAH)}] + [\mathrm{Ni([9]aneN_3)_2}]^{2+} \qquad (8)$$

$$[\mathrm{VO(DOCDA)}] + [\mathrm{Ni([9]aneN_3)_2}]^{3+} \xrightarrow[-\mathrm{H^+}]{+\mathrm{H_2O}} [\mathrm{VO_2(DOCDAH)}] + [\mathrm{Ni([9]aneN_3)_2}]^{2+} \qquad (9)$$

(I = 0.56 M) by using stopped-flow spectrophotometry. Pseudo-first-order conditions with the VO(TCDA) complex in large excess ([VO] = (1.6–9.6) $\times 10^{-3}$ M) over the oxidant ($[\mathrm{Ni^{III}}]$ = 1.5×10^{-4} M) were employed in acid aqueous solution ([H$^+$] = 0.02–0.56 M). Pseudo-first-order rate constants are listed in Table VI. A simple second-order rate law (eq 10) was established, and

$$-\mathrm{d}[\mathrm{Ni^{III}}]/\mathrm{d}t = k_{12}[\mathrm{VO}][\mathrm{Ni^{III}}] \qquad (10)$$

the second-order rate constant, k_{12}, was determined to be 685 M^{-1} s^{-1} at 25 °C (I = 0.56 M). This value was found to be independent of the acid concentration, the ionic strength employed, and the nature of the buffer system used.

The kinetics of the reaction between VO(DOCDA) and $[\mathrm{Ni([9]aneN_3)}]^{3+}$ were measured by using conventional spectrophotometry under conditions otherwise identical with those described for the reaction of VO(TCDA) with the $\mathrm{Ni^{III}}$ oxidant. Again a simple second-order rate law (eq 10) has been found; the numerical value of k_{13} is 14 M^{-1} s^{-1} at 25 °C (I = 0.56 M) (Table VI).

Since both reactants, the $\mathrm{Ni^{III}}$ and the vanadyl complexes, do not have labile coordination sites available at the respective metal ions, the electron-transfer step must be of the outer-sphere type. The question to be answered in the following section is as follows: What is the rate-determining step in eq 8 and 9? In principle two plausible possibilities are to be considered. The final oxidation products in acidic aqueous medium are not the $[\mathrm{V^VO(TCDA)}]^+$ or $[\mathrm{V^VO(DOCDA)}]^+$ cations but the neutral *cis*-dioxovanadium(V) complexes, and k_{12} (or k_{13}) or, alternatively, k_b in eq 11 and 12 could be rate-determining. The fact that the rate law does

$$[\mathrm{VOL}] + [\mathrm{Ni([9]aneN_3)_2}]^{3+} \xrightarrow{k_{12},\,k_{13}} [\mathrm{VOL}]^+ + [\mathrm{Ni([9]aneN_3)_2}]^{2+} \qquad (11)$$

$$[\mathrm{VOL}]^+ + \mathrm{H_2O} \xrightarrow{k_\mathrm{b}} [\mathrm{VO_2(LH)}] + \mathrm{H^+} \qquad (12)$$

not include an [H$^+$] dependence indicates that the outer-sphere electron-transfer step is rate-determining. If this is true, the reactivity difference of 49 between the rates of oxidation of VO(TCDA) and VO(DOCDA) by $[\mathrm{Ni([9]aneN_3)_2}]^{3+}$ (k_{12}/k_{13}) can be analyzed by using the Marcus cross relation for outer-sphere electron-transfer reactions (eq 13 and 14). If we assume that

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (13)$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)} \qquad (14)$$

the self-exchange rate constants k_{22} and k_{33} for the two vanadyl complexes and f_{12} and f_{13} are identical, we can write eq 15. Since

$$k_{12}/k_{13} = (K_{12}/K_{13})^{1/2} \qquad (15)$$

K_{12} and K_{13} are calculated from the known redox potentials of reductants and the oxidant,[26] the calculated reactivity difference between the redox reactions, k_{12}/k_{13}, is 45, which is in very good agreement with the experimental difference of reactivity.[27] This rough estimate corroborates the assignment of the outer-sphere electron-transfer step in eq 11 as the rate-determining step.

It is also possible to calculate the self-exchange rate constants k_{22} and k_{33} for the couples $[\mathrm{VO(TCDA)}]^{+/0}$ and $[\mathrm{VO(DOCDA)}]^{+/0}$. Since the driving force for the reaction between [VO(DOCDA)] and $[\mathrm{Ni([9]aneN_3)_2}]^{3+}$ is very small, f_{12} is set to unity and k_{22} = 0.54 M^{-1} s^{-1}. For VO(TCDA) a numerical value for f_{13} of 0.87 has been calculated, which yields k_{22} = 0.75 M^{-1} s^{-1}. It is instructive to compare these values with the self-exchange rate constant for the couple $\mathrm{VO(OH)^{2+}(aq)/VO(OH)^+(aq)}$, which has recently been determined by McAuley and co-workers[25] using the Marcus cross relation for the reaction between $[\mathrm{Ni^{III}([9]aneN_3)_2}]^{3+}$ and $\mathrm{VO(OH)^+(aq)}$. A numerical value of 7.0 M^{-1} s^{-1} (25 °C, I = 1.0 M) has been reported. This value is quite

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[24] McAuley, A.; Spencer, L.; West, P. R. *Can. J. Chem.* **1985**, *63*, 1198.

[25] Macartney, D. H.; McAuley, A.; Olubuyide, O. A. *Inorg. Chem.* **1985**, *24*, 307.

[26] Since only the ratio K_{12}/K_{13} is of importance in eq 15, the true redox potentials for the two vanadyl(IV) complexes *in aqueous solution* must not necessarily be known as long as the difference of the two redox potentials is the same in acetonitrile (measured) and water, which we assume here to be true.

[27] The rate constants k_{12} and k_{13} represent the product of the ion-pair formation constants between the vanadyl complexes and the oxidant $[\mathrm{Ni([9]aneN_3)_2}]^{3+}$, K_{IP} (M^{-1}), and the intramolecular electron-transfer rate constant, k_{et} (s^{-1}). Since the size and charge of both vanadyl complexes are the same, the observed reactivity difference is proposed to be due to differences of k_{et} for the two systems.

similar to those found in this work for the chelated vanadyl complexes VO(TCDA) and VO(DOCDA).

In summary, the analysis of the observed reactivity between VO(TCDA) or VO(DOCDA) and $[Ni([9]aneN_3)_2]^{3+}$ gives a consistent picture assuming the outer-sphere electron-transfer step to be rate-determining. The hydrolysis of the generated VOL species to the *cis*-dioxovanadium(V) complexes, which involves the unbinding of one coordinated pendant arm of the macrocyclic ligand, is a rapid subsequent step in reactions 8 and 9.

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Registry No. **1**, 114675-42-2; **2**, 114675-44-4; VO(DOCDA), 114675-43-3; $[VO(TCDA)]^+$, 114691-60-0; $[VO(DOCDA)]^+$, 114675-45-5; $[Ni([9]aneN_3)_2]^{3+}$, 86709-81-1; $Li_2(TCDA)$, 114691-59-7; $Li_2(DOCDA)$, 114675-41-1; $VO(acac)_2$, 3153-26-2; 1,4,7-triazacyclononane, 4730-54-5; 2-bromoacetic acid ethyl ester, 105-36-2; 1-oxa-4,7-diazacyclononane, 80289-59-4.

Supplementary Material Available: Tables of refined and calculated positions of hydrogen atoms, anisotropic thermal parameters, and intraligand bond distances and angles for $[VO(TCDA)]\cdot H_2O$ and $[VO_2(TCDAH)]\cdot 2H_2O$ and a view of the second molecule in $[VO_2(TCDAH)]\cdot H_2O$ (8 pages); listings of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of H_2O_2 Decomposition Catalyzed by Cu^{2+} in Alkaline Solution[1]

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The kinetics of the Cu^{2+}-catalyzed decomposition of hydrogen peroxide have been studied at pH 11–12. The disappearance of hydrogen peroxide and the appearance of dissolved dioxygen have been followed titrimetrically and potentiometrically. Alkaline decomposition in the presence of copper(II) is accompanied by formation of a superoxide–copper(I) complex, formally, $[HO_2–Cu(I)]$. The apparent complex formation constant $K_{app} = [HO_2–Cu(I)]/[H_2O]_f[Cu^{2+}]_f$, where $[H_2O_2]_f$ and $[Cu^{2+}]_f$ are the concentrations of free hydrogen peroxide and free copper(II) ion, respectively, has been determined at several pH values. The results are consistent with a complex of molecular formula $HO_2Cu(OH)_2^-$, which has extinction coefficient $\geq 1600\ M^{-1}\ cm^{-1}$ at 345 nm and acid dissociation constant $K_e = [O_2Cu(OH)_2^{2-}][H^+]/[HO_2Cu(OH)_2^-] = 3.55 \times 10^{-12}$ M. The experimental time course of the reaction (graphs of $[H_2O_2]$ vs time) can be obtained by integrating the rate law $-dy/dt = wy^2/(\breve{v} + sy + uy^2)$, where y is $[H_2O_2]$ and w, v, s, and u are complicated constants composed of rate constants and initial concentrations. Computer simulations with a mechanism in which complex formation is accompanied by reactions involving $OH^\bullet$, $HO_2^\bullet$, and $O_2^{\bullet-}$ radicals give excellent agreement with a variety of experimental observations. The relevance of the proposed mechanism to the Cu^{2+}-catalyzed decomposition of H_2O_2 in acid solution and to the Fe^{3+}-catalyzed reaction is discussed briefly.

Introduction

It has been known for about a century that the decomposition of H_2O_2 to H_2O and O_2 is drastically accelerated by many metal ions, among which Fe^{3+}/Fe^{2+} and Cu^{2+} have been investigated in depth.[2-6] Disagreements over mechanistic details, especially involving intermediate radicals or complexes, have lasted for decades.[7] There is evidence that the kinetics and mechanism of H_2O_2 decomposition catalyzed by iron and copper ions are dissimilar. This work focuses on the catalyst Cu^{2+}.

Sigel and colleagues[6] studied the kinetics of this reaction in acidic solution. A mechanism involving complexes but no radicals was suggested, which accounts for the experimental rate law. It assumes that, rather than changing its oxidation state, Cu^{2+} plays the role of a catalytic template that forms a bridge linking the two molecules of H_2O_2 that are going through oxidation and reduction.

Glasner[5] investigated the same reaction in alkaline solution with organic ligand present. He confirmed the formation of copper peroxide complex and used its absorbance to follow the reaction spectrophotometrically. Oxygen evolution out of the reaction solution was also measured. Both monitoring methods showed initial lags and fast subsequent increases in the reaction rate. Again, no radical was involved in the suggested mechanism.

However, the EPR experiment by Vierke[8] convincingly demonstrated the existence of $O_2^{\bullet-}$ and $OH^\bullet$ radicals in the decomposition of H_2O_2 catalyzed by Cu^{2+} at pH 12–13 in aqueous solution without organic ligands. Vierke further showed that when copper ion forms a complex (brown precipitate under his experimental conditions) with peroxide at the beginning of O_2 evolution, the EPR signal of copper(II) disappears. A new Cu(II) EPR signal, different from that of Cu^{2+}, CuO, or $Cu(OH)_2$, was detected after O_2 started to bubble and disappeared at the cessation of the bubbling. The molecular formula of neither the Cu(II) EPR-silent compound nor the EPR-active compound was identified.

We report here experiments carried out in strongly alkaline medium. We suggest a molecular formula for the Cu(II) EPR-silent copper peroxide complex, and we have measured its minimum extinction coefficient, as well as its equilibrium formation constant as a function of pH. We have determined the rate law valid in strongly alkaline solution and proposed a mechanism consistent with the experimentally observed rate law. We have fitted the integrated theoretical rates to the reaction progress curves

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