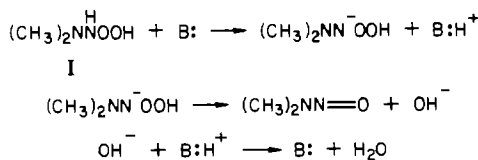
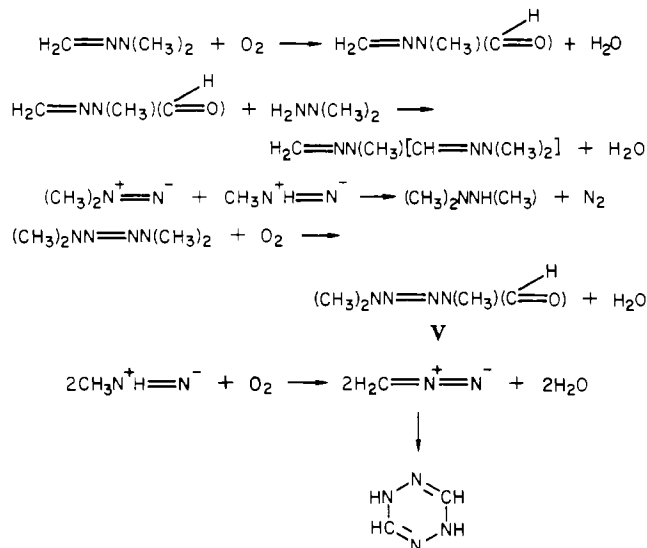


Scheme IV



Scheme V



formation of $(\text{CH}_3)_2\text{NN}=\text{CH}_2$ can be explained as previously reported by Sisler et al.^{1b} (Scheme II).

The formation of 1,1,4,4-tetramethyl-2-tetrazene can readily occur through the dimerization of dimethyldiazene. A reasonable pathway for the formation of formaldehyde methylhydrazone and its dimer, *sym*-hexahydro-1,4-dimethyltetrazene, would begin with the reaction of two molecules of II (Scheme III). Both III and IV are known compounds.^{10,14,15}

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The presence of III in the reaction product is confirmed by the presence of a typical quartet in the proton NMR spectrum at δ 6.3. The dimer IV is confirmed by the appropriate peaks in the mass spectrum. The retention times of III and IV (in benzene solution) in the gas chromatographic analysis are the same.

Other products confirmed by proton NMR, by mass spectra, and by gas chromatographic analysis include *N*-nitrosodimethylamine and water. The formation of *N*-nitrosodimethylamine and water can occur through the decomposition of I which Urry⁴ has indicated might be base catalyzed (Scheme IV). Though Urry⁴ and Loper⁵ have discussed the possibility of the formation of *N*-nitrosodimethylamine in the gas-phase reaction of dimethylhydrazine and air, no quantitative data concerning the extent of its formation were given. In our studies in the liquid phase, the amount of *N*-nitrosodimethylamine ranges between 1.5% and 13.9% of the reaction product as measured by gas chromatography. The magnitude of these yields combined with the carcinogenic character of *N*-nitrosodimethylamine make these results a basis for concern with respect to the utilization of dimethylhydrazine.

The identities of the remaining four products observed are inferred from gas chromatographic and mass spectral analyses. Scheme V reasonably accounts for the formation of some of these products. The formation of V has been reported as a product of the oxidation of 1,1,4,4-tetramethyl-2-tetrazene by chloramine.¹⁶

Acknowledgment. The authors gratefully acknowledge the support of the research by the Air Force Office of Scientific Research through a grant to the University of Florida.

Registry No. III, 36214-48-9; IV, 695-20-5; V, 20642-57-3; $(\text{CH}_3)_2\text{NNH}_2$, 57-14-7; O_2 , 7782-44-7; N_2 , 7727-37-9; CH_4 , 74-82-8; NH_3 , 7664-41-7; H_2O , 7732-18-5; $(\text{CH}_3)_2\text{NH}=\text{CH}_2$, 2035-89-4; $(\text{CH}_3)_2\text{NNO}$, 62-75-9; $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$, 6130-87-6; $\text{CH}_2=\text{NN}(\text{CH}_3)\text{CH}=\text{NN}(\text{CH}_3)_2$, 75400-49-6; $(\text{CH}_3)_2\text{NNH}(\text{CH}_3)$, 1741-01-1; $(\text{NHCH}=\text{N})_2$, 61626-05-9.

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Existence of Stereoselectivity in the Outer-Sphere Redox Reaction between Di- μ -oxo- μ -(propylenediaminetetraacetato)-bis[oxomolybdate(V)] and μ -Amido- μ -hyperoxo-bis[bis(ethylenediamine)cobalt(III)] in Aqueous Solution

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Received April 25, 1980

The oxidation of $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{R},\text{S-pdta})]^{2-}$ (1) (pdta = propylenediaminetetraacetate) with Δ, Δ - $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2^{(-)})\text{-Co}^{\text{III}}(\text{en})_2]^{4+}$ (2) (en = ethylenediamine) to give molybdenum(VI) species and μ -amido- μ -peroxo-dicobalt(III) complex exhibits stereoselectivity in aqueous solution of pH 3.5 and 4.6 at 25 °C at ionic strengths (*I*) from 0.2 to 2.0 M. An equimolar (2.69×10^{-3} M; M = mol dm⁻³) mixture of 1 and 2 undergoes redox reaction (stoichiometry 1:2) to leave the half amount of 1 unreacted, the enantiomeric excess depending on *I*; ca. 0.15% in favor of *R*-pdta complex at *I* = 0.2 M and ca. 0.25% in favor of *S*-pdta complex at *I* = 2.0 M. The pseudo-first-order rate constants (k_{obsd}) determined with racemic oxidant in the presence of an excess of the molybdenum(V) complex at 25 °C are expressed by $k_{\text{obsd}} = 2k_e K_{\text{IP}}[\text{Mo}_2]/(1 + K_{\text{IP}}[\text{Mo}_2])$, where K_{IP} and k_e are the ion-pair formation constant between the redox couple and the electron-transfer rate constant within the ion pair, respectively. K_{IP} (51 ± 7 M⁻¹ at *I* = 0.2 M) decreases and k_e (0.76 ± 0.07 s⁻¹ at *I* = 0.2 M) increases with increase in ionic strength. The difference in selectivity with ionic strength can be interpreted by assuming different selectivities for K_{IP} and k_e .

Introduction

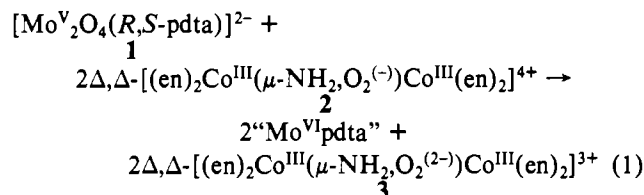
Existence of stereoselectivity in outer-sphere redox reactions has been discussed by several authors but remains uncertain.

Grossman and Wilkins measured the rate of reduction of various optically active iron(III) and cobalt(III) complexes with Δ - $[\text{Fe}^{\text{II}}(\text{R-pdta})]^{2-}$ (*R*-pdta = (*R*)-propylenediamine-

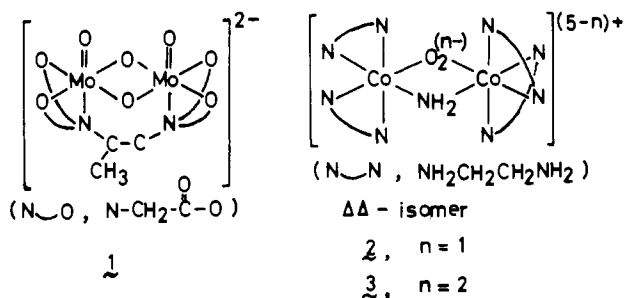
tetraacetate) but found no appreciable difference in rates between the enantiomers of oxidants.¹ Sutter and Hunt reported that the oxidation of $[\text{Cr}^{\text{II}}(\text{phen})_3]^{2+}$ (phen = 1,10-phenanthroline) with $\Delta\text{-}[\text{Co}^{\text{III}}(\text{phen})_3]^{3+}$ gave $\Delta\text{-}[\text{Cr}^{\text{III}}(\text{phen})_3]^{3+}$ with an optical purity as high as 89%, but their result was not reproduced by Kane-Maguire et al.³ The latter group further examined the optical activity of reaction products of various redox systems involving chromium(II) and optically active cobalt(III) complexes and concluded that no stereoselectivity was detected in outer-sphere redox processes.³ Recently Armstrong and Sykes examined the oxidation of reduced parsley ferredoxin containing the Fe(II, III) cluster $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{3-}$ (SR = coordinated cysteine of the peptide chain) with $\Delta\text{-}$ and $\Delta\text{-}\Delta\text{-}[\text{Co}^{\text{III}}(\text{en})_3]^{3+}$ (en = ethylenediamine), but no appreciable difference was found between the rates of oxidation.^{4,5}

Careful examination of these papers suggests that the following two points seem particularly important: (a) measurement of the rate constants involves an experimental error as high as 5%, while the extent of selectivity may be very small; (b) whenever optical activity of the reaction product between a racemic reductant and an optically active oxidant is examined, the product can racemize through electron self-exchange involving labile reductant (e.g., optically active chromium(III) complexes racemize quickly in the presence of chromium(II) compounds).

We thought that stereoselectivity may be more readily observed by use of binuclear complexes rather than uninuclear species and investigated the existence of stereoselectivity in the redox reaction (1).⁶ When a stoichiometrical excess of



1 was used, the unreacted part of **1** showed a small but un-



ambiguous optical activity. Other possible factors than the stereoselectivity affecting the optical activity of unreacted part of **1**, in the redox reaction, have been carefully examined, and their participation was denied. Thus the result provided a first

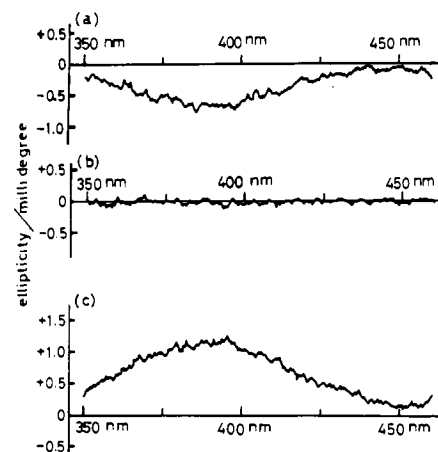


Figure 1. Examples of CD spectra of the recovered $[\text{Mo}_2\text{O}_4(\text{pdta})]^{2-}$, from the reaction mixture at (a) $I = 0.2$, (b) 0.5, and (c) 2.0 M. Concentrations of the molybdenum(V) dimer are (a) 2.63×10^{-3} , (b) 1.78×10^{-3} , and (c) 2.16×10^{-3} M, as determined by the intensity of absorption peak at 388 nm.

conclusive evidence for the existence of stereoselectivity in outer-sphere redox reactions between metal complexes. A preliminary account of this work was reported,⁷ and this paper deals with the details of the studies.

Experimental Section

Materials. Compounds **1** and **2** were prepared as sodium^{8,9} and chloride salts,¹⁰ respectively, and the latter was resolved with silver *d*-bromocamphorsulfonate by the known method.^{11,12} Other reagents were commercially obtained and used as received.

Measurement of Stereoselectivity of the Reaction. Aqueous solutions of **1** and the $\Delta\Delta$ isomer of **2** were mixed to give a solution (8 cm³) containing equimolar amounts (2.69×10^{-3} M; M = mol cm⁻³) of the reactants at appropriate ionic strengths ($I = 0.2$ –2.0 M, adjusted with LiClO_4), so that half of **1** remained unchanged after the redox reaction. So that the formation of precipitate (probably molybdate(VI) salt of the dicobalt ion(s)) during the course of the redox reaction was avoided, 1.34×10^{-3} M $\text{Na}_2\text{H}_2\text{edta}$ (edta = ethylenediaminetetraacetate) was added. The pH was kept at 4.6 with acetate buffer (total acetate concentration, 0.01 M). The redox reaction was completed within 1 h at 25 °C. The solution was diluted with water to make the ionic strength less than 0.1 M and passed through a column (1.8 cm in diameter, 4 cm in length) of QAE Sephadex A-25 resin in Cl⁻ form. The column was washed with water, and the orange band was eluted with ca. 0.5 M NaCl solution. The whole eluate was evaporated in a rotary evaporator to ca. 10 cm³, and its absorption and circular dichroism (CD) spectra were recorded.

The reaction mixtures were also treated with a cation-exchange column containing SP Sephadex C-25 resin in Na⁺ form. The dicobalt(III) species were absorbed. The orange eluates were concentrated to ca. 10 cm³, and the absorption and CD spectra were measured.

Kinetic Study. Kinetic studies were carried out under pseudo-first-order conditions with the molybdenum complex in at least 10-fold excess to the racemic μ -hyperoxo complex. The progress of the reaction was followed at 688 nm, where the μ -hyperoxo complex has a strong absorption peak ($\epsilon = 485$).¹⁰ First-order plots of the absorbance change gave straight lines, from the slope of which the first-order rate constant (k_{obs}) was estimated.

Measurements. The absorption and CD spectra were recorded with a Hitachi 323 spectrophotometer and a Jasco J-40 spectropolarimeter, respectively. The kinetic studies were carried out with a Hitachi 124

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Table I. CD Strength in $\Delta\epsilon$ at 387 nm of Unreacted $[\text{Mo}_2\text{O}_4(\text{pdta})]^{2-}$ and the Enantiomeric Excess^a

	<i>I</i>					
	0.2	0.35	0.5	1.0	1.5	2.0
$\Delta\epsilon/10^{-3}$ (pH 4.6)	-8	-2	0	+7	+11	+14
(pH 3.5)	-10					+17
<i>ee</i> ^b /%	0.15 (<i>R</i>)	0.036 (<i>R</i>)	0	0.13 (<i>S</i>)	0.20 (<i>S</i>)	0.25 (<i>S</i>)
(pH 3.5)	0.18 (<i>R</i>)					0.29 (<i>S</i>)

^a Values are subject to ca. 20% uncertainty. ^b *R* and *S* in parentheses indicate that the values are in favor of the *R*-pdta and the *S*-pdta complexes, respectively.

spectrophotometer with a Hitachi QPD-34 recorder. The pH was measured with an E300B pH meter of Metrohm Herisau.

Results and Discussion

I. Stereoselectivity of the Redox Reaction. a. Optical Activity of the Unreacted Molybdenum(V) Complex. The absorption spectra of the concentrated eluates of the anion-exchange chromatography coincided with that of $[\text{Mo}_2\text{O}_4(\text{R,S-pdta})]^{2-}$. Pure $[\text{Mo}_2\text{O}_4(\text{R-pdta})]^{2-}$ gives a negative CD peak at 387 nm with $\Delta\epsilon = -5.5$.⁸ Their CD spectra (Figure 1) give small but unambiguous peaks at 387 nm. Table I shows the $\Delta\epsilon_{\text{app}}$ values at 387 nm of the remaining $[\text{Mo}_2\text{O}_4(\text{pdta})]^{2-}$ at various ionic strengths. The $\Delta\epsilon_{\text{app}}$ values were reproducible within the range of ca. 20% uncertainty, and their values in Table I are the averages of at least three repeated experiments. The cation-exchange chromatography gave very similar values to those in Table I. Experiments were also carried out at pH 3.5 and ionic strengths 0.2 and 2.0 M, to find that pH does not give significant influence on the stereoselectivity in this region.

b. Absence of Resolution and Racemization during Ion Exchange. Studies with the optically pure $[\text{Mo}_2\text{O}_4(\text{R-pdta})]^{2-}$ complex solution disclosed that no racemization took place during the anion-exchange chromatography. When racemic $[\text{Mo}_2\text{O}_4(\text{R,S-pdta})]^{2-}$ was submitted to the anion-exchange chromatography, the whole lot of the eluate gave no CD pattern. When an aqueous solution of pH 4.6 and ionic strength <0.1 M containing racemic $[\text{Mo}_2\text{O}_4(\text{R,S-pdta})]^{2-}$, Δ,Δ - $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2^{2-})\text{Co}^{\text{III}}(\text{en})_2]^{3+}$ (reduction product of 1), sodium molybdate(VI), *R*-H₄pdta, and Na₂H₂edta (corresponding to the composition of the reaction mixture after the redox reaction completed, except that the Mo(V) complex is racemic) was treated with the anion-exchange column similarly, the eluted $[\text{Mo}_2\text{O}_4(\text{pdta})]^{2-}$ showed no CD pattern.

c. Self-Exchange and Related Reactions. No change in CD strength (at 387 nm) of a solution containing $[\text{Mo}_2\text{O}_4(\text{R-pdta})]^{2-}$ (3.03×10^{-3} M), sodium molybdate(VI) (6.08×10^{-3} M), and *R,S*-H₄pdta (3.08×10^{-3} M) (*I* = 0.2 M, pH 4.6) was observed over a period of 27 h at room temperature. Neither changed the absorption nor the CD strength (387 nm) of $[\text{Mo}_2\text{O}_4(\text{R-pdta})]^{2-}$ solution (1.64×10^{-3} M) in the presence of Na₂H₂edta (8.06×10^{-3} M) (*I* = 0.2 M, pH 4.6) over a period of 2 days at room temperature. Therefore neither the electron exchange between $[\text{Mo}_2\text{O}_4(\text{R-pdta})]^{2-}$ and Mo(VI) species nor the ligand substitution of $[\text{Mo}_2\text{O}_4(\text{R-pdta})]^{2-}$ with free edta⁴⁻ and its partly protonated ions (henceforth written as EDTA ion), takes place under the experimental conditions of the stereoselectivity.

The self-exchange rate between $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2^{2-})\text{Co}^{\text{III}}(\text{en})_2]^{4+}$ and $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2^{2-})\text{Co}^{\text{III}}(\text{en})_2]^{3+}$ was estimated by using optical isomers of the complexes as follows. When Δ,Δ isomer of the μ -hyperoxo complex was mixed with racemic μ -peroxo complex (both ca. 10^{-3} M), a rapid change in the CD spectrum was observed which completed within a few minutes at room temperature. The exchange rate constant is thus of a similar magnitude to the rate constant ($12.0 \text{ M}^{-1} \text{ s}^{-1}$) of the oxidation of $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2^{2-})\text{Co}^{\text{III}}(\text{en})_2]^{3+}$ with $[(\text{NH}_3)_4\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2^{2-})\text{Co}^{\text{III}}(\text{NH}_3)_4]^{4+}$.¹³ Optically

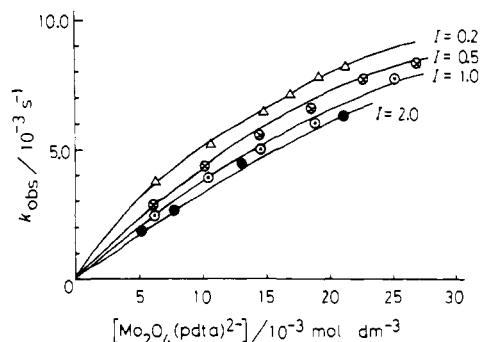


Figure 2. Dependence of k_{obs} on $[\text{Mo}_2]$ at various ionic strengths (25 °C, $[\mu\text{-O}_2^{2-}] = 1.03 \times 10^{-3}$ M, $[\text{EDTA}] = 5.2 \times 10^{-4}$ M, pH 4.6).

active isomers of both $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2^{2-})\text{Co}^{\text{III}}(\text{en})_2]^{4+}$ and its reduced form (μ -peroxo) do not racemize at all under the present experimental conditions. Hence, the rapid self-exchange proceeds with full retention of configuration and does not affect the stereoselectivity so far as optically pure μ -hyperoxo complex was used as oxidant.

Since Na₂H₂edta was added to the solutions for both the selectivity and the kinetic measurements, possible oxidation of EDTA ions with $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2^{2-})\text{Co}^{\text{III}}(\text{en})_2]^{4+}$ should be examined. They are oxidized only very slowly at pH ca. 3.5–4.6, and no significant influence is feasible on the present results.

d. Conclusion for the Existence of Stereoselectivity. The results in Table I must reflect the stereoselectivity of the redox reaction (1). It should be noted that not only the magnitude but also the sign of the CD peak of the remaining molybdenum(V) complex change as the ionic strength changes. The Δ,Δ isomer of 2 reacts more rapidly with the dimeric molybdenum(V) containing *S*-pdta than with that containing *R*-pdta at a low ionic strength, but the preference is reversed at a high ionic strength.

II. Kinetics of the Redox Reaction. a. Analogous Reaction Systems. Detailed kinetic results on redox systems similar to reaction 1 are available.^{14–16} Results for the reaction of $[\text{Mo}_2\text{O}_4(\text{edta})]^{2-}$ with $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\mu\text{-O}_2^{2-})\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$,¹⁴ $[\text{Fe}^{\text{III}}(\text{phen})_3]^{3+}$, and $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ ¹⁵ suggest that the oxidation proceeds through the outer-sphere mechanism and that the oxidation of the first molybdenum(V) ion in the dimer is the rate-determining step, which is followed by a rapid oxidation of the second molybdenum(V). There seems to be no example that hyperoxo-bridged dicobalt(III) complexes behave as inner-sphere oxidants.^{17,18} Reaction 1 must proceed also through

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- (15) Wharton, R. K.; Ojo, J. F.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* 1975, 1526.
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- (17) Sykes, A. G. *Chem. Br.* 1974, 10, 170.

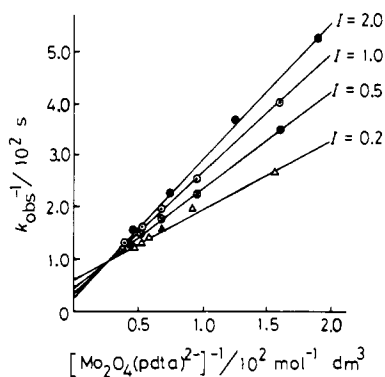


Figure 3. Dependence of k_{obs}^{-1} on $[\text{Mo}_2]^{-1}$ at various ionic strengths (reaction conditions are the same as those of Figure 3).

Table II. Kinetic Parameters for the Oxidation of $[\text{Mo}_2\text{O}_4(\text{pdt})]^{2-}$ with $[(\text{en})_2\text{Co}(\mu\text{-O}_2^{(-)})\text{Co}(\text{en})_2]^{4+}$ at 25 °C^a

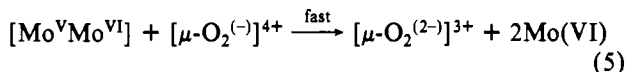
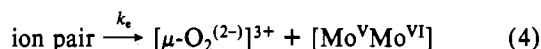
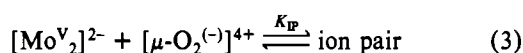
	<i>I</i>			
	0.2	0.5	1.0	2.0
$k_e/10^{-2} \text{ s}^{-1}$	0.76 ± 0.07	0.99 ± 0.05	1.20 ± 0.09	1.7 ± 0.5
$K_{\text{IP}}/\text{M}^{-1}$	51 ± 7	27 ± 2	18 ± 2	11 ± 3

^a Errors were determined by the least-square treatment with no weighing (confidence level, 0.7).

an outer-sphere mechanism. Kinetic behaviors (*vide infra*) and the stoichiometry of reaction 1 are consistent with the rate-determining oxidation of the first molybdenum(V) ion in the dimer.

b. Kinetics of the Present Reaction. The observed stereoselectivity suggests that the difference in the redox rate constants between the diastereomeric pairs of the oxidant and the reductant should be less than 1%, which is too small to be detected by the measurement of rate constants. The kinetic studies were carried out by use of the racemic reactants at 25 °C and pH 4.6. Dependence of the first-order rate constants (k_{obs}) on the concentrations of the molybdenum(V) complex is shown in Figure 2. The reciprocal plot, k_{obs}^{-1} vs. $[\text{Mo}_2]^{-1}$, is shown in Figure 3. These patterns are similar to those of the similar redox reactions, the oxidation of $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{edta})]^{2-}$ and $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{hedta})(\text{H}_2\text{O})]^-$ (hedta = *N*-(2-hydroxyethyl)-ethylenediamine-*N,N',N'*-triacetate) with $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\mu\text{-O}_2^{(-)})\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$.^{14,16} Hence the rate law (2) and the reaction scheme (3)–(5) should be applicable. K_{IP} and k_e are

$$\text{rate} = k_{\text{obs}}[\mu\text{-O}_2^{(-)}] = \frac{2k_e K_{\text{IP}}[\text{Mo}^{\text{V}}_2][\mu\text{-O}_2^{(-)}]}{(1 + K_{\text{IP}}[\text{Mo}^{\text{V}}_2])} \quad (2)$$



the ion-pair formation constants between the redox couple and the rate constant of electron transfer within the ion pair, respectively. The values of K_{IP} and k_e are shown in Table II. Both depend significantly on the ionic strength. The mechanism expressed by (3)–(5) includes neither dependence on pH nor dependence on the concentration of coexisting anionic species such as perchlorate and EDTA ions. Hence the given figures should be reckoned as conditional.

c. Interpretation of the Ionic-Strength Dependence of k_e . Individual values of K_{IP} and k_e have been evaluated for several redox systems between reactants with high and opposite charges.^{14,19} The dependence of these values on the ionic strength was examined for the oxidation of $[\text{Mo}_2\text{O}_4(\text{edta})]^{2-}$ with $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\mu\text{-O}_2^{(-)})\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$, where k_e showed no significant dependence on ionic strength in a rather narrow range, $I = 0.1 - 0.5 \text{ M}$.¹⁴ The dependence of k_e on I may vary with the nature of ion pair.

The ion pair formed by the present redox couple still possesses 2+ charge and thus can associate with other anionic species in the solution. Therefore, such species as $[(\mu\text{-O}_2^{(-)})^{4+}(\text{Mo}_2^{\text{V}})^{2-}\text{ClO}_4^-]$ and $[(\mu\text{-O}_2^{(-)})^{4+}(\text{Mo}_2^{\text{V}})^{2-}(\text{H}_2\text{edta})^{2-}]$ can exist in the solution. The kinetically determined term K_{IP} reflects the formation of all the "ion pairs" in which the electron transfer takes place. The relative abundance of these species should depend on the ionic strength. Consequently, k_e would depend on ionic strength, provided that the rates of electron transfer within these varying species are different from one another.

d. pH Dependence of the Rate Constant. The rate of reaction at identical concentrations of the reactants increases appreciably as the pH rises. For example, k_{obs} 's are $(2.37 \pm 0.03) \times 10^{-3}$ and $(3.70 \pm 0.05) \times 10^{-3} \text{ s}^{-1}$ at pH 3.2 and 4.6, respectively ($[\mu\text{-O}_2^{(-)}] = 1.25 \times 10^{-3} \text{ M}$ and $[\text{Mo}^{\text{V}}_2] = 7.17 \times 10^{-3} \text{ M}$, $[\text{EDTA}] = 1.8 \times 10^{-3} \text{ M}$, $I = 0.2$, 25 °C). Such a pH dependence is interpreted with difficulty, since both reactants are unlikely to be protonated or deprotonated around the given pH range.²⁰ The added EDTA can change the ratio among Hedta^{3-} , $\text{H}_2\text{edta}^{2-}$ and H_3edta^- in the given pH range. However, the oxidation of $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{R,S-pdt})]^{2-}$ with $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ in the absence of added EDTA also shows similar pH dependence (this oxidant is protonated with difficulty in this pH region, too). Hence the added EDTA does not seem to play an important role in this pH dependence. Further detailed kinetic studies are required to clarify this problem.

III. Ionic Strength Dependence of Stereoselectivity. Various ion-associating species, $[(\mu\text{-O}_2^{(-)})^{4+}(\text{Mo}_2^{\text{V}})^{2-}]^{2+}$, $[(\mu\text{-O}_2^{(-)})^{4+}(\text{Mo}_2^{\text{V}})^{2-}\text{ClO}_4^-]$, and $[(\mu\text{-O}_2^{(-)})^{4+}(\text{Mo}_2^{\text{V}})^{2-}\text{H}_2\text{edta}]$, would have different stereoselectivities for their formation constants and for the electron-transfer rate constants within them. However, the observed change in the overall stereoselectivity with ionic strength is so remarkable to be accounted for solely by the different stereoselectivities of the variety of ion-associating species.

The dependence of the stereoselectivity on ionic strength can be interpreted more reasonably by assuming that the two kinetic terms k_e and K_{IP} have different stereoselectivities and their extent is independent of ionic strength. The results in Table I can be accounted for by considering the following. k_e with Δ,Δ oxidant is larger for the *S*-pdt than for the *R*-pdt complex of molybdenum(V); the stereoselectivity of K_{IP} is the reverse and the extent larger than that of k_e . The rate of redox reaction under the given conditions must be governed by $k_e K_{\text{IP}}[\text{Mo}_2]$ at a high ionic strength where $K_{\text{IP}}[\text{Mo}_2]$ is much less than unity. The relative contribution of k_e increases as the ionic strength lowers, because $K_{\text{IP}}[\text{Mo}_2]$ in the denominator becomes larger.

This explanation is valid whenever the extent of stereoselectivity in the denominator of eq 2, $1 + K_{\text{IP}}[\text{Mo}_2]$, exceeded that of $2k_e K_{\text{IP}}$ in the numerator at an ionic strength less than 0.5. The ratio $2(k_e(\text{R}))(K_{\text{IP}}(\text{R}))/2(k_e(\text{S}))(K_{\text{IP}}(\text{S}))$ is at least 1.006, where $k_e(\text{R})$ and $K_{\text{IP}}(\text{R})$ denote the terms for the ox-

(18) Assignment of the inner-sphere mechanism for the oxidation of $[\text{Tl}^{\text{III}}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ with $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\mu\text{-O}_2^{(-)})\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$ should at present be regarded as uncertain: Thompson, G. A. K.; Sykes, A. G. *Inorg. Chem.* 1976, 15, 638; 1979, 18, 2025.

(19) Oliveira, L. A. A.; Giesbrecht, E.; Toma, H. E. *J. Chem. Soc., Dalton Trans.* 1979, 236 and references cited therein.

(20) The rate of oxidation of $[\text{Mo}_2^{\text{V}}\text{O}_4(\text{edta})]^{2-}$ with $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\mu\text{-O}_2^{(-)})\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$ in the absence of added EDTA is independent of $[\text{H}^+]$ in the range from 0.5 to 2.0 M.¹⁴

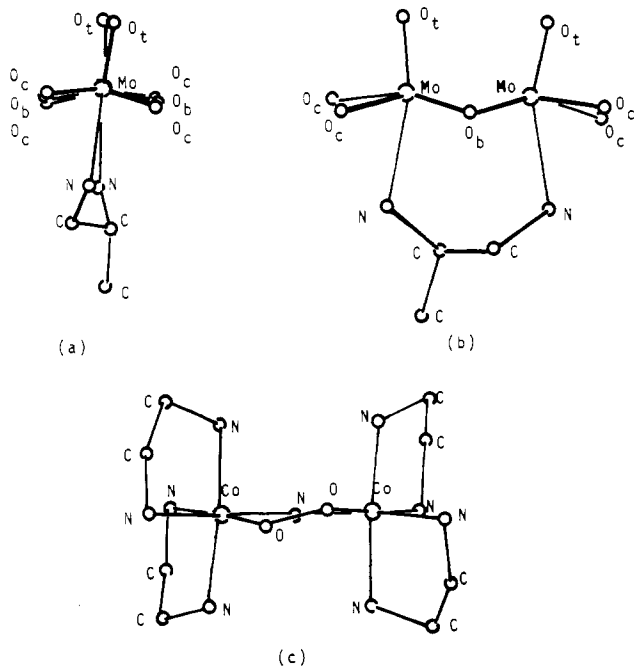


Figure 4. Projections of the structures of (a, b) $[\text{Mo}_2\text{O}_4(\text{R-pdta})]^{2-}$ (carboxylate arms are omitted for clarity)²⁴ and (c) Δ, Δ - $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2^{2-})\text{Co}^{\text{III}}(\text{en})_2]^{4+}$.²⁵

idation of $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{R-pdta})]^{2-}$ with Δ, Δ oxidant and $k_e(S)$ and $K_{\text{IP}}(S)$ for those of $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{S-pdta})]^{2-}$ with the same oxidant. This figure is derived from the enantiomeric excess at $I = 2.0$ M where the contribution of $K_{\text{IP}}[\text{Mo}_2]$ in the denominator is the smallest within the used ionic strength range, 0.2–2.0 M. [The contribution cannot be ignored since the increase in overall selectivity does not tend to saturate at $I = 2.0$ M.] For compensation of the stereoselectivity of the numerator $2k_eK_{\text{IP}}[\text{Mo}_2]$, eq 6 must hold at $I = 0.5$ M where no

$$(1 + (K_{\text{IP}}(R))[\text{Mo}_2]) / (1 + (K_{\text{IP}}(S))[\text{Mo}_2]) > 1.006$$

$$I = 0.5 \text{ M} \quad (6)$$

apparent selectivity is observed. This is rearranged to eq 7.

$$(1.006(K_{\text{IP}}(S))[\text{Mo}_2] + 0.006) / (K_{\text{IP}}(S))[\text{Mo}_2] <$$

$$(K_{\text{IP}}(R)) / (K_{\text{IP}}(S))$$

$$I = 0.5 \text{ M} \quad (7)$$

Relation 8 is derived by use of the experimental values 27 M^{-1}

$$K_{\text{IP}}(R) / K_{\text{IP}}(S) > 1.09 \quad (8)$$

and $2.69 \times 10^{-3} \text{ M}$ for $K_{\text{IP}}(S)$ and $[\text{Mo}_2]$ in eq 7, respectively. These estimations are based on eq 2 which is obtained under the pseudo-first-order condition with the molybdenum(V) dimer in large excess. The stereoselectivities were examined under the second-order conditions with comparable concentrations of the oxidant and the reductant, and such a treatment must be considered as an approximation. There seems to be no data available for the stereoselectivity of ion-pair formation between optically active metal complexes. However, that

between optically active metal complex cations and optically active carboxylate anions has been studied, and ratios above 1.09 have been given for some systems.²¹ The present ratio, 1.09, does not seem to be unreasonably big.

IV. Structural Aspect of the Stereoselectivity. a. Structure of the Reactants. Figure 4 shows the structure of the two reactants of reaction 1 determined by the X-ray diffraction method. The reductant $\text{Na}_2[\text{Mo}^{\text{V}}_2\text{O}_4(\text{R-pdta})] \cdot 3\text{H}_2\text{O}$ has four coordinated carboxylate oxygen atoms distorted tetrahedrally around the $\text{Mo}_2\text{O}_4^{2+}$ core and two terminal $\text{Mo}=\text{O}$ bonds twisted around the $\text{Mo}-\text{Mo}$ axis to the M direction²² with a torsion angle of 5.4° .^{8,23,24} Comparison of the CD spectrum in aqueous solution with that in KBr disk indicated that the structure is retained in aqueous solution.⁸ The two $\text{Co}-\text{O}$ bonds in the Δ, Δ isomer in a racemic $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2^{2-})\text{Co}^{\text{III}}(\text{en})_2](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ crystal are twisted around the $\text{O}-\text{O}$ axis by 23.4° to the M direction.²⁵ It provides another source of asymmetry than that due to the helical configuration of the two ethylenediamine rings on each cobalt(III) ion of the dimer.

b. Stereochemistry of the Selectivity. The present interpretation of stereoselectivity suggests that the favorable stereochemical situation for the ion-pair formation is not necessarily suitable for the electron transfer therein. Since the bond length and angles of the reactants would not change significantly in the ion pair, its stereochemistry can be discussed on the basis of the structural data of X-ray crystal analysis. The 3d electrons of the present molybdenum(V) dimer probably exist within the Mo_2O_4 core,²⁶ and the oxidant would accept an electron at the bridging dioxygen part. This moiety would approach the reductant most probably from the direction of the two terminal oxide ions. If the $\text{O}-\text{O}$ axis approached across the $\text{Mo}-\text{Mo}$ axis, the Δ, Δ isomer would experience less steric hindrance with the R -pdta complex than with the S -pdta complex. This is consistent with the observed stereoselectivity in K_{IP} .

Such a consideration cannot be applied to the electron-transfer process, because the stereoselectivity in this process is of reverse direction to that of the ion-pair formation. The bond lengths and angles of both the oxidant and the reductant should change significantly to reach the excited state for electron transfer. Such rearrangements would be subjected to a different kind of stereoselectivity which is responsible for the observed stereoselectivity in the electron-transfer process, k_e . Further discussion may be difficult on the basis of the present results alone.

Registry No. 1, 75520-36-4; 2, 62646-96-2; $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{R-pdta})]^{2-}$, 75520-37-5; $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{S-pdta})]^{2-}$, 75520-38-6.

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