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A Kinetic Study of Pressure Effect upon an Outer Sphere Electron-Transfer Reaction Involving Free Radicals

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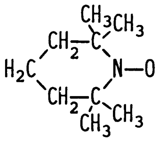
Synopsis. Volume of activation for the redox reaction between $[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^{(-)})Co^{III}(en)_2]^{4+}$ (en, ethylenediamine) and 2,2,6,6-tatramethyl-1-piperidinyloxyl radical is zero. The result endorses our previous discussion that the changes in solvation and in intrinsic volume of reactants are respectively responsible for determining the precursor and transition state.

Usefulness of pressure effect for elucidating the reaction mechanism of electron-transfer reactions has been widely understood,[1-3] but experimental data are available only for limited variety of redox pairs.[4] When the charge sign of the oxidant and reductant is different from each other, the equilibrium constant for the precursor formation K_{os} and the electron-transfer rate constant k_e are kinetically analyzed.[5-8] Hence the molar volume change accompanied by the precursor formation ΔV°_{os} and the activation volume of the electron-transfer stage $\Delta V^{\neq}{}_e$ are individually known, particularly when the charge numbers are high.[4,9-11] We have discussed that the ΔV°_{os} is mostly governed by the environmental effect, i.e. the observed positive values are due to the release of hydrated water molecules in the second hydration sphere on the formation of precursor ion pair.[10] Such a consideration may be endorsed by use of a reductant without charge. We have chosen 2,2,6,6-tetramethyl-1-pyperidinyloxyl (TMPNO) which is soluble in water and stable in air as reductant and binuclear cobalt(III) complex doubly bridged by hyperoxide and amide as oxidant. This paramagnetic complex has its localized unpaired electron at the hyperoxide moiety and the two Co^{III} atoms have low spin configuration, which is retained in the reduced form, diamagnetic μ-peroxo-μ-amido bridged species. Hence the change in overall structure before and after the redox reaction is expected to be very small. The stoichiometry of the reaction is as follows.

Table 1. Kinetic Data for the Redox Reaction between $[(en)_2Co^{III}(\mu\text{-}NH_2, O_2^{(-)})Co^{III}(en)_2]^{4+}$ and 2,2,6,6-Tetramethyl-1-piperidinyloxyl Radical in Aqueous Solution

t/°C	I/M	Buffer	pH	$k_{obsd}/10^4\ M^{-1}\ s^{-1}$
4.8	0.10	Acetate	3.92	1.30 ± 0.03
15.0	0.10	Perchlorate	2.85	2.57 ± 0.13
15.0	0.10	Perchlorate	3.95	2.75 ± 0.06
15.0	0.10	Acetate	3.92	2.71 ± 0.11
15.0	0.10	Acetate	5.00	2.68 ± 0.16
15.0	0.50	Acetate	3.95	4.56 ± 0.09
24.8	0.10	Acetate	3.92	5.17 ± 0.24
ΔH^{*}/kJ mol^{-1}		45.0 ± 0.3		
ΔS^{*}/J mol^{-1} K^{-1}		-3.7 ± 1.2		
$\Delta V^{*}{}_{obsd}$/cm^3 mol^{-1}		0.2 ± 0.5	(I=0.1 M)	
(cf. Fig. 1)		-1.4 ± 1.3	(I=0.5 M)	

$$[(en)_2Co^{III}(\mu\text{-}NH_2, O_2^{(-)})Co^{III}(en)_2]^{4+} + \text{TMPNO radical} \longrightarrow [(en)_2Co^{III}(\mu\text{-}NH_2, O_2^{(2-)})Co^{III}(en)_2]^{3+} + \text{TMPNO cation}$$



2,2,6,6-tetramethyl-1-pyperidinyloxyl (TMPNO)

Experimental

The oxidant was synthesized by the known method[12] in pure chloride form. Commercial TMPNO was sublimed in vacuo. pH Titration gave no sign of protonation at pH 2 to 11. The standard redox potentials for TMPNO· to $TMPNO^+ + e^-$ are +0.478 and +0.475 V vs. SCE at ionic strengths 0.1 and 0.5 M (NaCl), respectively. The pH was adjusted with acetate buffer (acetate concentration 0.01 M) or perchloric acid to 2.85 to 5.00. The ionic strength was adjusted to 0.1 and 0.5 M with sodium perchlorate ($M = mol\ dm^{-3}$).

The kinetics were followed at 4.8 to 24.8 °C under the following conditions: $[oxidant]=(0.73 \text{ to } 7.3)\times10^{-5}$ M, $[reductant]=(2.0 \text{ to } 10.0)\times10^{-4}$ M. A Union Giken Stopped-flow spectrophotometer was used for the kinetic measurement. The pressure effect was measured (up to 200 MPa) by a High Pressure Stopped-flow Apparatus FIT 3 exploited in Department of Chemistry, Nagoya University.[13] The pressure was measured with a strain-type gauge calibrated with a standard Heize gauge. The pressure remained constant within less than 1 MPa.

Results

When the kinetics were followed by this method at 306 nm (absorption peak of the oxidant) in the presence of a large excess of the reductant, the pseudo first order plots with respect to the oxidant concentration were linear for more than three half period of the reaction. The first order rate constant is independent of the initial concentration of the oxidant and proportional to that of reductant.

$$\text{Rate} = k_{obsd}[\mu\text{-}NH_2, O_2^{(-)}][\text{TMPNO}]$$

Table I shows that the rate constant is independent of

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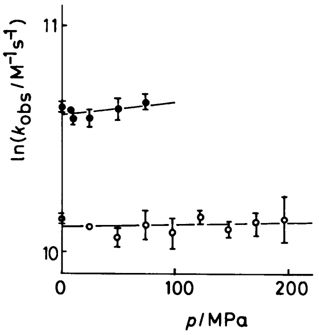

Fig. 1. Dependence of the observed second order rate constant upon the pressure.
○ at I=0.1 M, ● at I=0.5 M 15.0 °C
Bars indicate the range of 70% certainity.

the pH and the buffering agent. It increases significantly with increase in ionic strength. The activation parameters included in the Table clearly indicate that the volume of activation is zero (Fig. 1) and so is the activation entropy. Ligand substitution of the oxidant complex is very slow under the given conditions.

Discussion

It is generally understood that the influence of ionic strength upon reaction rates is feasible in the precursor formation stage rather than in the electron-transfer stage.[7] The observed increase in k_{obsd} with ionic strength can be interpreted that the interaction between the oxidant in less strongly hydrated form and the reductant results in effective precursor. Since the reductant is a chargeless radical, this fact implies that the precursor formation will not bring about significant change in the solvation state of the precursor formation, to make the ΔV°_{os} almost zero. Since $\Delta V^{\neq}_{obsd}=\Delta V^{\circ}_{os}+\Delta V^{\neq}_{e}$, the volume of activation at the electron-transfer stage is also very likely near to zero.

Consideration on the basis of crystallographic data of $[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^{(-)})Co^{III}(en)_2]^{4+}$,[14] $[(en)_2Co^{III}(\mu\text{-}NH_2, O_2^{(2-)})Co^{III}(en)_2]^{3+}$,[15] TMPNO,[16] and its oxidized cation[17] indicates that the change in molar volume of these species is not significant. The Co–Co distances of the hyperoxide- and peroxide bridged species are 3.25 and 3.27 Å, and the configuration of ethylenediamine ligand around Co^{III} as well as the Co–N distance is very similar to each other. The Co–O–O–Co moiety has planar (O–O 1.36 Å) and gauche (1.48 Å) structure, respectively, but the transition from O_2^- to O_2^{2-} will proceed without siginificant change in structure of that part. TMPNO and its oxidized cation have almost equal bond distances to each other including N–O (1.296 and 1.19 Å, respectively). The angles of N–O bond to the C–N–C plane of piperidine are 19.4 and 0°, respectively, but they are within the four methyl groups on 2- and 6- position and the small angle change will not cause big change in molar volumes of the two species. Thus the change in intrinsic molar volume of the oxidant and reductant on electron transfer will be very small. This fact indicates that the change in solvation state around the precursor will not be appreciable since the $\Delta V^{\neq}_{e}$ is near to zero. This consideration is supported by the very small absolute value of activation entropy.

When an electron is transferred from the chargeless TMPNO to the +4 oxidant in the precursor, a change in dipole moment may be expected, which could increase the hydration around the precursor, because +4 vs. 0 pair could give stronger hydration than +3 vs. +1 pair does. If this effect gave significant contribution to increase $\Delta V^{\neq}_{e}$ value, there should be some other contribution to compensate the increase in volume of the system. Careful examination of the molar volumes of participating species as well as the hydration around them did not suggest any possibility of decrease in volume of the system. Hence we conclude that in the present system both ΔV°_{os} and $\Delta V^{\neq}_{e}$ will be near to zero. The present result seems to support our previous conclusion that the contributions of change in solvation sphere and in the intrinsic volume of the reactants are respectively responsible for determining the precursor and the transition state of redox systems involving charged oxidant and reductant.

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