is 1,4,8,11-tetraazacyclotetradecane, proceeds by an outer-sphere mechanism.[36] Also, the oxidation of iodide by $Co^{3+}(aq)$ is believed to be an outer-sphere process, although the oxidation of Br^- and NCS^- occur by substitution-controlled inner-sphere pathways.[23] On the other hand, the oxidation of $IrCl_6^{3-}$ by $Cu^{III}(H_{-n}L)$ complexes appears to require an inner-sphere bridging chloride,[7,9,20,21] which suggests that the oxidation of iodide may also be inner sphere. Thus, there is presently no definitive evidence requiring that the oxidations of iodide by copper(III) be either inner-sphere or outer-sphere processes.

Reaction Path B. The slope of the plot of log k_B vs. $E_{III,II}/0.059$ is 0.95 ± 0.09 (Figure 3). Arguments similar to those presented for path A can be used to show that the slope of 0.95 indicates that reaction path B is not limited by the rate of electron transfer. They also show that for path B the reaction sequence given in eq 12 and 13 is not a possible alternative to the reaction proposed in eq 7.

A lower limit of the equilibrium constant K_B $(=K_0k_2/k_{-2})$ for reaction path B (eq 5 and 7) can be calculated from the reduction potentials in Table IV. The principle of microscopic reversibility[37,38] can then be used to evaluate a maximum value for k_{-2}, which is $(1.0 \pm 0.5) \times 10^5\ M^{-1}\ s^{-1}$. This value of k_{-2} is substantially less than might be expected for a diffusion- or substitution-limited reaction of I_2^- with $Cu^{II}(H_{-n}L)$. It is, however, consistent with the rate constants k_{ox}, which have been measured by pulse radiolysis for the oxidation of the copper(II) macrocyclic complexes $Cu^{II}Z^{2+}$ and $Cu^{II}Z'^{2+}$ (where Z is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and Z′ is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) by the Cl_2^- and Br_2^- radical anions. For the reaction of $Cu^{II}Z'^{2+}$ with Cl_2^- k_{ox} is $3.2 \times 10^8\ M^{-1}\ s^{-1}$ and with Br_2^- k_{ox} is $1 \times 10^7\ M^{-1}\ s^{-1}$.[39] These results suggest that the oxidation of copper(II)–macrocycle and –peptide complexes by halogen radical anions undergo a rate-limiting structural or electronic activation step prior to electron transfer. The copper(II)–peptide complexes are tetragonally distorted with water molecules in the axial coordination sites, while the copper(III)–peptide complexes have square-planar coordination geometries. Desolvation of the copper(II) complexes must occur in the course of their oxidation by the radical anions. This reaction also involves the breaking of the I–I bond of the I_2^- radical anion. Both the desolvation of the copper(II) complex and the breaking of the I–I bond will make significant contributions to the rate-limiting activation process. For the reverse reaction, namely, the oxidation of iodide to I_2^- by copper(III) in eq 7, the same (de)activation process is of necessity rate limiting and occurs after the electron transfer has been accomplished. That is, the transition state for reaction path B occurs at a point near the product (Cu(II) and I_2^-) end of the reaction coordinate.

Conclusions

The copper(III)–deprotonated peptide complexes behave both thermodynamically and kinetically as one-electron oxidizing agents in their reactions with iodide. These reactions occur by two kinetic pathways. Path A exhibits a first-order iodide dependence, and its rate is limited by the rate of electron transfer. Path B exhibits a second-order iodide dependence, and its rate is not electron transfer limited. The measured rate constants for reaction path A and microscopic reversibility considerations indicate that the reduction potential for the $I\cdot/I^-$ couple is less than or equal to 1.2 V.

Acknowledgment. This investigation was supported by Public Health Services Grant No. GM12152 from the National Institutes of General Medical Sciences. The authors also thank C. K. Murray and A. Hamburg for synthesizing the DGEN and Aib_3 ligands.

Registry No. $Cu^{III}(H_{-2}DGEN)^+$, 67202-40-8; $Cu^{III}(H_{-2}A_3)$, 69042-71-3; $Cu^{III}(H_{-2}L_3)$, 69042-72-4; $Cu^{III}(H_{-3}G_4a)$, 68550-44-7; $Cu^{III}(H_{-2}Aib_3)$, 69951-85-5; $Cu^{III}(H_{-3}G_4)^-$, 57692-61-2; I^-, 20461-54-5.

---

(37) Krupka, R. M.; Kaplan, H.; Laidler, K. J. *Trans. Faraday Soc.* **1966**, *62*, 2754.

(38) Boyd, R. K. *Chem. Rev.* **1977**, *77*, 93.

(39) Patterson, L. K. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1979**, *NSRDS-NBS 65*, 35, 39.

Contribution from the Laboratory of Analytical Chemistry,
Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan

Reactions of Hydrogen Peroxide with Metal Complexes. 5.[1] Mechanism of the Peroxo Complex Formation of (Nitrilotriacetato)dioxovanadate(V) As Studied by a High-Pressure Stopped-Flow Technique

SHIGENOBU FUNAHASHI, KOJI ISHIHARA, and MOTOHARU TANAKA*

Received January 18, 1980

A high-pressure stopped-flow apparatus has been exploited which enables us to follow reactions with a half-life longer than 0.1 s under pressure up to 1600 kg cm^{-2}. The rate for the formation of the peroxo complex of (nitrilotriacetato)dioxovanadate(V) $(VO_2(nta)^{2-})$ is expressed as $d[VO(O_2)(nta)^{2-}]/dt = (k_1 + k_2[H^+])[VO_2(nta)^{2-}][H_2O_2]$, where $k_1 = 7.05\ m^{-1}\ s^{-1}$, $k_2 = 1.46 \times 10^4\ m^{-2}\ s^{-1}$ at 25 °C and $I = 1.05\ m$ at atmospheric pressure and the volumes of activation for the k_1 and k_2 paths are -3.4 ± 0.5 and $1.5 \pm 0.5\ cm^3\ mol^{-1}$, respectively. An associative mechanism is most probably operative.

Introduction

Flow techniques have been introduced more than 50 years ago by Hartridge and Roughton.[2] The stopped-flow method has been utilized for studies of many kinds of reactions. We have developed a highly sensitive stopped-flow technique by use of a computer-assisted signal averaging device.[3] In contrast to the relaxation techniques, the application of the stopped-flow techniques is not limited to reversible reactions. Both techniques are complementary for studies of reactions in solution. Measurement of activation volumes is important

---

(1) Preliminary communication: Funahashi, S.; Ishihara, K.; Tanaka, M. *Inorg. Chim. Acta* **1979**, *35*, L351. Part 4: Funahashi, S.; Midorikawa, T.; Tanaka, M. *Inorg. Chem.* **1980**, *19*, 91.

(2) Hartridge, H.; Roughton, F. J. W. *Proc. R. Soc. London, Ser. A* **1923**, *104*, 376.

(3) Tanaka, M.; Funahashi, S.; Nagamura, T. Paper No. 63, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, PA, 1977.

0020-1669/81/1320-0051$01.00/0

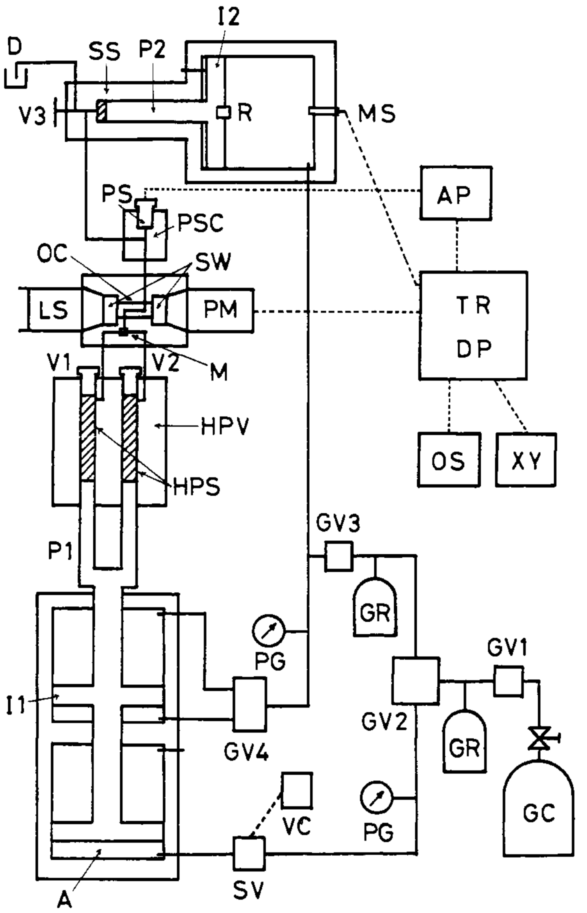


Figure 1. Schematic diagram of a high-pressure stopped-flow apparatus: V, high-pressure valve; GV, gas valve; P, piston; I, intensifier; SV, solenoid valve; VC, valve controller; A, actuator; HPS, high-pressure syringe; HPV, high-pressure vessel; M, mixer; OC, optical cell; SW, sapphire window; SS, stop syringe; MS, mechanical stop; PSC, pressure sensor cell; PS, pressure sensor (manganin or strain gauge); D, drain; GV1 and GV3, pressure reducing valve; GR, gas reservoir; GC, gas cylinder; PG, pressure gauge; LS, light source; PM, photomultiplier; TR, transient recorder; DP, data processor; OS, oscilloscope; AP, amplifier; XY, recorder.

for the elucidation of reaction mechanisms. Relaxation techniques under high pressure have been reported, e.g., temperature-jump, NMR, and ESR methods.[4] In 1977 Heremans et al. designed an apparatus capable of measuring the rates of reactions with a half-life of 20 ms at pressure up to 1200 kg cm^{-2} by putting a stopped-flow unit in a high-pressure bomb.[5] Recently Sasaki et al. have constructed a stopped-flow apparatus which enables them to study chemical reactions with a half-life longer than several milliseconds at hydrostatic pressure up to 3000 kg cm^{-2}.[6] In the present paper we describe a high-pressure stopped-flow apparatus with some different mechanics.

We have studied the reactions of hydrogen peroxide with some (aminopolycarboxylato)dioxovanadate(V) complexes in aqueous solution.[1,7,8] The large negative entropy of activation for the peroxo complex formation is ascribed to a highly oriented transition state and provides evidence for an associative mode of activation. In principle, the interpretation of volume change is based on inferred changes in nuclear positions. This involves a structural concept which should be intrinsically simpler to handle than the alternative concept of an entropy change which depends on inferred changes in both nuclear positions and energy.[9,10] Measurement of the activation volume for the reaction of (nitrilotriacetato)dioxovanadate(V) with hydrogen peroxide should provide some information on the reaction mechanism. This appears to be the first high-pressure study of vanadium solution chemistry.

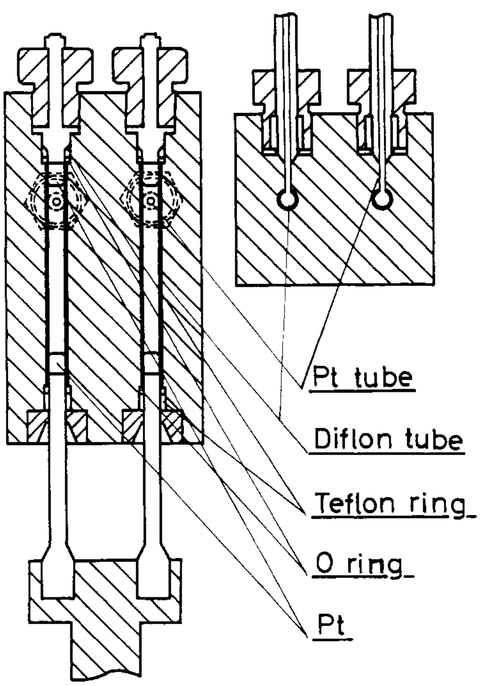


Figure 2. High-pressure syringe.

Experimental Section

High-Pressure Stopped-Flow Apparatus. The schematic diagram of the high-pressure stopped-flow apparatus with spectrophotometric detection is shown in Figure 1. A material for use in high-pressure equipment is high-strength stainless steel (SUS 630). Tubes made of platinum and Diflon (fluorocarbon polymer) are tightly inserted in the parts in contact with reactant solutions. A standard cone-type seal and O-ring seal are used for sealing pressure. Mixing of reactant solutions is made by a mixer of simple T jet type. The high-pressure optical cell made of Diflon with two sapphire windows is 10 mm in light-path length. The temperature was kept at 25 ± 0.1 °C by circulating thermostated water through channels around the high-pressure vessel, optical cell, and pressure sensor cell. High pressure is produced by an intensifier with an area ratio of 160. The pressure was measured by a manganin resistance pressure gauge or by a strain gauge (Sensotec Inc., Columbus, Ohio) which was calibrated by a Heise Bourdon gauge. In order for the pressure sensor to be protected, it was covered with a Teflon cap involving pressure-transmitting fluid (Silicone KF 96, Shin-Etsu Chemical Co., Ltd.). Figure 2 shows the details of the high-pressure syringes.

The operation has been carried out as follows. After high-pressure syringes (HPS) were filled with reactant solutions, the valves V1 and V2 were closed. The gas valve GV2 was opened, and the pistons P1 and P2 were pushed upward through the intensifiers I1 and I2 by constant nitrogen-gas pressure of 0–10 kg cm^{-2} until the desired pressure was generated by the gas valve GV1. After the application of pressure to the reactant solutions, about 5 min was required for the solution to come to within 0.1 °C of the initial temperature. The solenoid valve (SV), controlled by a valve controller (VC), was opened for a moment. By an actuator (A) the reactants in the high-pressure syringes were pushed through the mixer (M) and optical cell (OC) into the stop syringe (SS), where the flow was abruptly stopped when the rod (R) hit a mechanical stop (MS). The hitting triggered the valve controller and transient recorder. The progress of the reaction

---

(4) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407.
(5) Heremans, K.; Snauwaert, J.; Rijkenberg, J. *Proc. Int. Conf. High Pressure, 6th* **1977**.
(6) Takisawa, N.; Sasaki, M.; Amita, F.; Osugi, J. *Chem. Lett.* **1979**, 671. Sasaki, M.; Amita, F.; Osugi, J. *Rev. Sci. Instrum.* **1979**, *50*, 0073.
(7) Funahashi, S.; Haraguchi, K; Tanaka, M. *Inorg. Chem.* **1977**, *16*, 1349.
(8) Funahashi, S.; Ito, Y.; Tanaka, M. *J. Coord. Chem.* **1973**, *3*, 125.
(9) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303.
(10) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.

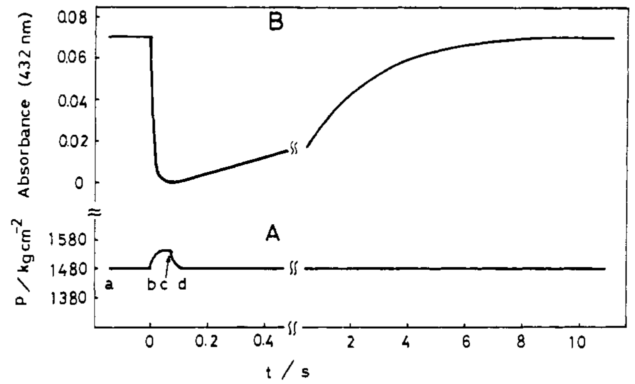


Figure 3. Changes of pressure and absorbance with time: A, pressure fluctuation with time (the pressure was followed with a strain gauge); B, a typical stopped-flow trace. The conditions are as follows: $C_{V\text{-}NTA} = 2.10 \times 10^{-4}$ m, $C_{H_2O_2} = 5.32 \times 10^{-3}$ m, $-\log [H^+] = 1.89$, $I = 1.05$ m, 25 °C, $P = 1480$ kg cm^{-2}.

in the portion of the stopped solution in an optical cell was monitored spectrally. After the pressure was released by a pressure reducing valve GV3, the used solution in the stop syringe was ejected through a drain tube (D) by opening of the valve V3. After the valve V3 was closed, the valves V1 and V2 were opened, and then P1 was pushed downward with the valve GV4.

Measurements. Solutions of $VO_2(nta)^{2-}$ and H_2O_2 were prepared as previously described.[7] The solutions were prepared at 298 K on the basis of the molar (mol dm^{-3} ≡ M) concentration scale. The molar concentrations of solutes in the solutions used in the kinetic studies (1.00 M $HClO_4$–$NaClO_4$) were converted to the pressure-independent molal (mol kg^{-1} ≡ m) scale. After a vanadium(V)–NTA complex solution was mixed with a hydrogen peroxide solution under various pressures, the reaction was followed spectrophotometrically at 432 nm, a wavelength of maximum absorption of the peroxo complex. The spectrophotometer and data processor used were those of a Union Giken RA1100 stopped-flow apparatus (Union Giken Co. Ltd.). The pressure during the reaction was also monitored by a pressure gauge.

The fluctuation of pressure during operations and a typical stopped-flow trace for the fastest reaction in the present study are shown in Figure 3. At the point b, SV is momentarily opened, and so the piston P1 rapidly transfers the reactant solutions from HPS to OC. The pressure in OC increases first to the point c and then returns to the initial pressure at the point d. The pressure jump up to 80 kg cm^{-2} and the slow recovery of pressure were observed. The rapid recovery of pressure cannot be achieved because of slow movement of the pistons due to the friction of O rings used in P and I. The higher the applied pressure, the larger is the friction force of O rings. The pressure jump at the initial time is less than 5% of the applied pressure and releases within 0.1 s. Since the half-life time of the reaction under our experimental conditions was larger than several seconds, such pressure perturbations did not affect the kinetic studies.

In an apparatus developed by Heremans et al.[5] and Sasaki et al.,[6] a stopped-flow unit is immersed in a high-pressure bomb filled with pressure-transmitting fluid. In both cases there are possibilities of contaminating reactant solutions in high-pressure syringes. In our case, high-pressure syringes are not in liquid and thus are much easier to handle. This is a considerable advantage of our apparatus. Another advantage is that the parts in contact with reactant solutions are made of acid-proof materials (platinum and Diflon).

Results

Over the pH range 2.2–4.2 at atmospheric pressure, the rate law for the formation of the peroxo complex has been given by eq 1,[7] where $k_1 = 7.41$ M^{-1} s^{-1} ($\Delta H^{\ddagger} = 39 \pm 1$ kJ mol^{-1},

$$d[VO(O_2)(nta)^{2-}]/dt = (k_1 + k_2[H^+])[VO_2(nta)^{2-}][H_2O_2] \quad (1)$$

$\Delta S^{\ddagger} = -96 \pm 9$ J K^{-1} mol^{-1}) and $k_2 = 1.86 \times 10^4$ M^{-2} s^{-1} ($\Delta H^{\ddagger} = 39 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -33 \pm 9$ J K^{-1} mol^{-1}) at 25 °C and $I = 1.00$ M. In the present study, the reaction was investigated over a wider range of pH 1.8–6.5, MES (2-(N-morpholino)ethanesulfonic acid)[11] being used as a pH buffer (pH 5.5–6.5).

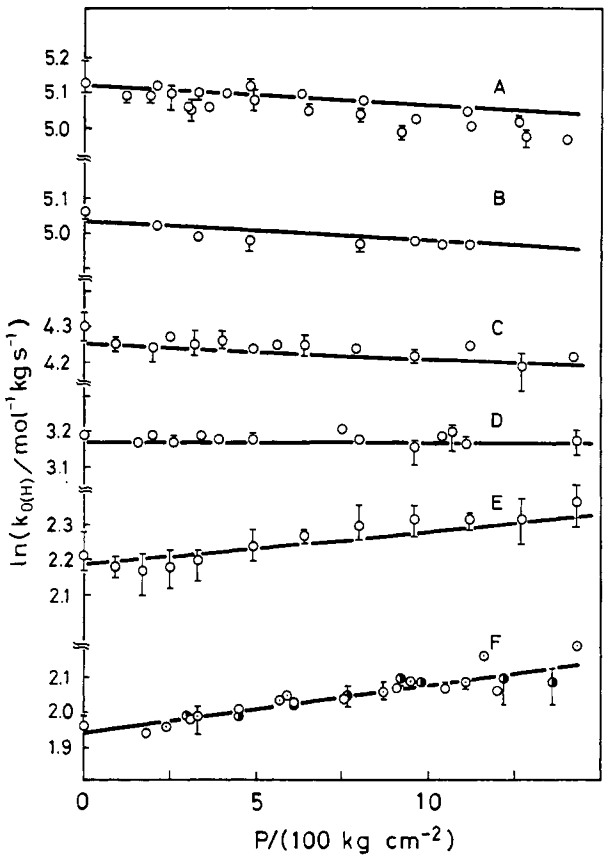


Figure 4. Pressure dependence of second-order rate constant $k_{0(H)}$ (conditions: 25 °C, $I = 1.05$ m ($NaClO_4$)). A: $[H^+] = 1.14 \times 10^{-2}$ m. B: $[H^+] = 1.04 \times 10^{-2}$ m. C: $[H^+] = 4.47 \times 10^{-3}$ m. D: $[H^+] = 1.19 \times 10^{-3}$ m. E: $[H^+] = 1.39 \times 10^{-4}$ m. F: ○, $[H^+] = 2.66 \times 10^{-6}$ m; ◑, 1.41×10^{-6} m; ⊙, 1.48×10^{-6} m. Each point is the average of three or more determinations. The solid curves were calculated by using the rate constants and activation volumes obtained.

The conditional second-order rate constants ($k_{0(H)} = k_1 + k_2[H^+]$) thus obtained were in excellent agreement with those reported previously.[7] The corresponding rate constants $k_{0(H)}$ were the same at atmospheric pressure and a given $[H^+]$ whether the reaction was carried out by the high-pressure stopped-flow assembly or the standard stopped-flow assembly (Union Giken RA1100). Rate constants k_1 and k_2 at 25 °C, $I = 1.05$ m, and atmospheric pressure were determined to be 7.05 ± 0.10 m^{-1} s^{-1} and $(1.46 \pm 0.05) \times 10^4$ m^{-2} s^{-1} (in molal units), respectively. Thus at pH higher than 5.5 the reaction proceeds via the proton-independent path,[12] while at pH lower than 2.3 the k_2 path predominates. Plots of values of ln $k_{0(H)}$ at a given $[H^+]$ against pressure P are shown in Figure 4. Plot A is for the k_2 path involving only the proton-dependent path and plot F is for the k_1 path involving the proton-in-

---

(11) Good, N. E.; Winget, G. D.; Winter, W.; Connolly, T. N.; Izawa, S.; Singh, R. M. M. *Biochemistry* **1966**, *5*, 467.

(12) The pH of a buffered solution should vary with the change in pressure. The volume change ΔV_{MES} for the protonation to the nitrogen atom of 2-(N-morpholino)ethanesulfonate is not available. The volume changes in the protonation of morpholine and 4-methylmorpholine are −7.4 cm^3 mol^{-1}.[13] ΔV remains practically unaffected on the introduction of a methyl group on the nitrogen atom of morpholine. This trend is similar to that shown by the aliphatic methylamine series.[14] Thus a ΔV_{MES} of about −7.4 cm^3 mol^{-1} may be expected. The ratio of the protonation constants at pressures of 1 and 1500 kg cm^{-2} is about 1.5. The pH of a buffered solution will become a little higher with increasing pressure. Since in the present case the reaction is independent of the hydrogen ion concentration at pH higher than 5.5, the variation of the pH of a buffered solution with change in pressure does not affect the rate.

(13) Cabani, S.; Mollica, V.; Lepori, L.; Lobo, S. T. *J. Phys. Chem.* **1977**, *81*, 982.

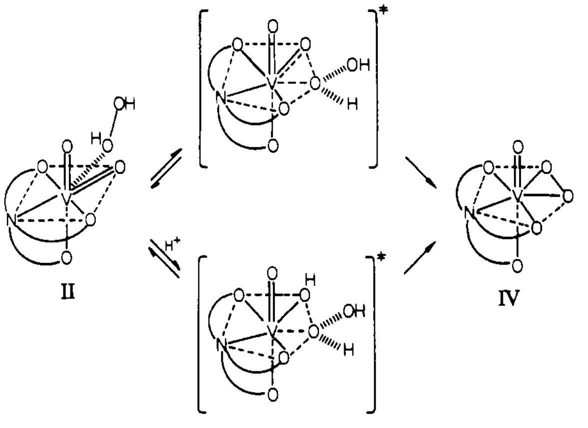
(14) Cabani, S.; Conti, G.; Lepori, L. *J. Phys. Chem.* **1974**, *78*, 1030.

Scheme I

$$\underset{\text{I}}{VO_2L} + H_2O_2 \rightleftharpoons \underset{\text{II}}{VO_2L\cdots H_2O_2} \rightarrow \underset{\text{III}}{VO_2L(H_2O_2)} \rightarrow \underset{\text{IV}}{VO(O_2)L}$$

Scheme II

$$\underset{\text{I}}{VO_2(nta)^{2-}} + H_2O_2 \rightleftharpoons \underset{\text{II}}{VO_2(nta)^{2-}\cdots H_2O_2}$$



III

dependent path. Both plots are linear within the experimental uncertainty. Thus the volumes of activation $\Delta V_1^\ddagger$ and $\Delta V_2^\ddagger$ for the k_1 path and k_2 path are assumed to be pressure independent, and the conditional second-order rate constant is expressed as eq 2, where k_1^0 and k_2^0 are corresponding rate

$$k_{0(H)} = k_1^0 \exp(-P\Delta V_1^\ddagger/RT) + k_2^0[H^+] \exp(-P\Delta V_2^\ddagger/RT) \quad (2)$$

constants at zero pressure. Values of k_1^0, k_2^0, $\Delta V_1^\ddagger$, and $\Delta V_2^\ddagger$ were obtained by a nonlinear least-squares fit to all eight sets of data (363 points) simultaneously:[15] $k_1^0 = 7.0 \pm 0.1$ m^{-1} s^{-1}, $k_2^0 = (1.4 \pm 0.1) \times 10^4$ m^{-2} s^{-1}, $\Delta V_1^\ddagger = -3.4 \pm 0.5$ cm^3 mol^{-1}, and $\Delta V_2^\ddagger = 1.5 \pm 0.5$ cm^3 mol^{-1}. Values of k_1^0 and k_2^0 are the same as corresponding values obtained at atmospheric pressure.

Discussion

Kinetic studies on the peroxo complex formation of (aminopolycarboxylato)dioxovanadate(V) have proposed an associative mechanism (Scheme I) through a seven-coordinate transition state for the reaction of hydrogen peroxide with VO_2L (V(V)-EDTA, V(V)-EDDA, and V(V)-DMEDDA complexes),[1] where $VO_2L\cdots H_2O_2$ (II) is a seven-coordinate intermediate involving H_2O_2 bonded as a monodentate at a face of the octahedron of VO_2L and the rate-determining step is the rearrangement of the associative complex (II) to the distorted pentagonal bipyramid (III). In these reactions, the proton does not contribute to the associate complex formation (I → II), but it assists the rearrangement step (II → III). The partial dissociation of metal-carboxylate bonds during the rate-determining step in the proton-independent path seems unlikely as pointed out from the mechanistic consideration.[1]

First, the volume effect of dissociation of a carboxylate group in the complex should be considered. A volume effect of about 13 cm^3 mol^{-1} is expected for the protonation of a carboxylate group.[4] The hydrated proton contributes only 1.5 cm^3 mol^{-1} of the 23.3 cm^3 mol^{-1} electrostriction associated with the self-ionization of water; the remaining electrostriction is attributable to the hydration of hydroxide ion.[16] There is the possibility of a predissociative type of mechanism, in which the positive $\Delta V^\ddagger$ contribution of partial breaking of vanadium-carboxylate bonds is compensated by a negative contribution from solvation due to the newly created charges. The dissociation of a carboxylate group in V(V)-NTA involves a cleavage of a metal-oxygen bond whereas the addition of a water molecule to the complex represents the reverse of this, a formation of a metal-oxygen bond. In this case, moderately negative contributions to $\Delta V^\ddagger$ are to be expected for the dissociation of a carboxylate group and somewhat larger and negative values for the association of a water molecule to the inner coordination sphere. Consequently, an interchange of an unprotonated carboxylate with a water molecule during the rate-determining step should result in a large and negative $\Delta V^\ddagger$ contribution, while the dissociation of a carboxylate without the subsequent addition of a water molecule should make a small and probably negative $\Delta V^\ddagger$ contribution. The dissociation of a protonated carboxylate without the addition of a water molecule should result in a considerably large and positive $\Delta V^\ddagger$ contribution. On the other hand, in the case of the interchange of a protonated carboxylate group with a water molecule, the expected $\Delta V^\ddagger$ contribution is smaller.

In the present system, if the interchange of an unprotonated carboxylate group and a H_2O_2 molecule in the inner sphere were operative in the k_1 path, a large negative contribution to $\Delta V_1^\ddagger$ should be expected. Actually the small negative value of $\Delta V_1^\ddagger$ may rule out such a predissociation and is consistent with an associative mechanism with the addition of a H_2O_2 molecule to the face of the octahedron and the subsequent rearrangement to the distorted pentagonal bipyramid. The H_2O_2-V bond formation and rearrangement must involve contraction.

In the k_2 path, the proton may assist the reaction either by dissociation of carboxylate coordinated to the central metal ion or by addition to oxo groups. In the case of the dissociation of carboxylate by protonation the small positive value of $\Delta V_2^\ddagger$ suggests that the coordination site vacated by the dissociation of protonated carboxylate should be occupied by a water molecule.

The thermodynamic parameters for the partial dissociation of carboxylate may be estimated from the difference of parameters for the formation of the MIDA and NTA complexes of vanadium(V): $\Delta H = -25$ kJ mol^{-1} and $\Delta S = 117$ J K^{-1} mol^{-1} for the MIDA complex; $\Delta H = \sim 0$ kJ mol^{-1} and $\Delta S = 263$ J K^{-1} mol^{-1} for the NTA complex.[17] Then taking into account $\Delta H = \sim 0$ kJ mol^{-1} and $\Delta S = 25$–46 J K^{-1} mol^{-1} for the protonation of the free carboxylate,[17] we estimate $\Delta H \simeq -25$ kJ mol^{-1} and $\Delta S \simeq -100$ to -121 J K^{-1} mol^{-1} for the proton-assisted partial dissociation of carboxylate in the vanadium complex. These values do not correspond to the difference between activation parameters in the k_1 and k_2 paths.

On the other hand, the protonation to the oxo group must involve a small, positive $\Delta V^\ddagger$ contribution judging from the small partial molar volume of a proton and the small electrostriction on the oxo group of vanadium, as expected from its very weak basicity. This corresponds to the findings. Moreover, since the enthalpy and entropy for protonation to an oxo group with very weak basicity are around zero kJ mol^{-1} and positive several tens J K^{-1} mol^{-1}, respectively, these values explain the difference of activation parameters for the k_1 and k_2 paths. After all consideration, we rule out the possibility of the proton-assisted dissociation of carboxylate in the k_2 path.

In conclusion, the proposed mechanism of the reaction of H_2O_2 with the octahedral $VO_2(nta)^{2-}$ complex to produce the pentagonal-bipyramidal $VO(O_2)(nta)^{2-}$ complex is shown in

---

(15) Nakagawa, T.; Oyanagi, Y. Program Library SALS (Statistical Analysis with Least-Squares Fitting), Nagoya University Computation Center, 1979.

(16) Noyes, R. M. *J. Am. Chem. Soc.* **1964**, *86*, 971.

(17) Yamada, S.; Nagase, J.; Funahashi, S.; Tanaka, M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 617.

Scheme II. II is an associative intermediate involving H_2O_2 bonded as a monodentate at a face of the octahedron of $VO_2(nta)^{2-}$. The rearrangement to the distorted pentagonal-bipyramidal transition state (III) from the associative complex (II) is enhanced by the protonation to an oxo group in the k_2 path.

There is no direct evidence to distinguish whether oxo oxygen or oxygen in hydrogen peroxide is released as a water molecule from the transition state (III). The oxygen exchange on vanadium(V) ion is very slow,[18] and mostly the oxygen exchange of oxyanion is not first order but second order in hydrogen ion concentration.[19,20] The strength of the V=O bond in vanadium(V) complexes estimated from IR spectra does not correspond to the reactivity of vanadium(V) complexes with H_2O_2.[1] Thus as shown in Scheme II it is likely that the peroxo in the product results from an oxo group of the V(V)–NTA complex and an oxygen atom of hydrogen peroxide.

Acknowledgment. We are grateful to the Ministry of Education, Science and Culture of Japan, for financial support (Shiken Kenkyu (2), No. 284025) for the construction of the high-pressure stopped-flow apparatus and for support of this work through Grant No. 347034.

Registry No. I, 59368-60-4; IV, 62126-17-4; H_2O_2, 7722-84-1.

---

(18) Murmann, R. K. *Inorg. Chem.* **1977**, *16*, 46.
(19) Gamsjäger, H.; Baertschi, P. *Helv. Chim. Acta* **1972**, *55*, 2154.
(20) Betts, R. H.; Voss, R. H. *Can. J. Chem.* **1970**, *48*, 2035.

Contribution from the Department of Chemistry, University of Alberta,
Edmonton, Alberta, Canada T6G 2G2

Kinetics of Solvent Water Exchange on Iron(III)

M. GRANT[1] and R. B. JORDAN*

Received April 24, 1980

Pulsed NMR methods have been used to measure the transverse and longitudinal relaxation rates of oxygen-17 in aqueous solutions of iron(III) (8.20×10^{-3}–0.315 *m*) and perchloric acid (0.34–3.89 *m*) from 0 to 140 °C. The results have been used to determine the kinetic parameters for solvent water exchange from $Fe(OH_2)_6^{3+}$ and $Fe(OH_2)_5OH^{2+}$. The values of k (s^{-1}, 25 °C), ΔH^* (kcal mol^{-1}), and ΔS^* (cal mol^{-1} deg^{-1}) are $(1.6 \pm 0.2) \times 10^2$, 15.3 ± 0.6, and 2.9 ± 1.6 for $Fe(OH_2)_6^{3+}$ and $(1.2 \pm 0.1) \times 10^5$, 10.14 ± 0.35, and 1.26 ± 0.95 for $Fe(OH_2)_5(OH)^{2+}$. The solvent exchange rates and various ligand substitution rates are most consistent with associative activation for substitution on $Fe(OH_2)_6^{3+}$ and dissociative activation for $Fe(OH_2)_5(OH)^{2+}$.

A standard method of determining the mechanism of ligand substitution on a metal ion is to compare the solvent exchange rate with the ligand substitution rate.[2] After correction for ion pair formation it has been found, at least for cobalt(II) and nickel(II), that the dissociative mechanism suggested by Eigen and Wilkins[3] is most consistent with the results. There have been a number of studies of ligand substitution on iron(III), but the mechanistic conclusions remain uncertain because of the lack of published water exchange rate data. The iron(III) system is complicated by the ease with which the $Fe(OH_2)_6^{3+}$ ion hydrolyzes and polymerizes.

This paper reports the results of oxygen-17 pulsed NMR relaxation time measurements on aqueous iron(III) perchloric acid solutions. The temperature and hydrogen ion dependence of the water solvent exchange rate has been determined.

Experimental Section

Materials. Ferric perchlorate stock solutions were prepared from two sources of iron. First, ammonium ferric sulfate (BDH AnalaR grade) was treated with an excess of concentrated NaOH solution, and the precipitated hydrated ferric oxide was dissolved in excess perchloric acid. After concentration of the resulting solution and cooling, crystals of $Fe(ClO_4)_3 \cdot 9H_2O$ were obtained and washed with concentrated perchloric acid. The damp crystals were dissolved in 1 M perchloric acid to give a stock solution about 0.7 M in iron(III) and 1.8 M in $HClO_4$. Second, high-purity iron (Alfa Products; 99.998% considering metallic impurities) was dissolved in concentrated nitric acid, and the solution was fumed with concentrated perchloric acid. The resulting crystals were treated as above to give a stock solution of similar composition.

The stock solutions were analyzed for iron both volumetrically by reduction to iron(II) with stannous chloride and by reoxidation with standard potassium dichromate[4] and spectrophotometrically as the tris(1,10-phenanthroline)iron(II) complex after reduction with hydroxylamine.[5] The methods gave concordant results. Manganese(II) is known to be a common impurity of iron compounds, and the very effective NMR line-broadening characteristics of the ion make it a highly undesirable contaminant. The two iron(III) stock solutions were analyzed for manganese spectrophotometrically as MnO_4^- after oxidation of the solution with periodate. The manganese concentration of the stock solutions was less than 2×10^{-6} M, and at these levels no contribution to the ^{17}O relaxation times from manganese(II) is possible.[6] The solutions were also analyzed for iron(II); the tests were negative, and $[\text{iron(II)}]/[\text{iron(III)}] \leq 5 \times 10^{-3}$.

The acid content of the stock solutions was measured by titration of the solutions with standard NaOH by using phenolphthalein[7] as indicator and verified by displacement of H^+ from a cation-exchange resin in the H^+ form.

Aluminum perchlorate was prepared from the nitrate salt (Fisher) by fuming a concentrated aqueous solution with concentrated perchloric acid. When the mixture was cooled, white crystals of $Al(ClO_4)_3 \cdot 6H_2O$ were precipitated and were washed with perchloric acid and dried at 100 °C for several hours. A stock solution in water was analyzed for aluminum gravimetrically as tris(8-quinolinolato)aluminum[4] and for perchloric acid by ion-exchange displacement of H^+.

Reagent grade sodium perchlorate (G. F. Smith) was recrystallized twice, and a 1 M solution was prepared and analyzed by cation

---

(1) On leave from the Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Australia.
(2) Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974; Chapter 4.
(3) Eigen, M.; Wilkins, R. G. *Adv. Chem. Ser.* **1965**, *No. 49*, 55.
(4) Vogel, A. I. "Quantitative Inorganic Analysis", 3rd ed.; Longman: London, 1961.
(5) Marczenko, Z. "Spectrophotometric Determination of the Elements"; Wiley: New York, 1976.
(6) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 308.
(7) Milburn, R. M.; Vosburgh, W. C. *J. Am. Chem. Soc.* **1955**, *77*, 1352.