BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2030—2038 (1970)

Oxidation of Vanadium(II) by Nitrate Ion

Kazuyoshi TANAKA

Department of Chemistry, College of Science, Rikkyo (St. Paul's) University, Nishi-Ikebukuro, Toshima-ku, Tokyo

(Received August 15, 1969)

The oxidation rates of vanadium(II) to vanadium(III) by nitrate ion were determined from the time dependence of the polarographic diffusion currents. As supporting electrolytes sodium perchlorate and sodium sulfate were used. The oxidation rates were linearly dependent on hydrogen ion concentration in strongly acidic solutions ($pH<2$) and independent in weakly acidic solutions ($pH>2$). Polarographic half-wave potentials, reversibility and diffusion currents indicated that vanadium(II) in sulfate medium formed a sulfato-complex or an ion-paired species which was oxidized faster than V^{2+} (hydrated) in perchlorate medium. The oxidation in sulfate medium proceeded mainly by a single two-electron oxidation, and further reaction between vanadium(II) and vanadium(IV) yielded a stable dimer of vanadium(III) detected by absorption experiments. The rates measured in various halide solutions, except fluoride, gave almost the same rate constants in perchlorate medium. The gaseous products from nitrate ion were identified as NO and N_2O by infrared spectrum measurements. The overall oxidation was proposed;

$$8V(II)+2NO_3^-+10H^+ \rightarrow 8V(III)+N_2O(g)+5H_2O$$

There have been a number of studies concerning the oxidation of vanadium(II) with oxidizing agents such as chlorate,[1] perchlorate,[2] oxygen and hydrogen peroxide,[3] and with higher oxidation states of metals such as vanadium(IV),[4] thallium(III),[5] chromium(III),[6] iron(III),[7] and uranium(VI).[8] The possibility of the reaction proceeding by way of a one- or a two-electron oxidation step is of interest. The vanadium is suitable for clarifying this problem because vanadium ions in aqueous solution are in various oxidation states from vanadium(II) to vanadium(V). Although the oxidation of cerium(III),[9] molybdenum(V),[10] and uranium(III)[11] by nitrate ion has been studied, no report has appeared concerning the oxidation of vanadium (II) by nitrate ion. The rates could be followed by the time dependence of polarographic diffusion current corresponding to the disappearance of vanadium(II) ion in the solution. Vanadium(II) species were polarographically investigated in various supporting electrolytes.[12,13] Many spectrophotometric measurements have been carried out in a strongly acidic solutions ($[H^+]>0.1$ M) because of the low extinction coefficient and high acidity of vanadium(II) stock solution. However, it was polarographically possible to determine the rate in weakly acidic solution of low vanadium(II) concentration.

Newton and Baker reported that the rate of reaction between vanadium(II) and vanadium(IV) changed with sulfate ion concentration, and the reaction intermediate VOV^{4+} was formed.[14] When the oxidation by nitrate ion proceeds by a single two-electron step, it is expected that the dimer of vanadium(III) may be formed and be stable in sulfate medium. This problem in particular is discussed in this paper.

Experimental

Materials. Vanadium(IV) perchlorate solutions were prepared from vanadyl sulfate solutions by adding $Ba(ClO_4)_2$ to precipitate $BaSO_4$. Vanadium(II) stock solutions were prepared by reduction of $VO(ClO_4)_2$

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[1] G. Gordon and P. H. Tewari, *J. Phys. Chem.*, **70**, 200 (1966).

[2] W. R King, Jr., and C. S. Garner, *ibid.*, **58**, 29 (1954).

[3] J. H. Swinehart, *Inorg. Chem.*, **4**, 1069 (1965).

[4] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **68**, 228 (1964).

[5] F. B. Baker, W. D. Brewer and T. W. Newton, *Inorg. Chem.*, **5**, 1294 (1966).

[6] E. Deutsh and H. Taube, *ibid.*, **7**, 1532 (1968).

[7] B. R. Baker, M. Orhanovic and N. Sutin, *J. Amer. Chem. Soc.*, **89**, 722 (1967).

[8] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **69**, 176 (1965).

[9] A. G. Sykes, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 10, Academic Press, Inc., New York (1967), p. 233.

[10] E. P. Guymon and J. T. Spence, *J. Phys. Chem.*, **70**, 1964 (1966).

[11] J. Koryta, *Collect. Czech. Chem. Commun.*, **20**, 667 (1955).

[12] J. J. Lingane, *J. Amer. Chem. Soc.*, **67**, 182 (1945).

[13] J. J. Lingane and L. Meites, *ibid.*, **73**, 2165 (1951).

[14] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).

solutions containing perchloric acid with zinc amalgam in a pure nitrogen stream. The vanadium(IV) concentration was spectrophotometrically determined using the absorption at 720 mμ, which is mainly due to vanadium(IV). The standard vanadium(IV) solutions were prepared by dissolving vanadium metal (>99.5 %) in a dilute nitric acid. Vanadium(II) concentration was also determined as vanadium(IV) produced by air oxidation in a concentrated perchloric acid solution.

Sodium nitrate solutions were prepared from Wako reagent grade chemicals which had been dried over concentrated sulfuric acid. As supporting electrolytes used for polarographic measurements, perchloric acid (70%), sulfuric acid and their salts, sodium fluoride, chloride, bromide, and iodide were also of reagent grade. Redistilled water was used.

Measurements. The proper amount of vanadium(II) solution was added to deaerated solution containing supporting electrolytes. After the solution was vigorously stirred with nitrogen gas, d.c. and a.c. polarographic measurements were performed at 25°C to obtain the values of half-wave potential and reversibility[15] of vanadium(II). The appropriate amount of sodium nitrate was added to the solution, and mixed by passing nitrogen gas. The time dependence of the polarographic diffusion current of vanadium(II) was recorded at a constant potential (−0.1 — 0.2V *vs.* SCE) where the diffusion current appeared. In the course of these measurements, the solution was protected from air oxidation by a stream of pure nitrogen gas. In order to follow the reactions, the sensitivity of the polarograph was set at 0.10 μA/mm, and the damping capacitance at 5 μF where the current change corresponds to the derease in vanadium(II) concentration. The ionic strength was adjusted to 0.5 by adding sodium perchlorate, except for experiments in which the rates at different ionic strengths were compared.

The visible spectra of the oxidation products were obtained as follows. After vanadium(II) solution was added to a deaerated sodium nitrate solution, the solution was mixed with nitrogen gas and then taken into a capped 1 cm cell in the spectrophotometer, and the time dependence of the absorption was measured. Gas analysis was performed in the following way. After the addition of nitrate ion to vanadium(II) solution in a vacuum vessel, the gases evolved were collected in a CaF_2 gas cell with liquid nitrogen to measure their infrared spectra in the rage 1000—4000 cm^{-1}. The experiments were performed at room temperature and all pH measurements were carried out after completion of the reactions.

Instruments. A Yanagimoto d.c. and a.c. polarograph Model PA-101 was used to obtain the polarograms and the time dependence of diffusion current of vanadium(II). An H-type cell with a saturated calomel electrode was used. The reaction vessel was large enough to hold more than 100 m*l*. The dropping time of the mercury electrode was measured by a Yanagimoto polarograph timer Model SY-2. The characteristic of dropping mercury was 0.830 mg/sec at a height of mercury reservoir of 72.2 cm. All pH measurements were made by a Towadenpa pH meter Model HM-5A. Visible absorption spectra were measured by a Hitachi Model EPV-2 and infrared spectra were recorded using JASCO Model DS-301 and DS-402G infrared spectrophotometers.

Results and Discussion

Polarographic Behavior of Vanadium(II). Linearity between vanadium(II) concentration and its diffusion current was necessary to obtain kinetic data from the time dependence of the diffusion current. Diffusion currents were measured at various concentrations of vanadium(II) in perchlorate, and sulfate media. Typical results are shown in Fig. 1. On adding vanadium(II) to the electrolyte solution, vanadium(II) was partially oxidized by air. It was found from the value of diffusion current, however, that about 90% of the vanadium ions were in the +2 oxidation state. From Fig. 1, it is polarographically possible to follow the decrease of vanadium(II) concentration by nitrate ion and calculate the rate constant of oxidation. As shown in Fig. 1, the diffusion currents in perchlorate medium are larger than those in sulfate medium. Although the diffusion currents in perchlorate medium were independent of hydrogen ion concentration, those in sulfate medium increased with hydrogen ion concentration and decreased with sulfate ion concentration. The polarographic half-wave potentials, diffusion currents and reversibility are shown in Table 1. The half-wave potentials were almost constant below pH 2 in perchlorate medium. However, they

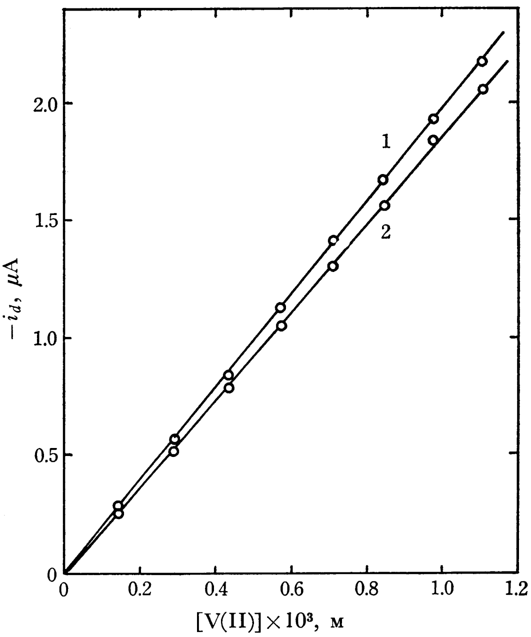

Fig. 1. Relation between vanadium(II) concentration and polarographic diffusion current at pH∼4 in the solutions:
1, 0.50 M $NaClO_4$; 2, 0.25 M Na_2SO_4.

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[15] M. Senda and I. Tachi, *J. Electrochem. Soc. Jap.*, **27**. 83 (1957).

Table 1. Half-wave potential, diffusion current, and reversibility of vanadium(II) at 25°C

pH	Perchlorate medium			pH	Sulfate medium		
	$-E_{1/2}$ (V *vs.* SCE)	$-i_d$ (μA)	$i_p/i_d\sqrt{\tau}$ ($\mho\cdot A^{-1}\cdot sec^{-1/2}$)		$-E_{1/2}$ (V *vs.* SCE)	$-i_d$ (μA)	$i_p/i_d\sqrt{\tau}$ ($\mho\cdot A^{-1}\cdot sec^{-1/2}$)
0.45	0.46	1.97	18.1	0.36[a]	0.50	1.93	6.4
0.69	0.46	1.96	20.3	0.58[a]	0.48	1.90	7.7
1.05	0.46	1.94	22.5	0.98[a]	0.49	1.88	11.2
2.01	0.46	1.95	23.6	1.95[b]	0.50	1.85	10.6
3.05	0.48	1.93	15.1	3.05[b]	0.51	1.82	8.8
4.01	0.50	1.96	10.5	3.94[b]	0.52	1.83	6.3
4.48	0.52	1.95	7.2	4.50[b]	0.53	1.80	4.4

a) H_2SO_4, $NaClO_4$ b) 0.05 M Na_2SO_4, $HClO_4$

shifted to more negative potential and the reversibility markedly decreased above pH 2. It was therefore concluded that vanadium(II) species was V^{2+} (hydrated) and the electro-oxidation product vanadium(III) was the same hydrated species in strongly acidic solution (pH<2). On the other hand, vanadium(III) in weakly acidic solution might form a hydrolyzed species which made the electrode reaction irreversible. In this case, the half-wave potential depends on hydrogen ion concentration. Lingane and Meites found that VO^+ in acetate buffer solution was reduced at more negative potential than VOH^{2+}.[16] However, it is more reasonable to conclude that a considerable amount of vanadium(III) ions in weakly acidic solution formed a dimer VOV^{4+}. Biermann and Wong reported that vanadium(II) species, above 2.5×10^{-3} M in perchloric acid, has a dimeric form, and below this concentration the polynucleation process seems incomplete.[17] From the diffusion currents obtained at various acidities, vanadium(II) species was, however, estimated to be mainly V^{2+}(hydrated) even in weakly acidic solution.

Although the diffusion currents in sulfate medium decreased both with sulfate ion concentration and with increasing pH values, they were linear with respect to vanadium(II) concentration. The half-wave potentials in sulfate medium were more negative than those in perchlorate medium at the same pH value. When sulfuric acid concentration decreased, the half-wave potential shifted to more positive potential and the reversibility became higher. In 0.25 M sodium sulfate, the half-wave potentials slightly shifted to more positive potential with the increase in vanadium(II) concentration, and became almost constant at the potential −0.53 V *vs.* SCE above 0.7×10^{-3} M vanadium(II). Thus, in the present work we could not obtained the results as published in which the half-wave potential is not affected by sulfate ion concentrations.[17] The second wave was observed at a more positive potential (~+0.03V *vs.* SCE) in weakly

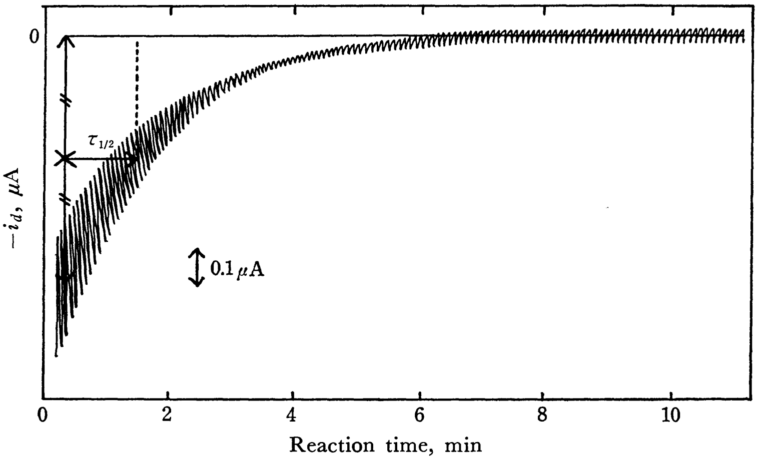

Fig. 2. Typical example of time dependence of polarographic diffusion current in 0.10 M perchloric acid at 25°C.
Initial concentration: 8.49×10^{-4} M vanadium(II), 1.84×10^{-2} M sodium nitrate

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[16] J. J. Lingane and L. Meites, *J. Amer. Chem. Soc.*, **70**, 2525 (1948).

[17] W. J. Bierman and W-K. Wong, *Can. J. Chem.*, **41**, 2510 (1963).

acidic sulfate medium, which corresponded to the oxidation wave of vanadium(III) to vanadium(IV). From these data, it was concluded that vanadium(II) in sulfate medium partially formed a sulfato-complex or an ion-paired species with sulfate ion and almost all vanadium(III) formed a sulfato-complex.

Zinc(II) ion was present in all of the solution used for the polarographic measurements and its concentrations were almost three times larger than those of vanadium(II). No influence of zinc ion could be observed in the polarograms of vanadium(II).

Measurement of Rate Constant. A typical time dependence of the diffusion current obtained is shown in Fig. 2. As all reactions were carried out in excess nitrate ion, the rate constants of the oxidation reaction could be calculated from the half-life time of the reaction ($\tau_{1/2}$ shown in Fig. 2) by

$$k=0.6931/\tau_{1/2} \qquad (1)$$

This relation is valid only if the rate of the oxidation is first-order with respect to vanadium(II). The logarithmic current-time plots in perchlorate, and sulfate media are shown in Fig. 3 and the rate constants calculated from Eq. (1) are listed in Table 2. From the results, the rates were indicated to be first-order with respect to vanadium(II) concentration, and the rate law is therefore given by

$$-\mathrm{d}[\mathrm{V(II)}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{V}^{2+}] \qquad (2)$$

where k_{obs} is equal to k in Eq. (1).

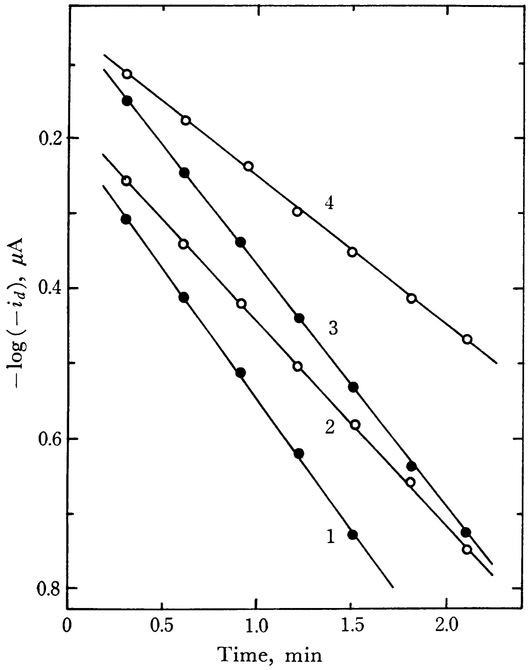

Fig. 3. Dependence of logarithmic current on time in the solutions:
1, 0.10 M H_2SO_4, pH 0.98; 2, 0.10 M $HClO_4$, pH 1.05; 3, 0.10 M Na_2SO_4, pH 4.29; 4, 0.50 M $NaClO_4$, pH 4.33. Initial concentration: *ca.* 8×10^{-4} M vanadium(II), 1.84×10^{-2} M sodium nitrate

Table 2. Dependence of k_{obs} on vanadium(II) concentration at 25°C[a)]

Perchlorate medium			Sulfate medium		
pH	10^4[V(II)] M	$10^3 k_{\mathrm{obs}}$ sec^{-1}	pH	10^4[V(II)] M	$10^3 k_{\mathrm{obs}}$ sec^{-1}
1.05	5.12	11.2	0.98[b)]	5.24	14.2
1.05	4.23	10.9	0.98	4.11	14.3
1.05	3.52	11.1	0.98	3.22	14.1
1.05	2.93	11.0	0.98	2.61	14.0
1.05	2.42	11.1	0.98	2.04	14.3
1.05	2.02	10.9	0.98	1.60	14.2
1.05	1.69	11.0	0.98	1.23	14.3
4.33	5.92	7.18	4.29[c)]	5.87	12.3
4.33	4.51	7.36	4.29	4.85	12.4
4.33	3.42	7.21	4.29	3.94	12.8
4.33	2.97	7.27	4.29	2.91	12.8
4.33	2.30	7.33	4.29	2.36	12.9
4.33	1.70	7.23	4.29	1.89	12.5
4.33	1.53	7.36	4.29	1.23	12.9

a) 1.84×10^{-2} M NO^{-}_{3} b) 0.10 M H_2SO_4
c) 0.10 M Na_2SO_4

The possibility for zinc ion to act as a catalytic impurity in this oxidation process was investigated by using electrically prepared vanadium(II). The rate constant ($k_{\mathrm{obs}}=6.96\times10^{-3}$ sec^{-1}) at pH 1.66 was almost the same as that ($k_{\mathrm{obs}}=6.81\times10^{-3}$ sec^{-1}) obtained using vanadium(II) prepared on zinc amalgam. Oxidation of vanadium(II) by perchlorate ion could not be detected until completion of the reaction by nitrate ion (about 30 min).

Dependence of Rate on Hydrogen Ion Concentration. The rate constants for strongly acidic solutions are plotted in Fig. 4. Sodium sulfate was added to sulfate medium in order to keep the sulfate ion concentration constant at 0.01 M assuming K_a of HSO_4^- to be 4.37×10^{-2} M.[18)] Perchloric acid was used to regulate the hydrogen ion concentration of the solution. As shown in Fig. 4, the rate constants in sulfate medium were larger than those in perchlorate medium, but in both cases they were linearly proportional to the hydrogen ion concentration. The rate constants measured in weakly acidic solutions are shown in Fig. 5. In sulfate medium, 0.05 M sodium sulfate was added to the solutions and the hydrogen ion concentration was adjusted with perchloric acid. The results gave the same relationship as in strongly acidic solutions, *viz.*,

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18) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-ion Complexes," The Chemical Soc., London (1964), p. 232.

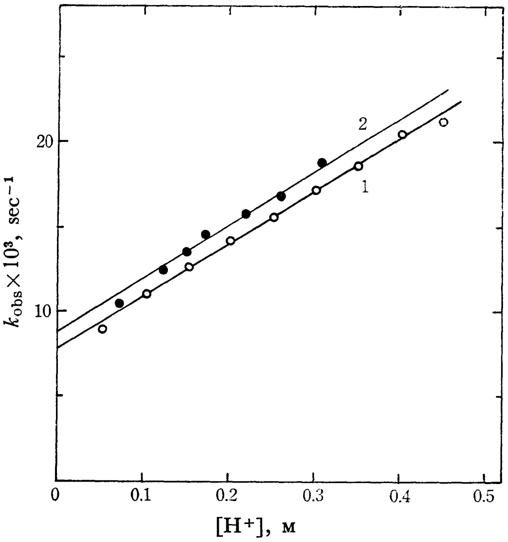

Fig. 4. Dependence of the first-order rate constant on hydrogen ion concentration at 25°C in the solution:
1, $HClO_4$; 2, $HClO_4$, 0.01 M [SO_4^{2-}].
Initial concentration: *ca.* 8×10^{-4} M vanadium(II), 1.83×10^{-2} M sodium nitrate

sulfate ion increased the rate of the oxidation reaction. Although the rate constants in both media were almost independent of hydrogen ion concentration above pH 2, they slightly increased above pH 3.5, particularly in sulfate medium. The kinetic data obtained shows that the rate laws can be expressed as follows:

$$\text{pH} < 2 \qquad k_{obs} = k_1[H^+] + k_2 \tag{3}$$

$$\text{pH} > 2 \qquad k_{obs} = \text{almost constant} \tag{4}$$

Dependence of Rate Constants on Ionic Strength. The effects of ionic strength on the rate constant are summarized in Table 3. The results in both media indicate that the rates decreased with the increase of ionic strengths. It has been reported that the rates of the reaction between vanadium(II) and vanadium(IV) increase with ionic strength, and are in good agreement with the extended form of Debye-Hückel's equation. Since the rate of reaction between a cation and a cation system may be increased by an anion which is used for adjusting ionic strength and which decreases the effective charge of the reaction,[4,19] it can be expected that the anion suppresses the rate of reaction between anionic oxidizing agent and the cation which forms an ion-paired species. The rates obtained are interpreted by assuming that vanadium(II) formed an ion-paired species with perchlorate ion. The larger rate constants obtained in sulfate medium are thought to indicate that the reaction proceeds mainly by another oxidation path as mentioned below.

TABLE 3. EFFECT OF IONIC STRENGTH ON k_{obs} AT 25°C

Perchlorate medium (pH 4.4)		Sulfate medium (pH 4.4)a)	
Ionic strength	10^3k_{obs} b) sec^{-1}	Ionic strength	10^3k_{obs} b) sec^{-1}
2.00	5.89	2.00	9.81
1.50	6.17	1.50	10.1
1.00	6.76	1.00	10.9
0.50	7.53	0.50	11.4
0.25	9.38	0.20	12.0

a) 0.10 M Na_2SO_4 b) 1.84×10^{-2} M NO_3^-

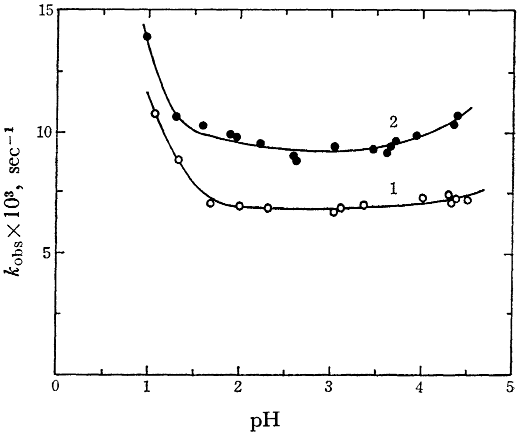

Fig. 5. Variation of the first-order rate constant by hydrogen ion concentration in the solution:
1, $HClO_4$, $NaClO_4$, 2, 0.05 M Na_2SO_4, $HClO_4$, $NaClO_4$.
Initial concentration: *ca.* 8×10^{-4} M vanadium(II), 1.84×10^{-2} M sodium nitrate

Nitrate Ion Dependence of Rate. The rates measured by varying the nitrate ion concentration in perchlorate medium are shown in Fig. 6. From

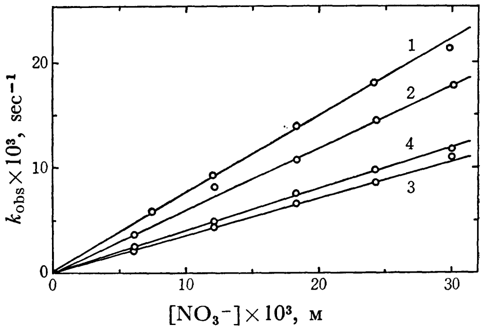

Fig. 6. Nitrate-ion-dependence of rate constant in perchlorate medium at pH 1: 0.80, 2: 1.08, 3: 3.09, 4: 4.38.
Initial concentration: *ca.* 8×10^{-4} M vanadium(II)

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[19] J. P. Candlin, J. Halpern and S. Nakamura, *J. Amer. Chem. Soc.*, **85**, 2517 (1963).

the results, the rates in various acid solutions were found to be first-order with respect to nitrate ion concentrations and are expressed by

$$k_{\text{obs}} = k_3[\text{NO}_3^-] \tag{5}$$

As indicated in Fig. 5, the increasing rate with pH above 3.5 in perchlorate medium is confirmed from the relation between the lines 3 and 4 in Fig. 6.

In sulfate medium, the rate increased with sulfate ion concentration and the intercepts of straight lines shown in Fig. 7 are not zero. This indicates that nitrate-ion-independent terms of the rate constants appeared. Even in sulfate medium, the rates were, however, first-order with respect to the nitrate ion concentration. The rate law is

$$k_{\text{obs}} = k_4 + k_5[\text{NO}_3^-] \tag{6}$$

When nitrate ion was not present in the solution, the diffusion current of vanadium(II) was almost constant for about 30 min, showing that no oxidation occurred by other oxidizing agents such as oxygen in the air. It was therefore concluded that the nitrate-ion-independent term was characteristic of the oxidation in the presence of sulfate ion, in which a sulfato-complex or an ion-paired species was oxidized faster than V^{2+} (hydrated).

After completion of oxidation, the polarograms indicated that the vanadium(III) concentration was about 50% of that of the initial vanadium(II). Since the polarographic wave in large excess of nitrate ion involved the catalytic wave,[20] the species of the reaction product vanadium(III) could not be determined. However, the diffusion current was not affected by vanadium(III) species.

Measurements of Visible Absorption Spectra. It was difficult to measure the rate of oxidation in a weakly acidic solution as used for the polarographic studies because of the small extinction coefficients of vanadium(II) and vanadium(III), and of the high acidity of vanadium(II) stock solution.[21] When sodium nitrate was added to the solution containing 2×10^{-2} M vanadium(II), the solution immediately exhibited a brown color, which gradually changed to green. Hydrogen ion in the vanadium(II) stock solution could be decreased somewhat by employing the experimental condition that hydrogen ion was reduced on zinc amalgam. When sodium nitrate was added to this solution, the brown color developed was so stable that absorption spectra could be measured. The spectra showed a peak at 425 mμ similar to that of the

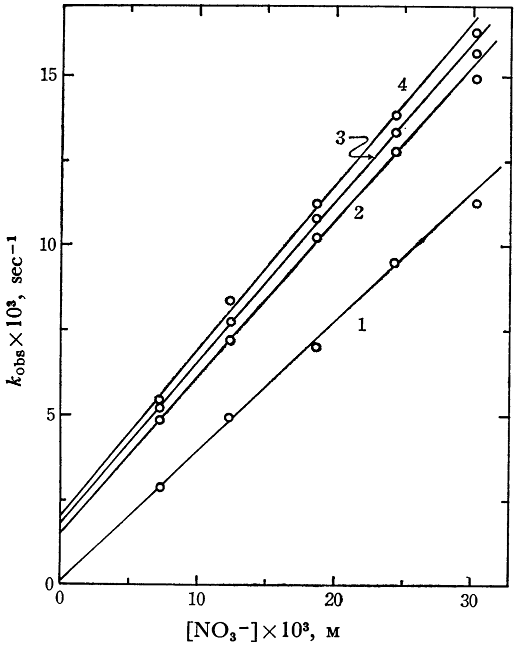

Fig. 7. Effect of sulfate ion on nitrate-ion-dependence of the first-order rate constant at pH∼4.4 in the solutions:

1, 0.50 M NaClO_4; 2, 0.05 M Na_2SO_4; 3, 0.01 M Na_2SO_4; 4, 0.15 M Na_2SO_4.

Initial concentration: *ca.* 8×10^{-4} M vanadium(II)

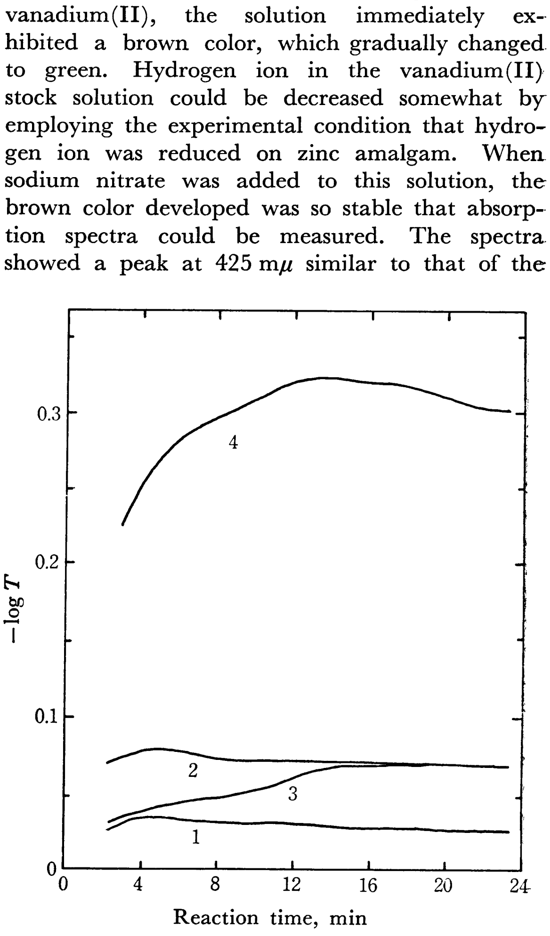

Fig. 8. Time dependence of absorbance at 425 mμ (μ=0.50):

1, 2.38×10^{-3} M vanadium(II) and 8.93×10^{-4} M sodium nitrate in 0.20 M HClO_4 (pH 0.80); 2, 1 in 0.20 M H_2SO_4 (pH 0.78); 3, 1.66×10^{-3} M vanadium(II) and 2.86×10^{-3} M sodium nitrate in 0.50 M NaClO_4 (pH 4.3); 4, 3 in 0.10 M Na_2SO_4 (pH 4.4)

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[20] J. W. Olver and J. W. Ross, Jr., *J. Phys. Chem.*, **66**, 1699 (1962).

[21] S. C. Furman and C. S. Garner, *J. Amer. Chem. Soc.*, **72**, 1785 (1950).

intermediate VOV^{4+} of the reaction between vanadium(II) and vanadium(IV).[14] Because of a large molar extinction coefficient of this species, it was possible to follow the rate of reaction producing VOV^{4+} in almost the same composition as used for the polarographic measurements. As indicated in Fig. 8, the absorbance at 425 mμ increased both with sulfate ion concentration and with decrease in hydrogen ion. Newton and Baker found that the rate of the reaction between vanadium(II) and vanadium(IV) increased to some extent with a small amount of sulfate ion, and the reaction yielded the intermediate VOV^{4+} which decomposed to monomer in a strongly acidic solution.[14] The time dependence of absorption at 425 mμ in perchlorate medium gave the decomposition rate of the dimer VOV^{4+} to monomer. The half-life time at pH 2.59 was about 1.8 hr. The resulting solution exhibited a yellow green color which was mainly due to the absorption of vanadium(III) monomer. The result indicates that there was a reaction path between vanadium(II) and vanadium(IV) in the oxidation by nitrate ion. It was therefore considered that nitrate ion mainly acted as a one-electron oxidizing agent in strongly acidic solutions and as a two-electron one in weakly acidic solution,[22] and that vanadium(IV) produced by a single two-electron oxidation then reacted with vanadium(II) to yield the dimer. Since vanadium(III) yielded the dimer above pH 2, the dimer was not produced only by the reaction between vanadium(II) and vanadium(IV). Accordingly the oxidation in weakly acidic solutions did not always proceed by a single two-electron oxidation path.

In the present work, the rate constant of the oxidation of vanadium(III) by nitrate ion polarographically measured at pH 1.33 was smaller than 7.7×10^{-5} sec^{-1} at 1.84×10^{-2} M nitrate ion, and this rate was considerably slow compared with that of vanadium(II) by nitrate ion. When sodium nitrate was added to a strongly acidic vanadium(II) solution, the solution first developed a green color which changed to blue corresponding to the absorption of VO^{2+}. This indicates that almost all vanadium ions were once in +3 oxidation state during the course of oxidation reaction, and the polarographic measurements, therefore, followed the overall oxidation of vanadium(II) to vanadium(III).

Effects of Sulfate and Halide Ion on the Rates. The typical effects of anions on the rates of oxidation are shown in Fig. 9. The rate increased with sulfate ion and became almost constant above 0.10 M sulfate ion. The results indicate that above this sulfate ion concentration almost all of vanadium(II) formed a sulfato-complex or an ion-paired species, and the rate of oxidation of this species was not affected any more by increasing sulfate ion concentration. Newton and Baker reported that the rate of the reaction between vanadium(II) and vanadium(IV) increased by adding 4×10^{-3} M sulfate ion. This increase is probably connected with the activation process.[4] These facts lead to the conclusion that the dimer in sulfate medium may be $VOV(SO_4)^{2+}$ and was fairly stable in the solution as discussed in the absorption experiments. It is also considered from the results given in Fig. 9 that a sulfato-complex or an ion-paired species was oxidized faster than V^{2+} (hydrated).

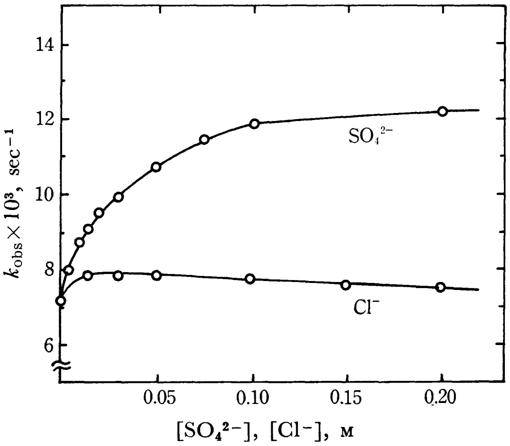

Fig. 9. Effects of sulfate and chloride ion on first-order rate constant at pH~4.4.
Initial concentration: *ca.* 8×10^{-4} M vanadium(II), 1.84×10^{-2} M sodium nitrate

The half-wave potentials, reversibility and oxidation rates of vanadium(II) by nitrate ion are summarized in Table 4. The half-wave potential in fluoride solution indicates that vanadium(III) formed a fluoro-complex,[13] and the oxidation rate was too fast to be measured by the polarographic method. The polarographic measurements of oxidation in halide solutions, except fluoride, gave almost the same rate constants as in perchlorate medium. From these half-wave potentials, it was considered that only weak complexing took place and therefore the rates were not so much affected by halide ion concentration. However, as shown in Fig. 9, the rate increases with a small amount of chloride ion and becomes gradually suppressed above 2.5×10^{-2} M chloride ion. It has been found that the reaction between vanadium(II) and vanadium(IV) is catalyzed by chloride ion, vanadium(IV) in the presence of a large amount of chloride ion forms a chloro-complex, and the chloride ion does not increase the rate any more.[4]

The reversibility increased from fluoride to iodide solution as shown in Table 4. It was found in the oxidation of titanium(III) by chlorate ion that the smaller the rate constant, the lower the

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22) M. Ardon and R. A. Plane, *ibid.*, **81**, 3197 (1957).

TABLE 4. EFFECTS OF SULFATE AND HALIDE IONS ON k_{obs} AT 25°C

Salt	Concentration M	pH	$-E_{1/2}$ V vs. sec	$i_p/i_d\sqrt{\tau}$ ℧·A^{-1}·$sec^{-1/2}$	10^3k_{obs}[a] sec^{-1}
NaF	0.20	7.20	0.67	2.0	very fast
NaCl	0.20	4.52	0.52	11.4	7.30
NaBr	0.20	4.40	0.53	28.3	7.84
NaI	0.20	4.42	0.54	42.8	7.56
Na_2SO_4	0.40	—	0.55	6.2	11.8

a) 1.84×10^{-2} M NO_3^-

reversibility.[23] However, the oxidation rates by nitrate ion increased with sulfate ion and the reversibility were lower than those in perchlorate medium. Although the rates in halide solutions, except fluoride, gave almost the same rate constants, reversibility was markedly varied. The discrepancies can be explained as follows: 1) the electrochemical oxidation product in sulfate medium may be so stable that the product makes the electrode reaction irreversible; 2) in halide solutions, the electron transfer of electrode reaction may be accelerated by halide ion specifically adsorbed on mercury.

Infrared Determination of Gaseous Products. When sodium nitrate was added to acidic vanadium(II) solutions, the solution immediately developed a brown color which gradually turned to green, yielding gaseous products. The gases produced in a vacuum line were collected in a gas cell using liquid nitrogen and determined by measuring their infrared spectra. The results are shown in Table 5. They indicate that NO and N_2O were predominant products in the ratio of 3 : 1.[25,26] However, this ratio in the polarographic measurements is considered to be more favorable to NO because of the large excess of nitrate ion. HNO_2 and NO_2 found in perchlorate medium might be produced by the oxidation of NO with oxygen in the traps, and their amounts negligibly small. The gaseous products immediately generated by the reaction between vanadium(II) and nitrite ion were also detected as NO and N_2O. The oxidizing power of nitrite ion was so strong that vanadium(IV) in acidic solution was easily oxidized to vanadium(V). Since there was such a low oxidation state of nitrogen as N_2O, it was expected that vanadium(II) would be oxidized by NO gas. NO gas easily produced by adding sodium nitrite to ferrous sulfate in sulfuric acid was bubbled through a vanadium(II) solution. The infrared spectrum of gas collected in the gas cell indicated the presence of N_2O. No N_2O was detected from the original NO gas. The solution bubbled for 3 hr developed a blue color corresponding to the absorption of vanadium(IV). The facts varified that vanadium(II) was oxidized to vanadium(IV) by NO gas, and the rate was very slow. However, all reactions investigated by the polarographic method were carried out with a considerable excess of nitrate ion to obtain feasible rates. Therefore, the amount of N_2O produced in the reaction was negligible with respect to the amount of NO. The gaseous products did not affect the time dependence of the diffusion current.

TABLE 5. INFRARED SPECTRUM MEASUREMENTS OF REACTION PRODUCTS FROM NITRATE ION

Perchlorate medium		Sulfate medium	
Observed NO str. Freq. (cm^{-1})	Compound	Observed NO str. Freq. (cm^{-1})	Compound
2223 s	N_2O	2233 s	N_2O
1873 s	NO	1871 s	NO
1678 w	HNO_2[24]	1290 s	N_2O
1620 w	NO_2		
1285 s	N_2O		

s : strong   w : weak

Reaction Mechanism. The changes of diffusion currents measured in a large excess of vanadium(II) over nitrate ion showed that the amount of vanadium(II) ions oxidized by nitrate ions was approximately four times larger than that of nitrate ions consumed. In fact, the ratio of vanadium(II) to nitrate ion was 3.7 : 1 in perchlorate medium and 3.9 : 1 in sulfate medium. Therefore, overall oxidation of vanadium(II) by nitrate ion is

$$8V^{2+} + 2NO_3^- + 10H^+ \rightarrow 8V^{3+} + N_2O + 5H_2O$$

The reaction processes involved the oxidation paths of vanadium(II) by vanadium(IV), NO_2^- and NO as mentioned above. Guymon and Spence reported that NO was a major product in the oxidation of molybdenum(V) by nitrate ion and that NO^+ was assumed to be the reactive intermediate.[10] For the oxidation of vanadium(II) by nitrate ion in

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23) K. Tanaka, K. Morinaga and K. Nakano, *Nippon Kagaku Zasshi*, **90**, 478 (1969).

24) T. A. Turney and G. A. Wright, *Chem. Rev.*, **59**, 497 (1959).

25) E. L. Saier and A. Pozefsky, *Anal. Chem.*, **26**, 1079 (1954).

26) G. M. Begun and W. H. Fletcher, *J. Chem. Phys.*, **28**, 414 (1958).

the present work, NO^+ was also assumed to be present as a reactive intermediate, and the following possible mechanisms in perchlorate medium were proposed.

$$V^{2+} + NO_3^- + H^+ \xrightarrow{k_I} V^{3+} + NO_2 + OH^- \quad (I)$$

$$V^{2+} + NO_3^- \xrightarrow{k_{II}} VO^{2+} + NO_2^- \quad (II)$$

$$V^{2+} + VO^{2+} \longrightarrow VOV^{4+} \quad (III)$$

$$2NO_2 \rightleftarrows N_2O_4 \quad (IV)$$

$$N_2O_4 \rightleftarrows NO^+ + NO_3^- \quad (V)$$

$$V^{2+} + NO^+ \longrightarrow V^{3+} + NO \quad (VI)$$

$$V^{2+} + NO_2^- + 2H^+ \longrightarrow V^{3+} + NO + H_2O \quad (VII)$$

$$2V^{2+} + 2NO + 2H^+ \longrightarrow 2V^{3+} + N_2O + H_2O \quad (VIII)$$

The oxidation rate corresponding to reaction(VII) was polarographically measured and gave a second-order rate constant of $3\times10^2\,\text{M}^{-1}\cdot\text{sec}^{-1}$ at pH 4.70. Thus, the rate of reaction (VII) is very fast and gaseous products such as NO and N_2O were generated. Frank and Spence investigated the oxidation of molybdenum(V) by nitrite ion, and found that the rate law was dependent on nitrite ion and hydrogen ion, but independent of molybdenum (V).[27] This leads to the conclusion that nitrite ions are in the following equilibrium:

$$H^+ + NO_2^- \rightleftarrows HNO_2 \quad (IX)$$

$$H^+ + HNO_2 \rightleftarrows NO^+ + H_2O \quad (X)$$

The true oxidation path of reaction(VII) was therefore considered to be the same as that of reaction(VI). Reaction (I) was the predominant oxidation path in strongly acidic solutions and reaction(II) in weakly acidic solutions. The polarographic determination of the reaction between vanadium(II) and vanadium(IV) was performed, and the rate constant obtained at pH 1.66 was $0.545\,\text{M}^{-1}\cdot\text{sec}^{-1}$, indicating that the rate was almost the same as that by nitrate ion.

Applying the steady-state condition to NO_2, NO_2^-, N_2O_4, NO^+, and VO^{2+}, the following rate law is obtained.

$$-d[V(II)]/dt = (2k_I[H^+] + 3k_{II})[V^{2+}][NO_3^-] \quad (7)$$

When hydrogen ion concentrations are low, that is, pH>2, Eq. (7) can be written as

$$-d[V(II)]/dt = 3k_{II}[V^{2+}][NO_3^-] \quad (8)$$

These formulas are in good agreement with the experimental rate laws, and the proposed mechanism is in line with kinetic data.

In sulfate medium, the following equilibrium between vanadium(II) and sulfate ion may exist below 0.1 M sulfate ion.

$$V^{2+} + SO_4^{2-} \rightleftarrows VSO_4 \quad (XI)$$

where VSO_4 shows a sulfato-complex or an ion-paired species. The oxidation rate of this species is faster than that in perchlorate medium, and the following oxidation paths may be involved.

$$VSO_4 + NO_3^- + H^+ \longrightarrow VSO_4^+ + NO_2 + OH^- \quad (I')$$

$$VSO_4 + NO_3^- \longrightarrow VOSO_4 + NO_2^- \quad (II')$$

$$V^{2+} + VOSO_4 \longrightarrow VOV(SO_4)^{2+} \quad (III')$$

As mentioned in the visible absorption experiments, the stable dimer of vanadium(III) in sulfate medium might be produced by reaction (III). However, it is difficult from the present data to interpret the nitrate-ion-independent term k_4 in Eq. (6), so that further work for the oxidation in sulfate medium is necessary.

Conocchioli *et al.* investigated the oxidation of iron(II) by hypochlorate ion and suggested that iron(IV) was produced as an intermediate by a single two-electron oxidation.[28] Oxidation of vanadium(II) by thallium(III) proceeds mainly by a single two-electron step.[5] When vanadium (II) was oxidized by hydrogen peroxide and oxygen, about 30% and 60%, respectively, vanadium(III) was formed by the reaction between vanadium(II) and vanadium (IV).[3] The results obtained for the oxidation of vanadium(II) by nitrate ion might show that reactions (I) and (II) proceed by one-electron oxidation, and reactions (II) and (III) by two-electron one, the latter occurring mainly in weakly acidic solutions, particularly in sulfate medium. The two-electron oxidation would also be possible in the reaction between vanadium(II) and nitrate ion. However, when sodium nitrite was added to acidic vanadium(II) solution, the solution did not exhibit a brown color. This shows that nitrate ion acted as a one-electron oxidizing agent.

The energy of activation was determined by measuring the rate of overall reactions at five temperatures, 15, 20, 25, 30, and 38°C.[29] The results obtained are shown in Table 6.

TABLE 6. ACTIVATION ENTHALPY AND ENTROPY OF OVERALL REACTION AT $\mu=0.50$

Composition[a)]	pH	$\Delta H^{\ddagger}$ Kcal	$\Delta S^{\ddagger}$ e.u.
0.50 M $NaClO_4$	4.45	13.3	−21.4
0.10 M Na_2SO_4	4.42	14.6	−11.9

a) 8.10×10^{-4} M V(II), 1.84×10^{-2} M NO_3^-

The author is indebted to Dr. E. Miki for the infrared spectrum measurements of gaseous products from nitrate ion.

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[27] J. A. Frank and J. T. Spence, *J. Phys. Chem.*, **68**, 2131 (1964).

[28] T. J. Conocchioli, E. J. Hamilton, Jr., and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 926 (1965).

[29] K. J. Laidler, "Reaction Kinetics," Vol. **1** Pergamon Press (1963), p. 84.