

Figure 1. Plot of $\log[(P_\infty - P)/P_\infty]$ vs. time for reactions at 45° and $\mu = 0.9$: ○, from $0.08 M \text{BH}_4^-$ with $0.82 M \text{NH}_4^+$; Δ, from $0.08 M \text{NH}_4^+$ with $0.82 M \text{BH}_4^-$.

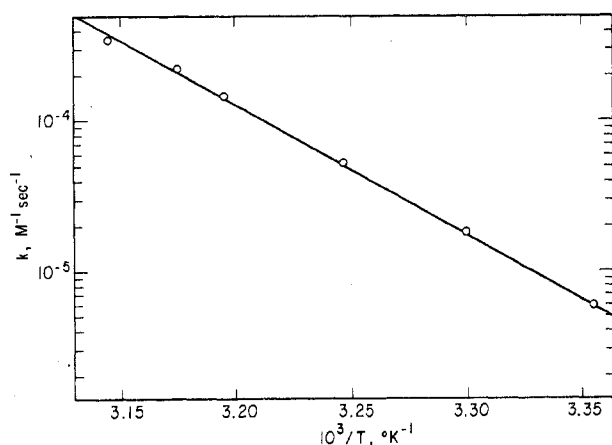


Figure 2. Temperature dependence of k at $\mu = 0.9$.

Table I. Rate Constants in Liquid Ammonia at $\mu = 0.9$

Temp, °C	$k, M^{-1} \text{sec}^{-1}$	Temp, °C	$k, M^{-1} \text{sec}^{-1}$
25	5.88×10^{-6}	40	$1.43 \times 10^{-4}^a$
30	1.79×10^{-5}	42	2.17×10^{-4}
35	5.04×10^{-5}	45	$3.40 \times 10^{-4}^b$

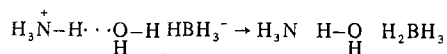
^a Average of 1.49×10^{-4} and 1.37×10^{-4} , from separate experiments. ^b This value was obtained in two experiments.

Table II. Rate Constants in Liquid Ammonia at 30°

Ionic strength	$[\text{BH}_4^-], M$	$[\text{NH}_4^+], M$	$k, M^{-1} \text{sec}^{-1}$
0.0098	0.00888	0.00094	2.07×10^{-3}
0.049	0.0446	0.0045	6.23×10^{-4}
0.20	0.1954	0.0046	1.94×10^{-4}
0.90	0.818	0.0818	1.79×10^{-5}
1.92 ^a	0.818	0.0818	4.95×10^{-6}

^a NaBr was added to increase the ionic strength.

involved:



Because hydrogen bonding is relatively unimportant in liquid ammonia, the analogous mechanism in liquid ammonia is unlikely.

The Bronsted-Bjerrum theory of ionic reaction leads to the expression

$$\log(k/k_0) = \frac{2\alpha Z_A Z_B \sqrt{\mu}}{1 + \beta\alpha\sqrt{\mu}}$$

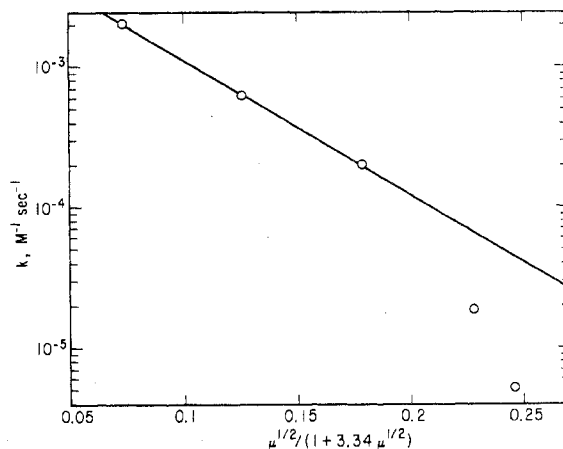


Figure 3. Ionic strength dependence of k at 30° . The line is drawn with the slope given by eq 2.

which was applied to rate constants measured at various ionic strengths at 30° (Table II). Using the dielectric constant⁵ of 16.5 for ammonia at 30° , we calculated⁶ $\alpha = 5.16$ and $\beta = 0.711$. A value for a of 4.7 \AA was used in constructing the Bronsted-Bjerrum plot of the data, shown in Figure 3. The experimental points at relatively low ionic strengths have a slope close to that predicted by eq 2, whereas the points at higher ionic strengths are low, probably because of the pairing of reactant ions with inert ions. Dewald and Browall⁷ correlated rate data for the reaction of the electron with the tri-*n*-butyl-*n*-propylammonium ion with the Bronsted-Bjerrum equation using a value for a of 6 \AA .

Acknowledgment. This work was supported by the Energy Research and Development Administration.

Registry No. BH_4^- , 16971-29-2; NH_4^+ , 14798-03-9.

References and Notes

- (1) R. E. Davis and C. G. Swain, *J. Am. Chem. Soc.*, **82**, 5949 (1960); R. E. Davis, C. L. Kibby, and C. G. Swain, *ibid.*, **82**, 5950 (1960); W. H. Stockmayer, R. R. Miller, and R. J. Zeto, *J. Phys. Chem.*, **65**, 1076 (1961); R. E. Mesmer and W. L. Jolly, *Inorg. Chem.*, **1**, 608 (1962); J. A. Gardiner and J. W. Collat, *J. Am. Chem. Soc.*, **86**, 3165 (1964); J. A. Gardiner and J. W. Collat, *ibid.*, **87**, 1692 (1965); F. T. Wang and W. L. Jolly, *Inorg. Chem.*, **11**, 1933 (1972).
- (2) D. L. Armstrong, Aerojet Engineering Corp. Annual Report No. 367, Defense Documentation Center File No. ATI50631, March 11, 1949.
- (3) E. Mayer, *Inorg. Chem.*, **11**, 866 (1972).
- (4) J. A. Gardiner and J. W. Collat, *J. Am. Chem. Soc.*, **87**, 1692 (1965).
- (5) J. Jander, "Anorganische und allgemeine Chemie in flüssigem Ammoniak", Wiley, New York, N.Y., 1966, p 23.
- (6) W. J. Moore, "Physical Chemistry", 3rd ed, Prentice-Hall, Englewood Cliffs, N.J., 1963, p 358.
- (7) R. R. Dewald and K. W. Browall, *Chem. Commun.*, 1511 (1968).

Contribution from the Department of Chemistry, Jadavpur University, Calcutta-32, India

Kinetics of the Oxidation of Antimony(III) by Vanadium(V)

Basanta B. Pal and Kalyan K. Sen Gupta*

Received June 13, 1974

AIC40377S

The kinetics of the oxidation of several organic¹ and inorganic²⁻⁵ compounds by vanadium(V) have been studied. Kinetic studies of the oxidation of antimony(III) by inorganic oxidants⁶⁻⁸ have also been reported. In continuation of our earlier work,⁹⁻¹² we have now studied the reaction between antimony(III) and vanadium(V) which has been incorporated in this report.

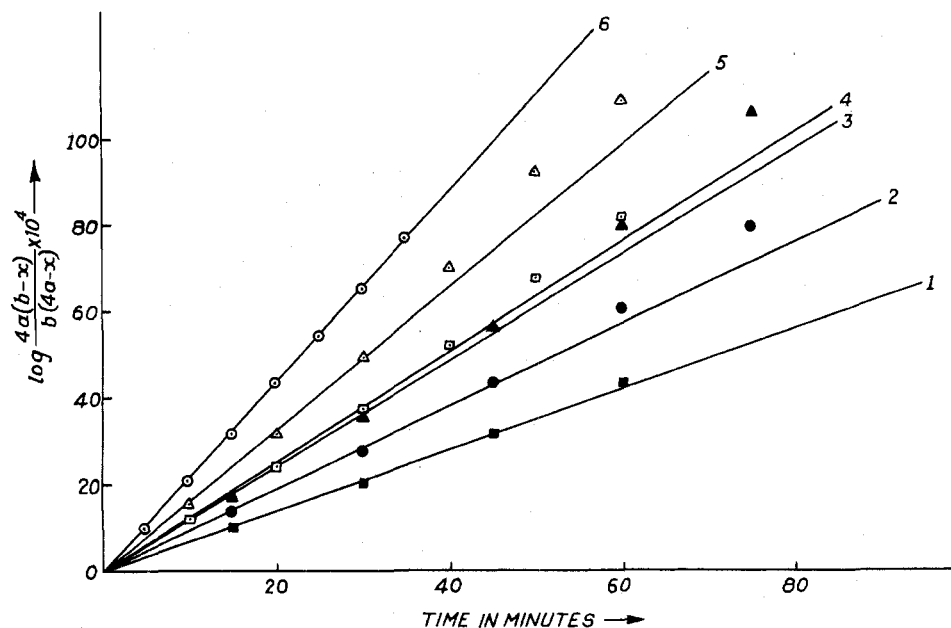


Figure 1. Influence of temperature on oxidation of Sb_2O_3 by V(V) in sulfuric acid medium ($[\text{vanadium(V)}] = 8.65 \times 10^{-3} \text{ M}$; $[\text{Sb}_2\text{O}_3] = 2.0 \times 10^{-3} \text{ M}$). Temperatures and H_2SO_4 concentrations for the various curves are as follows: (1) 40° , 4.0 M ; (2) 45° , 4.0 M ; (3) 45° , 4.5 M ; (4) 50° , 4.0 M ; (5) 55 and 50° , 4.0 and 4.5 M ; (6) 55° , 4.5 M .

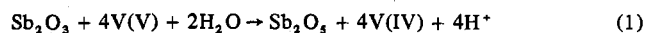
Experimental Section

Standard solutions of vanadium(V) in perchloric and sulfuric acids were prepared by dissolving ammonium metavanadate in known solutions of the respective acids. Antimony(III) solution in sulfuric acid was made by dissolving antimony(III) oxide (GR, E. Merck) in 50% sulfuric acid but the solution gradually hydrolyzed on keeping and fresh solutions were always prepared. For reactions in perchloric acid, antimony(III) oxide was allowed to stand overnight in contact with perchloric acid. The decanted solution was then used after dilution. Antimony(III) was standardized¹³ against potassium bromate using Methyl Red as a redox indicator. Acetic acid-water mixtures were prepared by adding requisite amounts of glacial acetic acid to the vanadium(V) solution.

Kinetic Measurements. The kinetics of reaction were followed as described earlier.⁹ Known concentrations of both antimony(III) and vanadium(V) were placed in two separate conical flasks which were placed in the thermostat for a sufficient time to attain the temperature ($\pm 0.1^\circ$). Two solutions were then mixed and at suitable intervals an aliquot part was withdrawn and quenched in a phosphoric acid-sulfuric acid mixture containing a known excess of ferrous ammonium sulfate solution. The unreacted ferrous solution was then titrated against vanadium(V) using sodium diphenylaminesulfonate as indicator. The reaction was followed up to 40% conversion of initial oxidant and generally four to eight experimental points were taken in each run for the calculation of rate constants. Antimony(V) did not interfere with the titration. Iron(III) which is generated by the oxidation of iron(II) with vanadium(V) would not react further with antimony(III), since the redox potential of the $\text{Fe(III)} \rightarrow \text{Fe(II)}$ couple is lowered¹⁴ to about 0.5 V in phosphoric acid and the potential is well below the potential of the $\text{Sb(V)} \rightarrow \text{Sb(III)}$ system which is 0.64 V.

Results

Stoichiometry. One mole of antimony(III) oxide consumed 4 mol of vanadium(V) in 6.0 M sulfuric acid in 72 hr at 35° and the reaction may be represented stoichiometrically by the equation



Rate Law. Equation 2 was used to evaluate the second-order rate constant, where "a" and "b" are the initial molar concentrations of antimony(III) oxide and vanadium(V), respectively, and "x" is the amount of vanadium(V) which has disappeared at time "t". The plots of $\log [4a(b-x)/b(4a-x)]$ against t gave straight lines passing through the origin

Table I. Variation of First-Order Rate Constants of the Oxidation of Sb_2O_3 by Vanadium(V) with Change in Substrate Concentrations

a			b		
$10^3 [\text{Sb}_2\text{O}_3], \text{ M}$	$10^5 k_1, \text{ sec}^{-1}$	$10^2 k_1 / [\text{Sb}_2\text{O}_3], \text{ M}^{-1} \text{ sec}^{-1}$	$10^3 [\text{Sb}_2\text{O}_3], \text{ M}$	$10^5 k_1, \text{ sec}^{-1}$	$10^2 k_1 / [\text{Sb}_2\text{O}_3], \text{ M}^{-1} \text{ sec}^{-1}$
2.29	2.71	1.18	1.50	0.62	0.42
3.33	4.6	1.38	2.10	0.93	0.44
4.59	6.4	1.39	2.53	1.12	0.44
5.17	7.3	1.41	3.12	1.39	0.45
6.45	9.1	1.41			

^a $[\text{Vanadium(V)}] = 2.17 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{SO}_4] = 4.8 \text{ M}$, temperature 45° . ^b $[\text{Vanadium(V)}] = 2.07 \times 10^{-3} \text{ M}$, $[\text{HClO}_4] = 5.0 \text{ M}$, temperature 45° .

$$k_2 = \frac{9.212}{t(b-4a)} \log \frac{4a(b-x)}{b(4a-x)} \quad b > 4a \quad (2)$$

(Figure 1) and the values of k_2 have been calculated from the gradient of such plots. The reproducibility was better than $\pm 3\%$.

Effect of Substrate Concentrations on Reaction Rate. The reactions were studied at constant $[\text{vanadium(V)}]_0$, but $[\text{Sb}_2\text{O}_3]_0$ was varied. The acid concentration was held constant in each run. The first-order rate constants were determined graphically from the plots of $\log [\text{vanadium(V)}]$ against time. The rate increases with the increase in $[\text{Sb}_2\text{O}_3]_0$. The plots of $1/k_1$ against $1/[\text{Sb}_2\text{O}_3]_0$ are linear, passing through the origin. The values of $k_1/[\text{Sb}_2\text{O}_3]_0$ are found to be 1.35×10^{-2} and $4.4 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ in sulfuric and perchloric acids, respectively (Table I). The results indicate that the concentration of any intermediate complex is small under the conditions studied.

Effect of Mineral Acids and Their Salts on the Rate. The rate was highly dependent on acidity which was varied by the addition of either sulfuric or perchloric acid. The reaction is acid catalyzed and is faster in sulfuric acid than in perchloric acid (Table II). The most widely used way of explaining the rate with acidity has been the Zucker-Hammett hypothesis^{17,18} where $\log k_1$ may be plotted against either $-\text{H}_0$, the Hammett acidity, or $\log [\text{HX}]$. The plots of $\log k_1$ against $\log [\text{HX}]$

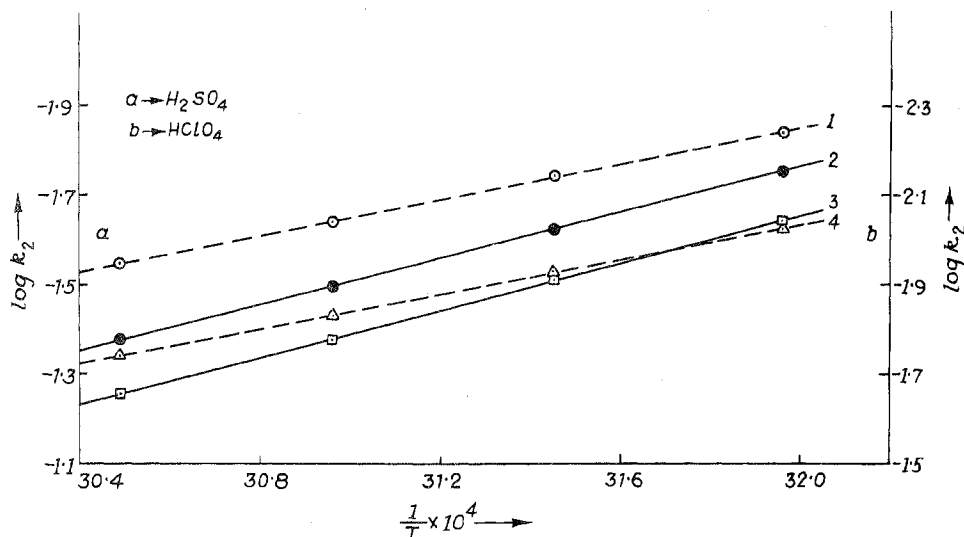


Figure 2. Plot of $\log k_2$ against $1/T$ ([vanadium(V)] = $8.65 \times 10^{-3} M$; $[Sb_2O_3] = 2.0 \times 10^{-3} M$). Acids used for the various curves are as follows: (1) 4.0 M $HClO_4$; (2) 4.0 M H_2SO_4 ; (3) 4.5 M H_2SO_4 ; (4) 5.0 M $HClO_4$.

Table II. Dependence of First-Order Rate Constants on the Oxidation of Sb_2O_3 by Vanadium(V) at Different Sulfuric and Perchloric Acid Concentrations^a

$[H_2SO_4], M$	$10^5 k_1, \text{sec}^{-1}$	$10^6 k_1 / [H_2SO_4]^2, M^{-2} \text{sec}^{-1}$	$[HClO_4], M$	$10^5 k_1, \text{sec}^{-1}$	$10^6 k_1 / [HClO_4]^2, M^{-2} \text{sec}^{-1}$
4.0	4.6	2.88	4.0	1.44	0.90
4.5	6.0	2.97	4.5	1.92	0.95
5.0	7.4	2.97	5.0	2.40	0.95
5.5	9.2	3.04	5.5	2.90	0.95
6.0	12.3	3.41			
6.5	15.4	3.64			
7.0	17.2	3.50			

^a [Vanadium(V)] = $8.0 \times 10^{-3} M$, $[Sb_2O_3] = 2.0 \times 10^{-3} M$, temperature 45° .

or $-H_0$ are linear up to acid concentrations of 5.5 M. The gradients of the former plots in both sulfuric and perchloric acids are the same (2.05) but are significantly less than unity for the other plots. The plots of $(\log k_1 + H_0)$ against $\log a_{H_2O}$ according to Bunnett¹⁶ are generally linear for the hydrolysis reactions in acid medium. The slopes define a parameter called "w" which is useful for the classification of reactions. A linear dependence of $(\log k_1 + H_0)$ against $\log a_{H_2O}$ is also observed in the present study. The values of $-H_0$ and a_{H_2O} at various acidities are taken from the reviews by Paul and Long¹⁵ and Bunnett,¹⁶ respectively. Values of Bunnett's parameter w are found to be 2.95 and 3.7 for sulfuric and perchloric acids, respectively. When w is positive, it is usually higher in perchloric acid than in sulfuric acid and the present result is in agreement with the observation made by Bunnett.¹⁶ Again, for similar hydrolytic reactions, wide variations in w values have been observed¹⁶ (-2 to +7). Consequently, the same type of mechanism may be operative in both of the acids considering that the present variations of w are not widely different. Again, the additions of sodium perchlorate (in perchloric acid), sodium sulfate, and sodium bisulfate (in sulfuric acid) do not seem to have any influence on the rate. Salt concentrations were varied up to 0.8 M, and constant values of $2.40 \times 10^{-2} M^{-1} \text{sec}^{-1}$ in 4.0 M sulfuric acid and $0.72 \times 10^{-2} M^{-1} \text{sec}^{-1}$ in 4.0 M perchloric acid have been obtained at constant concentrations of vanadium(V) and antimony(III) oxide of 8.65×10^{-3} and $2.0 \times 10^{-3} M$, respectively, at a constant temperature of 45° .

Effect of Solvent. The dielectric constant was varied by the addition of acetic acid (v/v) to the reaction mixture. The second-order rate constant increases with the increase in the

Table III. Dependence of Second-Order Rate Constants on the Oxidation of Sb_2O_3 by Vanadium(V) in Acetic Acid-Water Binary Mixtures at 50°

% acetic acid (v/v)	$10^3/D$	$10^2 k_2, M^{-1} \text{sec}^{-1}$	
		a	b
20	17.39	5.9	1.54
30	19.61	11.4	2.40
35	20.96		3.34
40	22.38	24.0	4.4
45	24.10	41	6.3
50	26.04	73	

^a [Vanadium(V)] = $8.50 \times 10^{-3} M$, $[Sb_2O_3] = 2.0 \times 10^{-3} M$, $[H_2SO_4] = 3.2 M$. ^b [Vanadium(V)] = $8.75 \times 10^{-3} M$, $[Sb_2O_3] = 1.44 \times 10^{-3} M$, $[HClO_4] = 3.0 M$.

Table IV. Second-Order Rate Constants at Different Temperatures and Various Thermodynamic Data in Sulfuric and Perchloric Acid Media of the Oxidation of Sb_2O_3 by Vanadium(V)^a

$[HX], M$	$10^2 k_2, M^{-1} \text{sec}^{-1}$				$\Delta H^\ddagger, \text{kcal/mol}$	$-\Delta S^\ddagger, \text{cal/(mol deg)}$
	40°	45°	50°	55°		
4.0 ^b	1.8	2.40	3.2	4.2	11.3 ± 0.5	32.7 ± 0.5
4.5 ^b	2.30	3.10	4.2	5.6	11.3 ± 0.5	32.1 ± 0.4
4.0 ^c	0.58	0.72	0.92	1.13	8.5 ± 0.5	43.6 ± 0.4
5.0 ^c	0.93	1.17	1.48	1.82	8.5 ± 0.5	42.7 ± 0.5

^a [Vanadium(V)] = $8.65 \times 10^{-3} M$, $[Sb_2O_3] = 2.0 \times 10^{-3} M$. ^b H_2SO_4 medium. ^c $HClO_4$ medium.

proportion of acetic acid (Table III). It has earlier been reported²⁰ that with the increase in proportion of acetic acid, the dielectric constant of the medium is mainly altered. The plots of $\log k_2$ against $1/D$ (D = dielectric constant) are linear and the gradients of both plots are positive. The values of dielectric constants for various acetic acid-water mixtures are due to Radhakrishna Murti et al.¹⁹

Activation Parameters. Runs were also made at different temperatures ranging between 40 and 55° and at intervals of 5° . The plots of $\log k_2$ vs. $1/T$ are linear (Figure 2); from the gradient of these the heats of activation have been computed. The other thermodynamic parameters have been determined (Table IV) with the aid of usual expressions which have been described earlier.⁹

Discussion

It is already known⁷ that antimony(III) and antimony(V) exist as oxy and hydroxy species but not as sulfate complexes in sulfuric acid medium. Moreover, the antimony(III) ion has

Table V. Activation Parameters for the Oxidation of Some Oxy Acids of Group 5B Elements by Vanadium(V)^a

Substrate	Medium	No. of electrons transferred	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/(mol deg)
H ₃ PO ₂ ¹⁰	H ₂ SO ₄	1	18.95	-5.1
H ₃ PO ₂ ¹⁰	HClO ₄	1	18.8	-5.7
H ₃ PO ₃ ¹²	H ₂ SO ₄	1	22.9	-6.9
H ₃ PO ₃ ¹²	HClO ₄	1	20.4	-15.2
C ₆ H ₅ PO ₂ H ₂ ¹¹	H ₂ SO ₄	1	28.8	15.3
C ₆ H ₅ PO ₂ H ₂ ¹¹	HClO ₄	2	12.2	-36.9
As ₂ O ₃ ⁹	H ₂ SO ₄	2	5.7	-50.8
As ₂ O ₃ ⁹	HClO ₄	2	7.6	-48.2
Sb ₂ O ₃	H ₂ SO ₄	2	11.3	-32.7
Sb ₂ O ₃	HClO ₄	2	8.5	-43.6

^a The polymerization test was applied in all of these cases, and in all of these one-electron-transfer reactions the addition of acrylamide yielded positive test.

a great tendency to hydrolyze²¹ and cationic compounds of antimony(III) exist as the so-called "antimonyl" ion, SbO⁺, and not as HSbO₂. Again, the increase in rate in acetic acid is so pronounced (unlike that in sulfuric and perchloric acid media) that the changes may be considered mainly due to changes in dielectric constant, and the positive slope of the plot of logarithm of the second-order rate constant against the reciprocal of the dielectric constant indicates that one of the reactive species is positively charged. The species^{1,9-12} of vanadium(V) like V(OH)₃HSO₄⁺ and V(OH)₃²⁺, which participate in many vanadium(V) oxidations, cannot be considered as the other reacting species in sulfuric and perchloric acids, respectively since the addition of perchlorate, bisulfate, or sulfate to the reaction mixture failed to alter the rate of reaction. The second-order dependence on mineral acids may be explained assuming (VO₂·2H₂SO₄)⁺ and V(OH)₂³⁺ as the reactive species for the respective cases of oxidation. However, the removal of a single electron from antimony(III) must result in the formation of a free-radical intermediate if vanadium(V) behaves as a one-electron-transfer oxidant. It is to be mentioned that neither has the antimony(IV) compound been isolated in the free state nor has its existence been established from spectral measurement.^{22,23} The addition of acrylamide to the reaction mixture failed to cause polymerization, suggesting that free radicals do not intervene in the oxidation-reduction reaction. Consequently, vanadium(V) may behave as a two-electron oxidant. Again, the kinetic evidence points to a transition state having vanadium(V), antimony(III) (possibly HSbO₂), two protons, and an unknown number of solvent molecules. The reactive species of vanadium(V) would therefore react with antimony(III) leading to the oxidation of the same to antimony(V). Vanadium(III) which is produced in the slowest step would further react with vanadium(V) producing 2 mol of vanadium(IV). The reaction between vanadium(III) and vanadium(V) is very fast.³

Although the slowest steps have been explained by a two-electron-transfer mechanism, an alternative path assuming vanadium(V) as a one-electron-transfer oxidant cannot be totally ruled out. In the oxidation of hydrazine by vanadium(V), Higginson et al.² have suggested that vanadium(V) behaves as both a 1- and 2-equiv oxidant. However, in an oxidation-reduction reaction between an ion of a transition element and a compound or ion derived from a nontransition element, the formation of a free radical or unstable oxidation state from the second reactant by a 1-equiv reaction is likely in some cases to be a more endothermic process than the corresponding 2-equiv reaction.²⁴ The exothermic process is able to lower the activation energy of reaction below that of the corresponding one-electron process.² The heats as well as entropies of activation are smaller than those obtained in

previous studies¹⁰⁻¹² where vanadium(V) behaves as a 1-equiv oxidant. The smaller activation parameters obtained in the present study lend further support to the view that vanadium(V) behaves as a 2-equiv oxidant. Corroborative evidences come from similar investigations concerning the oxidations of arsenic(III)⁹ and benzenephosphonous acid¹¹ by vanadium(V). These reactions where vanadium(V) behaves as a 2-equiv oxidant are also characterized by low activation parameters unlike the values which have been obtained in the oxidations of hypophosphorous¹⁰ and phosphorous acids¹² by vanadium(V) where the oxidant behaves as a one-electron reagent. The results presented in Table V would therefore support the contention that vanadium(V) behaves as a two-electron and not as a one-electron oxidant in the present study.

Registry No. Sb(III), 23713-48-6; V(V), 22537-31-1.

References and Notes

- J. S. Littler and W. A. Waters, "Oxidation in Organic Chemistry", K. B. Wiberg, Ed., Academic Press, New York, N.Y., 1965, Part A.
- W. C. E. Higginson, D. Sutton, and P. Wright, *J. Chem. Soc.*, 1380 (1953).
- D. T. Drye, W. C. E. Higginson, and P. Knowles, *J. Chem. Soc.*, 1137 (1962).
- N. J. Nicol and D. R. Rosseinsky, *Proc. Chem. Soc., London*, 16 (1963).
- A. G. Sykes, *J. Chem. Soc.*, 5549 (1961).
- S. K. Mishra and Y. K. Gupta, *J. Inorg. Nucl. Chem.*, 30, 2991 (1968).
- S. K. Mishra and Y. K. Gupta, *J. Chem. Soc. A*, 260 (1970).
- F. G. Soper, *J. Chem. Soc.*, 802 (1935).
- B. B. Pal, D. C. Mukherjee, and K. K. Sen Gupta, *J. Inorg. Nucl. Chem.*, 34, 3433 (1972).
- K. K. Sen Gupta, B. B. Pal, and D. C. Mukherjee, *Z. Phys. Chem. (Frankfurt am Main)*, 72, 230 (1970).
- K. K. Sen Gupta, J. K. Chaklader, B. B. Pal, and D. C. Mukherjee, *J. Chem. Soc., Perkin Trans. 1*, 926 (1973).
- K. K. Sen Gupta, B. B. Pal, and D. C. Mukherjee, *J. Chem. Soc., Dalton Trans.*, 224 (1974).
- A. I. Vogel, "A Text Book of Quantitative Inorganic Chemistry," Longmans, Green and Co., London, 1955, p 370.
- S. Glasstone, "An Introduction to Electrochemistry," Van Nostrand, New York, N.Y., 1962, p 290.
- M. A. Paul and F. A. Long, *Chem. Rev.*, 57, 1 (1957).
- J. F. Bunnett, *J. Am. Chem. Soc.*, 83, 4956 (1961).
- L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 1940, p 267.
- L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, 54, 2723 (1932).
- P. S. Radhakrishna Murti and S. C. Pati, *Indian J. Chem.*, 7, 687 (1969).
- N. Venkatasubramanian, *J. Sci. Ind. Res., Sect. B*, 20, 581 (1961).
- F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley Eastern Private Ltd., 1969, p 509.
- J. E. Whitney and N. Davidson, *J. Am. Chem. Soc.*, 69, 2076 (1947).
- A. A. Grinberg, "The Chemistry of Complex Compounds," 1st ed, Pergamon Press, London, 1962, p 127.
- W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 447 (1957).

Contribution from the Division of Chemistry,
National Research Council of Canada, Ottawa, Canada

Hydrostatic Pressure Effects upon the Metal-Chlorine Stretching Vibrations of Some 4-Substituted Pyridine Complexes of Zinc Chloride¹

P. T. T. Wong

Received October 29, 1974

AIC40750W

The symmetric and antisymmetric Zn-Cl stretching frequencies of a series of tetrahedral complexes of the form [Zn(4-Rpy)₂Cl₂], where 4-Rpy are 4-substituted pyridine derivatives, have been measured by both far-infrared and Raman spectroscopies.^{2,3} Substituents on the fourth position of the pyridine rings shift the Zn-Cl stretching frequencies and their magnitude can be correlated with the electron-releasing and -withdrawing abilities of the substituents. These results have been interpreted in terms of the change of the Zn-Cl bond nature induced by the substituents.^{2a}