

effect resulting from the higher electron density in the Fe—N=O bonds would be found in a higher  $\lambda, \delta(\text{FeNO})$  bending constant as compared to, say, the  $\lambda(\text{FeCN})$  bending constant.

The interaction force constants used in the present calculation and given in Table III are those which we initially judged to be important on the basis of the  $\text{Fe}(\text{CN})_5\text{NO}^{2-}$  structure. As shown in Table III, the stretch—stretch interaction constants involving linearly related bonds are important. Initial values for stretch—stretch interactions of C—Fe—C (axial and radial), N—Fe—C, and O—N—Fe bonds (Figure 3 of ref 2) were determined from linear triatomic calculations. The

interaction constants for internal coordinates located  $90^\circ$  (adjacent) to one another are of negligible importance and can be omitted from the force field in the present calculations. As indicated in the potential energy distribution, there is some interaction between the  $\text{FeC}(\text{axial})$  and  $\theta(\text{FeCN})$  coordinates which is reflected in the small interaction constant given in Table III.

**Acknowledgment.**—The authors wish to express their gratitude to Dr. Llewellyn H. Jones for his helpful suggestions in the preparation of the manuscript for this article.

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## Rate and Equilibrium Studies of the Monoazidovanadium(III) Ion<sup>1a,b</sup>

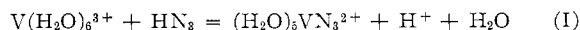
By JAMES H. ESPENSON<sup>1c</sup> AND JOHN R. PLADZIEWICZ

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Spectral studies have verified that only a single complex with the formula  $\text{VN}_3^{2+}$  is important in  $\text{V}(\text{III})\text{--HN}_3$  solutions. Even with favorable conditions ( $1\text{ M HN}_3$ ,  $0.025\text{ M H}^+$ ) conversion of  $\text{V}^{3+}$  to  $\text{VN}_3^{2+}$  is incomplete, and no higher complexes are formed. The equilibrium quotient for the reaction  $\text{V}^{3+} + \text{HN}_3 = \text{VN}_3^{2+} + \text{H}^+$  was evaluated spectrophotometrically, and from the kinetic data,  $Q$  is  $0.016 \pm 0.002$  at  $25.0^\circ$  and  $1.00\text{ M}$  ionic strength. The rate expression is  $d[\text{VN}_3^{2+}]/dt = \{c + d/[\text{H}^+]\}[\text{V}^{3+}][\text{HN}_3] - \{a + b[\text{H}^+]\}[\text{VN}_3^{2+}]$ . Respective values of the rate parameters  $a$ ,  $b$ ,  $c$ , and  $d$  (units:  $\text{M}$  and  $\text{sec}$ ) are 3.9, 24.8, 0.39, and 0.061 at  $25.0^\circ$ . The values of  $a$  and  $b$  were also determined at other temperatures giving  $\Delta H_a^\ddagger = 15.4 \pm 0.4$  and  $\Delta H_b^\ddagger = 10.2 \pm 0.4\text{ kcal mol}^{-1}$  and  $\Delta S_a^\ddagger = -4.3 \pm 1.4$ ,  $\Delta S_b^\ddagger = -17.9 \pm 1.4\text{ cal mol}^{-1}\text{ deg}^{-1}$ . The mechanism of the reaction, particularly the question of the role of the protons in the transition states, is discussed.

### Introduction

The principal equilibrium in dilute perchloric acid solutions of vanadium(III) and hydrozoic acid involves formation of a 1:1 complex of  $\text{V}^{3+}$  and  $\text{N}_3^-$ , as represented by the net equation shown in reaction I. This



process has not been studied previously. Yet the study of the equilibrium and kinetics of this reaction is important from at least three points of view.

First, the substitution mechanism followed in  $\text{V}(\text{III})$  reactions is open to question: do these reactions follow the pattern observed for many other octahedral complexes, where bond breaking controls the energetics of the activated complex,<sup>2-6</sup> or are the features of bond

making the ones that are more important? The latter mechanism has been invoked to account for the kinetic data obtained<sup>7</sup> in a study of the reaction of  $\text{V}^{3+}$  and  $\text{NCS}^-$ . Since the reactions of  $\text{V}^{3+}$  with  $\text{NCS}^-$  and  $\text{HC}_2\text{O}_4^-$  are the only  $\text{V}(\text{III})$ -substitution processes for which data are available, it is clear that additional studies are needed to provide a clearer picture of the mechanism.

Second, the complex in question,  $\text{VN}_3^{2+}$ , is the species formed when  $\text{V}(\text{H}_2\text{O})_6^{2+}$  is oxidized, using an inner-sphere mechanism, by an azido complex.<sup>8,9</sup> Whether an inner-sphere reaction does occur is of importance in understanding  $\text{V}(\text{II})$  redox mechanisms, and for the purposes of exploring these mechanisms the kinetic and equilibrium properties of  $\text{VN}_3^{2+}$  are needed.

Third, azide ion and hydrazoic acid substitutions have been an issue of continuing interest,<sup>5,10-13</sup> particularly with regard to understanding what role the protons play in such processes.

In this paper we report results on the following as-

(1) (a) Work was performed under the auspices of the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2653. (b) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969; see Abstracts, No. INOR 172. (c) Fellow of the Alfred P. Sloan Foundation, 1968-1970.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1963.

(3) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

(4) J. H. Espenson, *Inorg. Chem.*, **8**, 1554 (1969), and references therein. This paper points out that although bond breaking plays an important role in  $\text{Cr}(\text{III})$  substitution, bond making is not as unimportant as it appears to be for  $\text{Fe}(\text{III})$  and  $\text{Co}(\text{III})$  substitutions.

(5) T. W. Swaddle and G. Guastalla, *ibid.*, **8**, 1604 (1969).

(6) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

(7) B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, **6**, 1948 (1967).

(8) J. H. Espenson, *J. Am. Chem. Soc.*, **89**, 1276 (1967).

(9) K. M. Davies and J. H. Espenson, *ibid.*, **91**, 3093 (1969).

(10) D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).

(11) D. Seewald and N. Sutin, *ibid.*, **2**, 643 (1963).

(12) T. W. Swaddle and E. L. King, *ibid.*, **3**, 234 (1964).

(13) F. Accascina, F. P. Cavasino, and S. D'Alessandro, *J. Phys. Chem.*, **71**, 2474 (1967).

pects of reaction I: (a) identification of the formula of the complex formed upon reaction of  $V^{3+}$  and  $HN_3$ , (b) a spectrophotometric evaluation of the equilibrium quotient, (c) a stopped-flow kinetic study leading to rate expressions and rate constants for the forward and reverse reactions, (d) an independent evaluation of the equilibrium quotient using the rate data, and (e) values of the activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the aquation reaction.

### Experimental Section

**Materials.**—Solutions of vanadium(III) perchlorate were prepared and analyzed as described in an earlier publication,<sup>14</sup> using oxovanadium(IV) perchlorate solutions prepared both from reaction of the sulfate with barium perchlorate and electrochemically from vanadium pentoxide.<sup>15</sup> Two independent sources of hydrazoic acid were also used. In the first case solutions of doubly recrystallized sodium azide were passed through a column of Dowex 50W-X8 cation-exchange resin in the hydrogen ion form.<sup>16</sup> The second preparation involved steam distillation of the hydrazoic acid formed upon slow acidification of sodium azide solutions as described by Brauer.<sup>17</sup> Solutions of hydrazoic acid were analyzed by titration with standard base, and in some instances the concentration was verified by addition of excess cerium(IV) (which oxidizes hydrazoic acid cleanly to nitrogen) followed by back-titration with iron(II).<sup>18</sup> Lithium perchlorate was prepared from the carbonate and was twice recrystallized from water. All other reagents, including perchloric acid, were reagent grade chemicals used without further purification. Conductivity water was used throughout. Air-sensitive vanadium(III) solutions were handled and used under a nitrogen atmosphere and transferred using syringe techniques.

**Procedures.**—Spectra were measured using a Cary Model 14 recording spectrophotometer. In those instances where temperature control was required, as for example in the spectrophotometric evaluation of the equilibrium quotient, a metal cell jacket through which constant-temperature water was circulating was employed.

The rate studies were carried out using the stopped-flow technique. The instrument employed<sup>20</sup> was that manufactured by the Atom Mech Machine Co. (based on the design of Dulz and Sutin<sup>19</sup>). The temperature was maintained to within  $\pm 0.1^\circ$  in the rate experiment.

The rate experiments fell into several different categories, depending generally on the concentration conditions chosen which can cause one limiting form or another of a complicated expression to dominate and depending also on the direction from which equilibrium was approached. The nature of these experiments will be stated along with their results in a later section. The effect of changing ionic strength was not investigated; in all experiments an appropriate quantity of lithium perchlorate was added to maintain ionic strength at 1.00 *M*.

### Results

**Formula and Stability of the Complex.**—Prominent spectral changes that are especially marked at wavelengths near 350 nm occur upon mixing solutions of vanadium(III) and hydrazoic acid. The absorbance of the mixed solution exceeds the sum of the contributions from comparable but separate solutions of  $V^{3+}$  and  $HN_3$  by a very substantial amount, and the intensity

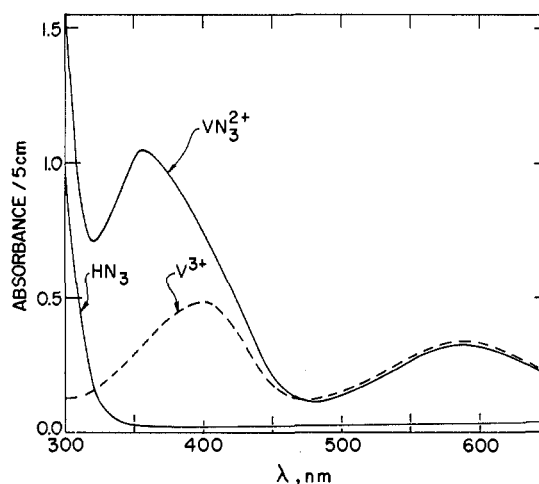


Figure 1.—Absorption spectra of  $V^{3+}$  and  $HN_3$  solutions separately and mixed at the concentrations specified;  $[V^{3+}] = 0.01$  *M*,  $[HN_3] = 0.050$  *M*,  $[H^+] = 0.1$  *M*,  $\mu = 1.0$  *M*,  $25.0^\circ$ .

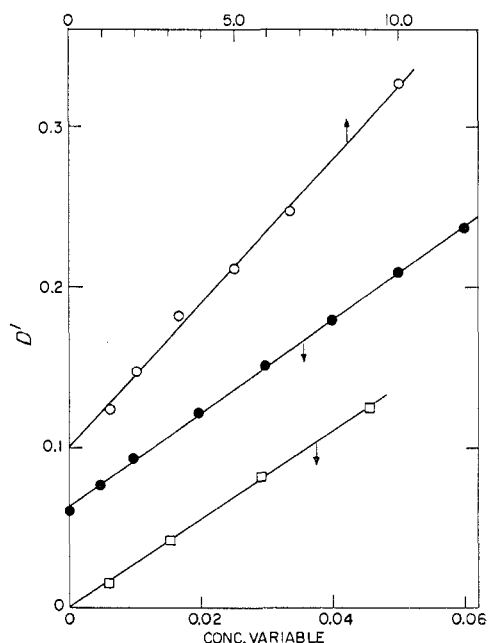


Figure 2.—A plot of the absorbance at  $\lambda$  355 nm and  $25.0^\circ$  per unit path length,  $D'$ , vs. concentration variables: lower line, vs.  $[V^{3+}]$  at 0.010 *M*  $HN_3$ , 0.10 *M*  $H^+$  (lower abscissa scale);  $D'$  values plotted were corrected<sup>20</sup> for the absorbance of  $V^{3+}$  and for the small contribution from  $HN_3$ ; middle line, vs.  $[HN_3]$  at 0.010 *M*  $V^{3+}$ , 0.10 *M*  $H^+$  (lower abscissa scale); upper line, vs.  $1/[H^+]$  at 0.020 *M*  $V^{3+}$ , 0.040 *M*  $HN_3$  (upper abscissa scale).

of the new absorption band centered at  $\lambda$  355 nm increases with an increase in concentration of either reactant. Typical absorption spectra showing the individual components as well as the mixed solution are depicted in Figure 1. Further absorption changes occur in the uv region at still shorter wavelengths, but those bands are obscured by  $HN_3$  absorption and no effort was made to study them.

The intensity of the absorbance at  $\lambda$  355 nm is a measure of the extent to which complex formation between V(III) and  $HN_3$  occurs. The intensity was monitored as a function of each of three concentration variables,  $V^{3+}$ ,  $HN_3$ , and  $H^+$ . The results of these variations, depicted in Figure 2, established that the pre-

(14) J. H. Espenson and L. A. Krug, *Inorg. Chem.*, **8**, 2633 (1969).

(15) J. H. Espenson and R. J. Christensen, *J. Am. Chem. Soc.*, **91**, 7311 (1969).

(16) D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, **57**, 1131 (1961).

(17) G. Brauer, "Handbook of Preparative Inorganic Chemistry," 2nd ed, Academic Press, New York, N. Y., 1963.

(18) J. W. Arnold, *Ind. Eng. Chem., Anal. Ed.*, **17**, 215 (1945)

(19) C. Dulz and N. Sutin, *Inorg. Chem.*, **3**, 917 (1964).

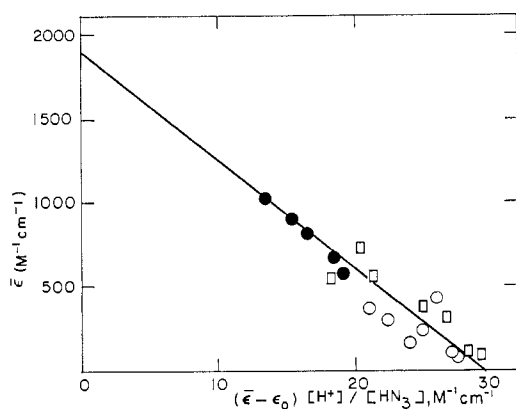


Figure 3.—Evaluation of the stability constant and molar absorption of  $\text{VN}_3^{2+}$  at  $\lambda$  355 nm according to eq 4. Symbols refer to 0.010  $M$   $\text{H}^+$  (closed circles), 0.025  $M$   $\text{H}^+$  (open squares), and 0.050  $M$   $\text{H}^+$  (open circles).

dominant complexed species is  $\text{VN}_3^{2+}$  and evaluated the product of its stability constant and molar absorptivity. The total absorbance per unit path length,  $D'$ , is given by the expression

$$D' = \epsilon_0[\text{V}^{3+}] + \epsilon_1[\text{VN}_3^{2+}] \quad (1)$$

which upon substitution for  $[\text{VN}_3^{2+}]$  from

$$Q = \frac{[\text{VN}_3^{2+}][\text{H}^+]}{[\text{V}^{3+}][\text{HN}_3]} \quad (2)$$

becomes

$$D' = \epsilon_0[\text{V}^{3+}] + \epsilon_1 Q [\text{V}^{3+}][\text{HN}_3]/[\text{H}^+] \quad (3)$$

From the slopes<sup>20</sup> of the lines presented in Figure 2, the average value of  $\epsilon_1 Q$  is 28.8  $M^{-1} \text{cm}^{-1}$ .

The  $\epsilon_1 Q$  product cannot be resolved into its separate values by such studies because at the concentrations studied only a small fraction of the limiting reagent was converted to the complex. Consequently additional experiments were done with substantially higher  $\text{HN}_3$  concentrations, 0.05–0.95  $M$ , and with lower  $[\text{H}^+]$ , 0.01–0.05  $M$ , also to favor formation of the complex. The  $\text{V(III)}$  concentration in those experiments was ca.  $10^{-3} M$ . An apparent molar absorptivity of  $\text{V(III)}$ ,  $\bar{\epsilon}$ , is calculated from the expression  $\bar{\epsilon} = \Delta D/C_v$ , where  $\Delta D$  is the absorbance enhancement per centimeter of optical path and  $C_v$  is the formal (total)  $\text{V(III)}$  concentration. From the concentration dependence of  $\bar{\epsilon}$  the separate values of  $\epsilon_1$  and  $Q$  can be resolved according to the relation

$$\bar{\epsilon} = \epsilon_1 - Q^{-1}(\bar{\epsilon}[\text{H}^+][\text{HN}_3]^{-1}) \quad (4)$$

Evaluation of  $\epsilon_1$  and  $Q$  were made graphically in accord with eq 4 as shown in Figure 3. The values found are  $\epsilon_1 = 1.9 \pm 0.2 \times 10^3 M^{-1} \text{cm}^{-1}$  and  $Q = 0.0155 \pm 0.002$ . The relatively large error limits are due to the complex having such a low stability that its concentration, even in most favorable concentration limits, was never predominant. (The average extent

(20) The correction for  $\text{V}^{3+}$  was made by measuring the absorbance of otherwise identical solutions containing no  $\text{HN}_3$  in the series of solutions where  $[\text{V}^{3+}]$  was the concentration variable. The correction was made at each  $\text{V}^{3+}$  concentration although  $\text{V}^{3+}$  obeyed Beer's law under the conditions employed, with  $\epsilon_0$  5.1  $M^{-1} \text{cm}^{-1}$  at 0.10  $M$   $\text{H}^+$ ,  $\mu = 1.00 M$ , and 25.0°.

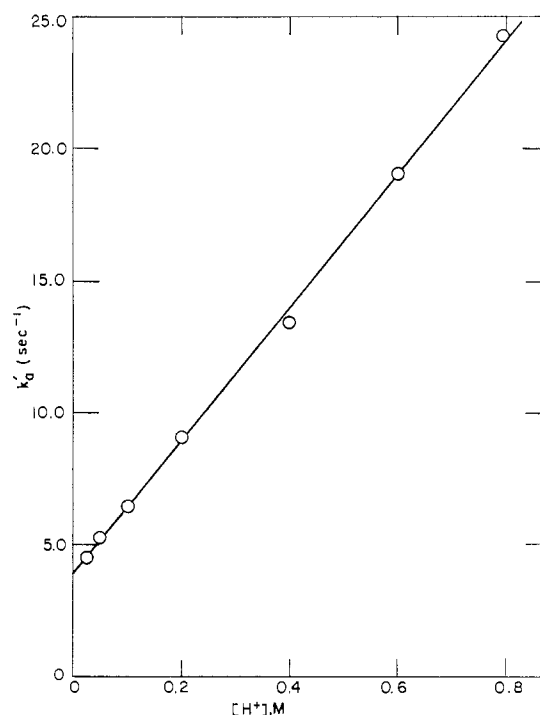


Figure 4.—The linear dependence of the aquation rate constant upon  $[\text{H}^+]$  according to eq 7.

of  $\text{V(III)}$  complexation in the 19 experiments on which the values are based was 21%, ranging from 3 to 54%.)

**Rate Equations and Kinetic Data.**—The hydrogen ion concentration in each experiment was high relative to the concentration of  $\text{VN}_3^{2+}$  formed and thus effectively constant during the course of each run. The rate expression given by (5) was assumed where  $k_f'$  and  $k_a'$

$$d[\text{VN}_3^{2+}]/dt = k_f'[\text{V}^{3+}][\text{HN}_3] - k_a'[\text{VN}_3^{2+}] \quad (5)$$

are apparent rate constants at some particular  $[\text{H}^+]$ , their values being also related to  $Q$ :  $k_f'[\text{H}^+]/k_a' = Q$ . The rate of approach to equilibrium will follow pseudo-first-order kinetics provided either that one reactant (say  $\text{HN}_3$ ) is in great excess or that the reactant present at low concentration is not significantly converted to  $\text{VN}_3^{2+}$ . The pseudo-first-order rate constant under such conditions is given<sup>10,11</sup> by

$$k_{\text{exptl}} = k_a' + k_f'\{[\text{HN}_3]_{\text{eq}} + [\text{V}^{3+}]_{\text{eq}}\} \quad (6)$$

Several series of experiments were done under conditions where the concentration of  $\text{VN}_3^{2+}$  was far smaller than that of  $\text{V}^{3+}$  or  $\text{HN}_3$ . In that limit  $k_{\text{exptl}}$  is simply  $k_a'$ . That is, the first-order rate constant for the approach to equilibrium is not dependent on the concentration of either reactant. The kinetic data obtained under such conditions, summarized in Table I, are independent of  $[\text{V}^{3+}]$  and of  $[\text{HN}_3]$  consistent with the prediction made for that concentration limit. When  $k_a'$  is evaluated at different  $[\text{H}^+]$ , the value varies linearly with  $[\text{H}^+]$ , eq 7, as shown in Figure 4. Values

$$k_a' = a + b[\text{H}^+] \quad (7)$$

are  $a = 3.9 \text{sec}^{-1}$  and  $b = 24.8 M^{-1} \text{sec}^{-1}$  at 25.0°,  $\mu = 1.00 M$ .

**Formation Rate Studies.**—Evaluation of  $k_f'$  requires

TABLE I  
AQUATION RATE OF AZIDOVANADIUM(III) ION<sup>a</sup>  
AT DIFFERENT HYDROGEN ION CONCENTRATIONS

[V <sup>3+</sup> ], M	[HN <sub>3</sub> ], M	<i>k</i> <sub>exptl</sub> , sec <sup>-1</sup>	[V <sup>3+</sup> ], M	[HN <sub>3</sub> ], M	<i>k</i> <sub>exptl</sub> , sec <sup>-1</sup>
—[H <sup>+</sup> ] = 0.0250 M—			—[H <sup>+</sup> ] = 0.200 M—		
0.0050	0.030	4.66	0.020	0.020	9.44
0.0090	0.020	4.80	0.020	0.050	9.11
0.0090	0.030	4.85	0.035	0.035	9.13
0.0135	0.0135	4.72	0.050	0.020	9.21
0.020	0.0050	4.90	0.100	0.020	9.43
0.020	0.0090	4.92			
—[H <sup>+</sup> ] = 0.0500 M—			—[H <sup>+</sup> ] = 0.400 M—		
0.015	0.020	5.32	0.050	0.070	13.5
0.015	0.030	5.33	0.060	0.060	13.4
0.020	0.020	5.34	0.070	0.070	13.3
—[H <sup>+</sup> ] = 0.100 M—			—[H <sup>+</sup> ] = 0.600 M—		
0.020	0.040	6.45	0.0533	0.070	19.0
0.030	0.030	6.80	0.0533	0.090	18.8
0.040	0.020	6.87	0.0533	0.110	19.2
—[H <sup>+</sup> ] = 0.800 M—			—[H <sup>+</sup> ] = 0.800 M—		
			0.027	0.180	23.9
			0.027	0.200	24.4

<sup>a</sup> Ionic strength maintained at 1.00 M using lithium perchlorate.

experiments at higher reactant concentrations to force the equilibrium toward formation of a higher concentration of the complex. Because of the low stability of the complex, only at the higher [HN<sub>3</sub>] and the lower [H<sup>+</sup>] will the second term in eq 6 contribute to an appreciable extent.

Studies of the dependence of *k<sub>f</sub>* upon [HN<sub>3</sub>] (at higher concentrations) were carried out at four [H<sup>+</sup>]: 0.025, 0.050, 0.100, and 0.200 M. Only at the lowest [H<sup>+</sup>], however, was the effect of [HN<sub>3</sub>] of measurable magnitude. The results at 0.025 M H<sup>+</sup> are depicted in Figure 5, where a plot of *k*<sub>exptl</sub> vs. {[V<sup>3+</sup>] + [HN<sub>3</sub>]} is shown. The dependence is linear as required by eq 6, and in accord with the very small stability of the complex the slopes of such plots at the other three [H<sup>+</sup>] were all quite small, being essentially within experimental error of zero. (Also, the error in *k*<sub>exptl</sub> becomes greater at higher [H<sup>+</sup>] because less complex is formed and the absorbance changes become quite small.) The slope at 0.025 M H<sup>+</sup> is 2.9 ± 0.3 M<sup>-1</sup> sec<sup>-1</sup>; from the relation  $Q = k_f'[H^+]/k_a'$  the value  $Q = 0.016 \pm 0.002$  (25.0°, μ = 1.00 M) was then calculated. This value of *Q* is in agreement, within the experimental error, with that from the direct spectrophotometric evaluation which gave  $Q = 0.0155 \pm 0.002$ .

The form of the rate expression for the forward direction of reaction I is given by eq 8 and is based upon a

$$d[\text{VN}_3^{2+}]/dt = \{c + d/[\text{H}^+]\}[\text{V}^{3+}][\text{HN}_3] \quad (8)$$

combination of eq 7 and the expression for *Q*, eq 2. The form of the H<sup>+</sup> dependence given in eq 8 could not be checked, however, since only at the lowest [H<sup>+</sup>] studied, 0.025 M, could *k<sub>f</sub>'* be evaluated. The rate parameters are related to *Q* and to one another as shown in eq 9,

$$Q = k_f'[H^+]/k_a' = d/a = c/b \quad (9)$$

The values of *c* and *d* are 0.39 ± 0.05 M<sup>-1</sup> sec<sup>-1</sup> and 0.061 ± 0.007 sec<sup>-1</sup> at 25.0°, μ = 1.00 M, respectively.

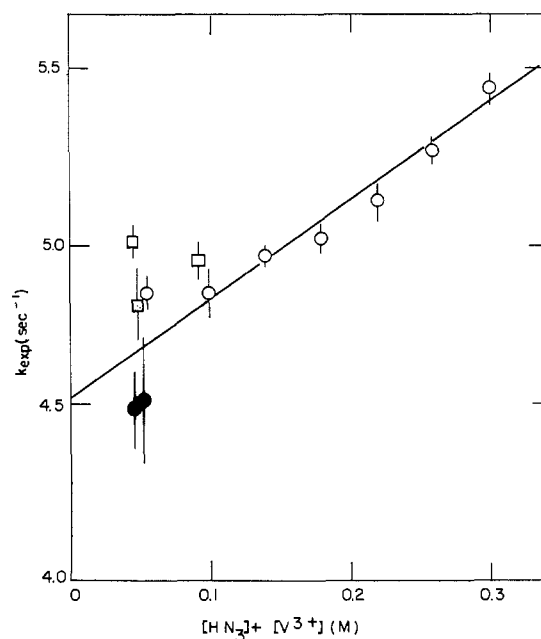


Figure 5.—Dependence of *k*<sub>exptl</sub> upon concentration of the excess reagent at 0.025 M H<sup>+</sup> according to eq 6. Points refer to experiments with excess HN<sub>3</sub> (open circles) and with excess V<sup>3+</sup> (open squares) and to rates for dilution of solutions already at equilibrium (closed circles).

**Temperature Dependence of Aquation.**—Experiments to evaluate the aquation rate of VN<sub>3</sub><sup>2+</sup> similar to those described in an earlier section were carried out at other temperatures. Table II summarizes the results of those experiments.

TABLE II  
AQUATION RATE OF AZIDOVANADIUM(III)  
ION AT VARIOUS TEMPERATURES<sup>a</sup>

[H <sup>+</sup> ], M	[V <sup>3+</sup> ], M	<i>k</i> <sub>exptl</sub> , sec <sup>-1</sup>			
		15.8°	20.4°	29.6°	34.2°
0.0500	0.0200	2.24 ± 0.04	3.36 ± 0.03	7.33 ± 0.07	10.8 ± 0.4
0.100	0.0300	3.10 ± 0.19	4.57 ± 0.12	9.4 ± 0.1	12.5 ± 0.3
0.200	0.0350	4.34 ± 0.08	6.14 ± 0.14	12.1 ± 0.2	17.5 ± 0.3
0.400	0.0850	7.27 ± 0.10	10.2 ± 0.2	19.4 ± 0.3	25.4 ± 0.7

<sup>a</sup> μ = 1.00 M (LiClO<sub>4</sub>). <sup>b</sup> Uncertainty is the average deviation of four repeat determinations using the same solutions; the value of *k*<sub>exptl</sub> represents essentially just *k<sub>a</sub>* under these conditions.

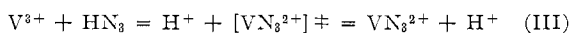
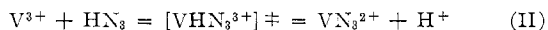
The fit of these data to the hydrogen ion dependence of eq 7 and to the temperature dependence, according to the Eyring equation, of rate constants *a* and *b* was carried out simultaneously. A nonlinear least-squares computer program<sup>21</sup> was used in this computation, in which each value of *k*<sub>exptl</sub> was weighted by the reciprocal of its square (since the per cent uncertainty in a given value was roughly constant). Values of the activation parameters and the standard deviations calculated by the program are Δ*H*<sup>‡</sup> = 15.4 ± 0.4 and 10.2 ± 0.4 kcal mol<sup>-1</sup> and Δ*S*<sup>‡</sup> = -4.3 ± 1.4 and -17.9 ± 1.4 cal mol<sup>-1</sup> deg<sup>-1</sup>, for *a* and *b*, respectively.

(21) The computer program was supplied by Drs. T. W. Newton and R. H. Moore based on a report from Los Alamos Scientific Laboratory: LA 2367 plus addenda.

## Interpretation and Discussion

The form of the overall rate expression, eq 10, establishes that two parallel pathways exist. The reaction  $d[\text{VN}_3^{2+}]/dt = \{c + d/[\text{H}^+]\}[\text{V}^{3+}][\text{HN}_3] - \{a + b[\text{H}^+]\}[\text{VN}_3^{2+}]$  (10)

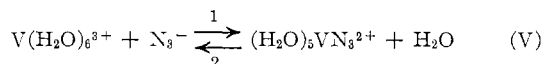
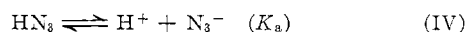
scheme can be represented in terms of the "net activation processes,"<sup>22</sup> which show the formation of the activated complexes from the *predominant forms* of the reactants (which are not necessarily the reactive forms)



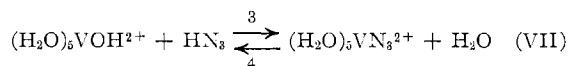
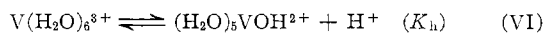
The first of these corresponds to the substitution of  $\text{HN}_3$  molecules into the primary coordination sphere of  $\text{V}(\text{H}_2\text{O})_6^{3+}$  and in that respect is formally similar to substitutions of other  $\text{HX}$  or  $\text{X}^-$  groups on  $\text{V}(\text{III})$  as well as on other metal ions. The details of the mechanism, particularly whether in the transition state bond making or bond breaking dominates, will be discussed later.

The second activation process, reaction III, has associated with it the same "proton ambiguity" common to any substitution of an anion of a weak acid in the coordination sphere of a hydrated cation. The two general mechanisms that account for such a rate term are as shown in Schemes I and II. The rate constants for the mechanisms are  $d = K_a k_1$ ,  $a = k_2$  for Scheme I and  $d = K_h k_3$ ,  $a = k_4$  for Scheme II.

## SCHEME I



## SCHEME II



An approach to making a distinction between these has been a comparison of  $\Delta S^\ddagger$  values for aquation of azido complexes, where the proton ambiguity exists, and for isothiocyanato complexes, where it does not. A value of  $\Delta S^\ddagger$  for the azido much more positive than that for the isothiocyanato was found for the present reaction, as was the case in a number of other complexes as summarized in Table III. The conclusion we draw is the same as that drawn by Swaddle and King<sup>12</sup> for  $\text{Cr}(\text{III})$  and by Swaddle and Guastalla<sup>5</sup> for  $\text{Co}(\text{III})$ : acid hydrolysis of  $(\text{H}_2\text{O})_5\text{VN}_3^{2+}$  yields  $(\text{H}_2\text{O})_5\text{VOH}^{2+} + \text{HN}_3$  and not  $\text{V}(\text{H}_2\text{O})_6^{3+} + \text{N}_3^-$ , as the primary products. In effect this argues in favor of the mechanism shown in Scheme II. Swaddle and Guastalla<sup>5</sup> considered a further distinction in the case of  $(\text{NH}_3)_5\text{CoN}_3^{2+}$ : to decide whether the transition state for which they favored  $[\text{Co}(\text{NH}_3)_5\text{OH} \cdots \text{HN}_3]$  as concluded here was formed from the reaction of  $(\text{NH}_3)_5\text{CoOH}_2^{3+}$  and  $\text{N}_3^-$  with proton transfer or from  $(\text{NH}_3)_5\text{CoOH}^{2+}$  and  $\text{HN}_3$ . This issue does not appear to be a fruitful

(22) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

TABLE III

ENTROPY OF ACTIVATION OF  $\text{N}_3^-$  AND  $\text{NCS}^-$  COMPLEXES

Complex	$-\Delta S^\ddagger$ , <sup>a</sup> cal mol <sup>-1</sup> deg <sup>-1</sup>		$\Delta(\Delta S^\ddagger)$ , <sup>b</sup> cal mol <sup>-1</sup> deg <sup>-1</sup>
	$\text{X}^- = \text{N}_3^-$	$\text{X}^- = \text{NCS}^-$	
$(\text{H}_2\text{O})_5\text{CrX}^{2+}$	+16.2 <sup>c</sup>	-3.5 <sup>d</sup>	+20
$(\text{H}_2\text{O})_5\text{FeX}^{2+}$	-3 <sup>e</sup>	-10 <sup>f</sup>	+7
$(\text{NH}_3)_5\text{CoX}^{2+}$	+3.5 <sup>g</sup>	-9.4 <sup>h</sup>	+23
$(\text{H}_2\text{O})_5\text{VX}^{2+}$	-4.3 <sup>i</sup>	-22.6 <sup>j</sup>	+18

<sup>a</sup> For acid hydrolysis (aquation) by the rate term  $k[\text{MX}]^{2+}$ . <sup>b</sup>  $\Delta S^\ddagger(\text{MN}_3^{2+}) - \Delta S^\ddagger(\text{MNCS}^{2+})$ . <sup>c</sup> Reference 12. <sup>d</sup> C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955). <sup>e</sup> Reference 10. <sup>f</sup> J. F. Below, Jr., R. E. Connick, and C. P. Coppel, *J. Am. Chem. Soc.*, **80**, 2961 (1958). <sup>g</sup> G. C. Lalor and E. A. Moelwyn Hughes, *J. Chem. Soc.*, 1560 (1963). <sup>h</sup> A. W. Adamson and R. G. Wilkins, *J. Am. Chem. Soc.*, **76**, 3379 (1954). <sup>i</sup> This work. <sup>j</sup> Reference 7.

matter for argument for either  $\text{Co}(\text{III})$  or  $\text{V}(\text{III})$ , as there is no experimental basis for the distinction unless one knows independently the rates of solvent exchange for the two forms and also whether the complexation rate is controlled primarily by bond breaking (the latter does appear to be the case for  $(\text{NH}_3)_5\text{CoX}^{2+}$  complexes<sup>23</sup>). In Scheme II the particular aquo ligand that is deprotonated is not necessarily the leaving group. In fact, the interpretation generally offered is that conversion of  $\text{H}_2\text{O}$  to  $\text{OH}^-$  results in  $\pi$  bonding between  $\text{M}(\text{III})$  and  $\text{OH}^-$  thereby promoting dissociation of the *trans* ligand. In support of this, the anation of the hydroxo complex  $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$  (where the  $\text{OH}^-$  would necessarily be replaced) is of negligible importance compared to that of  $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ .

Table IV summarizes the kinetic and thermodynamic

TABLE IV

## KINETICS AND THERMODYNAMICS OF MONOAZIDO COMPLEX FORMATION FOR TRIPROPOSITIVE METAL IONS



$$d[\text{MN}_3^{2+}]/dt = \{c + d/[\text{H}^+]\}[\text{M}^{3+}][\text{HN}_3] - \{a + b[\text{H}^+]\}[\text{MN}_3^{2+}]$$

Rate or equilibrium parameter <sup>a</sup>	Metal ion			
	$\text{Fe}^{3+}$ <sup>b</sup>	$\text{Cr}^{3+}$ <sup>c</sup>	$\text{Co}(\text{NH}_3)_5^{2+}$ <sup>f</sup>	$\text{V}^{3+}$ <sup>g</sup>
$a$ , sec <sup>-1</sup>	20.0	$1.2 \times 10^{-7}$	$2.2 \times 10^{-9}$	3.9
$b$ , M <sup>-1</sup> sec <sup>-1</sup>	5.1	$1.5 \times 10^{-8}$	$9 \times 10^{-9}$	24.8
$c$ , M <sup>-1</sup> sec <sup>-1</sup>	2.6	...	$(5.2 \times 10^{-10})^d$	0.39
$d$ , sec <sup>-1</sup>	10.1	...	$(1.2 \times 10^{-10})^e$	0.061
$Q$	0.51	...	0.06	0.0155
$\Delta H_a^\ddagger$ , kcal mol <sup>-1</sup>	14.7	32.4	33.4	15.4
$\Delta H_b^\ddagger$ , kcal mol <sup>-1</sup>	19.6	23.2	25.9	10.2
$\Delta S_a^\ddagger$ , cal mol <sup>-1</sup> deg <sup>-1</sup>	-3.2	+16.2	+13.5	-4.3
$\Delta S_b^\ddagger$ , cal mol <sup>-1</sup> deg <sup>-1</sup>	+11	-8.3	-8.0	-17.9

<sup>a</sup> Values at 25.0°,  $\mu = 1.00$  M, except  $\text{Cr}^{3+}$ , 30°. <sup>b</sup> Reference 10. <sup>c</sup> Reference 12. <sup>d</sup> Estimated from  $Q$  and the value of rate constant  $b$ .<sup>5</sup> <sup>e</sup> Computed from published data expressed in the form of the above rate equation using  $K_a$  for  $\text{NH}_3$ .<sup>24</sup> <sup>f</sup> References 5 and 12. <sup>g</sup> This work.

parameters for the known monoazido complexes of tripositive metal cations. The greater stability of the  $\text{Fe}^{3+}$  complex may arise from  $\pi$ -bonding effects.<sup>24</sup> Because  $\text{V}(\text{III})$  has fewer d electrons than  $\text{Co}(\text{III})$ , the very low stability quotient of  $\text{VN}_3^{2+}$  may be attributed to the negligible extent of back-bonding to azide ion.

(23) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

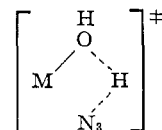
(24) Reference 2, pp 169-172.

For the reasons cited by Sutin and coworkers<sup>7</sup> the anation reaction of  $V^{3+}$  with  $SCN^-$  has considerably more  $SN_2$  character than, for example, the corresponding reactions of  $Fe^{3+}$  and  $(NH_3)_5CoH_2O^{3+}$ . In the latter cases<sup>2,3,5,6,10,11,23</sup> the predominant rate-determining feature is the dissociation of a coordinated water molecule from the ion pair  $M^{3+}, NCS^-$ . Cr(III) appears to follow a mechanism<sup>4</sup> intermediate in character between that ascribed to V(III), on the one hand, and to Fe(III) and Co(III), on the other. In view of the mechanistic differences, the very low value of 0.004 for the ratio  $k_{HN_3}/k_{NCS}$  for  $V^{3+}$  is not surprising since a ligand dependence is expected for an  $SN_2$  process.

The rate term  $d[L_5MOH_2^{3+}][HN_3]/[H^+]$ , or its equivalent  $k_3[L_5MOH^{2+}][HN_3]$ , provides an important pathway for all four M(III)'s listed in Table IV, whereas the term  $k_3'[L_5MOH^{2+}][NCS^-]$  contributes appreciably only for  $Fe^{3+}$  and  $Cr^{3+}$  and not for  $V^{3+}$ <sup>25</sup> and  $(NH_3)_5Co^{3+}$ . The origin of the second term arises from the  $\pi$ -bonding effect of  $OH^-$  in dissociative mechanisms where the  $OH^-$  is retained in the primary product as with Fe(III) and Cr(III). In  $(NH_3)_5CoOH^{2+}$ , on the other hand,  $OH^-$  is not retained, but rather it is

(25) Sutin, *et al.*<sup>7</sup> gave an upper limit of  $0.03 \text{ sec}^{-1}$  for the value of  $k$  in the term  $k[V^{3+}][SCN^-]/[H^+]$  which leads to the value  $\leq 22 \text{ M}^{-1} \text{ sec}^{-1}$  for the second-order rate constant for  $VOH^{2+} + NCS^-$  using  $K_h = 1.4 \times 10^{-3}$  for  $V^{3+}$ ; L. Pajdowski, *J. Inorg. Nucl. Chem.*, **28**, 443 (1966). From the results obtained here the value of  $k_3$  for  $VOH^{2+} + HN_3$  in Scheme II is  $44 \text{ M}^{-1} \text{ sec}^{-1}$  ( $k_3 = k/K_h$ ).

the leaving group. The effect of  $OH^-$  would be far less if bond breaking is not the main rate-controlling aspect, as appears to be the case with  $V^{3+}$ . The reactivity of  $MOH^{2+}$  toward  $HN_3$  (or of  $M^{3+}$  toward  $N_3^-$ ) in all cases supports Swaddle and Guastalla's contention<sup>5</sup> that a specific effect is present in the azide case, which may be the hydrogen bonding of azide ion



The second-order rate constant  $k_1$  for the reaction of  $V(H_2O)_6^{3+}$  and  $N_3^-$ , were Scheme I and not Scheme II responsible for the rate term  $d[V^{3+}][HN_3]/[H^+]$ , can be computed from the value of  $d$  and the acid dissociation constant of  $HN_3$ . The latter value<sup>26</sup> is  $Q_a = 7 \times 10^{-5} \text{ M}$ , giving  $k_1 = 9 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$ . This is a value somewhat higher than that for  $SCN^-$  ( $114 \text{ M}^{-1} \text{ sec}^{-1}$ ) or for oxalic acid<sup>27</sup> ( $6.9 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$ ). Because bond making predominates, it is not possible to state the  $k_1$  value is unreasonably high on that basis alone, although the other lines of evidence strongly suggest Scheme II is the correct mechanism.

(26) M. Quintin, *Compt. Rend.*, **210**, 625 (1940).

(27) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968). In this reaction the dependence on  $[H^+]$  apparently was not examined, so resolution of this rate constant into true second-order rate constants is not possible.

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## The Preparation of $\beta$ -Molybdenum Nitride

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The preparation of pure  $\beta$ -molybdenum nitride, stable at room temperature, is achieved by reaction of the elements catalyzed by calcium nitride. The X-ray powder diffraction pattern is indexed using a tetragonal unit cell,  $a = 8.41 \text{ \AA}$  and  $c = 8.05 \text{ \AA}$ . The suggested formula is  $Mo_{16}N_7$ . The compound has a temperature-independent paramagnetism above  $175^\circ\text{K}$ . Below this temperature, Curie-Weiss behavior is observed.

In the investigation of the system Ca-Mo-N<sup>1</sup> it was found that the mixtures with Ca:Mo ratios less than 5 gave rise to a phase other than hexagonal  $Ca_5MoN_5$ . The new phase was first thought to be a second ternary nitride. The diffraction pattern was later identified as that of  $\beta$ -molybdenum nitride which had been characterized by Hägg<sup>2</sup> as a metastable molybdenum nitride formed in the reaction between molybdenum and ammonia at temperatures above  $600^\circ$ . It was always contaminated with the  $\alpha$ -molybdenum phase and  $Mo_2N$  in samples obtained by quenching from temperatures above  $600^\circ$ . The phase was identified by the presence in the X-ray powder diffraction

pattern of reflections which could be indexed on the basis of a tetragonal unit cell with  $a = 4.180 \text{ \AA}$  and  $c = 4.016 \text{ \AA}$ . It was estimated to contain 28 atom % nitrogen.

The products we obtained by reactions occurring at  $750^\circ$  and with slow cooling were uncontaminated by either  $\alpha$ -molybdenum or  $Mo_2N$ . This paper describes the preparations and properties of pure  $\beta$ -molybdenum nitride.

### Experimental Section

The materials and general procedures are similar to those to be described.<sup>1</sup> The heat treatment of the intimate mixtures of calcium nitride and molybdenum which gave the best results involved heating for 1 day at  $450^\circ$  and for 2 weeks at  $750^\circ$ . The pressure of nitrogen was maintained at about 1 atm. The mix-

(1) R. Karam and R. Ward, to be submitted for publication.

(2) G. Hägg, *Z. Physik. Chem.*, **7**, 339 (1930).