

Then introducing (3A) and (6A) into (2A)

$$\Delta S_0 = R \ln K_0^0 - RTb \frac{d \ln D}{dT} + R \ln \gamma_{\pm}^2 - RT \ln \gamma_{\pm}^2 \left( \frac{d \ln D}{dT} + \frac{1}{T} \right) \quad (7A)$$

also

$$\Delta H_0 = \Delta G_0 + T \Delta S_0 = -RT \left( 1 + \frac{d \ln D}{d \ln T} \right) (b + \ln \gamma_{\pm}^2) \quad (8A)$$

In water at  $T = 298.15^\circ\text{K}$  and  $I = 0.1$  with  $a = 5 \times 10^{-8}$  cm for a 2:1 electrolyte the following quantities are calculated:  $K_0^0 = 0.3157$ ,  $b = 2.855$ ,  $\ln \gamma_{\pm}^2 =$

$-0.9759$ . This together with  $d \ln D/dT = -4.6 \times 10^{-3} \text{ deg}^{-1}$  gives  $\Delta S_0 = -2.2910 + 7.7804 - 1.939 - 0.7204 = 2.83 \text{ cal}/(\text{mol deg})$  and  $\Delta H_0 = -592.42 - (0.3715)(2.855) - 0.9759 = 414 \text{ cal/mol}$ . One may compare these two figures with the corresponding values at zero ionic strength  $\Delta S_0 = 5.49 \text{ cal}/(\text{mol deg})$  and  $\Delta H_0 = 628 \text{ cal/mol}$  to convince one's self that the differences are small but significant.

In order to have a check on the reliability of this calculation, the Fuoss function  $K_0^0 e^{b\gamma_{\pm}^2}$  has been calculated at 0, 25, and  $50^\circ$  giving  $K_0 = 1.976$ , 2.057, and  $2.175 M^{-1}$ , respectively. A plot of  $\ln K_0$  vs.  $1/T$  was slightly concave. Least-squares fitting to a straight line gave average values from slope and intercept  $\Delta H_0 = 333 \text{ cal/mol}$  and  $\Delta S_0 = 2.57 \text{ cal}/(\text{mol deg})$  in fair accord with the corresponding quantities calculated above.

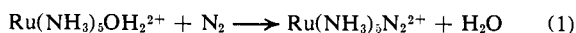
## Kinetics and Mechanism for the Production of a Dinitrogen Complex

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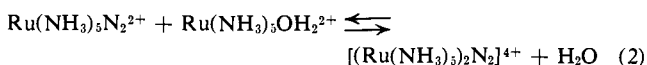
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**Abstract:** The kinetics for the attack of NO(aq) upon  $\text{Ru}(\text{NH}_3)_6^{3+}$  have been investigated from pH 3 to 12.8. The reaction proceeds through a two step rate law. Below a pH  $\sim 7$ , the product corresponds to substitution of NO onto  $\text{Ru}(\text{NH}_3)_6^{3+}$  yielding  $\text{Ru}(\text{NH}_3)_5\text{NO}^{3+}$ . Above pH 8.3, the product results exclusively in the production of  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$ . While there is no significant acid dependent path below pH 7, the reaction is first order in hydroxide ion above pH 8.3. Both paths exhibit first-order behavior in  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $[\text{NO}]_{\text{aq}}$ . While the values of  $\Delta H^\ddagger$  are similar for the two paths, the values of  $\Delta S^\ddagger$  are quite different. Labeling studies in alkaline solution indicate that the NO attacks the ammine ligand (possibly after the NO coordinates to the metal center). The results are discussed with respect to the importance of ion-pair formation, and criteria for parallel reactions in other metal complexes are offered.

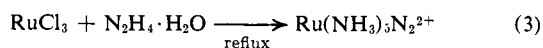
Since the original discovery of the dinitrogen complex  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$ , several alternative methods of preparation have arisen. These preparative methods have found application to other metal systems and can be loosely grouped into at least five mechanistic classifications: (I) metal complex +  $\text{N}_2$  (+ ligands), *e.g.*<sup>1</sup>



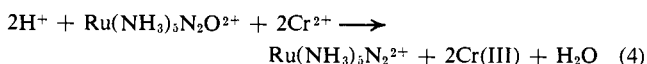
(II) reaction of a dinitrogen complex to produce another dinitrogen complex, *e.g.*<sup>2</sup>



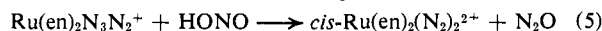
(III) metal complex + nitrogen-containing reagent (*e.g.*,  $\text{N}_2\text{H}_4$ ,  $\text{N}_3^-$ ), *e.g.*<sup>3</sup>



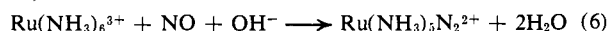
(IV) external reduction (or oxidation) of a nitrogen-containing ligand, *e.g.*<sup>4</sup>



(V) redox-coupling reaction, *e.g.*<sup>5</sup>



The last category offers the greatest possibility of new and interesting mechanisms of dinitrogen formation. In the course of our work on nitrosyl complexes, we discovered another example of method V. The reaction results in the quantitative<sup>6</sup> production of  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$



In addition, the reaction is simple to run, rapid, and requires no external reducing agents.<sup>6</sup> Because of the advantages cited above, we are now able to report a detailed study of the mechanism of this reaction. The results lend some insight into why this particular reaction proceeds and allow one to draw upon these results to predict other systems where similar reactions may occur.

### Experimental Section

**Materials.** All reagents used were of primary standard grade.  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ , purchased from Matthey-Bishop, was recrystallized according to previously described procedures.<sup>7</sup> Nitric oxide was

(1) D. Harrison and H. Taube, *J. Amer. Chem. Soc.*, **89**, 5706 (1967).

(2) D. Harrison and H. Taube, *Science*, **159**, 320 (1968).

(3) (a) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965);

(b) using  $\text{NH}_3$  instead: J. Chatt and J. Fergusson, *ibid.*, 126 (1968).

(4) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **91**, 6874 (1969).

(5) L. Kane-Maguire, P. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **90**, 5295 (1968).

(6) S. Pell and J. N. Armor, *J. Amer. Chem. Soc.*, **94**, 686 (1972).

(7) J. N. Armor, Ph.D. Thesis, Stanford University, June 1970.

vigorously scrubbed through towers of molecular sieve ( $-78^\circ$ ), solid NaOH, 8 M NaOH, and 0.1 M NaCl as previously described. Argon was scrubbed through  $\text{Cr}^{2+}$  towers to remove all traces of oxygen. The last scrubbing tower was thermostated ( $\pm 0.1^\circ$ ) in the same bath as the reaction solution. In order to vary the NO in solution, analyzed, certified gas mixtures were obtained from Matheson (22.5 and 59.5% NO, remainder as Ar). These were also scrubbed in the same manner as the pure NO(g). The  $[\text{NO}]_{\text{eq}}$  was adjusted according to the atmospheric pressure at the time. (The solubility of NO was also corrected for small pressure variations with the use of a standard solubility curve.<sup>8</sup>)

**Kinetics.** All kinetics were performed under pseudo-first-order conditions in NO and in  $\text{OH}^-$ . The desired buffer solution was degassed with argon using a Zwickel<sup>7,9,10</sup> flask fitted with a heavy rubber septum cap. After 30 min, the NO flow was initiated and maintained for  $>45$  min. A concentrated solution of  $\text{Ru}(\text{NH}_3)_6^{3+}$ , previously degassed with argon, was injected into the Zwickel flask. The volume of ruthenium (0.5 ml) was much smaller than that contained in the reaction flask (20 ml). The Zwickel flask was adapted in such a way to permit rapid mixing of the solutions and transfer of the product solution (by rotation of a four-way stopcock) into a 1-cm spectrophotometric cell. The cell and its adaptor<sup>8</sup> were removed from the flask and transferred to the thermostated cell compartment of a Cary 14 recording spectrophotometer. Because of the distance between the hood and Cary 14, the entire process could not be completed in less than 30 sec. A few experiments were performed by injecting a small volume of the ruthenium solution directly into the cell (fitted with a heavy serum cup) containing the NO-saturated buffer solution. The results were identical.

Attempts were made to follow the rate of the reaction using a Durrum-Gibson stop-flow spectrophotometer. While the rate constants did show dramatic increases with increase in pH, the rate constants were not as reproducible as those obtained from the Cary 14. Unlike the all-glass system described above, the stop-flow method suffered from (1) having to use syringes to transfer the reactant solutions, (2) mixing an NO-saturated solution with an argon-saturated solution, and (3) relying upon repetitive flushing of reaction syringes to ensure against  $\text{O}_2$  contamination. Part of the problem must lie with the NO, since we have had considerable success with this method using  $\text{Cr}^{2+}$  (air sensitive) as a reductant in electron-transfer reactions.

Rate constants were obtained by determining the slope of plots of  $\ln(A_\infty - A)$  vs. time. The plots were linear for greater than four half-lives and extrapolation of the lines to zero-time provided values of the initial absorbance to within 8% of that calculated from previously determined values of extinction coefficient. Most of the runs were recorded at 221 nm where at pH  $\sim 8.8$  ( $0.025$  M Borax,  $1.0$  M NaCl)  $\epsilon_{\text{Ru}(\text{NH}_3)_6\text{N}_2^{2+}} 1.8 \times 10^4$ ,  $\epsilon_{\text{Ru}(\text{NH}_3)_6^{3+}} 3.0 \times 10^2$ ,  $\epsilon_{\text{Ru}(\text{NH}_3)_6\text{NO}^{2+}} 1.8 \times 10^3$ ,  $\epsilon_{\text{NO}} \sim 110$ , and  $\epsilon_{\text{Borax}} < 110$   $M^{-1} \text{ cm}^{-1}$ . Rate constants were also measured at 225, 228, and 280 nm and were independent of wavelength. The first three wavelengths represent the formation of  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$ , and the last value represents the decomposition of  $\text{Ru}(\text{NH}_3)_6^{3+}$  (in a 5-cm cell). It is noteworthy to point out that contamination by  $\text{NO}_2^-$  ( $\lambda_M$  220,  $\epsilon$   $4.8 \times 10^3$   $M^{-1} \text{ cm}^{-1}$ )<sup>11</sup> or  $\text{NO}_2$  (in particular broad, intense absorption at 260–280) would not permit recording the absorbances that were observed; therefore, we constantly had internal checks on any  $\text{NO}_2$  contamination that might have occurred.

Activation parameters were obtained by Eyring plots of  $\ln(k/T)$  vs.  $1/T$ . Values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were obtained using a linear least-squares computer program. Errors are reported to within one standard deviation.

**Product Analyses.** The presence of  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{X}_2$  as the only ruthenium containing product ( $[\text{Ru}(\text{NH}_3)_6]^{3+} = 3 \times 10^{-3}$  M, pH 9.2 and 12,  $\text{NO} = 1.9 \times 10^{-3}$  M,  $T = 25^\circ$ ) was confirmed by several methods. The uv spectra ( $\lambda_M$  221 nm,  $\epsilon$   $1.8 \times 10^4$   $M^{-1} \text{ cm}^{-1}$ )<sup>12</sup> of the product solution and all solids obtained from it were identical with that previously reported for  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{X}_2$ . Gas chromatographic analysis of the product gases (molecular sieve and Porapak Q columns in series) indicated that upon addition of  $\text{Fe}^{3+}$ , which is known to liberate  $\text{N}_2$  from the complex,  $\text{N}_2$  was the

only gaseous product. The yield of  $\text{N}_2$  was  $0.95 (\pm 0.05)$  mol per mol of ruthenium treated. Addition of solid NaBr to the product solution precipitated  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Br}_2$  in  $>75\%$  yield. This product has an ir spectrum identical with that previously reported<sup>13</sup> for  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Br}_2$ . Rotary evaporation of the product solution to dryness produced a material displaying an ir spectrum identical with that reported for  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Br}_2$ . (No  $\nu_{\text{NO}}$  was observed in the ir spectrum of this material.<sup>14</sup>)

**Labeling Experiments.** The preparation and isolation of the  $\text{Ru}(\text{NH}_3)_5^{29}\text{N}_2^{2+}$  were achieved in the following manner. A solution of 0.01 M NaOH (25 ml) was placed inside a two-necked, round-bottom flask. Onto one neck of the flask was mounted a bulb containing the solid  $[\text{Ru}(\text{NH}_3)_6]\text{Br}_3$  (170  $\mu\text{mol}$ ) (in such a way that when the bulb was rotated  $180^\circ$  the solid could be directly added to the solution). The entire unit was mounted onto a vacuum line and the solution degassed by successive freeze, pump, and thaw cycles.  $^{15}\text{NO}$  (NO as 99%  $^{15}\text{N}$ ) was admitted into the flask to a final pressure of  $\sim 1$  atm. After the solution was vigorously stirred for a few minutes, the solid  $[\text{Ru}(\text{NH}_3)_6]\text{Br}_3$  was added to the NaOH solution. The solution immediately turned deep yellow and then became lighter in color. After 5 min, the NO was removed by evacuation of the flask and its contents. After opening the flask to the atmosphere, some solid NaBr was added to immediately precipitate  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Br}_2$ . The solid was filtered and washed with methanol and ether. The solid was isolated in 75% yield and the uv spectrum ( $\lambda_M$  221,  $\epsilon$   $1.8 \times 10^4$   $M^{-1} \text{ cm}^{-1}$ ) corresponded to  $>95\%$   $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Br}_2$ . While these analyses were being performed, a Nujol mull of the solid was prepared and the ir spectrum of the material was recorded. (The time from the addition of the ruthenium complex to the NaOH solution until the ir was recorded amounted to 20 min.)

**pH Control.** The following buffers were used to control the pH of the reaction solutions:  $\text{H}_2\text{PO}_4^- - \text{OH}^-$  (pH 6–8.5), Borax-HCl (8–9.2), Borax- $\text{OH}^-$  (9.2–10.8),  $\text{HPO}_4^{2-} - \text{OH}^-$  (pH 10.0–12), and NaOH (pH  $>12$ ). In order to test for specific base effects, the concentrations of some of the sodium salts of the above anions were varied from 0.005 to 0.075 M. In addition, sufficient overlap of pH for two different buffer systems permitted a test of the effect of various anions. The desired pH was determined by calculation using the standard tables<sup>15</sup> available. The solutions were checked using a Beckmann Expando-matic pH meter and the observed values were corrected for  $\text{Na}^+$  effects. The meter was standardized using standard buffers of 6.86, 7.41, 8.00, 9.18, 10.01, 11.00, and 12.00 at  $25^\circ$  and using the temperature corrections supplied with the standard buffers. The  $\text{OH}^-$  concentration was then determined using adjusted values of  $K_w$  (as a function of temperature<sup>16</sup> and ionic strength<sup>17–19</sup>), and the value of  $[\text{H}^+]$  was determined from the pH reading.

In particular the hydroxide concentration in solution was estimated in the following manner. The observed pH was subtracted from the  $\text{p}K_w$  of water at a particular temperature.<sup>16</sup> The value of  $\text{p}K_w$  had been previously adjusted for activity effects using values of  $\gamma_{\text{H}^+}\gamma_{\text{OH}^-}/a_{\text{H}_2\text{O}}$  reported in the literature for NaCl<sup>18</sup> and NaBr<sup>19</sup> (for NaTFMS and  $\text{NaClO}_4$  runs); the results of these calculations actually gives  $[\text{OH}^-]/\gamma_{\text{H}^+}$ . The assumption was made that the single ion activity coefficient of  $\text{H}^+$  is approximately one. (This does correspond to the value determined mathematically.<sup>20</sup>)

**Ionic Strength.** For most experiments, the ionic strength was maintained constant with NaCl. In some experiments, the buffer concentrations were adjusted to test for specific base catalysis (while compensating for ionic strength effects with NaCl). The effect of the anions upon the rate constant was also measured by using NaBr, NaTFMS,<sup>21</sup> or  $\text{NaClO}_4$  in place of NaCl.

**Solubility of NO.** Nitric oxide (aqueous) was determined by reaction of a NO-saturated solution of the buffer with a large excess

(13) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).

(14) S. Pell and J. N. Armor, *Inorg. Chem.*, **12**, 873 (1973).

(15) R. G. Bates and V. E. Bower, *Anal. Chem.*, **28**, 1322 (1956).

(16) H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

(17) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1958.

(18) H. S. Harned and G. E. Mannweiler, *J. Amer. Chem. Soc.*, **57**, 1873 (1935).

(19) H. S. Harned and W. S. Hamer, *J. Amer. Chem. Soc.*, **55**, 4496 (1933).

(20) J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

(21) TFMS<sup>-</sup> = trifluoromethylsulfonate anion.

(8) J. N. Armor, *J. Chem. Eng. Data*, in press.

(9) A. M. Zwickel, Ph.D. Thesis, University of Chicago, 1959.

(10) A. M. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **83**, 793 (1961).

(11) W. A. Seddon, J. W. Fletcher, and F. C. Sopchysyn, *Can. J. Chem.*, **51**, 1123 (1973).

(12) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 6170 (1970).

Table I. Rate Constants for Formation of  $\text{Ru}(\text{NH}_3)_6\text{N}_2^{2+}$  <sup>a</sup> at 25°

NO <sup>b</sup>	pH <sup>c-e</sup>	$\mu$	$k_{\text{obsd}} \times 10^3, f$ sec <sup>-1</sup>	$k_{\text{NO}}, g$ M <sup>-1</sup> sec <sup>-1</sup>	$k_{\text{OH}} \times 10^{-5}, h$ M <sup>-2</sup> sec <sup>-1</sup>
100	6.94	1.1	0.530	0.366	23 <sup>e</sup>
	7.18		0.626	0.441	16 <sup>e</sup>
	7.84		1.02	0.699	5.5
	7.94		1.09	0.762	4.7
	8.13		1.33	0.941	3.7
	8.30		1.48	1.06	2.8
	8.36		1.66	1.15	2.7
	8.47		2.36	1.65	3.0
	8.55		2.88	1.95	3.0
	8.59		2.71	1.94	2.7
	8.67		2.76	1.89	2.2
	8.76		4.22	2.85	2.7
	8.77		4.20	2.83	2.6 <sup>i,k</sup>
	9.12		8.15	5.90	2.5 <sup>j,n</sup>
	9.32		13.6	9.25	2.4
	9.43		16.1	11.4	2.3
	9.75		31.4	23.4	2.2
59.5	7.22		0.412	0.461	15
	8.02		0.716	0.861	4.4
	8.30		1.04	1.16	3.1
	8.77		2.47	2.80	2.6
	8.77		2.44	3.05	2.8
	9.16		5.16	5.78	2.2
	9.43		10.5	12.0	2.4
	9.75		19.8	22.6	2.2
	10.06		35.0	39.8	1.9 <sup>l</sup>
	10.11		34.5	43.3	1.9 <sup>l</sup>
22.5	8.30		0.395	1.24	3.3
	8.77		0.920	2.80	2.5
	9.43		3.66	11.3	2.3
	9.75		7.52	23.7	2.4
	10.05		13.5	43.7	2.1 <sup>l</sup>
	10.06		11.0	35.0	1.7 <sup>l</sup>
	10.63		38	1.2 × 10 <sup>2</sup>	2.1 <sup>m</sup>
100	8.89	0.58	7.64	4.96	3.2
59.5	8.16	0.18	1.66	1.57	6.1
100	9.08	0.18	14.6	8.60	4.1 <sup>m</sup>
22.5	9.08	0.18	3.30	8.31	3.9
59.5	9.08	0.18	9.60	9.06	4.3
59.5	9.51	0.18	23.0	23.6	4.1
22.5	9.78	0.18	15.8	41.0	3.9

<sup>a</sup>  $[\text{Ru}(\text{NH}_3)_6]^{3+} \sim 4.5 \times 10^{-5} \text{ M}$ ,  $T 25.0^\circ$ , observed at  $\lambda 221 \text{ nm}$ .

<sup>b</sup>  $[\text{NO}]$  expressed as per cent NO (balanced with argon). The actual concentration depends on the electrolyte concentration and the atmospheric pressure, e.g., at  $25.0^\circ$  (760 mm) (corrected to  $0^\circ$ ) in  $1.0 \text{ M NaCl } 1.38 \times 10^{-3} \text{ M}$ ; in  $0.1 \text{ M NaCl } 1.62 \times 10^{-3} \text{ M}$  (ref 8). <sup>c</sup> pH readings used to calculate  $[\text{OH}^-]$  after allowing for salt effects upon  $\text{p}K_w$  of water and assuming  $\gamma_{\text{H}} \sim 1$ . <sup>d</sup> Read to three significant figures (to right of decimal) and rounded to two figures. Borax buffer at  $\sim 0.2 \text{ M}$  unless otherwise noted. <sup>e</sup>  $\text{H}_2\text{PO}_4^- - \text{OH}^-$  buffer. <sup>f</sup> Error  $\sim \pm 2\%$ . <sup>g</sup>  $k_{\text{NO}} = k_{\text{obsd}}/[\text{NO}_{\text{aq}}]$ ; error  $\sim \pm 4\%$ . <sup>h</sup>  $k_{\text{OH}} = k_{\text{NO}}/[\text{OH}^-]$ , error  $\sim \pm 8\%$ . <sup>i</sup>  $\lambda 280 \text{ nm}$ ,  $[\text{Ru}(\text{NH}_3)_6]^{3+} = 1.27 \times 10^{-4} \text{ M}$ . <sup>j</sup> Same rate after 40 min or 3.5 hr of NO saturation prior to  $\text{Ru}(\text{NH}_3)_6^{3+}$  injection. <sup>k</sup> Same rate with  $[\text{Ru}(\text{NH}_3)_6]^{3+} = 3.34 \times 10^{-6} \text{ M}$  and with Borax at 0.005 and 0.050 M. <sup>l</sup>  $\text{HPO}_4^{2-} - \text{OH}^-$  buffer. <sup>m</sup> Rapid reaction. <sup>n</sup> Includes runs at  $\lambda 228 \text{ nm}$ .

of an oxygen saturated solution of water. The  $\text{NO}_2^-$  produced<sup>22,23</sup> was then determined by spectrophotometric means using the sulfanilamide method of analysis ( $\lambda_{\text{M}} 540 \text{ nm}$ ,  $\epsilon 5.42 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>24,25</sup> As a secondary check an NO saturated solution at pH 3 was treated with a very small volume of  $\text{Cr}^{2+}$ .  $\text{Cr}^{2+}$  has been

(22) D. Yost and H. Russel, "Synthetic Inorganic Chemistry," Prentice-Hall, New York, N. Y., 1944, p 79.

(23) W. Jolly, "The Chemistry of the Non-Metals," Prentice-Hall, Englewood, N. J., 1966, p 82.

(24) M. B. Shinn, *Ind. Eng. Chem.*, 13, 33 (1941).

(25) W. A. Seddon and H. C. Sutton, *Trans. Faraday Soc.*, 59, 2323 (1963).

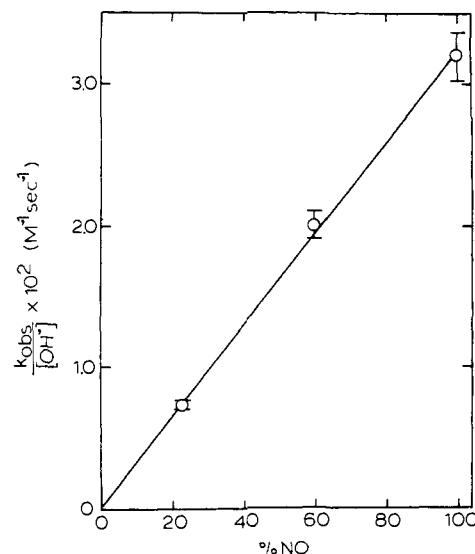


Figure 1. Dependence of  $k_{\text{obsd}}/[\text{OH}^-]$  upon  $[\text{NO}]_{\text{aq}}$ :  $T 25.0^\circ$ ,  $\mu = 1.1$ , pH 9.2–9.7. The coordinate representing  $[\text{NO}]_{\text{aq}}$  is expressed as per cent NO in an Ar–NO gas mixture. Average  $[\text{Ru}(\text{NH}_3)_6]^{3+} \sim 4.5 \times 10^{-5} \text{ M}$ .

shown to react quantitatively with NO to produce  $\text{CrNO}^{2+}$  ( $\lambda_{\text{M}} 450 \text{ nm}$ ,  $\epsilon 121 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>26</sup> With the  $\text{Cr}^{2+}$  maintained at a slight excess (predetermined by the  $\text{O}_2$  method of analysis), the yield of  $\text{CrNO}^{2+}$  was identical with that predicted by the standard method of analysis. The solubility of NO was determined as a function of pH (pH 0–13), ionic strength, atmospheric pressure, and temperature. These results will be compiled in a separate article,<sup>8</sup> although they were used to calculate the third-order rate constants to be reported and can be obtained by dividing the values of  $k_{\text{obsd}}$  by  $k_{\text{NO}}$ . In short, the NO solubility in water was the same as those values published in the past at  $25.0^\circ$  and at  $5.2^\circ$ .<sup>28</sup> The solubility of NO decreased with increasing electrolyte. Most importantly, the solubility remained fairly constant from pH 2 to 12 (in both  $\text{Cl}^-$  and  $\text{ClO}_4^-$  media).

## Results

All rate data were collected under pseudo-first-order conditions ( $[\text{Ru}(\text{NH}_3)_6]^{3+}$   $3.3 \times 10^{-6}$ – $1.27 \times 10^{-4} \text{ M}$ ,  $\text{NO } 4.38 \times 10^{-4}$ – $1.95 \times 10^{-3} \text{ M}$ , and  $[\text{buffer}] 5.0 \times 10^{-3}$ – $7.5 \times 10^{-2} \text{ M}$ ). Plots of  $\ln(A - A_\infty)$  at 280 nm and  $\ln(A_\infty - A)$  at 221, 225, and 228 nm were linear beyond four half-lives (Table I). The independence of the observed rate constant upon varying the ruthenium concentration and the linearity of the first-order plots indicate that the reaction is first order in ruthenium. Plots (e.g., Figure 1) of the observed rate constant/ $[\text{OH}^-]$  (over a pH range of 9.2–9.7) vs. the nitric oxide concentration in solution indicate that the reaction is first order in  $\text{NO}_{\text{aq}}$ . Due to the dramatic increase in  $k_{\text{obsd}}$  with pH (of the order of  $10^6$ ) a log–log plot is required to adequately display the data. Figure 2 describes the dependence of the log of  $k_{\text{obsd}}/[\text{NO}_{\text{aq}}]$  as a function of pH. The initial curvature prior to pH 8.3 can be explained by a secondary path which is only significant below a pH 8.3. Beyond a pH of 8.3, the reaction is first order in  $\text{OH}^-$  to a pH of at least 10.6 at  $25.0^\circ$  or at least 11.9 at  $5.2^\circ$ . The rate law for the re-

(26) J. N. Armor and M. Buchbinder, *Inorg. Chem.*, 12, 1086 (1973).

(27) A. Seidell and N. F. Linke, "Solubilities of Inorganic and Organic Compounds," Vol. II, 4th ed, American Chemical Society, Washington, D. C., 1965, pp 790 and 791.

(28) "International Critical Tables," Vol. III, E. W. Washburn, Ed., McGraw-Hill, New York, N. Y., 1928, p 259.

Table II. Dependence of Rate Constants upon the Medium at Low Ionic Strengths<sup>a</sup>

[Borax] × 10 <sup>2</sup> , M	[NaCl] × 10 <sup>2</sup> , M	pH <sup>d</sup>	μ	k <sub>obsd</sub> × 10 <sup>3</sup> , sec <sup>-1</sup>	k <sub>NO</sub> , M <sup>-1</sup> sec <sup>-1</sup>	k <sub>OH</sub> × 10 <sup>-6</sup> , M <sup>-2</sup> sec <sup>-1</sup>
0.50		9.184	0.015	39.4	35.8	19 <sup>e</sup>
0.50		9.184	0.015	14.0	33.5	18 <sup>b</sup>
0.75		9.166	0.023	11.6	28.0	14 <sup>b</sup>
1.0		9.178	0.030	29.8	27.6	13 <sup>e</sup>
1.0		9.178	0.030	10.3	25.1	12 <sup>b</sup>
2.5		9.175	0.075	5.47	13.8	5.9 <sup>b</sup>
2.5		9.175	0.075	21.5	12.3	5.3
5.0		9.190	0.15	12.5	7.40	2.8
7.5		9.210	0.22	8.50	5.15	1.7
7.5		9.210	0.22	2.00	5.20	1.8 <sup>b</sup>
0.50	0.646	9.166	0.022	13.2	32.3	17 <sup>b</sup>
0.50	1.94	9.130	0.034	10.2	25.1	13 <sup>b</sup>
0.50	4.04	9.100	0.055	7.87	19.8	11 <sup>b</sup>
0.50	8.08	9.062	0.096	6.00	15.4	8.3 <sup>b</sup>
2.0	4.0	9.137	0.10	5.41	17.4	7.9 <sup>b</sup>
0.5	0.14	9.024	0.15	14.3	8.51	4.6
0.83	0.13	9.049	0.16	15.6	9.29	4.8
1.0	0.13	9.055	0.16	16.6	9.88	5.3
0.7	0.12	9.059	0.17	14.5	8.63	4.3 <sup>b</sup>
2.5	0.10	9.079	0.18	3.3	8.31	3.9
2.5	0.10	9.079	0.18	9.6	9.06	4.3 <sup>e</sup>
2.5	0.10	9.079	0.18	14.9	8.57	4.2
5.0	0.05	9.147	0.20	12.5	7.48	4.1

<sup>a</sup> [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> ~ 4.5 × 10<sup>-5</sup> M, T 25.0°, [NO] = 100%. <sup>b</sup> [NO] = 22.5%. <sup>c</sup> The hydrolysis of Borax is not substantial enough to significantly alter [Borax]. <sup>d</sup> pH of Borax solutions varies irregularly with [Borax] (refer to R. Bates, "Determination of pH," Wiley, New York, N. Y., 1964, p 84). <sup>e</sup> [NO] = 59.5%.

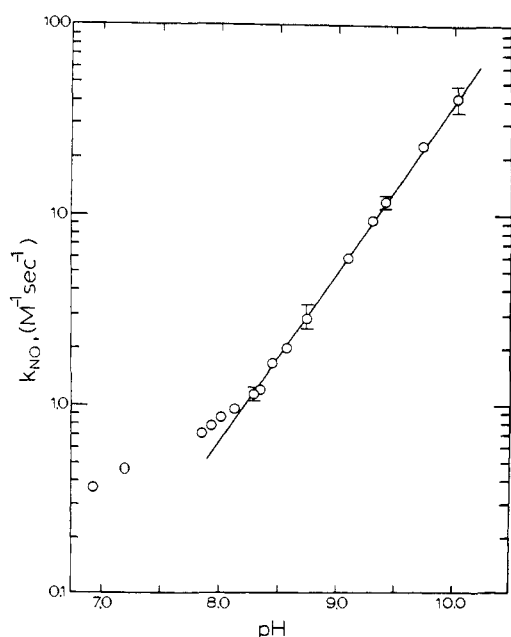
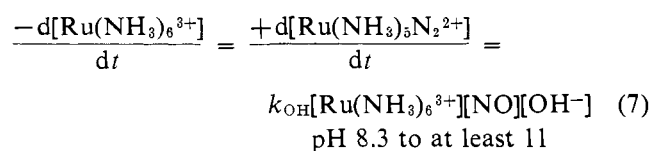


Figure 2. Dependence of log  $k_{\text{obsd}}/[\text{NO}]_{\text{aq}}$  vs. pH: T 25.0°, μ = 1.1. Average [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> ~ 4.5 × 10<sup>-5</sup> M.

action in basic solution is



The data displayed in Table I represent a summary of the dependence of the observed rate constant upon the variables cited above. At μ = 0.18,  $k_{\text{OH}} = 4.1 \pm 0.2 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1}$  (25.0°) (mean of five experiments, pH > 8.9). At μ = 1.1,  $k_{\text{OH}} = 2.2 \pm 0.3 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1}$  (25.0°) (mean of >14 experiments, pH > 9.0).

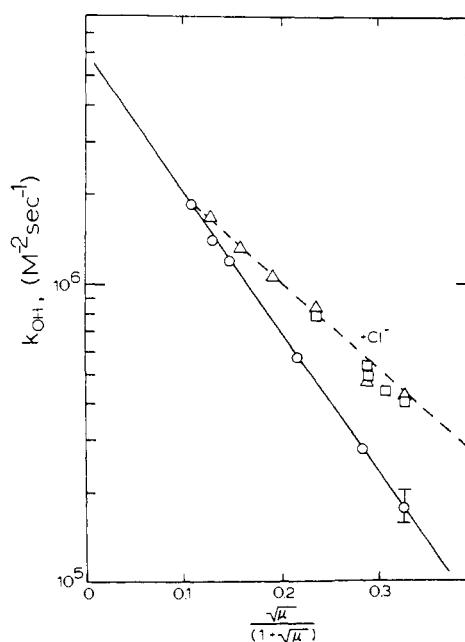


Figure 3. Ionic strength dependence of  $k_{\text{OH}}$ : T 25.0°; pH ~ 9.1 (see Table II); average [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> ~ 4.5 × 10<sup>-5</sup> M; ○, Borax only; ▽, 0.005 M Borax + Cl<sup>-</sup>; □, 0.01–0.025 M Borax + Cl<sup>-</sup>.

While most of the experiments in Table I were performed in 0.02 M Borax, additional data were obtained as a function of both the Borax and Cl<sup>-</sup> concentrations. The values in Table I indicated only a small decrease in  $k_{\text{OH}}$  with increasing ionic strength. However, from Table II one can observe that prior to an ionic strength of 0.15, the rate is markedly dependent upon ionic strength. Working in a Borax buffer, two trends emerge, which are displayed in Figure 3. Plots of log  $k_{\text{OH}}$  vs.  $\sqrt{\mu}/(1 + \sqrt{\mu})$  (Figure 3) using only Borax to control ionic strength (0.0050–0.075 M) were linear and had a slope of -4.9. However, if varying amounts of

Cl<sup>-</sup> were added to increase the ionic strength, another linear dependence emerged with a slope of -2.9. It is important to note that  $k_{\text{OH}}$  is constant at  $\mu = 0.16 \pm 0.02$  despite a variation of a factor of 5 in the Borax concentration. Similar observations can be made at  $\mu = 0.10$  and  $\mu = 0.03$ . However, above 0.05 M Borax, adding Cl<sup>-</sup> did not increase the value of  $k_{\text{OH}}$  to those values obtained earlier at lower levels of Borax with added Cl<sup>-</sup>. It would appear that Borax is either inhibiting the rate or that Cl<sup>-</sup> is accelerating the rate; but in the presence of added Cl<sup>-</sup>, the value of  $k_{\text{OH}}$  is independent of the [Borax] below 0.025 M.

Some additional results can be introduced to emphasize the importance of the medium in this reaction. Table III described the effect of various salts upon the

Table III. Ionic Strength Effects with Various Salts

Salt	pH <sup>a</sup>	$\mu$	$k_{\text{obsd}} \times 10^3, \text{ sec}^{-1}$	$k_{\text{OH}}, \text{ M}^{-1} \text{ sec}^{-1}$	$k_{\text{OH}} \times 10^5, \text{ M}^{-2} \text{ sec}^{-1}$
NaBr	8.77	1.1	4.29	3.00	2.8
NaBr	9.07	1.1	8.24	5.76	2.7
NaTFMS <sup>d</sup>	8.98	1.1	11.8	8.22	4.7
NaTFMS	9.11	0.18	18.2	10.5	4.7
NaClO <sub>4</sub>	8.92	1.1	2.07 <sup>e</sup>	6.18	5.1
NaClO <sub>4</sub>	8.95	0.18	19.1	11.5	7.3
NaCl	8.76	1.1	4.22	2.85	2.7
NaCl	9.08	0.18	14.6	8.60	4.1

<sup>a</sup> Using  $K_w$  adjusted with NaBr activity coefficients (ref 19). <sup>b</sup>  $T$  25.0°, [Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>] =  $4.5 \times 10^{-5}$  M; 0.025 M Borax; [NO] = 100%. <sup>c</sup> Includes solubility determinations for the various salt solutions. <sup>d</sup> TFMS = trifluoromethylsulfonate. <sup>e</sup> [NO] = 22.5%.

value of  $k_{\text{OH}}$ . The value of  $k_{\text{OH}}$  for NaBr at  $\mu = 1.1$  is very similar to that obtained in NaCl, but the values of  $k_{\text{OH}}$  for NaTFMS and NaClO<sub>4</sub> are larger and yet very similar to one another. Again for NaClO<sub>4</sub> the rate increases with decreasing ionic strength. One would expect Cl<sup>-</sup> to be about as effective as Br<sup>-</sup> in ion pairing with Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>.<sup>29,30</sup> On the other hand, ClO<sub>4</sub><sup>-</sup> or TFMS<sup>-</sup> would not be expected to result in substantial ion-pair formation.<sup>31</sup>

The overlap of different buffers was tested in the pH 10 region at  $\mu = 1.1$  and 0.18. From Table I, the value of  $k_{\text{OH}}$  did decrease somewhat in the HPO<sub>4</sub><sup>2-</sup>-OH<sup>-</sup> buffer (with respect to Borax-OH<sup>-</sup>). It was difficult to assess whether this was due to (1) the attainment of a more correct value of  $k_{\text{OH}}$  as one gets further away from the pH independent path, (2) another specific base effect, or (3) the leveling off of the value of  $k_{\text{NO}}$  (indicating saturation in pH).

Using only NaOH as the buffer, a kinetic run at pH 12.0 ( $T$  5.2°  $\mu = 0.11$ ) was already over within the time required to reach the Cary 14 (30 sec). This would suggest that the rate still was not saturated in [OH<sup>-</sup>] before pH 12 (at 5°).

By lowering the temperature for the kinetic runs, we hoped to extend our range of pH measurements (using the Cary 14 to monitor the rate of the reaction). At 5.2°, between pH 9.28 and 10.70 (Borax buffers) the

(29) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 36 (1953).

(30) E. L. King, J. Espenson, and R. E. Visco, *J. Amer. Chem. Soc.*, **63**, 755 (1959).

(31) F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, **75**, 1463 (1953); A. Scott and H. Taube, *Inorg. Chem.*, **10**, 62 (1971).

value  $k_{\text{OH}}$  was constant ( $1.2 \pm 0.2 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1}$ ) (Table IV). However, when the buffer was changed

Table IV. Rate Data at 5.2°<sup>a</sup>

pH at 5° <sup>b</sup>	$\mu$	$k_{\text{obsd}} \times 10^3, \text{ sec}^{-1}$	$k_{\text{NO}}$	$k_{\text{OH}} \times 10^5, \text{ M}^{-2} \text{ sec}^{-1}$
9.28	0.175	2.20 <sup>c</sup>	.876	1.4 <sup>d</sup>
9.71	0.175	1.10	1.82	1.1 <sup>d</sup>
9.83	0.175	1.60	2.65	1.2 <sup>d</sup>
10.08	0.175	2.91	4.80	1.3 <sup>d</sup>
10.32	0.175	5.00	9.14	1.3 <sup>d</sup>
10.64	0.175	8.26	15.1	1.1 <sup>d</sup>
11.35	0.24	12.8	21.9	0.30 <sup>e</sup>
11.60	0.24	21.0	38	0.28 <sup>e</sup>
11.90	0.24	38	66	0.25 <sup>e</sup>
11.21	0.044	9.76	17.4	0.40 <sup>e</sup>
11.16	0.073	7.90	13.9	0.35 <sup>e</sup>
11.12	0.15	5.04	8.84	0.21 <sup>e</sup>
10.88	0.24	5.18	8.89	0.35 <sup>e</sup>

<sup>a</sup> [Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>] =  $4.5 \times 10^{-5}$  M,  $T$  5.2°, 22.5% NO, NaCl as the supporting electrolyte. <sup>b</sup> Using  $pK_w$  at  $\infty$  dilution of 14.734 and corrected to 14.494 at  $\mu = 0.175$  and 14.47 at  $\mu = 0.24$ . <sup>c</sup> At 100% NO. <sup>d</sup> Borax-OH<sup>-</sup> buffer. <sup>e</sup> HPO<sub>4</sub><sup>2-</sup>-OH<sup>-</sup> buffer.

to HPO<sub>4</sub><sup>2-</sup>-OH<sup>-</sup> the rate fell by a factor of ~3. Further investigation revealed that at a constant ionic strength (over a pH region of 10.88-11.90) the value of  $k_{\text{OH}}$  was  $0.30 \pm 0.05 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1}$ , and the value of  $k_{\text{OH}}$  also demonstrated a marked dependence upon the concentration of the HPO<sub>4</sub><sup>2-</sup>-OH<sup>-</sup> buffer. A plot of  $\log k_{\text{OH}}$  vs.  $\sqrt{\mu}/(1 + \sqrt{\mu})$  gave a slope of -2.7 (between  $\mu = 0.044$  and 0.15), and the addition of Cl<sup>-</sup> seemed to accelerate the reaction. Thus, the results in Table IV parallel those obtained at 25.0° and serve to further emphasize the importance of the ionic media and the possibility of ion pair formation. The significant difference in  $k_{\text{OH}}$  at 5.2° for the two buffer systems studied might indicate a more important (temperature accentuated) path involving ion pair formation between PO<sub>4</sub><sup>3-</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>. Moreover, the pH 12 (NaOH only) experiment discussed earlier suggests that the rate still has not achieved saturation in [OH<sup>-</sup>].

The values at 5.2° noted above do not rule out the possibility of a saturation effect in the value of  $k_{\text{NO}}$ . One might argue that the  $pK_a$  of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> might increase with the decrease in temperature, and this now seems to be the case.<sup>32</sup> With this in mind, we sought to make use of the values of  $k_{\text{OH}}$  obtained from the stop-flow studies. The rate constants obtained from the stop-flow measurements were about a factor of 2 faster than those obtained using the Cary 14. Despite larger variations in the former values, we were able to obtain the following consistency from the stop-flow data: at a pH of 9.2, pH ~11 (HPO<sub>4</sub><sup>2-</sup>-OH<sup>-</sup> buffer), pH 11.8 (NaOH), and a pH of 12.8,  $k_{\text{OH}} \sim 1 \times 10^6 \text{ M}^{-2} \text{ sec}^{-1}$  (all having  $\mu \sim 0.1$  and  $T$  25.0°). Thus, it would appear that the lack of accuracy does not obscure the important fact that the value of  $k_{\text{OH}}$  does not appear to attain a saturation level (at least to a pH of ~12.8).

**Activation Parameters.** In order to obtain further insight into the mechanism of our reaction, the values of  $k_{\text{OH}}$  were obtained at pH ~9.1 at 5.2, 15.0, and 25.0°. Within the error limits of the data, the plots of  $\ln(k/T)$  vs.  $1/T$  demonstrated no curvature. The data in

(32) D. Waysbort and G. Navon, *J. Phys. Chem.*, **77**, 960 (1973).

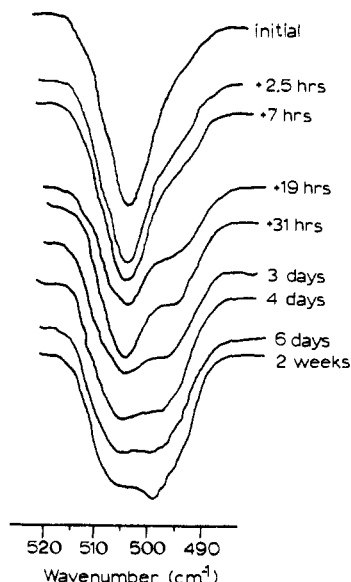


Figure 4. Reaction of  $^{15}\text{NO}$  with  $\text{Ru}(\text{NH}_3)_6^{3+}$  at  $0.01\text{ M OH}^-$ ,  $T\ 25.0^\circ$ . The initial spectrum corresponds to 20 min after the reaction was initiated. The product was isolated as the  $\text{Br}^-$  salt and suspended in Nujol. All spectra recorded at low temperature by attaching the  $\text{KBr}$  plates (containing the Nujol mull) to a liquid- $\text{N}_2$  cooled cold finger.

Table V. Rate Constants for the Action of  $\text{NO}$  upon  $\text{Ru}(\text{NH}_3)_6^{3+}$  at pH 9 and 3 as a Function of Temperature

pH <sup>a</sup>	Temp <sup>b</sup>	$\mu^c$	$k_{\text{obsd}} \times 10^3, \text{d}$ $\text{sec}^{-1}$	$k_{\text{NO}} \times 10^1, \text{e}$ $\text{M}^{-1} \text{sec}^{-1}$	$k_{\text{OH}} \times 10^{-5}, \text{f}$ $\text{M}^{-2} \text{sec}^{-1}$
9.08	25.0	0.18	14.6	98.9	$4.1 \pm 0.2$
9.16	15.0	0.18	6.52	29.0	$2.6 \pm 0.1$
9.28	5.2	0.18	2.20	8.86	$1.5 \pm 0.1$
3.02	25.0	0.10	359	$1.99 \pm 0.10$	
3.02	15.0	0.10	249	$1.11 \pm 0.05$	
3.02	5.2	0.10	166	$0.667 \pm 0.03$	

<sup>a</sup> Using  $K_w$  at  $\mu = 0.18$  at  $5.2^\circ$ ,  $3.210 \times 10^{-15}$ ; at  $15.0^\circ$ ,  $7.862 \times 10^{-16}$ ; and at  $25.0^\circ$ ,  $1.765 \times 10^{-14}$ . <sup>b</sup>  $\pm 0.05^\circ$ . <sup>c</sup> Ionic strength maintained with  $\text{NaCl}$ ;  $0.025\text{ M Borax}$  at pH  $\sim 9$ , where  $\lambda\ 221\text{ nm}$ ;  $1.0 \times 10^{-3}\text{ M HCl}$  at pH  $\sim 3$ , where  $\lambda\ 280\text{ nm}$ . <sup>d</sup>  $[\text{Ru}(\text{NH}_3)_6^{3+}] = 4 \times 10^{-5}\text{ M}$ , 100%  $\text{NO}$ . <sup>e</sup>  $k_{\text{obsd}}/[\text{NO}]$ . <sup>f</sup>  $k_{\text{obsd}}/[\text{NO}][\text{OH}^-]$ .

Table V give rise to values of  $\Delta H^\ddagger = 7.8 \pm 1.0\text{ kcal/mol}$  and  $\Delta S^\ddagger = -6.7 \pm 3.3\text{ eu}$ . It also proved useful to obtain the activation parameters for the previously reported substitution reaction at pH 3,  $\mu = 0.10$  with  $\text{Cl}^-$ . An Eyring plot of these data gave values of  $\Delta H^\ddagger = 8.5 \pm 0.8\text{ kcal/mol}$  and  $\Delta S^\ddagger = -33 \pm 3\text{ eu}$ .

**Labeling Experiments.** Although previous studies<sup>6</sup> indicated that the only dinitrogen product of the reaction between  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $^{15}\text{NO}$  at pH 12 was  $\text{Ru}(\text{NH}_3)_5^{2+}^{29}\text{N}_2$ , we did not know the initial mode of attack by the  $^{15}\text{NO}$ . In the past, we have demonstrated that a significant difference exists in the  $\delta_{\text{Ru}-\text{N}_2}$  band in the  $500\text{-cm}^{-1}$  region of the infrared spectrum for  $\text{Ru}-^{15}\text{N}^{14}\text{N}$  and  $\text{Ru}-^{14}\text{N}^{15}\text{N}$ .<sup>33,34</sup> In particular, the half-time for intramolecular isomerization of dinitrogen on ruthenium is  $\sim 3$  days (at room temperature).<sup>33</sup> The differences between the alternative modes of  $^{29}\text{N}_2$  binding ( $9\text{ cm}^{-1}$ ) are such that one can easily determine the exact nature of  $^{15}\text{N}$  bonding in a sample of  $[\text{Ru}$

$(\text{NH}_3)_5^{29}\text{N}_2]\text{Br}_2$ . Our reaction enabled us to isolate the  $^{29}\text{N}_2$  product within 20 min. Even though the reaction is over by this time, the ir spectra (Figure 4) demonstrated that the initial product was essentially pure  $[(\text{NH}_3)_5\text{Ru}-^{14}\text{N}^{15}\text{N}]\text{Br}_2$ . This product proceeded to isomerize on the same time scale as those samples prepared by the alternative  $\text{N}_2\text{O}$  method of preparation.<sup>35</sup> These results dictate that the initial dinitrogen product results in attack by one  $^{15}\text{NO}$  molecule upon the coordinated metal-amine complex. Further, the time for isomerization of  $^{29}\text{N}_2$  requires that the ammine does not come off and attack the nitric oxide ( $\text{Ru}(\text{NH}_3)_6^{3+}$  is inert to substitution)<sup>36</sup> and that the  $\text{NO}$  does not insert itself between the metal-amine bond. The labeled product above can be produced in two ways: (1) attack of  $\text{NO}$  upon a coordinated metal amide or (2) attack of  $\text{NO}$  upon the metal center with collapse to a species resembling a direct attack on the metal amide.

## Discussion

In acid solution (pH 1–3), it has been demonstrated that  $\text{NO}$  reacts with  $\text{Ru}(\text{NH}_3)_6^{3+}$  to produce  $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$ , quantitatively.<sup>36</sup> It has been suggested that a convenient bond making mechanism exists for the paramagnetic  $\text{NO}$  because  $\text{Ru}(\text{III})$  with a low spin  $d^5$  electron structure has an unpaired electron which can be engaged by the odd electron of  $\text{NO}$ .<sup>36,37</sup> A similar mechanism has recently been advanced for the  $\text{Np}(\text{III})$  reduction of  $\text{Ru}(\text{NH}_3)_6^{3+}$ . The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were  $3.9\text{ kcal/mol}$  and  $-48\text{ eu}$ .<sup>38</sup> The mechanism for the nitric oxide reaction suggested above takes on added weight when one recalls that we now report activation parameters of  $\Delta H^\ddagger = 8.5\text{ kcal/mol}$  and  $\Delta S^\ddagger = -33\text{ eu}$  at pH 3. The value of  $\Delta S^\ddagger$  is suggestive of a highly organized activated complex and is in line with other bimolecular reactions.

With these results in mind, the curvature in Figure 2 exhibited at lower pH is consistent with a two step rate law

$$-\frac{d[\text{Ru}(\text{NH}_3)_6^{3+}]}{dt} = \text{substitution} + \text{redox} = k_{\text{H}}[\text{Ru}(\text{NH}_3)_6^{3+}][\text{NO}] + k_{\text{OH}}[\text{Ru}(\text{NH}_3)_6^{3+}][\text{NO}][\text{OH}^-] \quad (8)$$

One can imagine obtaining a value of  $k_{\text{H}} = 0.20\text{ M}^{-1}\text{sec}^{-1}$ <sup>36</sup> by extrapolation of our value of  $\log(k_{\text{obsd}}/[\text{NO}])$  to pH 3. The curvature is also consistent with the dependence of the yield of  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$  upon pH.<sup>6</sup> Using the values of  $k_{\text{H}}$  and  $k_{\text{OH}}$  above, one can estimate the contribution of each step in the overall rate law. Thus, at a pH of  $\sim 8$  rate =  $(2.0 \times 10^{-1}\text{ M}^{-1}\text{sec}^{-1}) \cdot [\text{Ru}(\text{III})][\text{NO}] + (4.1 \times 10^5\text{ M}^{-2}\text{sec}^{-1})[\text{Ru}(\text{III})][\text{NO}] \cdot (1.0 \times 10^{-14}/1.0 \times 10^{-8})$ , the redox path contributes about 67% to the observed rate of disappearance of  $\text{Ru}(\text{NH}_3)_6^{3+}$ . This corresponds very nicely with the dependence of the  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$  yield upon pH ( $\sim 50\%$  yield at pH  $\sim 8$ ).<sup>6</sup>

(35) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **93**, 6476 (1971).

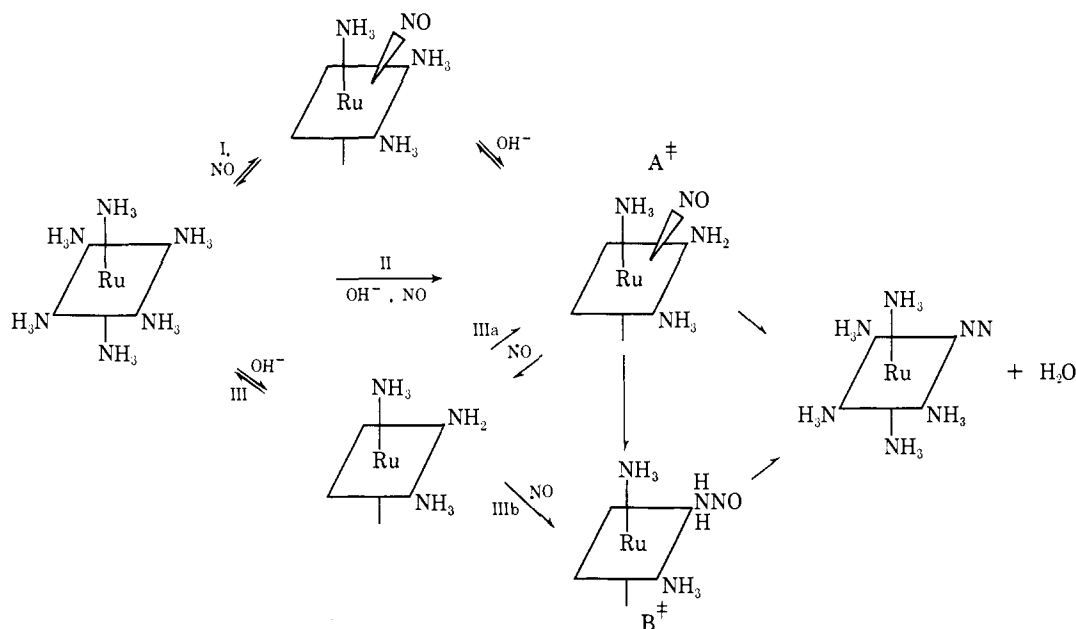
(36) J. N. Armor, H. Scheidegger, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 5928 (1968).

(37) P. Ford, J. R. Kuempel, and H. Taube, *Inorg. Chem.*, **7**, 1976 (1968).

(38) D. K. Lavalley, C. Lavalley, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **12**, 570 (1973).

(33) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 2560 (1970).  
(34) S. Pell, R. Mann, H. Taube, and J. N. Armor, *Inorg. Chem.*, in press.

Scheme I



Keeping in mind the results<sup>6</sup> of our earlier communication [(1)  $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$  is the only product above a pH of 8.45 (41% at pH 7.76); (2)  $\text{Ru}(\text{NH}_3)_6^{2+} + \text{NO} + \text{OH}^- \rightarrow \text{no Ru-N}_2$ ; (3)  $\text{Ru}(\text{NH}_3)_6^{3+} + \text{OH}^- + \text{NO}_2^- \rightarrow \text{no Ru-N}_2$ ; (4)  $\text{Ru}(\text{NH}_3)_6^{2+} + \text{OH}^- + \text{NO}_2^- \rightarrow \text{no Ru-N}_2$ ; and (5)  $\text{Ru}(\text{NH}_3)_6^{3+} + \text{NO}_2 + \text{OH}^- \rightarrow \text{no Ru-N}_2$ ], three possible mechanisms emerge from a consideration of the above results<sup>39</sup> (Scheme I). I involves attack of NO upon  $\text{Ru}(\text{NH}_3)_6^{3+}$  followed by deprotonation of the ammine and collapse of the seven-coordinate species into the product. II involves a concerted, termolecular reaction with positioning of the NO and  $\text{OH}^-$  molecules at a metal-ammine site. III requires deprotonation of the ammine followed by attack of the NO at the amide (IIIa) or, less likely,<sup>40</sup> upon the edge of the octahedron (IIIb). The rate law requires that NO,  $\text{OH}^-$ , and  $\text{Ru}(\text{NH}_3)_6^{3+}$  are directly involved in the formation of the activated complex. The amido nitrosyl ( $\text{A}^\ddagger$ ) (or the *n*-nitroso ammine ( $\text{B}^\ddagger$ )) in the next to last step of each of the three schemes above is assumed to closely resemble the composition of the activated complex. The last step corresponds to a rapid rearrangement (or decomposition) of these species into the final dinitrogen product. The basis for these interpretations follows from the absence of any definite saturation effect in  $\text{OH}^-$  over a  $10^6$  range in rate constants. The  $\text{OH}^-$  is involved in reaching the activated complex, but the expected sigmoidal effect may be obscured by other equilibria (such as ion pairing, pH dependence of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ru}(\text{NH}_3)_6\text{NO}]^{3+}$ ,  $[\text{Ru}(\text{NH}_3)_6^{3+}, \text{X}^-]$ , etc.). Experiments at low levels of  $[\text{NO}]_{\text{aq}}$  were impractical; however, the data displayed in Figure 1 extrapolate to intersect at the origin.

Although attack by  $\text{OH}^-$  (with abstraction of the  $\text{H}^+$  from the coordinated ammine) is expected to be rapid, preequilibria components in  $\text{OH}^-$  and NO with

$[\text{Ru}(\text{NH}_3)_6]^{3+}$  have been considered in order to account for the first-order behavior of these species in the rate law. The preequilibria steps in NO and  $\text{OH}^-$  are meant to indicate that both these species are important in achieving the activated complex. Since no intermediate species were observed at 225 or 280 nm on the stop-flow, we will assume these equilibria are achieved rapidly and completely with no stable intermediates being formed along the way (or, alternatively, both the forward steps are fast).

An  $\text{S}_{\text{N}}1$  mechanism is unlikely since this would demand that the amide bond to ruthenium is severed. Also such a result would require that a scrambled product initially be observed in our labeled studies.

One might rule out the termolecular reaction (II) due to the small value of  $\Delta S^\ddagger$  observed for our reaction at high pH. A large, negative entropy of activation is often associated with a termolecular reaction. For example, a reported termolecular reaction in aqueous media between  $\text{H}_2\text{O}_2$ ,  $\text{H}^+$ , and  $\text{I}^-$  displays a  $\Delta S^\ddagger = -21$  eu.<sup>41</sup> However, the involvement of a +3 metal complex instead of a +1 species (supposedly  $\text{H}_3\text{O}_2^+$ ) in the  $\text{H}_2\text{O}_2$  reaction would tend to lower the value of  $\Delta S^\ddagger$  expected for a termolecular reaction.<sup>42</sup> With this in mind, a termolecular reaction would be consistent with our value of  $\Delta S^\ddagger$ . In addition, the prolonged treatment of  $\text{Ru}(\text{NH}_3)_5\text{NO}^{3+}$  with aqueous ammonia produces  $\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})^{2+}$ , while further treatment of the same complex with 0.1 M NaOH produces  $\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NH}_2)^{2+}$ .<sup>7</sup> Bottomley has recently observed a 30% yield of a dinitrogen complex after 48 hr from a 0.025 M solution of  $\text{Ru}(\text{NH}_3)_5\text{NO}^{3+}$  in 0.5 M NaOH.<sup>43</sup> Thus, it would appear that the octahedral complex of ruthenium nitrosyl does not proceed completely through a single mechanism for dinitrogen formation. In addition, our earlier communication<sup>6</sup> indicated substantial substitution of NO on  $\text{Ru}(\text{NH}_3)_5$ -

(39) A reviewer has offered the additional possibility of an outer-sphere complex with  $\text{Ru}(\text{NH}_3)_6^{3+}$  or  $\text{Ru}(\text{NH}_3)_5\text{NH}_2^{2+}$ . Since this basically is implied in achieving the sequence of events offered in II, we will not pursue this possibility any further.

(40) If the attack by NO involves the reduction of the NO, it would seem more likely to occur at a coordinated amide (unhindered and having a more accessible pair of electrons).

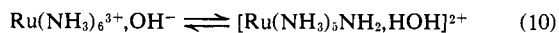
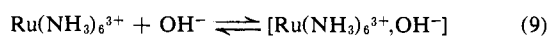
(41) H. A. Liebafsky and A. Mohammad, *J. Amer. Chem. Soc.*, **55**, 3977 (1933).

(42) The authors wish to thank Professor J. Halpern for offering this possibility.

(43) F. Bottomley and J. R. Crawford, *J. Chem. Soc., Dalton Trans.*, 2145 (1972).

$\text{OH}^{2+}$ . This would suggest that the simultaneous attack of both NO and  $\text{OH}^-$  upon  $\text{Ru}(\text{NH}_3)_6^{3+}$  is important in the production of a major dinitrogen containing product.

I and III (Scheme I) are quite similar and depend upon the  $pK_a$  of the coordinated ammine. Waysbort and Navon have recently reported a value of 12.5<sup>44</sup> for the  $pK_a$  of  $\text{Ru}(\text{NH}_3)_6^{3+}$ . It has since been determined that the method of analysis is very dependent upon the medium involved<sup>45</sup> and the temperature.<sup>32</sup> Recently, they have modified the mechanism for H exchange on  $\text{Ru}(\text{NH}_3)_6^{3+}$  in alkaline solution to include not only a step involving amide formation but also ion-pair formation<sup>45</sup>



The importance of ion pair formation in reactions of the +3 ruthenium hexaammine complex has already been emphasized in the data presented. It was observed that high levels of Borax caused an inhibition in  $k_{\text{OH}}$ . In addition,  $\text{NaClO}_4$  and  $\text{NaTFMS}$  (poor potential ion-pair agents) accelerated the value of  $k_{\text{OH}}$  (*vs.* Borax,  $\text{NaCl}$ , or  $\text{NaBr}$ ). Increasing levels of  $\text{PO}_4^{3-}$  (in the  $\text{HPO}_4^{2-}$ - $\text{OH}^-$  buffer) caused an apparent inhibition in the rate. All these observations are indicative of ion-pair formation. In addition, the slopes obtained from the Debye-Hückel rate law plots suggest the importance of secondary salt effects.<sup>46</sup> One would have certainly expected a slope of approximately zero in such a plot where NO is implicated in the rate determining step (recall that  $k_{\text{OH}}$  is the same for both 22.5 and 100% NO in 0.005 M Borax).

In both I and III, ion pair equilibria may also be considered. They have not been included in these simplified schemes. The observed deceleration in the third-order rate constants in the presence of potential ion-pair agents suggests that ion pairing may inhibit the rate by raising the  $pK_a$  of  $\text{Ru}(\text{NH}_3)_6^{3+}$  or  $[\text{Ru}(\text{NH}_3)_6(\text{NO})]^{2+}$ . If the  $pK_a$  of the ion pair  $\text{Ru}(\text{NH}_3)_6^{3+}, \text{X}^-$  is still  $\sim 12$ ,<sup>45</sup> we cannot accurately assess the importance of the deprotonation step in our mechanism under the restrictions imposed by our rapid reaction. Thus, the fact that the plot of  $\log k_{\text{NO}}$  *vs.* pH does not level out at high pH does not eliminate prior amide formation. If III is the preferred pathway, the absence of sigmoidal behavior in Figure 2 does suggest that the  $pK_a$  of  $\text{Ru}(\text{NH}_3)_6^{3+}, \text{X}^-$  may still be greater than 11. On the other hand, if the reaction had occurred *via* I, one might expect the  $pK_a$  of a seven-coordinate  $[\text{Ru}(\text{NH}_3)_6(\text{NO})]^{3+}$  (perhaps as  $\text{Ru}(\text{IV}), \text{NO}^-$ ) to be more acidic than that for  $\text{Ru}(\text{NH}_3)_6^{3+}$ . If this were the case a hydroxide-independent pathway should emerge at a pH lower than 12. However, the effects of  $\text{X}^-$  and of temperature on the  $pK_a$  of such a species are unknown. The values of  $k_{\text{OH}}$  appear to be fairly constant over the broad pH region 8.5  $\rightarrow$  12.8. The extended region of pH dependence may also be indicative of two pH sensitive equilibria operating in this reaction.

The differences in I and III would require that NO

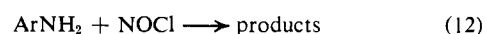
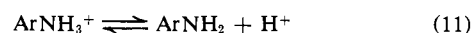
(44) D. Waysbort and G. Navon, *Chem. Commun.*, 1410 (1971); the value of 12.5 for the  $pK_a$  of  $\text{Ru}(\text{NH}_3)_6^{3+}$  cannot be calculated from the values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  provided in this paper.

(45) J. N. Armor, *J. Inorg. Nucl. Chem.*, **35**, 2067 (1973).

(46) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

attack the amide complex in III where diazotization can proceed readily. However, in I, the initial attack by NO in the metal would facilitate removal of the ammine proton by  $\text{OH}^-$ . The amide nitrosyl could then collapse to yield the dinitrogen complex. The latter suggests a base induced redox reaction between  $\text{NH}_2^-$  and NO (or  $\text{NO}^+$ ). By way of comparison, it has been reported that  $\text{NaNH}_2$  does react with  $\text{NOCl}$  to produce  $\text{N}_2$ .<sup>47</sup>

It is known that  $\text{NOCl}$  is the nitrosylating agent in the diazotization of aniline by  $\text{HNO}_2$  in the presence of  $\text{Cl}^-$ . It has been shown that the rate data for the diazotization implicate  $\text{NOCl}$  attack upon aniline<sup>48</sup>



Reaction 12 proceeds to produce an aryl nitrosoamine which then decomposes with the production of the diazonium salt. The observed rate constant demonstrates an acceleration in rate by a factor of  $\sim 10$  between 0 and 25° ( $\Delta H^\ddagger = 17.0$ , kcal/mol  $\Delta S^\ddagger = 6.1$  eu).<sup>49</sup> However, using the  $pK_a$  of aniline, the apparent  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  reduce to 5.56 kcal/mol and +3.1 eu for step 12 in the reaction.<sup>49</sup>

Our reaction suggests that the ultimate destruction of the organic diazonium salt occurs because of the inability of the organic residue to absorb the positive charge. However, ruthenium can do this by back-bonding into the ligand. Any final mechanism must reflect the ionic strength dependencies discussed earlier in the article. The precedence for ion-pair formation has already been established in this and analogous systems.<sup>32,45</sup> The presence of ion pairs in our reaction suggests that they might inhibit the primary reaction sufficiently by altering the  $pK_a$  of the ruthenium ammine or by providing less reactive species for NO attack. The slight deceleration in  $k_{\text{OH}}$  with increasing ionic strength ( $\mu > 0.1$ ) is still predicted in the final mechanism. However, the magnitude of such a secondary salt effect cannot be readily predicted.<sup>50</sup> Insufficient amide is formed at pH < 7, and the seven-coordinate species proceeds to undergo a substitution reaction. This suggests that a reason for the inability of  $\text{Ru}(\text{NH}_3)_5\text{OH}^{2+}$  to produce dinitrogen complexes<sup>6</sup> in a reaction parallel to that for  $\text{Ru}(\text{NH}_3)_6^{3+}$  might be due to a higher  $pK_a$  for the coordinated amines of the pentaammine, which results in substitution (*i.e.*,  $k_{\text{H}} \gg k_{\text{OH}}[\text{OH}^-]$  for  $\text{Ru}(\text{NH}_3)_5\text{X}^{2+}$ ).

Beyond the points already discussed above, it is difficult to definitely distinguish which mechanism best represents the observed reaction. Initial attack by NO (instead of  $\text{OH}^-$ ) upon  $\text{Ru}(\text{NH}_3)_6^{3+}$  is attractive because of the parallel which exists in acid solution. However, the parallel ceases beyond this point because amide formation induces a dramatic change in the product of the reaction.

Additional analogies to our reaction exist in the literature. Copper(II) catalyzes<sup>51</sup> the reaction of NO with diethylamine to produce the nitrosamine and

(47) J. W. Mellor, "Inorganic and Theoretical Chemistry," Vol. VIII, Longmans, Green and Co., New York, N. Y., p 257.

(48) H. Schmid and E. Hallaba, *Montash. Chem.*, **87**, 560 (1956).

(49) Calculated from the data given in ref 48.

(50) A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 150.

(51) W. Brackman and P. Smit, *Recl. Trav. Chim. Pays-Bas*, **84**, 357, 373 (1965).



$\text{N}_2\text{O}$ . The proposed mechanism is quite complicated and involves copper(II) in combination with NO functioning as the nitrosylating agent of the amine. By comparison with our study, one might expect that the lability of Cu(II) and the fact that no dinitrogen complex of either oxidation state of copper has been reported is suggestive that the *N*-nitroso amine simply breaks away from the copper center and then undergoes further decomposition.

The reaction of  $\text{Ru}(\text{NH}_3)_6^{3+}$  with  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{OH}^-$ , and  $\text{O}_2$  to produce  $(\text{NH}_3)_5\text{RuNH}_2\text{SO}_3^{2+}$  has been demonstrated<sup>52</sup> to proceed only in basic solution. Considering the substitution inertness of  $\text{Ru}(\text{NH}_3)_6^{3+}$  and the high yields obtained for the sulfamate product, it would appear that attack also proceeds on  $\text{Ru}-\text{NH}_2^-$ . However, one cannot rule out initial attack by  $\text{S}_2\text{O}_3^{2-}$  upon the octahedron, which facilitates removal of the ammine proton.

In conclusion, we have determined the kinetics and mechanism of the reaction between NO and  $\text{Ru}(\text{NH}_3)_6^{3+}$  from pH 3 to ~11. Beyond pH 8.3, the reaction is first order in Ru(III), NO, and  $\text{OH}^-$ , with attack by NO upon the deprotonated ammine complex. A

(52) J. N. Armor and H. Taube, *Inorg. Chem.*, 10, 1570 (1971).

dramatic variation of  $\sim 10^6$  exists in the rate constants for the acid and base components of the rate law. In acid solution, substitution of the coordinated ammine is important; however, in basic solution, the reaction may proceed *via* a concerted or stepwise attack of NO and  $\text{OH}^-$  upon  $\text{Ru}(\text{NH}_3)_6^{3+}$ . The dinitrogen complex is not produced when either  $\text{Ru}(\text{NH}_3)_6^{3+}$  or  $\text{Ru}(\text{NH}_3)_6^{2+}$  is treated with  $\text{NO}_2^-$  in alkaline solution. In general, this suggests that any metal ammine complex which is used in this synthetically useful preparation for dinitrogen complexes ought to be one which undergoes reaction with  $\text{NO}_{\text{aq}}$  and has easily dissociable ammine protons (along with other criteria for metal-nitrogen complex stabilization).<sup>53,54</sup>

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(53) Yu. G. Borod'ko and A. E. Shilov, *Russ. Chem. Rev.*, 38, 355 (1969).

(54) J. E. Fergusson and J. L. Love, *Rev. Pure Appl. Chem.*, 20, 33 (1970).

## Derivative Chemistry of Metallocarboranes. Nido 11-Atom Metallocarboranes and Their Lewis Base Adducts

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Contribution No. 3135 from the Department of Chemistry, University of California, Los Angeles, California 90024. Received May 10, 1973

**Abstract:** The reaction between  $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$  or  $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_9\text{H}_{10}]^-$  and pyridine affords the nido adducts  $X[9-(\eta\text{-C}_5\text{H}_5)\text{-}11\text{-C}_5\text{H}_5\text{N-}7,8,9\text{-C}_2\text{CoB}_9\text{H}_{10}]$  and  $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,9'\text{-Co-}11'\text{-C}_5\text{H}_5\text{N-}7',8'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ , respectively. Oxidation of these species with  $\text{FeCl}_3$  affords the substituted closo compounds  $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}7\text{-C}_5\text{H}_5\text{N-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_9]^+$  and  $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}7'\text{-C}_5\text{H}_5\text{N-}2',4'\text{-C}_2\text{B}_9\text{H}_9]$ . Analogous compounds were prepared from  $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$  with piperidine in place of pyridine. The unsubstituted nido metallocarboranes  $X[9-(\eta\text{-C}_5\text{H}_5)\text{-}7,8,9\text{-C}_2\text{CoB}_9\text{H}_{11}]^-$  and  $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,9'\text{-Co-}7',8'\text{-C}_2\text{B}_9\text{H}_{11}]^{2-}$  were prepared by degradation of the icosahedral compounds  $[3-(\eta\text{-C}_5\text{H}_5)\text{-}1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}]$  and  $[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,3'\text{-Co-}1',2'\text{-C}_2\text{B}_9\text{H}_{11}]^-$ . These compounds could be reversibly protonated to give  $X[9-(\eta\text{-C}_5\text{H}_5)\text{-}7,8,9\text{-C}_2\text{CoB}_9\text{H}_{12}]$  and  $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,9'\text{-Co-}7',8'\text{-C}_2\text{CoB}_9\text{H}_{12}]^-$  which eliminate hydrogen on heating to give  $[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,3,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$  and  $[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',3'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ . The chemical changes resulting from the replacement of a polyhedral  $\{\text{BH}\}^{2+}$  moiety by  $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$  or  $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^{2+}$  are discussed.

Although a large number of metallocarboranes have been prepared<sup>1-17</sup> since the first report of  $[1,2-$

- (1) M. F. Hawthorne and G. B. Dunks, *Science*, 178, 462 (1972).
- (2) R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.
- (3) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, and P. Wegner, *J. Amer. Chem. Soc.*, 90, 879 (1968).
- (4) T. A. George and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 91, 5475 (1969).
- (5) G. B. Dunks, Ph.D. Dissertation, University of California, Riverside, Calif., 1970.
- (6) W. J. Evans and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 93, 3063 (1971).
- (7) G. B. Dunks, M. M. McKown, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 93, 2541 (1971).
- (8) L. J. Todd, A. R. Burke, A. P. Garber, H. T. Silverstein, and B. N. Storhoff, *Inorg. Chem.*, 9, 2175 (1970).
- (9) J. L. Little, P. S. Welcker, N. J. Loy, and L. J. Todd, *Inorg. Chem.*, 9, 63 (1970).
- (10) L. J. Todd, *et al.*, *J. Organometal. Chem.*, 50, 93 (1973).

$\text{C}_2\text{B}_9\text{H}_{11}\text{-}3,3'\text{-Fe-}1',2'\text{-C}_2\text{B}_9\text{H}_{11}]^-$  in 1965,<sup>18,19</sup> compara-

- (11) J. L. Spencer, M. Green, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1178 (1972).
- (12) L. G. Sneddon and R. N. Grimes, *J. Amer. Chem. Soc.*, 94, 7161 (1972).
- (13) R. N. Grimes, *J. Amer. Chem. Soc.*, 93, 261 (1971).
- (14) V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 95, 2830 (1973).
- (15) R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *J. Amer. Chem. Soc.*, 94, 1865 (1972).
- (16) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *J. Amer. Chem. Soc.*, 95, 3046 (1973).
- (17) J. W. Howard and R. N. Grimes, *Inorg. Chem.*, 11, 263 (1972).
- (18) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Amer. Chem. Soc.*, 87, 1818 (1965).
- (19) The first commo metallocarborane was originally treated as a  $\pi$ -bonded metal complex of the (3)-1,2-B<sub>2</sub>C<sub>2</sub>H<sub>11</sub><sup>2-</sup> ligand (ref 18). However, using the newest IUPAC nomenclature rules this compound should be named as a commo polyhedral structure, *i.e.*,  $[1,2,3\text{-C}_2\text{FeB}_9\text{H}_{11}(3\text{-commo-}3')1',2',3'\text{-C}_2\text{FeB}_9\text{H}_{11}]^-$ . Since a reader not versed in the details of replacement nomenclature might be led to the