Reduction of Nitrous Oxide in the Presence of Pentaammineaquoruthenium(II)[1]

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Abstract: The specific rate for the reduction of $Ru(NH_3)_5N_2O^{2+}$ by Cr^{2+} at 25° and $\mu = 0.07$ is $8.2 \times 10^2\ M^{-1}\ sec^{-1}$, approximately 10^8 times greater than the rate of reduction of free N_2O by Cr^{2+}. The rate increases markedly with the concentration of chloride ion; this sensitivity of the rate to chloride ion suggests that Cr^{2+} attacks $Ru(NH_3)_5N_2O^{2+}$ by an outer-sphere mechanism. Whereas when Cr^{2+} reduces N_2O in the presence of $Ru(NH_3)_5OH_2^{2+}$, substitution on Ru(II) is rate determining for the formation of the nitrogen complex, in the same concentration range with V^{2+} as reducing agent, substitution becomes rate determining only at high concentration of V^{2+}. The value for the specific rate at which $Ru(NH_3)_5OH_2^{2+}$ is converted to $Ru(NH_3)_5N_2O^{2+}$, as determined from an analysis of kinetic data for the V^{2+} system, agrees with that determined with Cr^{2+} as reducing agent, and with the direct measurement. The reactivity of N_2O toward V^{2+} is increased *ca.* 10^7-fold when N_2O enters the coordination sphere of Ru(II). Reduction of $Ru(NH_3)_5N_2O^{2+}$ by either $V(H_2O)_6^{2+}$ or $Ru(NH_3)_5OH_2^{2+}$ is slow enough so that substitution on the reducing agent can precede attack on coordinated N_2O.

In an earlier paper,[2] equilibrium and kinetic data on the reaction were reported. There too was re-

$$Ru(NH_3)_5OH_2^{2+} + N_2O = Ru(NH_3)_5N_2O^{2+} + H_2O \qquad (1)$$

ported the fact that N_2O is reduced by Cr^{2+} virtually as rapidly as the oxide enters the coordination sphere of Ru(II). The kinetic data on this reaction yielded measurements of the rate of the N_2O–Ru(II) association reaction, but not of the rate at which Cr^{2+} reduces coordinated N_2O. It seemed of interest to get a quantitative measure of the increase in reactivity toward Cr^{2+} of N_2O when it enters the coordination sphere of Ru(II), and to extend the investigation to at least one other reducing agent. Accordingly, we undertook to measure the rate at which $Ru(NH_3)_5N_2O^{2+}$ is reduced by Cr^{2+}, and to extend the work to the system with V^{2+} in place of Cr^{2+}. The results of these two sets of investigations, as well as those obtained in a study of the reduction of N_2O by $Ru(NH_3)_5OH_2^{2+}$, are reported in this paper.

Experimental Section

Standard operations such as the preparation of Cr^{2+} and V^{2+} are described in the thesis[1] or in related publications, and only the general procedures followed in studying the reactions of interest are dealt with in this section.

Reactions with Cr^{2+}. The reaction of N_2O with Cr^{2+} is very slow, and only two experiments on the rate of the direct reaction were done. A solution of Cr^{2+} (8.4×10^{-3} *M* in 8.6×10^{-2} *M* HCl) was saturated with N_2O (2.47×10^{-2} *M*) and transferred to a 10-cm spectrophotometric cell. The progress of the reaction was followed over a period of 5 months by observing the growth of the absorption bands at 408 and 573 nm characteristic of $Cr(H_2O)_6^{3+}$. In a companion solution using argon in place of N_2O, no change in absorption was observed in the 5-month time period.

To measure the direct reaction of $Ru(NH_3)_5N_2O^{2+}$ with Cr^{2+}, a stopped-flow[3] method was used. All reactant solutions were presaturated with N_2O. One of the solutions fed to the mixing chamber contained the Cr^{2+}, and the other was a solution in which reaction 1 had reached equilibrium. It should be noted that the equilibrium in reaction 1 readjusts very slowly compared to the rate of reduction of the N_2O complex and therefore only the preformed N_2O complex is reduced in the stopped-flow experiments.

The solutions containing Cr^{2+} were prepared from chromium(III)–trifluoromethyl sulfonate, or chromium(III) chloride, the former supplied by courtesy of A. Scott. Both solutions were deoxygenated using N_2O and were reduced with amalgamated Zn for 3 hr. When the Cr(III) was completely reduced, a 5% excess of Cr^{2+} was added to an N_2O-saturated solution containing $Ru(NH_3)_5Cl^{2+}$ using a side arm mounted on the storage flask. A period of 5 min was allowed for reaction 1 to reach equilibrium before the solutions were used, and solutions were not kept beyond 1 hr. Observations were made from 221 (formation of $Ru(NH_3)_5N_2^{2+}$) to 248 nm ($Ru(NH_3)_5N_2O^{2+}$ has a maximum at 238 nm).

Reactions with V^{2+}. Vanadium(II) as V^{2+} was generated by using zinc amalgam to reduce vanadium(IV) chloride.[1] After the solution containing V^{2+} was separated from the reducing agent, it was saturated with deoxygenated N_2O, and then, in large excess, it was injected into a solution containing $Ru(NH_3)_5Cl^{2+}$. Reduction of Ru(III) by V(II) is rapid compared to the reactions of present interest.[4] The progress of the reduction of N_2O in the presence of $Ru(NH_3)_5OH_2^{2+}$ was followed spectrophotometrically, observing the growth of the peak at 221 nm characteristic of the product $Ru(NH_3)_5N_2^{2+}$.

A single experiment was done to measure the rate of reduction by V^{2+} of free N_2O. The reaction mixture was saturated in N_2O and contained V^{2+} and HCl at 9.5×10^{-3} *M* and 1.03×10^{-2} *M*, respectively. The reaction was followed spectrophotometrically at 580 nm. The reaction is so slow that only a rough value for the rate was obtained even after a reaction time exceeding 6 months.

Reduction by $Ru(NH_3)_5OH_2^{2+}$. The reduction of N_2O by Ru(II) was referred to in an earlier communication[2] as complicating the measurement by the static method of the affinity of N_2O for Ru(II). We made an attempt to determine the kinetics of the reaction and to measure its rate.

The solutions of $Ru(NH_3)_5OH_2^{2+}$ were produced by reducing $Ru(NH_3)_5Cl^{2+}$ (6.6×10^{-4}–2.7×10^{-3} *M*) in HCl (7×10^{-2}–7×10^{-3} *M*), using zinc amalgam or hydrogen on platinum. The Ru(II) was transferred by means of a syringe to the N_2O-saturated reaction medium contained in a Zwickel flask, and from this the reaction mixture was transferred, without contact with air, to 0.10-cm spectrophotometer cells. The spectra were scanned periodically from 400 to 200 nm. The approach to association equilibrium (reaction 1) is rapid compared to the subsequent changes. Initially the formation of $Ru(NH_3)_5N_2^{2+}$ at the expense of $Ru(NH_3)_5N_2O^{2+}$ is seen, and in a second phase absorption characteristic of $[Ru(NH_3)_5]_2N_2^{4+}$ develops. Kinetic data were collected only for the initial phase.

Unless otherwise mentioned, argon was used as the inert gas. All spectra were recorded on the Cary 15 spectrophotometer.

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[1] Taken in part from Ph.D. thesis of J. N. Armor, 1970, Stanford University.

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

[3] We acknowledge with thanks the help of A. Zanella in the stopped-flow experiments.

[4] J. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).

Table I. The Reduction of $Ru(NH_3)_5N_2O^{2+}$ by Cr^{2+} [a,b]

Expt no.	$Cr^{2+} \times 10^3$, M	$[Cl^-]$, M	λ, nm	k, M^{-1} sec^{-1} [c] $\times 10^{-3}$	No. of runs
1	1.50	1.12×10^{-3}	246	0.82 ± 0.03	6
1	1.50	1.12×10^{-3}	238	0.93 ± 0.06	3
1	1.50	1.12×10^{-3}	221	1.02 ± 0.04	2
2	1.50	3.23×10^{-2}	246	1.13 ± 0.08	8
3	1.51	0.066	238–248	1.45 ± 0.03	8
4	1.51	0.066	246	1.39 ± 0.16	5
4	1.51	0.066	238	1.46 ± 0.20	4
5	1.52	0.066	246	1.40 ± 0.10	9
6	3.03	0.066	246	1.32 ± 0.07	5
7	4.55	0.066	246	1.31 ± 0.01	4
8	5.05	0.066	246–221	1.32 ± 0.12	4
9	1.51	0.0144	238–233	0.63 ± 0.05	6
9	1.51	0.0144	221	0.79 ± 0.03	2

[a] Temperature = 25°; Ru(II) = 1.50×10^{-4} M except in experiment 7, where it was 1.35×10^{-4} M; $\mu = 0.071$–0.072, except in experiment 9, where it was 0.019. [HCl] or HTFMS (trifluoromethylsulfonic acid) was used to fix the ionic strength except in experiment 4, where HCl was reduced to 1.25×10^{-2} M and NaCl was used to maintain ionic strength. [b] Concentration of N_2O in solution = 2.47×10^{-2} M. At this level of N_2O only 10.0% of the Ru(II) is complexed, and only the complexed Ru(II) reacts in the course of the experiments. [c] There is a systematic trend, k appearing to be larger at short wavelengths, but its significance is obscure. The values of A_∞ tended to drift rather severely at shorter wavelength, and the difficulty in fixing the appropriate value is undoubtedly at least partly responsible for the apparent effect of wavelength.

Reaction solutions were equilibrated at 25.0° in a constant-temperature bath. Nitrous oxide (Liquid Carbonic) and argon were freed from O_2 by passing them through two scrubbing towers containing Cr^{2+} and were transported through all-glass systems. Trifluoromethylsulfonic acid was supplied through the courtesy of 3M Co.

Results

Reductions Using Cr^{2+}. The observations on the stoichiometry of the reaction of Cr^{2+} with N_2O in the presence of $Ru(NH_3)_5H_2O^{2+}$ have not been reported in substantial form and are included in this paper.

In one series of experiments, $Ru(NH_3)_5Cl^{2+}$ was brought into reaction with Cr^{2+} in the presence of N_2O, allowing enough time for the reduction of N_2O to be complete (*ca.* 1 hr.). A solution containing Fe^{3+} was added, and the residual reducing agent determined, developing the color of Fe^{2+} with *o*-phenanthroline. With the time for analysis sufficiently short (3 min or so), $Ru(NH_3)_5N_2^{2+}$ does not respond to Fe^{3+} as a reducing agent, at least under the conditions used for analysis. The results for the series is summarized in the following, where the four numbers given for each experiment represent $[Cr_2^{2+}]_0 \times 10^4$, $[Ru(NH_3)_5Cl^{2+}]_0 \times 10^4$, per cent loss of reducing power predicted, and per cent loss of reducing power observed: (1) 56.7, 5.57, 30.2, 29.5; (2) 56.3, 5.69, 30.3, 30.2; (3) 4.95, 3.93, 30.8, 29.1; (4) 90.9, 48.7, 69.6, 69.6; (5) 6.73, 0.627, 29.4, 28.5; (6) 4.61, 0.63, 41.0, 39.7.

The chromium(III) products obtained in an experiment with $[Ru(NH_3)_5Cl^{2+}]_0 = 7.5 \times 10^{-3}$ M, $[Cr^{2+}]_0 = 2.14 \times 10^{-2}$ M, $[HCl] = 3 \times 10^{-2}$ M, $[Cl^-]_0 = 0.13$ M, and $\mu = 0.22$ were separated by ion-exchange chromatography, and the amounts were determined. The results, a mean of two experiments, showed the percentages of $CrCl^{2+}$, Cr^{3+}, and "dimer" to be 60, 39, and 0.5. Note that some, but not all, of the $CrCl^{2+}$ arises in the reduction of Ru(III) by Cr^{2+}.

The yield of $Ru(NH_3)_5N_2^{2+}$ was not affected by the rate of addition of excess Cr^{2+} to the solution containing $Ru(NH_3)_5OH_2^{2+}$ and N_2O. In one experiment 10 equiv of Cr^{2+} was added all at once, in another 1 equiv (*i.e.*, enough to generate $Ru(NH_3)_5OH_2^{2+}$) was first added, followed by an additional equiv over a period of 1 hr, N_2O being passed through continuously. Using Fe^{3+} in excess as oxidant for each solution, it was found that 1 mol (±10%) of N_2 was formed for each mole of ruthenium ammine used.

The experiments on kinetics were done with Cr^{2+} in excess, and the plots of ln $(A_t - A_\infty)$ *vs.* time conformed well to pseudo-first-order behavior, being linear to beyond five half-lives. The results of the kinetic analysis are shown in Table I. The specific rate k_{Cr} is defined by

$$\frac{-d[Ru(NH_3)_5N_2O^{2+}]}{dt} = k_{Cr}[Cr^{2+}][Ru(NH_3)_5N_2O^{2+}] = \frac{d[Ru(NH_3)_5N_2^{2+}]}{dt}$$

The specific rate k_{Cr} is observed to be independent of $[Cr^{2+}]$ and of [HCl], but to decrease with a decrease in ionic strength and to increase with $[Cl^-]$ at constant ionic strength. The variation of k_{Cr} with $[Cl^-]$ is given by the expression

$$k_{Cr} = 8.2 \times 10^2\ M^{-1}\ \text{sec}^{-1} + (9.0 \times 10^3\ M^{-2}\ \text{sec}^{-1})[Cl^-]$$

In the direct reaction of Cr^{2+} with free N_2O, it was assumed that 2 mol of Cr^{2+} is required to reduce 1 mol of N_2O, and the second-order rate constant for the consumption of N_2O was observed as 6.5×10^{-6} M^{-1} sec^{-1} at 23 ± 2° in 8.6×10^{-2} M HCl. In the two experiments done, N_2O was in excess kept at 1 atm so that the variation of rate with $[N_2O]$ was not studied; the formation of Cr^{3+} did, however, conform to pseudo-first-order behavior.

Vanadium(II) as Reducing Agent. Preliminary experiments were done to ensure that V(III), which is produced when V^{2+} is oxidized, does not interfere in the reaction. To this end, V^{2+} in stoichiometric amount was used to generate $Ru(NH_3)_5OH_2^{2+}$ from $Ru(NH_3)_5Cl^{2+}$, thereby being oxidized to V(III), and the rate of approach to equilibrium for reaction 1 was measured. The results were fully consistent with those obtained using either Cr^{2+} or zinc amalgam to produce Ru(II), and we therefore conclude that V(III) at the level formed in the experiments is inert in the system on our time scale.

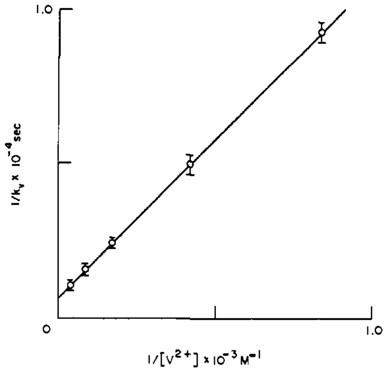

Figure 1. The plot of $1/k_v$ for the formation of $Ru(NH_3)_5N_2^{2+}$ as a function of the reciprocal of the concentration of vanadium(II) in solution (temperature = 25.0°, μ = 0.10).

Only superficial product studies on the vanadium component were done. A solution containing V^{2+}, HCl, N_2O, and $Ru(NH_3)_5Cl^{2+}$, initially 0.02, 0.04, 0.025, and 2.9×10^{-3} *M*, respectively, turns from violet to gray immediately, and then almost colorless over a period of 5 min. At no time is there apparent the brown color characteristic[5] of $[VOV]^{4+}$. There is no reason to believe that the change in oxidation state for vanadium is other than 2+ to 3+ in the system, either in terms of mechanism or of net change.

Addition of NaBr to the above solution produced a cream-colored solid. The ir and uv–visible spectra were identical with those reported[6,7] for $[Ru(NH_3)_5N_2]Br_2$ in the solid and solution, respectively. The yield based on ruthenium was 84% which, when account is taken of solubility, corresponds to a substantially quantitative reaction. The absorbance changes at 221 nm in the kinetic experiments also indicate essentially quantitative formation of the nitrogen complex.

The kinetic experiments were done with the concentration of Ru(II) much lower than that of V^{2+}, and this in turn lower than that of N_2O. The kinetic data conformed well to pseudo-first-order behavior, thus showing that the rate is first order in Ru(II). The pseudo-first-order rate constants, k_v, are entered in Table II.

Inspection of the data in Table II shows that k_v is independent of $[H^+]$. The variation with $[V^{2+}]$ requires analysis. A plot of k_v against $[V^{2+}]$ reveals that k_v increases with $[V^{2+}]$, but the plot shows rate saturation at high values of $[V^{2+}]$. When $1/k_v$ is plotted against $1/[V^{2+}]$ (Figure 1), the dependence of rate on $[V^{2+}]$ is seen to be of the form

$$k_v = a[V^{2+}]/(b + [V^{2+}])$$

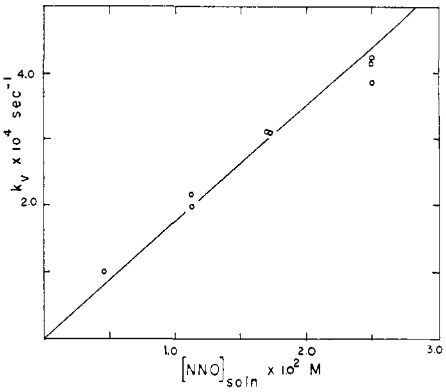

Figure 2. Plot of k_v for the formation of the $Ru(NH_3)_5N_2^{2+}$ complex as a function of the concentration of nitrous oxide in solution (temperature = 25°, $[V^{2+}] = 6.2 \times 10^{-3}$ *M*; $[Ru(II)] = 5.9 \times 10^{-5}$ *M*, μ = 0.08–0.10).

Figure 2 shows the variation of k_v with $[N_2O]$. With $[V^{2+}] = 0.6 \times 10^{-2}$ *M*, the rate law approximates first-order dependence on $[V^{2+}]$ (note that the value of the constant in the denominator of the rate law given below is 1.6×10^{-2}) and under these conditions, to the extent that the species Ru(II) is depleted by formation of the nitrous oxide complex, the specific rate k_v must show a saturation effect in $[N_2O]$. According to the equilibrium measurements made earlier, when N_2O is at 1 atm (or $[N_2O](aq) = 2.47 \times 10^{-2}$ *M*) approximately 10% of the reactant Ru(II) is complexed, and the rate would then be about 10% lower than would be the case were the affinity of N_2O for $Ru(NH_3)_5OH_2^{2+}$ insignificantly small. By expressing the rate in terms of actual $[Ru(NH_3)_5OH_2^{2+}]$ rather than total reactant Ru(II), the specific rates are independent of this effect. The approximate rate law expressing the data in these terms is

$$\frac{d[Ru(NH_3)_5N_2]}{dt} = \frac{7.0 \times 10^{-2}[V^{2+}][Ru(NH_3)_5OH_2^{2+}][N_2O]}{1.6 \times 10^{-2} + [V^{2+}]}$$

Table II. Rate of Formation of $Ru(NH_3)_5N_2^{2+}$ for the Reaction of Excess V^{2+} with N_2O in the Presence of $Ru(NH_3)_5OH_2^{2+}$ [a]

$[V^{2+}]_0 \times 10^3$ *M*	[HCl] $\times 10^2$ *M*	μ	$k_v \times 10^4$ sec^{-1}
0.460	10.3	0.12	0.520
0.460	10.3	0.11	0.570
1.20	10.4	0.11	1.04
1.20	2.21	0.11	1.11
2.40	2.30	0.11	2.18
2.40	2.30	0.11	1.92
6.16	1.78	0.10	4.17
6.16	7.96	0.10	3.85
6.16	7.96	0.10	4.24
12.2	1.49	0.07	6.03
12.2	1.49	0.07	6.17
12.2	1.49	0.08	6.11
25.9	3.13	0.11	9.88
25.9	3.13	0.11	10.3

[a] Temperature = 25.0°; $[Ru(II)]_0 = 5.8\text{–}5.9 \times 10^{-5}$ *M*; $[N_2O] = 2.47 \times 10^{-2}$ *M*; λ 221 nm.

This rate law is valid only in the limit that $[V^{2+}] \ll 1.6 \times 10^{-2}$ *M*. At high V^{2+}, the rate of formation of the N_2O complex becomes rate determining and the saturation effect in $[N_2O]$ must disappear.

In the experiment on the reduction of free N_2O by V^{2+}, the change in absorption corresponded to a change in $[V^{2+}]$ by approximately 5%. Assuming that the reaction is first order in each of $[V^{2+}]$ and $[N_2O]$, a

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

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

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

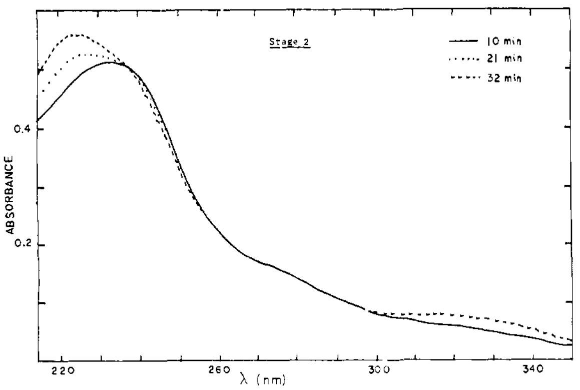

Figure 3. Absorbance changes in a solution with [$Ru(NH_3)_5OH_2^{2+}$] = 10^{-3} *M*, saturated with N_2O.

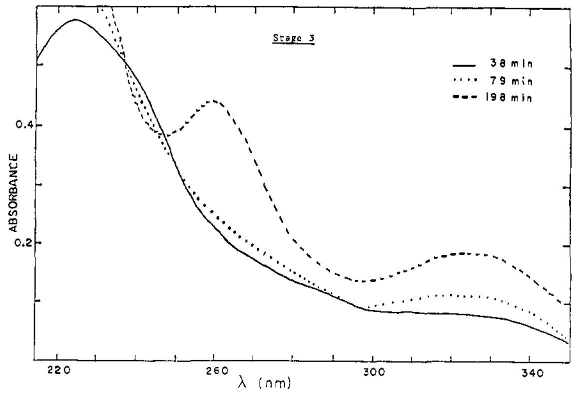

Figure 4. Continuation of experiment introduced in Figure 3.

second-order specific rate of $\sim 10^{-7}$ M^{-1} sec^{-1} is calculated for the rate of consumption of N_2O by V^{2+}.

Reduction by $Ru(NH_3)_5OH_2^{2+}$. Working at 0.01 *M* $Ru(NH_3)_5OH_2^{2+}$, Diamantis and Sparrow[8] showed that such solutions saturated with N_2O produced $Ru(NH_3)_5N_2^{2+}$ and $[Ru(NH_3)_5]_2N_2^{4+}$ after *ca.* 3 hr. In our earlier work[2] we found that when Ru(II) is sufficiently dilute, these reactions are not rapid enough to interfere seriously with the study of the association of N_2O with $Ru(NH_3)_5OH_2^{2+}$, but we also found that the net reduction of N_2O in the presence of $Ru(NH_3)_5OH_2^{2+}$ is strongly catalyzed by surfaces such as platinized Pt or amalgamated Zn. We have attempted in the course of the present work to measure the rate of reduction of N_2O by $Ru(NH_3)_5OH_2^{2+}$ in homogeneous solution.

Figures 3 and 4 illustrate the time scale of the changes in spectrum which occur when a solution of $Ru(NH_3)_5OH_2^{2+}$ at 10^{-3} *M* is saturated with N_2O. After 10 min the maximum at 238 nm characteristic of the complex is the prominent feature. After 20 min has elapsed, the maximum has shifted toward the spectral region where [$Ru(NH_3)_5N_2^{2+}$] shows a maximum. After 198 min absorption characteristic of $[Ru(NH_3)_5]_2N_2^{4+}$ is clearly evident, and absorption ($\sim$320 nm) due to a mixture of $Ru(NH_3)_5OH_2^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ is prominent. When the concentration of $Ru(NH_3)_5OH_2^{2+}$ is reduced, the time scale for the production of $Ru(NH_3)_5N_2^{2+}$ is much increased. In Figure 5 is shown the change with time of the spectrum of a solution 3.3×10^{-4} *M* in $Ru(NH_3)_5OH_2^{2+}$ in the presence of N_2O. The concentration here corresponds to that used in the experiments which served to establish the affinity of N_2O for $Ru(NH_3)_5OH_2^{2+}$.

In the present work on the kinetics of the production of $Ru(NH_3)_5N_2^{2+}$ in the system, we restricted attention to the early phases of the reaction. Expressing the rate law in the form

$$\frac{d[Ru(NH_3)_5N_2^{2+}]}{dt} = k[Ru(NH_3)_5OH_2^{2+}][Ru(NH_3)_5N_2O^{2+}]$$

we found the coefficient *k* to be approximately 2×10^{-2} M^{-1} sec^{-1}. This value is not offered with confidence, however; in addition to the difficulty of extracting a rate constant in such a complex reaction sequence, there is no guarantee that surface catalysis was eliminated in our work.

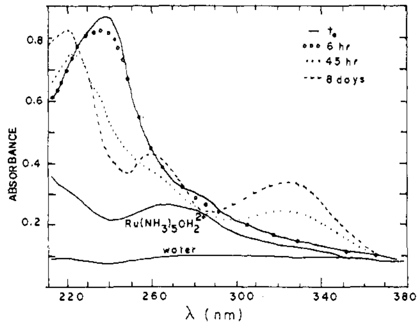

Figure 5. Spectra for the decay of the nitrous oxide complex at 20.1°, $[Ru(II)]_{tot_0} = 3.29 \times 10^{-4}$ *M*, [HCl] = 1.07×10^{-2} *M* (solution saturated with nitrous oxide).

One observation made in the course of the experiments on the reduction as catalyzed by surfaces merits mention. When H_2 on Pt was used to reduce Ru(III) to Ru(II), and the H_2 gas stream was replaced by N_2O, bubbles appeared on the surface of the Pt. This seems to indicate that in the surface-catalyzed reaction, N_2 formed on reduction of N_2O is not necessarily incorporated into the coordination sphere of Ru(II).

Discussion

The new kinetic data provide a measure of the activation by $Ru(NH_3)_5^{2+}$ of N_2O toward reduction by Cr^{2+}. The increase in rate when N_2O enters the coordination sphere is a factor of about 10^8. The added work has, however, not illuminated the following basic question. Is the effect of Ru(II) exerted solely in its capacity as a back-bonding metal ion, or does the ruthenium center cooperate in the valence change (reactions 2 and 3)?

$$Ru(NH_3)_5N_2O^{2+} + Cr^{2+} \xrightarrow{H^+} Ru(NH_3)_5N_2^{3+} + CrOH^{2+} \quad (2)$$

$$Ru(NH_3)_5N_2^{3+} + Cr^{2+} = Ru(NH_3)_5N_2^{2+} + Cr^{3+} \quad (3)$$

A search for the intermediate $Ru(NH_3)_5N_2^{3+}$ was made by adding Cr^{2+} slowly to the Ru(II)–N_2O system, so as to give the intermediate an opportunity to release N_2, but the experiments on this point met with no success. Under all conditions, the formation of the Allen and Senoff ion was complete. The sensitivity of the rate of reduction by Cr^{2+} to the presence of Cl^- is characteristic of an outer-sphere

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[8] A. A. Diamantis and G. J. Sparrow, *Chem. Commun.*, 469 (1969).

rather than an inner-sphere reduction. It should be noted that when $Co(NH_3)_5OH_2{}^{3+}$ is reduced by Cr^{2+} in the presence of 0.10 *M* Cl^-, there is virtually no increase in rate of reduction over a similar reaction at the same ionic strength with $ClO_4{}^-$ as the only anion.[9] By contrast, when $Co(NH_3)_6{}^{3+}$ is the reactant, the rate of reduction is enhanced *ca.* 14-fold by 0.1 *M* Cl^-.[10] If, as this comparison suggests, we are dealing with an outer-sphere initial attack, the oxide ion eventually released from the coordinated N_2O would not be transferred to Cr in the first step, eq 2, though it might be transferred in a subsequent reaction. Tracer work on the transfer of oxygen to chromium could clearly be of help in advancing our understanding of the mechanism of the reaction. The fact that Cr^{3+} rather than dimer is product suggests that Cr^{2+} is oxidized by a one-electron rather than a two-electron change.[11] Tracer work might also further illuminate this important issue.

The kinetic data obtained with V^{2+} can be accounted for by the mechanism

$$Ru(NH_3)_5OH_2{}^{2+} + N_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ru(NH_3)_5N_2O^{2+} + H_2O \qquad (4)$$

$$Ru(NH_3)_5N_2O^{2+} + V^{2+} \xrightarrow{k_v'} \text{products } (Ru(NH_3)_5N_2{}^{2+}) \qquad (5)$$

On that basis

$$\frac{-d[Ru(NH_3)_5OH_2{}^{2+}]}{dt} = \frac{k_f[Ru(NH_3)_5OH_2{}^{2+}][N_2O][V^{2+}]}{k_r/k_v' + [V^{2+}]}$$

Comparison of this form of the rate law with that obtained experimentally shows that k_f as determined here is 7×10^{-2} M^{-1} sec^{-1} at 25°, which agrees well with the value of 7.6×10^{-2} extrapolated from the earlier measurements[2] for Cr^{2+} at 6.8° and 20.1°. The saturation in rate with $[V^{2+}]$ simply reflects the fact that at high $[V^{2+}]$ this agent reacts with $Ru(NH_3)_5N_2O^{2+}$ rapidly enough so that the N_2O complex is not maintained at equilibrium with $Ru(NH_3)_5OH_2{}^{2+}$ and N_2O. From the coefficient k_fk_v'/k_r, by introducing the equilibrium constant for reaction 1 at 25° (extrapolated from the earlier data[2] as 4.5), the second-order rate constant for k_v' is calculated as 1.0. Thus, with V^{2+} as the reducing agent, the rate of reduction of N_2O is increased *ca.* 10^7-fold when it enters the coordination sphere of Ru(II).

The values recorded for the rates at which either $V(H_2O)_6{}^{2+}$ or $Ru(NH_3)_5OH_2{}^{2+}$ reacts with coordinated N_2O are compatible with substitution at the reducing agent preceding electron transfer. The rates are low enough so that in both cases substitution may be rate determining. Thus, the rate difference for free *vs.* coordinated N_2O in the case of V^{2+} may not be directly comparable to the case of Cr^{2+}, and the factor of 10^7 may be a lower limit on the rate increase in the former case.

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