Inorg. Chem. **1987**, *26*, 2437-2440

Contribution from the Departments of Chemistry, King's College London, London W8 7AH, U.K., and State University of New York at Stony Brook, Stony Brook, New York 11794

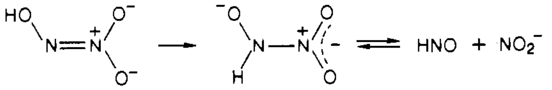
Reaction between Trioxodinitrate and the Pentaamminenitrosylruthenium(II) Cation

Mohammad Javaid Akhtar,[1b] Francis T. Bonner,*[1b] Martin N. Hughes,*[1a] Chun-Su Lu,[1b,c] Helen L. Wallis,[1a] and Peter E. Wimbledon[1a]

Received December 5, 1986

The reaction between $N_2O_3^{2-}$ and $Ru(NH_3)_5NO^{3+}$ has been studied over the pH range 6–14. In the region around pH 10, reaction results in rapid formation of NO followed by much slower formation of N_2O and N_2, in relative proportions that vary with pH. The use of ^{15}N-labeled trioxodinitrate ($^-ON^1{=}N^2O_2^-$) shows that NO derives predominantly from the N-1 atom and N_2O derives substantially from N-1 but with some admixture of either N-2 or NO^+ nitrogen. The minor product N_2 appears to be formed entirely by self-decomposition of the nitrosyl complex. There is a rapid initial reaction in which free NO is produced, which reflects one-electron oxidation of $N_2O_3^{2-}$ by the NO^+ group of $Ru(NH_3)_5NO^{3+}$ and is interpreted as resulting in a complex of Ru(II) containing radical NO and NO^+ from trioxodinitrate. This species then rearranges in a relatively slow process to form a yellow complex (λ_{max} = 350 nm), accompanied by release of N_2O. This reaction is first order in complex but independent of trioxodinitrate concentration. It is postulated that it proceeds via an intermediate $Ru^{III}(NO^-)(NO^+)$ species, formed via internal electron transfer, and that the final yellow species is a Ru(III) complex. The plot of k_1 vs. pH is bell-shaped, corresponding to rate-controlling protonation equilibria involving species with pK_a values of 7.2 and 12.2.

The decomposition of trioxodinitrate in aqueous solution is affected by nitrite in a pH-dependent manner.[2] At pH ≥3, added nitrite causes a reduction in the decomposition rate, showing that the initial cleavage of $HN_2O_3^-$ into HNO and NO_2^- (eq 1 and 2) is reversible, as has been confirmed by ^{15}N studies.[3] Since



(1)

$$HNO + HNO \longrightarrow N_2O + H_2O \qquad (2)$$

this eliminates the possibility of direct N═N bond cleavage, it was proposed[2] and recently shown[4] that tautomerization (eq 1) is a rate-controlling precursor to N–N single bond cleavage in which HNO and NO_2^- are formed. Further evidence has been reported in studies of the reaction between trioxodinitrate and hemoglobin, in which case an interpretation[5] suggesting that NO and HNO_2^- are primary cleavage products has been disproven.[4,6-8] At pH ≤3, nitrite is responsible for a free-radical chain reaction that yields NO as the exclusive gas product. Distinct rate laws have been found to hold at different temperatures for this HNO_2-catalyzed process, the change occurring at 17 °C at pH 3.90 and at 7 °C at pH 3.05.[2] The low-temperature process exhibits nearly zero activation energy.

This study was undertaken because the cation $Ru(NH_3)_5(NO)^{3+}$ acts as an agent of nitrosation toward a range of nucleophiles[9] and appeared to offer opportunity to study the NO-producing nitrosation process at relatively high pH, i.e. under conditions at which trioxodinitrate chemistry is less complex than at low pH. The ruthenium nitrosyl cation is converted into a nitro complex under alkaline conditions, in an equilibrium process that has been characterized.[10]

Experimental Section

$Na_2N_2O_3$, prepared from $C_3H_7ONO_2$ and NH_2OH, displayed a value ϵ = 8300 cm^{-1} M^{-1}, identical with the literature value.[11] The complex

Table I. Gas Products of the $N_2O_3^{2-}$–$Ru(NH_3)_5NO^{3+}$ Reaction[a]

pH	buffer	I/M	% N_2	% NO	% N_2O	n_{N_2O}:n_{NO}
1. $[N_2O_3^{2-}] = [RuNO^{3+}] = 1.0 \times 10^{-3}$ M						
5.53	acetate		2.8	7.5	90.0	12.0
9.75	borate		5.3	40.2	54.5	1.4
11.1	NaOH		18.9	45.6	35.5	0.8
14.0	NaOH	1.0	20.4	22.0	57.6	2.6
2. $[N_2O_3^{2-}] = 2.0 \times 10^{-3}$ M; $[RuNO^{3+}] = 1.0 \times 10^{-3}$ M						
5.53	acetate	0.25	3.2	9.1	87.7	9.6
9.75	borate	0.25	5.6	45.0	49.4	1.1
10.85	borate	0.25	7.8	32.0	60.2	1.9
12.00	NaOH	0.25	9.8	56.4	33.8	0.6
13.00	NaOH	0.25	14.2	46.0	39.8	0.9
14.00	NaOH	1.0	21.7	25.i	53.1	2.1
3. $[N_2O_3^{2-}] = 1.0 \times 10^{-3}$ M; $[RuNO^{3+}] = 1.0 \times 10^{-4}$ M						
6.21	acetate					9.3
7.48	acetate					2.8
9.02	borate					1.3
9.80	borate					1.3
10.9	borate					1.5

[a] Conditions: T = 25.0 °C; reaction time 180 min.

$[Ru(NH_3)_5NO]Cl_3$ was prepared by a literature method[12] and characterized by elemental analysis. Other reagents were of the best available grade.

Kinetic runs, carried out under N_2, were initiated by addition of a solution of $[Ru(NH_3)_5NO]Cl_3$ to a solution containing all other components, at 25 °C and with $Na_2N_2O_3$ usually in excess. Samples withdrawn at measured times were run into known volumes of 4 M NaOH, and optical densities were measured at 365 nm (Unicam SP6-550 spectrophotometer). A few runs were initiated by injection of Ru complex solution through a rubber cap and followed directly in 1-cm quartz cells at 350 nm to monitor formation of a reaction product in the range pH 8.05–9.05. Ionic strength control was maintained by using $NaClO_4$.

Gas products were analyzed by employing a vacuum-line–interfaced GC system,[13] using CF_4 as internal reference, and with mechanical vibration in time dependence studies.[14] $Na_2O^{15}NNO_2$ and $Na_2ON^{15}NO_2$[15,16] were employed in tracer experiments, with mass spectrometry carried out on an AEI MS-30 instrument (Stony Brook Mass Spectrometry Facility).

Results

At equimolar concentrations (0.02 M) reaction between trioxodinitrate and $Ru(NH_3)_5(NO)^{3+}$ exhibits vigorous gas evolution that is most pronounced at pH ~10, and development of a yellow color in the solution, characterized by λ_{max} = 350 nm. At pH

---

[1] (a) Kings College London. (b) State University of New York at Stony Brook. (c) Beijing Medical University, Beijing, People's Republic of China.

[2] Hughes, M. N.; Wimbledon, P. E. *J. Chem. Soc., Dalton Trans.* **1977**, 1650.

[3] Akhtar, M. J.; Lutz, C. A.; Bonner, F. T. *Inorg. Chem.* **1979**, *18*, 2369.

[4] Donald, C. E.; Hughes, M. N.; Thompson, J. M.; Bonner, F. T. *Inorg. Chem.* **1986**, *25*, 2676.

[5] Doyle, M. P.; Mahapatro, S. N. *J. Am. Chem. Soc.* **1984**, *106*, 3678.

[6] Bazylinski, D. A.; Hollocher, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 7982.

[7] Bazylinski, D. A.; Goretski, J.; Hollocher, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 7986.

[8] Bazylinski, D. A.; Hollocher, T. C. *Inorg. Chem.* **1985**, *24*, 4285.

[9] Bottomley, F.; Crawford, J. R. *J. Chem. Soc., Dalton Trans.* **1972**, 2145.

[10] Hughes, M. N.; Wallis, H. L.; Wimbledon, P. E., unpublished work.

[11] Addison, C. C.; Gamlen, G. A.; Thomson, R. *J. Chem. Soc.* **1952**, 338.

[12] Armor, J. N.; Scheidegger, H. A.; Taube, H. *J. Am. Chem. Soc.* **1968** *90*, 5928.

[13] Pearsall, K. A.; Bonner, F. T. *J. Chromatogr.* **1980**, *200*, 224.

[14] Bonner, F. T.; Pearsall, K. A. *Inorg. Chem.* **1982**, *21*, 1973.

[15] Bonner, F. T.; Ravid, B. *Inorg. Chem.* **1975**, *14*, 558.

[16] Bonner, F. T.; Degani, H.; Akhtar, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 3739.

0020-1669/87/1326-2437$01.50/0

Table II. Time Course of Gas Evolution for the $N_2O_3^{2-}$–$Ru(NH_3)_5(NO)^{3+}$ Reaction[a]

1. $10^5 n_0(Ru) = 2.10$; $10^5 n_0(N_2O_3^{2-}) = 6.50$

t/min	3	10	17	35	45	60	90	120	4320
$10^5 n(NO)$	1.98	1.98	2.01	1.69	1.65	1.67	1.71	1.68	1.72
$10^5 n(N_2O)$	0.51	0.79	0.94	0.96	1.17	1.15	1.87	2.16	3.29
$10^5 n_N$(total)	3.00	3.56	3.89	3.61	3.99	3.97	5.45	6.00	8.30

2. $10^5 n_0(Ru) = 2.54$; $10^5 n_0(N_2O_3^{2-}) = 15.79$

t/min	10	17	25	45	90	120	1260
$10^5 n(NO)$	2.69	2.69	2.19	2.38	2.43	2.44	2.38
$10^5 n(N_2O)$	1.75	2.15	1.93	3.10	4.66	5.63	8.61
$10^5 n_N$(total)	6.19	6.99	6.05	8.58	9.32	13.70	19.60

[a] Conditions: $T = 25$ °C; pH 9.7, borate buffer.

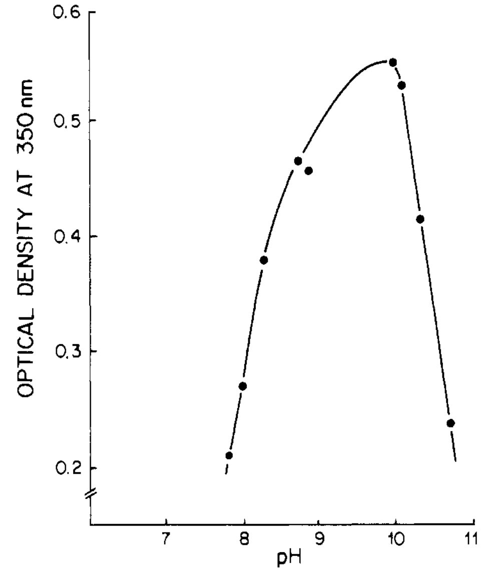


Figure 1. Maximum values of optical density for production of the yellow ruthenium complex ($\lambda_{max} = 350$ nm) at 25 °C and various pH levels.

<9.8 the yellow color is stable, although the extent of its formation (Figure 1) decreases with decreasing pH. At pH >9.8 the color decays with time, and it is not observed at all at pH >11. This behavior was found to be independent of buffer type and concentration.

Gas products were identified to be NO, N_2O, and N_2. Details of their formation are shown in Table I and Figure 2, where it is seen that the percentage of NO passes through a maximum and that of N_2O a minimum, at about pH 10. The ratio n_{N_2O}:n_{NO} is ≥10 at pH 5.5 and displays a minimum value <1 in the range pH 11–12 under equimolar and 2:1 stoichiometries. Dinitrogen is a relatively minor product, whose appearance can be attributed to the known self-decomposition of $Ru(NH_3)_5NO^{3+}$.[17]

Data on the time course of gas evolution (Table II) show that formation of NO is complete within the first 3 min, while N_2O is produced more slowly; a subsequent small decline in n_{NO} probably results from reaction with the Ru complex. In these experiments, with $N_2O_3^{2-}$ in excess, NO is produced in approximately 1:1 ratio with the consumption of $Ru(NH_3)_5(NO)^{3+}$. For an overall 1:1 stoichiometry, assuming that all N atoms of $N_2O_3^{2-}$ and NO^+ appear among the gas products, the maximum production of gas-phase N should be $3n_0$(Ru). In the observed gas production this value is exceeded, showing that some of the N_2O is produced by self-decomposition of $N_2O_3^{2-}$, an effect that is enhanced by increased excess of $N_2O_3^{2-}$ (experiment 2, Table II).

Mass spectrometric data on the gas products of reaction between $Ru(NH_3)_5(NO)^{3+}$ and $N_2O_3^{2-}$ labeled in each of the two nonequivalent nitrogen positions (Table III) show that at pH 9.8 the NO product derives predominantly from the N-1 position of trioxodinitrate, with a small admixture from N-2, and that N_2O derives largely from N-1, but with a small contribution from N-2 that is not large enough to account for the remaining nitrogen. Accordingly, N_2O must also derive in part from the NO^+ group of the Ru complex. The results at pH 7.1 show a higher proportion of N-1 nitrogen in the N_2O product and an increasing ^{15}N content with increasing $N_2O_3^{2-}$ concentration, reflecting the expected effect of self-decomposition. The near-randomness of isotopic distribution in N_2O supports an assumption that this product is formed predominantly by dimerization of a monomeric species, i.e. HNO or NO^-. Reliable measurements of the ^{15}N content of NO produced at the lower pH 7.1 were not available because of small sample size and difficulty of separation. Similarly, although measurements indicated an apparent minor content of N-1 nitrogen in N_2, it is entirely attributable to a small inclusion of unseparated NO, and we are confident that self-decomposition of $Ru(NH_3)_5(NO)^{3+}$ is the essential sole source of this product.

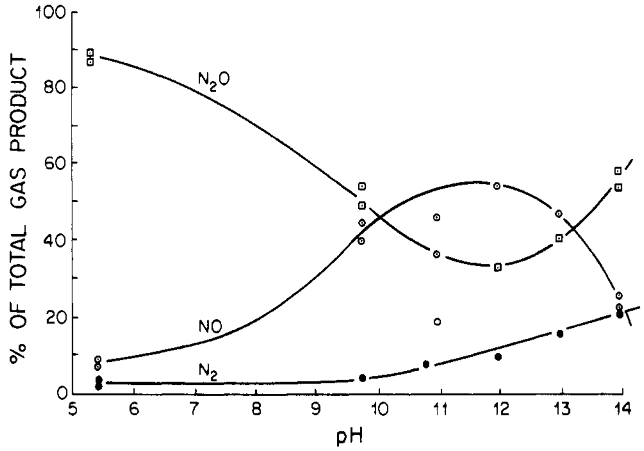


Figure 2. Dependence of gas products of the $N_2O_3^{2-}$–$Ru(NH_3)_5(NO)^{3+}$ reaction upon pH.

Table III. Mass Spectrometry of Gas Products of Reaction with ^{15}N-Labeled Trioxodinitrate[a]

pH	n_{Ru}:$n_{N_2O_3^{2-}}$	*m/e* 46	*m/e* 45	*m/e* 44	% $^{15}N(N_2O)$	% $^{15}N(NO)$
		1. $RuNO^{3+}$ + $^-O^{15}NNO_2^-$				
9.8[b]	1:1	0.431	0.503	0.066	68.3	91.6
9.8	1:2	0.488	0.467	0.045	72.1	86.0
7.1[c]	3:1	0.646	0.346	0.008	81.9	
7.1	1:1	0.768	0.227	0.005	88.1	
7.1	1:3	0.788	0.207	0.005	89.1	
		2. $RuNO^{3+}$ + $^-ON^{15}NO_2^-$				
9.8	1:2	0.003	0.115	0.882	6.1	4.0

[a] Conditions: $T = 25.0$ °C; reaction time ~8 h; 95.0% ^{15}N. [b] Borate buffer. [c] Phosphate buffer.

Kinetic studies were carried out at 25 °C, usually at ionic strength 0.25 M and with $N_2O_3^{2-}$ in stoichiometric excess. The rate of reaction was found independent of buffer type and concentration and only slightly affected by variation of ionic strength. Measurements were made by running reaction samples into 4 M NaOH, with the objective of converting the unreacted nitrosyl complex into the nitro form and measuring its concentration by using the known absorption at 365 nm. However, it was subse-

---

[17] Bottomley, F.; Clarkson, S. G.; Kiremire, E. M. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1909.

Table IV. Measured First-Order Rate Constants for the $N_2O_3^{2-}$-$Ru(NH_3)_5(NO)^{3+}$ Reaction[a]

pH	$10^2[N_2O_3^{2-}]$/M	$10^4[RuNO^{3+}]$/M	$10^3k_1/s^{-1}$
		I = 0.25 M	
10.4	1.0	5.0	12.8
10.4	1.0	5.0	12.3
10.4	1.0	10.0	13.0
10.4	0.50	5.0	13.1
10.4	0.375	5.0	10.9
10.4	0.25	5.0	10.9
5.6	1.0	5.0	1.50
6.37	1.0	5.0	1.70
6.80	1.0	5.0	5.20
7.38	1.0	5.0	9.20
8.21	1.0	5.0	14.2
8.91	1.0	5.0	13.9
9.74	1.0	5.0	16.1
10.9	1.0	5.0	15.4
11.2	1.0	5.0	15.2
		I = 1.0 M	
7.31	1.0	5.0	11.3
7.98	1.0	5.0	15.1
9.01	1.0	5.0	15.4
10.1	1.0	5.0	17.7
11.1	1.0	5.0	20.2
12.5	1.0	5.0	4.7
14.0	1.0	5.0	0.49

[a] T = 25.0 °C.

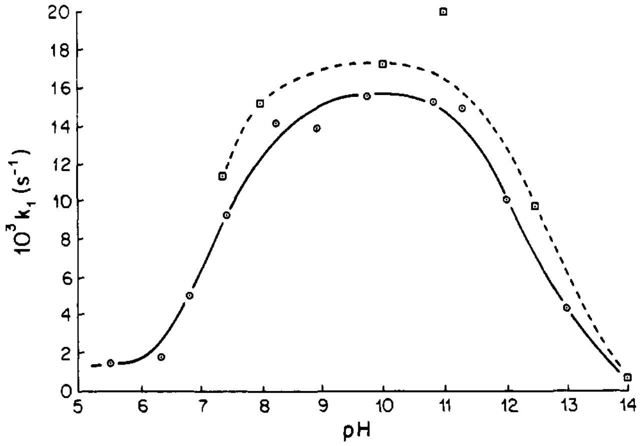


Figure 3. Dependence of k_1 upon pH: circles, I = 0.25 M; squares, I = 1.0 M.

quently realized that the initial, NO-producing reaction occurs rapidly and that the kinetic measurements as carried out must relate to a subsequent, slower reaction of a second Ru complex (which we designate species A) that forms along with NO. This species must still contain an NO^+ group, because it is converted reversibly in alkali to a species showing the absorption characteristic of a nitro complex. Species A then rearranges to give the yellow compound absorbing at 350 nm (which we designate species B) and N_2O. Species B does not rearrange in alkali to give a nitro complex.

Rigorously linear plots of log A_{365} vs. time were obtained, showing the reaction to be first order in Ru complex. Measured values of the rate constant k_1 (Table IV) were found independent of both Ru complex concentration and $[N_2O_3^{2-}]$. The latter observation confirms that the observed kinetics relate to rearrangement of a Ru complex and not to reaction with trioxodinitrate. The pH dependence of k_1 (Figure 3) exhibits a maximum at about pH 10, and the bell-shaped plot suggests rate-controlling protonation equilibria characterized by pK_a values of about 7.2 and 12.2. The reaction rate is only slightly increased by increasing ionic strength.

The process characterized by k_1 exhibits a pH-dependent lag phase (see Figure 4). At pH 5.6 the onset of reaction is delayed by 7 min, but the lag time decreases with increasing pH until at pH 8 the reaction begins immediately upon the mixing of reagents. At pH >10 the lag phase reappears and increases with pH. The pH-dependent lag phase may be accounted for by assuming an NO-producing reaction that is slower at pH values other than those around 10. Direct monitoring of the formation of the yellow Ru complex product species B at 350 nm also shows the presence of a lag phase at certain pH values and a pH dependence of rate constant similar to that shown in Figure 3.

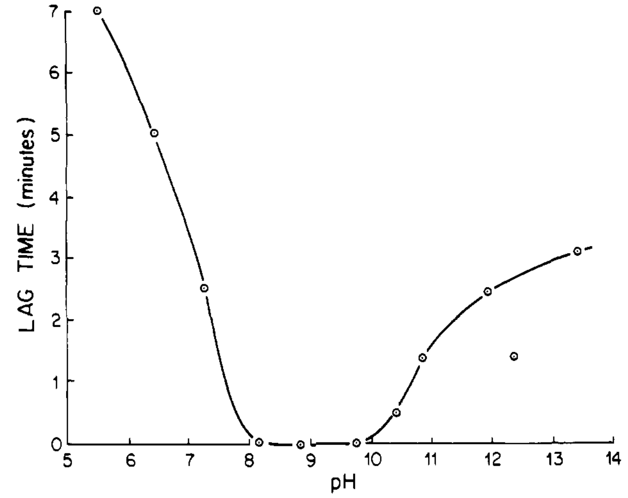


Figure 4. Dependence of lag time for onset of reaction upon pH (T = 25 °C).

Unsuccessful attempts were made to isolate species B as a solid. Although stable in acidic solution, the yellow color is lost when a solution at pH 8 is made alkaline. The color reappears when the pH is restored to 8, but not quantitatively, in agreement with its known instability at high pH.

The reaction sequence eq 3 and 4 is consistent with the evidence described above. Equation 4 includes the possibility that conversion A → B may proceed via an intermediate species X. While

$$Ru(NH_3)_5(NO)^{3+} + N_2O_3^{2-} \xrightarrow{\text{fast}} \text{species A} + NO \qquad (3)$$

$$\text{species A} \rightarrow X \xrightarrow[\text{slow}]{k_1} \text{species B} + N_2O \qquad (4)$$

trioxodinitrate consists of $HN_2O_3^-$ and $N_2O_3^{2-}$ in varying proportions over the pH range studied, the kinetics results give no information concerning which if not both of these species is the reactive participant.

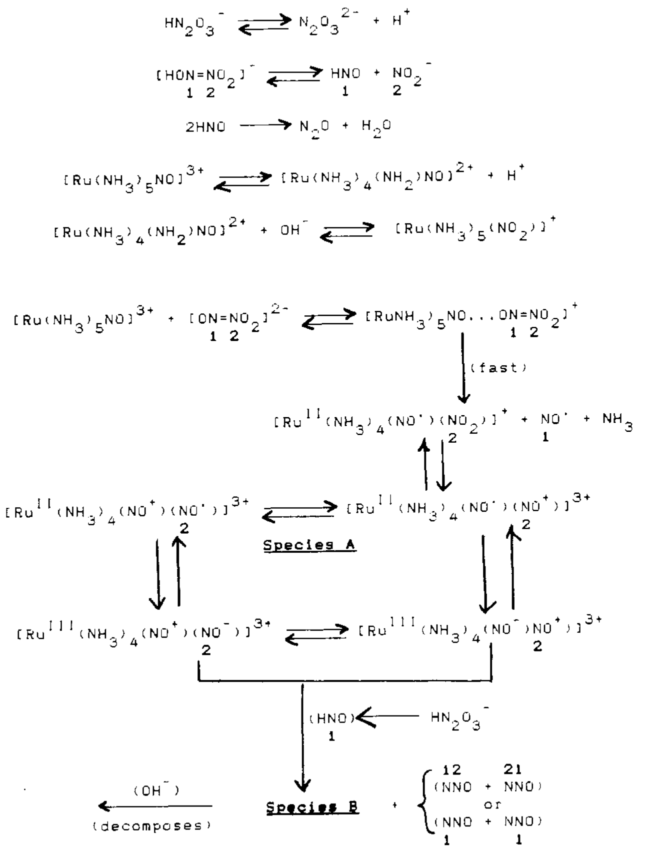
Discussion

The reaction of $N_2O_3^{2-}$ with $Ru(NH_3)_5(NO)^{3+}$ probably occurs via ion-pair formation, followed by attack of the nitrosyl group on trioxodinitrate. The rapid production of NO is consistent with a one-electron oxidation of trioxodinitrate accompanied by cleavage of its N=N bond. It is known that $Ru(NH_3)_5(NO)^{3+}$ is susceptible to one-electron reduction to form $Ru(NH_3)_5(NO)^{2+}$, in which radical NO is coordinated to Ru(II).[18-20] Similar observations have been made in the case of $Fe(CN)_5(NO)^{3-}$.[21] The compound $Ru(NH_3)_5(NO^\bullet)^{2+}$ has a lifetime of seconds,[19] but other NO radical complexes of Ru(II) are much more stable.[20] Reduction of the NO^+ group in $Ru(NH_3)_5NO^+$ thus appears the most likely source of $N_2O_3^{2-}$ oxidation, and it is therefore appropriate to suggest that species A contains an NO radical. It must also contain either an NO^+ group or a group that can be readily converted to NO^+, since species A is known to be reversibly converted to a nitro complex at high pH. The most likely origin of this group is the nitrite fragment released upon one-electron oxidation of trioxodinitrate. The process characterized by k_1 is

---

(18) Armor, J. N. *Inorg. Chem.* **1973**, *12*, 1959.
(19) Armor, J. N.; Hoffman, M. Z. *Inorg. Chem.* **1975**, *14*, 444.
(20) Callahan, R. W.; Brown, G. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 894.
(21) Oosterhuis, W. T.; Lang, G. *J. Chem. Phys.* **1969**, *50*, 4381.

Scheme I



then one in which species A must rearrange to form yellow species B, with simultaneous production of N_2O. While our evidence is not sufficient to determine the detailed nature of this process, we speculate that an intermediate Ru(III) species containing NO^- may form by internal electron transfer and that loss of NO^- then leads to release of N_2O. While we have not succeeded in identifying species B, we note that it should be a Ru(III) complex, that we know it to be unstable in alkali, and that while the composition of its assumed precursor suggests that it may contain an NO^+ group, it does not analyze as a nitro complex.

The pH dependences of product distribution and k_1 may be explained in part by the conversion of pentaamminenitrosylruthenium(II) cation to the nitro species. This species would be unable to oxidize trioxodinitrate, so that as pH is increased, the rate of NO production would be expected to fall and the rate of conversion A → B to decrease as the fraction of complex present in the active form decreases. The apparent p*K* value 12.2 obtained from the pH–k_1 plot is consistent with the known pH dependence of the formation of nitro complex. We have not succeeded in identifying a protonation equilibrium associated with the apparent p*K* value 7.2 obtained at the low-pH end of the k_1–pH plot, which may indicate the presence of a competing reaction.

The interpretations described above are summarized in Scheme I. It accommodates the evidence for production of NO from trioxodinitrate atom N-1 and for formation of some N_2O from N-1 (via NO^- produced in self-decomposition) in combination with a second N atom, whose origin is partly N-2 and partly NO^+. The N-2 and NO^+ nitrogen atoms become equivalent in Scheme I.

Finally, we call attention to the fact that the key step in this mechanism consists of an attack by the ruthenium-bound NO^+ group upon trioxodinitrate that results in rapid cleavage of its N=N bond. This feature is consistent with previously presented evidence that the catalytic cleavage of trioxodinitric acid to yield NO is initiated by HNO_2 nitrosation.[2]

Acknowledgment. We acknowledge the award of SERC studentships (to P.E.W. and H.L.W.) and the financial support of NATO (F.T.B. and M.N.H.) and the People's Republic of China (C.-S.L.).

Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Assessment of the π-Acceptor Capability of Selected Ligands Based on the Photoelectron Spectra of Ruthenium Ammine Complexes

Rex E. Shepherd,* Andrew Proctor, Wayne W. Henderson, and Terry K. Myser

Received March 24, 1987

ESCA spectra have been recorded for a series of Ru^{II} and Ru^{III} ammine complexes of general formula $[(NH_3)_5RuL]X_n$ (X^- = PF_6^-, Cl^-). Binding energy regions of the C_{1s}, $Ru_{3d_{3/2}}$, $Ru_{3d_{5/2}}$, and $Ru_{3p_{3/2}}$ photopeaks were studied. Binding energies were determined by using nonlinear-least-squares curve fitting. Δ equal to the binding energy difference for ($C_{1s} - Ru_{3d_{5/2}}$) has been used to assign a fractional increase in charge at the Ru^{II} center when L = a series of π-acceptor ligands: *N*-methylpyrazinium (CH_3pz^+), CO, dimethyl acetylenedicarboxylate ester (dmad), CO, pyrazine (pz), pyridine (py), and CH_3CN. Authentic Ru^{II} and Ru^{III} oxidation states were assumed for $[Ru(en)_3]ZnCl_4$, $\Delta = 5.1$ eV, and $[Ru(NH_3)_6]Cl_3$, $\Delta = 2.5$ eV, respectively. The π-acceptor order and effective Ru oxidation state were determined to be as follows: CH_3pz^+, 3.01 > CO, 2.88 > dmad, 2.73 > pz, 2.51 > CH_3CN, 2.31 > py, 2.20. Δ was also found to be linear in the value of $E_{1/2}$ for the $(NH_3)_5RuL^{3+/2+}$ couple. π-Donor ligands exhibit little influence on Δ for Ru^{III} derivatives; $\Delta = 2.4 \pm 0.1$ eV for 3,5-dimethylpyrazole, 4-(dimethylamino)pyridine, and 4-aminopyridine.

Introduction

Electron spectroscopy for chemical analysis (ESCA) is a technique that is used to determine the binding energies of core electrons. The binding energy is dependent not only on the given core level and atom of interest but also on initial- and final-state effects. Changes in the initial-state charge of the atom give rise to a small but measurable chemical shift. In addition, the final-state relaxation energy contributions, caused by screening of the core hole created by photoemission, give rise to considerable absolute binding energy shifts. If one assumes that relaxation energy contributions are constant in a series of similar compounds, then ESCA data can be approximately correlated with effective changes in oxidation state for the atom of interest and with the charge-transfer electron distributions. Previous work includes studies with platinum complexes,[1] ruthenium complexes,[2,3]

---

(1) Cook, C. D.; Wan, K. Y.; Gelius, U.; Hamrin, K.; Johansson, G.; Olsson, E.; Siegbahn, H.; Nordling, C.; Siegbahn, K. *J. Am. Chem. Soc.* **1971**, *93*, 1904.

(2) (a) Citrin, P. H. *J. Am. Chem. Soc.* **1973**, *95*, 6472. (b) Citrin, P. H.; Ginsberg, A. P. *J. Am. Chem. Soc.* **1981**, *103*, 3673.

(3) Matsumura-Inoue, T.; Ikemoto, I.; Umezawa, Y. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *102*, 131.

0020-1669/87/1326-2440$01.50/0 © 1987 American Chemical Society