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gram of **4b** with that of the mixture of isomers of **4** confirmed the cis isomer as the major constituent. The GC–mass spectrometry analysis of **5** shows the expected three components with the largest GC peak assigned to (on the basis of the ^{31}P NMR spectrum) the cis isomer, **5b**. The first eluted compound shows a major fragmentation route involving cleavage of the aryl–phosphazene bond. This behavior is typical of a geminal isomer[27] and so allows assignment of **5a**. Geminal phosphazene isomers generally have the smallest GC retention times. The non-geminal isomers **5b** and **5c** show the expected fragmentation patterns[27] with formation of linear phosphazene ions being an important feature. The intensities of the peaks assigned to the cis isomer are greater than those of the trans isomer. This is in agreement with the behavior of phenyl fluorocyclotriphosphazenes,[27] thus adding addition evidence to the GC peak assignments. The isomer ratio (from GC) for **5a**:**5b**:**5c** is 1:2.8:1.1. The GC–mass spectrometry analysis of **4** shows the gen (**a**):cis (**4b**):trans (**4c**) ratio to be 1:6.1:1.5. A curious feature of the mass spectrum of the geminal, **4a**, isomer is the importance of the loss of a propenyl group and the formation of linear ions becoming competitive with phosphazene–aryl cleavage. The reason for the selective cleavage of the propenyl group in this case is unclear, but once it is severed from the aryl ring, there will be a more pronounced positive charge on that ring and it will be more likely to migrate to the adjacent ring nitrogen atom and eliminate as an aryl nitrene, a process which ultimately produces the linear phosphazene fragment seen in the mass spectrum.[27]

The observed substitution pattern for reactions of lithio-α-methylstyrenes with **1** is similar to that of the corresponding phenyllithium reaction;[23] i.e., regio- and stereoisomers are observed with non-geminal regioselectivity and cis stereoselectivity being observed. We have previously shown[6] that steric effects are reasonable for the formation of non-geminal, as opposed to the expected[2,7] geminal, products in the reactions of organolithium reagents with **1**. Further evidence for the importance of steric effects is found in the cis:trans ratio for the para vs. meta (**5a**,**b**) α-methylstyrene derivatives. The cis selectivity is significantly reduced with the propenyl substituent in the meta position, where it might be expeected to experience significant transannular repulsions with another substituent in a cis configuration. The question of the cis preference in these reactions is an interesting one. If only steric effects were involved, then one would expepect a strong trans preference, as is shown in the reactions of *tert*-butyllithium with **1**.[6] We believe the observed cis preference is due to an electrostatic interaction of the electron-deficient aryl substituent on the phosphazene ring[9,10] and the electron-rich incoming organolithium reagent. This interaction favors approach of the incoming reagent on the same side of the ring as the aryl substituent, which is in place, thus leading to the formation of the cis isomer. The fact that an approximately 1:1 cis:trans ratio is observed in the formation of (*p*-(dimetylamino)phenyl)tetrafluorocyclotriphosphazenes[28] is related to the exceptionally strong electron-donating ability of the dimethylamino group. The transfer of electron density from the dimethylamino group to the phenyl ring reduces the electron-deficient nature of the aryl groups, and hence, less electrostatic attraction with the incoming reagent occurs.

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Supplementary Material Available: Table I (major mass spectral fragments and their relative intensities) (3 pages). Ordering information is given on any current masthead page.

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Kinetic and Isotopic Studies on the Reaction between Trioxodinitrate and the Hexaammineruthenium(III) Cation

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The reaction between trioxodinitrate and the hexaammineruthenium(III) cation has been studied over the pH range 4.7–13.4. The products are nitrite, N_2O, NO, and a trace of N_2. Isotopic-labeling experiments confirm that the major source of the gaseous products is the N-1 nitrogen atom in trioxodinitrate, with a small contribution from the N-2 (two-oxygen-containing) position. The reaction is first order in both ruthenium complex and in trioxodinitrate. The rate exhibits a maximum at about pH 11.2, with a second-order rate constant $k_2 = 45.8$ M^{-1} s^{-1} at 2 °C. Variation of rate constant with pH allows the determination of pK_a values of 9.25 and 13.20 for $HN_2O_3^-$ and $Ru(NH_3)_6^{3+}$, respectively, in good agreement with literature values. The kinetic data are consistent with pathways involving $N_2O_3^{2-}$ and $Ru(NH_3)_6^{3+}$ as reactive species, or $HN_2O_3^-$ and $Ru(NH_3)_5(NH_2)^{2+}$. The latter alternative leads to an unreasonably high value of the second-order rate constant ($k_2' = k_2K_a(HN_2O_3^-)/K_a(Ru) = 2.5 \times 10^5$ M^{-1} s^{-1}), however, and is considered unlikely.

Aspects of the solution chemistry of trioxodinitrate have been clarified in recent years. These include the mechanism of self-decomposition[2,3] and the stabilization of the $HN_2O_3^-$ ion by added nitrite.[4,5] The decomposition in the range pH ≥4 occurs by cleavage of the N–N bond in the monoprotonated anion $HN_2O_3^-$, with formation of nitrosyl hydride (HNO) and nitrite, followed by rapid dimerization of HNO to yield N_2O. A recent proposal that the primary products are HNO_2^- and NO, rather than HNO and NO_2^-,[6] has been subjected to a direct experimental test and disproven.[7] Under more acidic conditions (pH <3) decomposition occurs by a nitrous acid catalyzed free-radical process to yield NO exclusively.

We now describe the previously unreported reaction between trioxodinitrate and hexaammineruthenium(III) trichloride over the pH range 4.7–13.4. Our interest in this reaction arose from studies of the reaction of the nitrosylpentaammineruthenium(II)

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cation with trioxodinitrate, in which an attempt was made to clarify the reactions between trioxodinitrate and nitrosating agents. The course of the trioxodinitrate–hexaammineruthenium(III) reaction depends upon the reactant stoichiometry. The use of excess trioxodinitrate leads to secondary reactions between that species and the ruthenium products of the primary reaction. This paper deals largely with the reaction under conditions of excess ruthenium(III) complex, or with 1:1 stoichiometry.

Experimental Section

Sodium trioxodinitrate was prepared by a literature method[8] but recrystallized from 0.1 M alkali rather than water. The infrared spectrum showed the absence of bands assignable to carbonate or nitrite, while solutions in dilute alkali gave an extinction coefficient at 248 nm (λ_{max}) identical with the literature value of 8300 M^{-1} cm^{-1}. Samples were stored in vacuo. The labeled compounds $Na_2O^{15}NNO_2$ and $Na_2ON^{15}NO_2$ (99% ^{15}N) were synthesized as described elsewhere.[5,9]

Hexaammineruthenium(III) chloride was obtained from Johnson Matthey and its purity confirmed by analysis for ruthenium. All other chemicals were the best available grade.

Constant ionic strength buffers (acetate, phosphate, borate, butylamine) were made up to literature specifications.[10] Values of pH were measured with a Kent 6075 pH meter.

Kinetic runs were carried out directly in the cell compartment of a Unicam SP6-550 spectrometer, coupled to a Phillips PM 8251 recorder. The temperature of the cell compartment was regulated by circulating water from an ice–water tank. The temperature of solutions in the cells was 2 °C. A slow flow of dinitrogen was passed through the cell compartment to prevent condensation of water vapor on the cells. Reaction was initiated by adding weighed quantities of $Ru(NH_3)_6Cl_3$, and then $Na_2N_2O_3$, to a deoxygenated solution containing all other components in the cell after temperature equilibration. Exact concentrations of $Na_2N_2O_3$ were obtained by extrapolation of optical density to the time of mixing. The reaction was followed at λ_{max} (248 nm for $N_2O_3^{2-}$, 233 nm for $HN_2O_3^-$), as appropriate for the pH conditions employed.

Nitrite was determined by the standard colorimetric method, employing sulfanilic acid and β-naphthol. Samples of the final reaction solution were first passed down a Zeo-Karb 325 cation-exchange column in the Na^+ form to remove ruthenium complex cations. Analysis for nitrite was repeated for each reaction solution at hourly intervals to check on the possibility of slower reactions taking place.

Gas stoichiometric measurements were carried out in Y-shaped vessels on the vacuum line. Weighed quantities of $Ru(NH_3)_6Cl_3$ and $Na_2N_2O_3$ were added separately to deaerated solutions in the two legs of the vessel, of composition and volume calculated to give the desired pH and total volume (normally 20.0 mL) upon mixing. Purified CF_4 gas was admitted at measured partial pressure and reaction initiated by rotation of the vessel. Gas-phase samples were then withdrawn at measured intervals through a helical trap at 195 K to remove H_2O vapor, and transferred to storage bulbs by Toepler pump. Gas samples were then analyzed by gas chromatography employing a vacuum-line-interfaced GC system[11] and partial pressures and molar quantities of products N_2, N_2O, and NO calculated on the basis of the CF_4 reference gas, as described elsewhere.[12]

Results

The existence of a reaction between trioxodinitrate and hexaammineruthenium(III) cation was confirmed by rapid, repetitive scanning of the UV–vis spectra of reaction solutions, which showed the reaction to be very fast at about pH 11 and much slower at pH values of 7 and 13. The spectra showed the loss of the absorption due to trioxodinitrate and the formation of a new species having an intense absorption at around 215 nm, attributed to nitrite. These studies showed that the spectrum of $[Ru(NH_3)_6]Cl_3$ varied with pH at high pH values, due to the formation[13,14] of the deprotonated species $Ru(NH_3)_5(NH_2)^{2+}$. Solutions of pH 12 and higher are deep yellow due to the formation of this compound, which has an absorption at 402 nm (ϵ = 2800 M^{-1} cm^{-1}). The amidoruthenium(III) complex is a reactive species that has been implicated in several reactions.[13–15] It slowly undergoes hydrolysis to give $Ru(NH_3)_5(OH)^{2+}$, which has an absorption maximum at 295 nm with $\epsilon = 2100$ M^{-1} cm^{-1}.

Table I. Production of Nitrate[a]

pH	$10^6(\Delta[Na_2N_2O_3])$/mol	$10^6(\Delta[NaNO_2])$/mol immediate	1 h	2 h	$\Delta[NaNO_2]_i/\Delta[N_2N_2O_3]$
13.0	2.0	2.20	2.19		1.10
12.7	1.71	2.88	2.54	2.55	1.68
12.0	1.86	1.88	1.68	1.34	1.01
11.3	1.29	1.86	1.68	1.53	1.44
8.86	2.14	3.34	3.26		1.56
8.60	1.29	1.30	1.38	1.05	1.01
8.16	1.86	3.28	3.25	3.01	1.76
7.67	1.57	2.46	2.18		1.57

[a] Conditions: 2 °C; $[Na_2N_2O_3]$ in the range (2.6–4.28) × 10^{-5} M; $[Ru(NH_3)_6^{3+}]$ in 10-fold excess.

Experiments on the $N_2O_3^{2-}$–$Ru(NH_3)_6^{3+}$ reaction in dilute alkali with excess ruthenium complex show changes in the UV–vis spectra of the ruthenium complex over about 1 h. The band at about 402 nm due to $Ru(NH_3)_5(NH_2)^{2+}$ loses intensity, while there is substantial enhancement of the band at 274 nm and the appearance of a new absorption at about 370 nm. This was thought to result from the formation of the nitropentaammineruthenium(II) cation (literature spectrum: 272, 363 nm). In experiments at pH 13.4 there was no visually detectable formation of gas.

Addition of $Na_2N_2O_3$ to solutions of $Ru(NH_3)_6Cl_3$ in water or in buffer solutions (pH 7.1–10.8) at room temperature resulted in very rapid reaction, as shown by the evolution of gas and a deepening in intensity of the yellow color of the reaction solution. Under these pH conditions there is no formation of $Ru(NH_3)_5(NH_2)^{2+}$, as shown by the lack of intensity at 402 nm. At pH 4.7 the rate of reaction was very slow, comparable to the rate of self-decomposition of trioxodinitrate to N_2O and nitrite.

Stoichiometry. The production of nitrite, suggested by UV measurements, was confirmed quantitatively by colorimetric means. Table I gives the yield of nitrite for reactions with a 10-fold excess of $[Ru(NH_3)_6]Cl_3$ over $Na_2N_2O_3$. The situation is complicated in that while about half of the experiments suggest a 1:1 production of nitrite from trioxodinitrate, other experiments show higher yields of nitrite, suggesting the presence of an additional pathway leading to nitrite. No obvious correlation with specific experimental conditions could be discerned. Analysis of completed reaction solutions showed a slight loss of nitrite with time, presumably due to the reaction of nitrite with excess $Ru(NH_3)_6^{3+}$.

Preliminary analysis of gas products showed the presence of major amounts of N_2O and NO and small amounts of N_2. Results at pH 4.67 show that N_2O is the predominant product, but this appears to arise from self-decomposition of trioxodinitrate, as the relative importance of this reaction increases with decreasing pH. Approximately equal amounts of N_2O and NO were obtained at pH 7.10. A complication may arise in assessing the analytical data at higher pH, as NO reacts rapidly with $Ru(NH_3)_6^{3+}$ in a hydroxide-dependent reaction to give the pentaammine(dinitrogen)ruthenium(II) cation. At lower pH values $Ru(NH_3)_5NO^{3+}$ is formed by reaction of NO with $Ru(NH_3)_6^{3+}$, but the dinitrogen complex is the sole product at pH 8.5. The kinetics of these reactions between NO and $Ru(NH_3)_6^{3+}$ have been studied;[16] their effect may be decreased production of NO and the possible formation of N_2. at pH 13.4, the $N_2O_3^{2-}$–$Ru(NH_3)_6^{3+}$ reaction gives only N_2.

Table II gives quantitative data on the distribution of NO and N_2O gas products at pH 4.7, 7.1, and 10.8 and information on the time course of gas production at pH 7.1. The latter data make it clear that gas products are formed within the time period covered by kinetic studies. The results show that the product ratio n_{NO}/n_{N_2O} tends to increase with pH; at pH 10.8 NO is the major

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Table II. Analysis of Gas Products[a]

buffer	pH	$10^5 n_{Ru}$	$10^5 n_{N_2O_3^{2-}}$	$10^5 n_{NO}$	$10^5 n_{N_2O}$	time/min	$(2n_{N_2O} + n_{NO})/n_{N_2O_3^{2-}}$
acetate	4.7	2.1	1.9	0.867	1.04	120	
phosphate	7.1	4.53	2.28	0.701	0.414	15	0.671
				0.877	0.548	30	0.865
				0.944	0.586	60	0.928
				0.962	0.606	90	0.954
				0.970	0.623	120	0.972
		4.44	4.73	1.032	0.678	5	0.505
				1.438	1.575	20	0.970
				1.675	1.813	35	1.121
				1.874	1.889	45	1.195
				1.751	1.879	60	1.165
				1.761	1.997	120	1.217
		4.57	4.14	2.35		12	
				2.58	1.13	20	1.169
				2.91	1.30	30	1.331
				2.82	1.21	40	1.287
				2.98	1.28	60	1.338
				2.57	1.10	75	1.152
				2.48	1.11	90	1.135
				2.59	1.14	120	1.176
				2.53	1.25	1420	1.215
borate	10.8	2.23	2.16	0.944	0.224	1200	0.644

[a] Conditions: total volume 20.0 mL; t = 25.0 °C.

Table III. Mass Spectrometry of Gas Products of Reaction between $Ru(NH_3)_6^{3+}$ and ^{15}N-Labeled $N_2O_3^{2-}$[a]

	3:1; N-2[b]	3:1; N-1	1:1; N-1	1:3; N-1	1:3; N-1
% 46, N_2O	0.16	97.28	96.21	95.99	84.99
% 45, N_2O	11.25	1.97	3.23	3.67	13.91
% 44, N_2O	88.59	0.40	0.56	0.33	1.10
% ^{15}N, N_2O	5.8	98.3	.7.8	97.8	91.9
% ^{15}N, NO	3.2	84.5			92.4
% ^{15}N, N_2		3.5			1.0

[a] Conditions: pH 7.1; t = 25 °C; reaction time ≥4 h; ^{15}N purity 99%. [b] Stoichiometric ratio, $Ru(NH_3)_6^{3+}$:$N_2O_3^{2-}$; position of ^{15}N label in $N_2O_3^{2-}$.

Table IV. Rate Constants for the Hexaammineruthenium(III)–Trioxodinitrate Reaction[a]

pH	$10^4 \times [Ru(NH_3)_6^{3+}]$/M	k_2/$M^{-1}\,s^{-1}$	$10^{14} \times K_a(Ru)$	$10^{10} \times K_a(HN_2O_3^-)$	$k_{2(max)}$/$M^{-1}\,s^{-1}$
13.30	4.46	19.9	6.45		51.4
13.08	7.75	23.5	7.79		45.8
13.00	6.65	28.2	6.13		50.5
13.00	5.33	27.0	6.56		48.4
12.90	5.81	32.0	5.31		52.2
12.85	5.99	30.0	7.30		46.9
12.69	6.01	34.9	6.20		48.5
12.48	6.91	37.9	6.06		47.0
12.30	7.11	39.4	7.76		45.6
12.08	7.68	42.1	6.72		46.1
12.00	5.17	40.2			43.5
11.30	4.84	42.8			44.0
11.20	10.2	44.8			46.1
11.10	5.01	47.3			48.7
10.90	8.53	42.4			44.0
10.40	9.21	38.5		2.19	42.1
10.30	8.72	37.1		2.21	41.4
9.86	5.46	31.7		3.17	41.8
8.92	5.33	15.0		5.91	56.3
8.80	7.27	11.9		5.61	55.4
8.78	6.91	(13.1)		(6.41)	(63.0)
8.63	7.69	11.5		7.92	(73.2)
8.60	6.20	9.70		6.84	(65.7)
8.60	10.4	9.60			
8.60	19.8	9.88			
8.42	9.62	6.00		5.92	(58.3)
8.41	4.59	5.34		5.17	52.9
8.07	9.43	3.71		7.55	76.1
8.00	4.97	4.02			
7.12	9.30	0.513			

[a] Conditions: t = 2.0 °C; I = 0.20 M; $Na_2N_2O_3$ concentration range (2.5–5) × 10^{-5}/M.

gas product. The mass balance column for the pH 7.1 series with excess $Ru(NH_3)_6^{3+}$ shows a very nearly 1:1 relation between gas product nitrogen atoms and initial moles of reactant trioxodinitrate. The values for nearly 1:1 stoichiometric conditions exceed unity to the extent of about 20%. In most reaction systems examined, N_2 was observed as a minor product, to the extent of a few percent. Molar quantities of N_2 have not been included in Table II, and N_2 has not been included in the mass balance calculations because its appearance is probably due to one or more secondary reactions, possibly involving ammine ligands. Formation of $^{29}N_2$ is consistent with attack of ^{15}NO upon an ammine group (see following section).

Tracer Experiments. Results of experiments employing ^{15}N-labeled trioxodinitrate are shown in Table III. Experiments carried out with ^{15}N in the N-1 position ($Na_2O^{15}NNO_2$) of trioxodinitrate show that there is relatively little effect of varying the ratio of reactants. Although there is some discrepancy between the two measurements carried out at 1:3 stoichiometry, the general conclusion is clear, that the N-1 nitrogen is the major but not exclusive source of nitrogen atoms in both N_2O and NO produced in the reaction. This conclusion is confirmed by the single experiment carried out with ^{15}N in the N-2 position ($-ON^{15}NO_2^-$). Yields of N_2 were small, and mass spectrometry was not accomplished in all cases, but limited data indicate the presence of minor amounts of $^{29}N_2$.

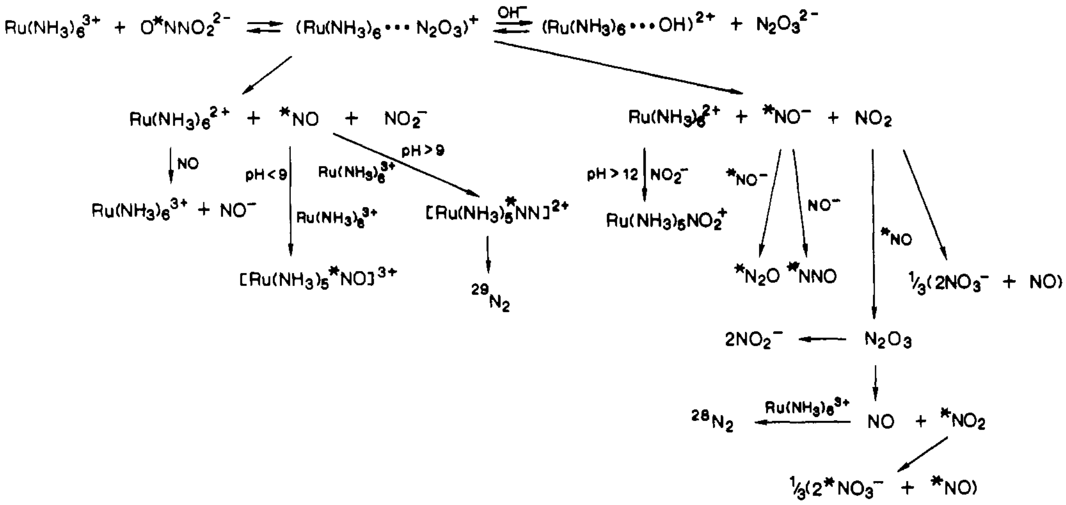
Kinetic Studies. These were carried out at an ionic strength of 0.2 M, usually maintained with LiCl, at 2 °C and over the pH range 7.1–13.3. Pseudo-first-order conditions were arranged with the ruthenium complex in excess over trioxodinitrate by a factor of 10–40. The reaction is of first order in trioxodinitrate, good straight-line plots of log ($D_t - D_\infty$) against time being obtained for at least 2 half-lives, and usually for 3. The results are given in Table IV. The reaction is also of first order in ruthenium complex, as shown by the constancy of values of the second-order rate constant $k_2 = k_{obsd}/[Ru(NH_3)_6^{3+}]$, where k_{obsd} is the measured first-order rate constant. Values of k_2 vary with pH, giving a bell-shaped plot (Figure 1). This suggests that the reaction rate is controlled by two protonation equilibria, with approximate pK_a values 9.25 and 13.20, namely protonation of $N_2O_3^{2-}$ to form $HN_2O_3^-$ and the conversion of $Ru(NH_3)_6^{3+}$ to the amido complex $Ru(NH_3)_5(NH_2)^{2+}$. Literature values of these pK_a's are 9.36 ($HN_2O_3^-$)[3] and 13.1 ($Ru(NH_3)_6^{3+}$),[14] in good agreement with the values found in the present work. The pK_a value for $Ru(NH_3)_6^{3+}$

Table V. Ionic Strength Effect at pH 8.7[a]

I/M	0.0139	0.0220	0.0299	0.0390	0.046	0.054	0.079
$10^4[Ru(NH_3)_6^{3+}]$/M	6.07	6.30	5.62	6.60	5.43	5.49	6.27
$10^2k_1/s^{-1}$	8.74	5.40	4.66	4.24	3.02	2.81	1.60
$k_2/M^{-1}\ s^{-1}$	144	85.7	82.9	64.2	55.6	51.1	25.5

[a] Conditions: borate buffer; t = 2.0 °C; $[Na_2N_2O_3] \simeq 5 \times 10^{-5}$ M.

Scheme I



relates to an apparent dissociation constant at 0.1 M ionic strength, which includes an ion-pair formation constant for $[Ru(NH_3)_6]^{3+}\cdot OH^-$.

It may be shown that, under pH conditions where the rate is governed by the $Ru(NH_3)_6^{3+} \rightleftarrows Ru(NH_3)_5(NH_2)^{2+}$ equilibrium, a plot of $1/k_2$ against $1/[H^+]$ should be a straight line, with an intercept of $1/k_2$(max) and a slope of K_a/k_2(max), where K_a is the dissociation constant of the hexaammine complex and k_2(max) is the value of the second-order rate constant when the ruthenium complex cation is present entirely in the hexaammine form. From the data in Table IV it may be shown that k_2(max) = 45.8 $M^{-1}\ s^{-1}$ and $K_a = 7.56 \times 10^{-14}$ M (pK_a = 13.12). The value of k_2(max) obtained this way is probably a better value than that read from the graph of k_2 against pH (Figure 1). Values of K_a have also been calculated from the relation $K_a = [H^+](k_2(\max) - k_2)/k_2$. These are shown in Table IV and give a mean value for pK_a of 13.18.

A similar treatment may be applied to the results obtained at lower pH, where the kinetics are assumed to be controlled by the protonation of $N_2O_3^{2-}$. A plot of $1/k_2$ vs. $[H^+]$ should yield a straight line with intercept $1/k_2$(max) and slope $1/K_ak_2$(max) where K_a is the dissociation constant of the monoprotonated trioxodinitrate ion. The value of k_2(max) obtained from these data (45.5 $M^{-1}\ s^{-1}$) is closely similar to that found above, as anticipated. Table IV contains values of $K_a(HN_2O_3^- = N_2O_3^{2-} + H^+)$ obtained with use of this value of k_2(max) and the relationship $K_a = [H^+]k_2/(k_2(\max) - k_2)$. There is some scatter in values of K_a, usually associated with pH values where k_2 is close to k_2(max), but for the pH range 8.92–8.07 the mean value for $K_a = 6.42 \times 10^{-10}$ M, with pK_a = 9.19.

The close agreement between these experimental values for the two pK_a's and those available in the literature confirms the analysis of the kinetic data. Alternatively, the literature pK_a values could be used to calculate the concentrations of $[N_2O_3^{2-}]$ and $[Ru(NH_3)_6^{3+}]$ at each pH studied and hence the true second-order rate constants evaluated at each pH (eq 1–3). These values of k_2(max) are given in Table IV, column 6. Again they are reasonably constant, although more consistent values are obtained if the value $pK_a(HN_2O_3^-)$ = 9.20 is used.

$$\text{rate} = k_1[\text{“}Na_2N_2O_3\text{”}] \tag{1}$$

$$= k_2[\text{“}Na_2N_2O_3\text{”}][\text{“Ru”}] \tag{2}$$

$$= k_2(\max)\ [N_2O_3^{2-}][Ru(NH_3)_6^{3+}] \tag{3}$$

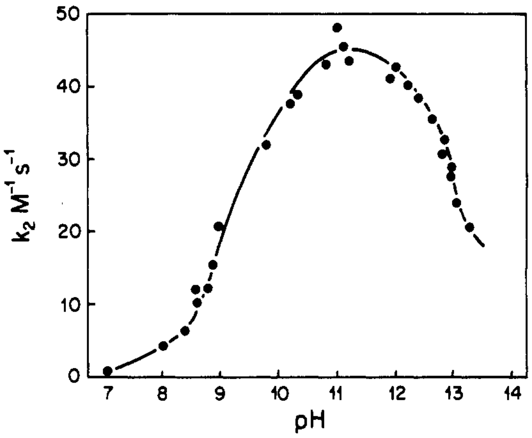


Figure 1. Dependence of second-order rate constant on pH for the reaction between $Ru(NH_3)_6^{3+}$ and $N_2O_3^{2-}$ at 2 °C.

The ionic strength effect was measured at pH 8.7 in borate buffer over the range I = 0.0139–0.079 M at $[Na_2N_2O_3] = 5 \times 10^{-5}$ M and $[Ru(NH_3)_6]^{3+} = (5.43\text{–}6.62) \times 10^{-4}$ M. Values of k_2 decrease with increase in ionic strength, as shown in Table V for LiCl. A plot of log k_2 against $I^{1/2}$ is linear with best slope (by "least squares") of −4.6. Similar experiments with $NaClO_4$ give a value of −1.9. These results do not contain any allowance for the effect of ionic strength on the pK_a for $HN_2O_3^-$.

Discussion

The kinetics results have been interpreted in terms of reaction between the species $N_2O_3^{2-}$ and $Ru(NH_3)_6^{3+}$. It should be noted, however, that the rate law eq 3 may be rewritten in terms of the species $HN_2O_3^-$ and $Ru(NH_3)_5(NH_2)^{2+}$. The second-order rate constant for this case is given by eq 4. With use of literature

$$k_2' = k_2(\max)\ K_a(HN_2O_3^-)/K_a(Ru) \tag{4}$$

values for the pK_a's, $k_2' = 2.5 \times 10^5\ M^{-1}\ s^{-1}$ at 2 °C. Although this alternative formulation is consistent with the known reactivity of amido complexes, the rate constant appears to be orders of magnitude too high for reactions of Ru(III) and so will not be considered further.

It is clear from other work on $Ru(NH_3)_6^{3+}$ that ion pairing will be an important factor and that the reaction is likely to involve the ion pair between $Ru(NH_3)_6^{3+}$ and $N_2O_3^{2-}$. The negative salt effect produced by added LiCl could then result from displacement of trioxodinitrate from the ion pair by chloride ion. The smaller effect produced by the use of $NaClO_4$ could result from the lowered ability of ClO_4^- compared to that of Cl^- to compete with $N_2O_3^{2-}$. Such competition for ion-pair formation has been observed. Sulfate or phosphate prevents the formation of the yellow color due to the amidopentaammineruthenium(III) cation in solutions around pH 13 by ion pairing with the hexaammineruthenium(III) cation and so preventing ion pair formation with hydroxide ion.[13,16] The fall in reactivity at high pH in the present study is thus due initially to the displacement of trioxodinitrate from the ion pair by OH^-, which is the first stage in the formation of the deprotonated complex.[16]

Ruthenium(III) is a substitution-inert center[17,18] but undergoes facile electron transfer to the more labile Ru(II). An example of a fast reaction involving Ru(III) is that with NO to give $Ru(NH_3)_5N_2^{2+}$ with rate constant 21.9 M^{-1} s^{-1} at 5.2 °C and pH 11.35. This reaction involves the amido species, and so the second-order rate constant continues to increase with pH. The reaction between $Ru(NH_3)_6^{3+}$ and $N_2O_3^{2-}$ represents unusually high reactivity of the hexaammineruthenium(III) cation, having a second-order rate constant at pH 11.2 and 2 °C of 44.8 M^{-1} s^{-1}.

Formation of a trioxodinitrate complex of Ru(III) as the first stage of the reaction seems unlikely, although bidentate complexes of $N_2O_3^{2-}$ are known.[19] An outer-sphere reaction involving oxidative cleavage of $N_2O_3^{2-}$ could occur by two pathways, giving $NO + NO_2^-$ or $NO^- + NO_2$. The former pathway seems more likely. The stoichiometric data suggest that at least 1 mol of nitrite is liberated per mole of $N_2O_3^{2-}$. Cleavage of the $N_2O_3^{2-}$ may occur synchronously with electron transfer from the (NO^-) fragment to Ru(III), generating Ru(II) and NO. The resulting NO may react with excess $Ru(NH_3)_6^{3+}$ to give N_2 at pH values greater than about 9, and the nitrosylpentaammineruthenium(II) cation at lower pH. The alternative cleavage to give NO^- and NO_2 may account for the formation of N_2O. In the case of N-1-labeled trioxodinitrate ($O^{15}NNO_2^{2-}$), this will give $^{46}N_2O$. If the two cleavage reactions occur together, NO and NO_2 will be products. These combine in aqueous solution to give N_2O_3 and hence nitrite and could accommodate NO_2^- production at a stoichiometry greater than 1:1. Combination of NO and NO_2 in aqueous solution is postulated to give the symmetrical isomer ONONO rather than the more stable form $ONNO_2$.[20] This allows the exchange of nitrogen atoms between NO and NO_2 and hence the formation of ^{14}NO and $^{45}N_2O$ in reactions with $O^{15}NNO_2^{2-}$. The $^{45}N_2O$ is suggested to result from reaction between $^{15}NO^-$ and $^{14}NO^-$ produced by reduction of ^{14}NO by $Ru(NH_3)_6^{2+}$. These reactions are summarized in Scheme I.

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Registry No. $Ru(NH_3)_6^{3+}$, 18943-33-4; $N_2O_3^{2-}$, 15435-67-3.

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Kinetics and Mechanism of the Reaction between *trans*-Dioxotetracyanotungstate(IV) and Azide in Aqueous Solution

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The reaction of *trans*-$[WO_2(CN)_4]^{4-}$ with N_3^- has been studied in the pH range 6–10. The kinetic data indicate that the protonated form *trans*-$[WO(H_2O)(CN)_4]^{2-}$ is the only reactive species and that the aquo ligand is substituted by the N_3^- ion according to the reaction

$$[WO(H_2O)(CN)_4] + N_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [WO(N_3)(CN)_4]^{3-} + H_2O$$

The values of k_1 and k_{-1} are 4.2 (1) M^{-1} s^{-1} and 0.20 (6) s^{-1}, respectively, at 25 °C. The value of $\Delta V^*(k_1)$ (+10.6 (5) cm^3 mol^{-1}) is indicative of a dissociatively activated substitution process.

Introduction

trans-Dioxotetracyanotungstate(IV) and -molybdate(IV) ions may be protonated to form the oxo–hydroxo and oxo–aquo complexes,[1,2] reactions 1 and 2.

$$[MO_2(CN)_4]^{4-} + H^+ \rightleftharpoons [MO(OH)(CN)_4]^{3-} \qquad (1)$$

$$[MO(OH)(CN)_4]^{3-} + H^+ \rightleftharpoons [MO(H_2O)(CN)_4]^{2-} \qquad (2)$$

The existence of the protonated forms was duly established by means of the structure determination of $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$,[3] $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$,[3] and $(PPh_4)_2[MoO(H_2O)(CN)_4]\cdot 4H_2O$.[4]

These structure determinations, as well as the structural data of $[MoO_2(CN)_4]^{4-}$,[5] showed that the $Mo{=}O$ and $Mo{-}OH$ bonds are much stronger than the $Mo{-}OH_2$ bond. It was recently discovered that the bidentate ligand, 1,10-phenanthroline (Phen), reacts with *trans*-$[MoO_2(CN)_4]^{4-}$ with the formation of the

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