bromide are based on the fundamental frequencies reported by Hawkins and Carpenter[12] and by Miller and Carlson[14] which have already been discussed; the maximum difference between the literature value and the present value for any fundamental is 5 cm^{-1} for the tetrachloride and 10 cm^{-1} for the tetrabromide. The data in the JANAF tables for zirconium tetrachloride are in error owing to their being based on a grossly inaccurate value[24] for $\nu_1(a_1)$ (315 cm^{-1} *vs.* the correct value of 377 cm^{-1}) and on estimated values for $\nu_2(e)$ and $\nu_4(t_2)$ (these being in error by up to 6 cm^{-1}). The data in the JANAF tables for the halides TiI_4, $ZrBr_4$, and ZrI_4 are entirely based on estimated values for the four fundamentals in each case; these estimates are in error to the maximum extent of 63 cm^{-1} for titanium tetraiodide, 9 cm^{-1} for zirconium tetrabromide, and 17 cm^{-1} for zirconium tetraiodide. Tables VII–XII therefore place, for the first time, the very close similarities between the tetrahalides of zirconium and hafnium on a quantitative basis.[25]

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Kinetics and Mechanism of the Reduction of Hydrazoic Acid by Chromium(II) and Vanadium(II)

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The rates of reduction of HN_3 by V(II) and Cr(II) are reported. Both reactions produce 1 mol of N_2 and 1 mol of NH_3 and consume 2 mol of reductant. Both reductions proceed by mixed second-order kinetics with the rate constant independent of $[H^+]$ over the range 0.1–1.0 *M*. For the rate law defined by $-d[HN_3]/dt = k[HN_3][\text{reductant}]$, the rate parameters are: for Cr^{2+} $k = 18\ M^{-1}\ sec^{-1}$, $\Delta H^{\ddagger} = 7.1$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -29$ cal mol^{-1} deg^{-1}; for V^{2+} $k = 2.8 \times 10^{-2}\ M^{-1}\ sec^{-1}$, $\Delta H^{\ddagger} = 14.4$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -17$ cal mol^{-1} deg^{-1}, all at 25°. The reaction of Cr^{2+} with HN_3 produces a Cr–N bond in the first step. The fate of the unstable species produced thereafter is discussed.

Introduction

The role a reducible ligand plays in redox reactions between metal ions has become a topic of considerable interest since Nordmeyer and Taube produced convincing evidence of a radical ion intermediate in the Cr^{2+} reduction of isonicotinamidepentaamminecobalt(III) complex.[1] One feature of this interest involves the study of the rate and mechanism of reduction of free ligands. A detailed study of the V^{2+} reduction of cobalt(III)–azide complexes[2] made information about the V^{2+} reduction of hydrazoic acid necessary. Several preliminary experiments indicated that the Cr^{2+} reduction of HN_3, which has been examined previously,[3,4] was not satisfactorily understood. In this report a description of the kinetics and mechanism of the reduction of HN_3 by these two reagents is given. Of interest in these noncomplimentary reactions is the fate of unstable, intermediate, oxidation states; these are discussed.

Experimental Section

Reagents and Analyses.—The sodium azide was an Eastman product and was recrystallized from water as described by Browne.[5] A solution of this solid was analyzed by adding the NaN_3 solution to excess Ce(IV) and titrating that excess with standard Fe(II) solution to a ferroin end point.[6]

Solutions of Cr(II) were derived from Cr(III) solutions by reduction with amalgamated Zn. The Cr(III) stock solution was prepared by H_2O_2 reduction of CrO_3 in $HClO_4$. Total Cr(III) content was determined by oxidation with peroxide of an aliquot made basic using ϵ 4815 at 3730 Å.[7] The $[ClO_4^-]$ of the stock Cr(III) solution was determined by ion exchange of an aliquot on Dowex 50W-X8 in the H^+ form and titration of the acid released with standard base. Reducing power of the Cr(II) solution was measured by adding an aliquot to deaerated Ce(IV) solution in H_2SO_4 medium[8] followed by titration of the excess Ce(IV) with standard Fe(II). The concentration of total cations (exclusive of H^+) was determined by heating an aliquot of the Cr(II) solution with excess EDTA buffered at pH 5 for 5–15 min at 80°;[9] after raising the pH to 10 with NH_3-NH_4Cl buffer, the excess EDTA was titrated with standard Zn^{2+} to an Erio-Black-T end point.

Solutions of VO^{2+} were prepared either by electrolytic reduction of V_2O_5 in $HClO_4$ acid or by treatment of a solution of $VOSO_4$ with an anion-exchange resin in the ClO_4^- form. No differences in rate behavior between the two solutions were observed. Reduction was accomplished with amalgamated Zn. When not in use this solution of V(II) was stored at −78° in order to prevent reduction of ClO_4^-. Total V was determined spectrophotometrically as the peroxide complex;[10] $[ClO_4^-]$ was determined as outlined above. Analysis for total reducing power utilized the ceriometric technique described for [Cr(II)], except that the excess Ce(IV) was titrated with Fe(II) in a solution >5 *M* in H_2SO_4 in order to reduce VO_2^+ before $Fe(phen)_3^{3+}$.[11] The $[V^{2+}] + [V^{3+}] + [Zn^{2+}]$ was determined by an EDTA titration after oxidation of V^{2+} with ClO_3^- or NO_3^-.

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Ion-exchange studies were carried out on Dowex 50-X2 resin, 200–400 mesh.

Kinetic Studies.—The reduction of HN_3 liberates N_2 which causes bubbles to form on the walls of the reaction vessel. This feature combined with the relatively small difference in absorbance of reactants and products makes spectrophotometric monitoring of reaction progress difficult. Nevertheless, it was found that this technique was adequate if care was exercised. In particular, visual observation of the reaction cells was used to confirm the lack of light-scattering bubbles in the vessel. Because this approach was not possible on the stopped-flow spectrometer, this instrument was used in only a few runs. A typical experiment involved deaerating a solution of appropriate medium with a stream of N_2 or Ar, followed by thermostating of the cell and its contents. A deaerated solution of NaN_3 and the reductant were then added with syringe techniques and mixed, and the course of the reaction was observed on a thermostated Cary Model 14 spectrophotometer. The raw kinetic data were analyzed by a nonlinear least-squares program that minimizes the sum of the squared deviation between calculated and observed data points with weighting appropriate to the variable observed (absorbance on the Cary, transmittance on the Durrum stopped-flow spectrophotometer) by a Newton–Gauss technique.[12] Usually the calculated absorbance was within 0.002 absorbance unit of the observed up to greater than 95% reaction. The uncertainty in individual rate constants was usually 1.5%.

Results

Stoichiometry.—Ardon and Mayer[3] have indicated that $Cr(H_2O)_5NH_3^{3+}$ (hereafter denoted $CrNH_3^{3+}$) is one of the Cr(III) products of the reduction of HN_3 by Cr^{2+}. This result has been substantiated here by ion-exchange separation. In ClO_4^- media, the other dominant Cr(III) product is $Cr(H_2O)_6{}^{3+}$ and 1 mol of N_2 per mol of HN_3 is produced as measured by the volume of gas evolved. Table I gives analytical data in support of the dominant stoichiometry

$$2Cr^{2+} + HN_3 + 2H^+ = CrNH_3^{3+} + Cr^{3+} + N_2$$

TABLE I

STOICHIOMETRIC RESULTS FOR REDUCTION OF HN_3 BY Cr^{2+}

Initial concentrations, M		Per mol of HN_3 reduced: Mol of Cr(III) product			Mol of N_2 product
$[Cr^{2+}]_0$	$[HN_3]_0$	$CrNH_3^{3+}$	Cr^{3+}	$CrCl^{2+}$	N_2
1.75×10^{-1}	$6.75 \times 10^{-2\,a}$	...	...	...	1.01
1.55×10^{-2}	$6.59 \times 10^{-3\,b}$	...	...	...	1.02
1.71×10^{-2}	$9.28 \times 10^{-3\,c}$	0.90[d]	0.89[d]	...	...
7.25×10^{-2}	$4.58 \times 10^{-2\,e}$	0.90[f]	0.88[f]		...
8.18×10^{-2}	$4.48 \times 10^{-2\,e}$	0.92[g]	0.88[g]		...
1.71×10^{-2}	$9.28 \times 10^{-3\,h}$	0.97	...	1.00	...
5.70×10^{-3}	$2.29 \times 10^{-2\,i}$	1.02	...	1.02	...
1.58×10^{-2}	$1.05 \times 10^{-2\,j}$	0.96		0.87	...

[a] $[H^+] = 0.59$ M. [b] $[H^+] = 0.91$ M. [c] $[H^+] = 0.88$ M. [d] Yield of dimer is 0.05 mol per mol of HN_3 reduced (0.10 mol of Cr(III)). [e] $[H^+] = 1.07$ M. [f] Yield of dimer is 0.047 mol per mol of HN_3 reduced. Yield of CrN_3^{2+} is 0.017 mol per mol HN_3 reduced. [g] Yield of dimer is 0.040 mol per mol of HN_3 reduced; of CrN_3^{2+}, 0.024 mol per mol of HN_3 reduced. [h] $[Cl^-] = 0.88$ M, $[H^+] = 0.91$ M. [i] $[Cl^-] = 0.226$ M, $[H^+] = 0.96$ M. [j] $[Cl^-] = 0.088$ M, $[H^+] = 0.93$ M.

At the concentrations used in the kinetic experiments, CrN_3^{2+} [3] is produced in, at most, trace concentrations; the dimer containing 1 mol of nitrogen per 2 mol of Cr(III)[3] accounts for about 8–10% of the total Cr(III). It has also been reported[3] that $CrCl^{2+}$ is formed as a product in preference to Cr^{3+} in 1 N HCl. Experiments summarized in Table I extend the range in which this statement is true to lower concentrations of Cl^-.

The V^{2+} reduction of HN_3 also produces a gas as a product. Spectrophotometric analysis of the solution after reaction of V^{2+} with HN_3 was carried out using literature values for the extinction coefficient.[13,14] For a solution originally 0.051 M in V^{2+}, 0.004 M in V^{3+}, and 0.021 M in HN_3, the final concentrations were 0.0084 M in V^{2+} and 0.0465 M in V^{3+}. This result indicates that the stoichiometry is adequately represented by

$$2V^{2+} + HN_3 + 3H^+ = 2V^{3+} + NH_4^+ + N_2$$

Kinetics.—The Cr^{2+} reduction of HN_3 was followed at $I = 1.0$ M over a range of $[Cr^{2+}]$ of $(0.4–45.2) \times 10^{-3}$ M, $[HN_3]$ of $(0.40–3.3) \times 10^{-3}$ M, $[H^+]$ of 0.16–1.00 M, $[Cl^-]$ of 0.0–0.99 M and a temperature range of 15.1–34.8°. Most reactions were monitored at 4020 Å. Within the rather large experimental errors all data are consistent with the rate law

$$\frac{-d[HN_3]}{dt} = k[Cr^{2+}][HN_3]$$

with k independent of $[H^+]$ over the indicated range and of $[Cl^-]$. The data in Table II include the observed values of k. From a nonlinear least-squares computation using individual temperature–rate constant values, the activation parameters were obtained.

TABLE II

RATE DATA FOR REDUCTION OF HN_3 BY Cr^{2+}, $I = 1.0$ M $HClO_4$

	10^3 M		M^{-1} sec^{-1}	
Temp, °C	$[Cr^{2+}]_0$	$[HN_3]_0$	k_{obsd}	k_{calcd}[j]
11.9	2.53	1.14	12.7[a]	9.7
12.4	2.39	1.67	11.3	10.0
12.4	2.49	1.67	11.0	10.0
12.7	3.13	1.26	9.8	10.1
15.1	4.97	2.13	12.2	11.3
15.1	1.80	1.44	12.4	11.3
15.3	2.08	1.01	10.6	11.4
17.0	1.19	0.51	12.8	12.3
17.1	2.21	0.72	9.4[b]	12.4
17.1	2.72	1.01	13.8	12.4
17.1	2.10	1.11	13.2	12.4
17.2	1.98	1.32	16.2[c]	12.5
17.2	3.35	3.30	16.7[c]	12.5
17.2	5.77	2.20	8.8[c]	12.5
24.9	1.69	0.84	17.2[d]	17.6
24.9	1.63	1.74	17.8	17.6
24.9	2.71	0.75	18.6	17.6
25.0	2.51	1.73	20.9[e]	17.7
25.0	1.73	1.73	14.8	17.7
25.0	1.81	0.90	21.4	17 7
25.0	1.81	0.90	17.8[f]	17.7
25.0	0.85	0.50	19.6	17.7
25.1	1.18	0.88	16.8	17.8
25.2	2.72	0.56	21.1	17.9
25.2	0.82	0.53	21.4[g]	17.9
25.2	2.52	1.57	20.9	17.9
25.2	1.84	1.32	21.6	17.9
25.2	24.4	0.53	25.8[h]	17.9
25.3	39.0	0.53	27.8[i]	18.0
26.0	45.2	0.40	14.6	18.5
34.8	0.42	0.55	26.4[c]	26.9
34.8	1.27	1.12	31.1[c]	26.9

[a] $[Cl^-] = 0.89$ M. [b] $[H^+] = 0.24$ M, $[Li^+] = 0.76$ M. [c] Wavelength of observation 2700 Å. [d] $[Cl^-] = 0.99$ M. [e] $[H^+] = 0.16$ M, $[Li^+] = 0.84$ M. [f] $[Cl^-] = 0.28$ M. [g] Wavelength of observation 2500 Å. [h] $[H^+] = 0.87$ M, $I = 1.0$ M with Cr^{2+}. [i] $[H^+] = 0.58$ M, $I = 1.0$ M with Cr^{2+} and Li^+. [j] Calculated from the activation parameters given in the text.

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[12] This program, RHODON36, is based on the method outlined by R. H. Moore and R. K. Ziegler, Report LA 2367, Los Alamos Scientific Laboratory. The functional relationship used to relate absorbance to time is variable to allow equal equivalent concentration experiments to be analyzed.

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This fit yields $k_{298°} = 17.8 \pm 2.4\ M^{-1}\ \text{sec}^{-1}$, $\Delta H^{\ddagger} = 7.1 \pm 0.8$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -28.9 \pm 2.9$ cal mol^{-1} deg^{-1}. This rate constant is in reasonable agreement with the earlier report,[4] but the activation data differ considerably.

The reduction of HN_3 by V^{2+} was studied over the temperature range of 18.9–35.3° at $I = 1.0\ M$, with the reagent concentrations varied over the limits: $[V^{2+}]$, $(0.91–3.62) \times 10^{-2}\ M$; $[HN_3]$, $(0.30–2.65) \times 10^{-2}\ M$; $[H^+]$, 0.09–0.94 M. The individual runs are described in Table III. The least-squares analysis yields $k_{298°} = (2.83 \pm 0.32) \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$, $\Delta H^{\ddagger} = 14.4 \pm 0.6$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -17.3 \pm 2.0$ cal mol^{-1} deg^{-1} for the second-order rate law

$$\frac{-d[HN_3]}{dt} = k[V^{2+}][HN_3]$$

with k independent of $[H^+]$ over the indicated range.

TABLE III
RATE DATA FOR REDUCTION OF HN_3 BY V^{2+},[a]
$I = 1.0\ M$

	M			$\times 10^2\ M^{-1}\ \text{sec}^{-1}$	
	$\times 10^2$				
Temp, °C	$[V^{2+}]_0$	$[HN_3]$	$[H^+]$	k_{calcd}[b]	k_{obsd}
18.9	1.48	1.08	0.13	1.66	1.52
	2.75	0.77	0.76		1.68
	1.87	1.18	0.12		1.57
24.9	2.96	0.39	0.79	2.81	3.02
	1.77	0.35	0.87		2.74
	2.70	0.78	0.13		3.34
	0.92	0.38	0.93		2.61
25.0	1.02	0.30	0.94	2.83	3.44
	1.85	0.36	0.88		3.15
	1.03	1.14	0.79		2.88
	2.04	1.09	0.78		2.97
34.8	0.92	0.38	0.94	6.34	6.3
	1.72	0.37	0.88		5.8
	2.96	0.85	0.83		5.4
	2.96	0.85	0.09		7.5
35.3	2.61	2.30	0.64	6.6	6.9
	3.62	1.09	0.72		6.9
	1.57	2.65	0.56		6.6

[a] Wavelength of observation, 3050 Å. [b] Calculated from the activation parameters given in the text.

Stoichiometry of Mixed Reductant Experiments.—In trying to establish the details of the mechanism of the Cr^{2+} reduction of HN_3 it was necessary to ask if a reagent could be found that would compete with Cr^{2+} for any intermediate that might be found in the reduction. V^{2+} is such a reagent. The experiment that establishes this point involves the reaction of HN_3 with a mixture of V^{2+} and Cr^{2+}. Since the reactivity of Cr^{2+} is 600 times as great as is that of V^{2+}, the initial step in the reduction of HN_3 in this mixed reductant medium must involve Cr^{2+}. If V^{2+} does compete with Cr^{2+} for an intermediate, then some V(III) will be produced in reaction 4; it is known that Cr^{2+} reduces V^{3+} at a rate low[15,16] compared to the Cr^{2+} reduction of HN_3, thus affording the opportunity to assess the V(III) concentration after the reduction of HN_3 is substantially complete. In an experiment with $[Cr^{2+}]_0 = 2.68 \times 10^{-3}\ M$, $[V^{2+}]_0 = 2.71 \times 10^{-3}\ M$, and $[HN_3]_0 = 1.36 \times 10^{-3}\ M$ the absorbance at 5700 Å was monitored. Since V^{2+} and V^{3+} are isosbestic at this wavelength, the only absorbance change is due to Cr^{2+} being oxidized to Cr(III). If it is assumed that $CrNH_3^{3+}$ is produced in yield equivalent to the initial concentration of HN_3 (see below), then the quantity of Cr(III) produced from intermediate reduction can be calculated from the known extinction coefficients of the various Cr species after the reduction of HN_3 is complete (≅200 sec). Such a calculation yields the result that 0.4 mol of Cr^{3+} and, by difference, 0.6 mol of V^{3+} are produced per mol of HN_3 destroyed. This production of V^{3+} is confirmed by noting a relatively slow change in absorbance with time at 5700 Å as the excess Cr^{2+} reacts with the V^{3+} produced to yield V^{2+} and Cr^{3+}. The assumption that $CrNH_3^{3+}$ is produced in the reaction was confirmed by ion-exchange experiments. These experiments showed that more than 0.82 mol of $CrNH_3^{3+}$ is produced per mol of HN_3 reduced. (Incomplete separation of V from $CrNH_3^{3+}$ results in the establishment of only a limit.) It is to be noted that the absorptivities of Cr^{3+} and $CrNH_3^{3+}$ differ only slightly at 5700 Å (14.6 and 17.4 M^{-1} cm^{-1}, respectively) and hence the conclusion that V^{3+} is produced in this experiment is not very sensitive to the exact yield of $CrNH_3^{3+}$.

Discussion

The mechanism of the reduction of HN_3 by either Cr^{2+} or V^{2+} proceeds through a transition state that contains one molecule of reductant and one of hydrazoic acid. Because the latter is a two-electron oxidant, this rate behavior demands that an intermediate oxidation state of one of the two reagents be formed. One of two formal schemes seems most likely

SCHEME I

$$M^{2+} + HN_3 \overset{H^+}{=} M(IV) + NH_4 + N_2 \tag{1}$$

$$M^{2+} + M(IV) = 2M(III) \tag{2}$$

SCHEME II

$$M^{2+} + HN_3 = M(III) + N(-II) + N_2 \tag{3}$$

$$N(-II) + M^{2+} = M(III) + NH_4^+ \tag{4}$$

There is by now a large body of evidence on the expected behavior of reactions such as (2). In both the V^{2+} reduction of VO^{2+}[17] and the Cr^{2+} reduction of systems in which Cr(IV) is expected to be present,[18] a dimeric species is found. In the former case this species is unstable with respect to a rather rapid decomposition to 2 mol of V^{3+},[19] but the Cr(III) dimer decomposes only slowly. Ion-exchange separations of the product of the Cr^{2+} reduction of HN_3 show no evidence of $Cr_2(OH)_2^{4+}$. In addition, there was found no evidence for the presence of the highly colored dimer of V(III) in the V^{2+} reduction of HN_3. These data indicate that Scheme II is a more appropriate mechanism for the reduction of HN_3 by V^{2+} and Cr^{2+}. The establishment of this feature of the mechanism does not complete a definition of either reaction's course, because it does not specifically account for the details of the stoichiometric properties of the reduction.

The detailed features of the rate and stoichiometry of the Cr^{2+} reduction of HN_3 that must be taken into account in writing the mechanism of this reduction

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are (1) the production of 1 mol of $CrNH_3^{3+}$ per mol of Cr^{3+}, (2) the presence of small quantities of a dimeric species, written here as $Cr_2NH_2^{5+}$ although the binding mode is unknown, and (3) the production of $CrCl^{2+}$ in the presence of Cl^- even at concentrations of 0.088 *M*.

From the experimental results described above a plausible mechanism for the Cr^{2+} reduction of HN_3 consistent with the data is

$$Cr^{2+} + HN_3 \xrightarrow{k} Cr\overset{H}{N}N_2^{2+} \qquad (5)$$

$$Cr\overset{H}{N}N_2 + H^+ \longrightarrow CrNH_2^{3+} + N_2 \qquad (6)$$

$$CrNH_2^{3+} + Cr^{2+} \longrightarrow Cr_2NH_2^{5+} \qquad (7)$$

$$CrNH_2^{3+} + Cr^{2+} \xrightarrow{H^+} CrNH_3^{3+} + Cr^{3+} \qquad (8)$$

$$CrNH_2^{3+} + Cl^- + H^+ \longrightarrow CrNH_3^{3+} + Cl \qquad (9)$$

$$Cr^{2+} + Cl \longrightarrow CrCl^{2+} \qquad (10)$$

Reaction 5 is required by the $[H^+]$-independent rate law and the trapping experiments with V^{2+}. Reaction 6 seems plausible in acidic aqueous solution. The fate of $CrNH_2^{3+}$ is indicated by reactions 7–9. The first seems to be the only plausible means of producing the dimeric Cr(III) product, although there is no evidence demanding bridging through NH_2^- in preference to bridging through OH^-. Reactions 9 and 10 must be invoked to explain the high yield of $CrCl^{2+}$, even at $[Cl^-]$ of 0.088 *M*. To argue that $CrCl^{2+}$ arises from a nonbridging ligand effect of Cl^- on the reductant Cr^{2+} assigns too great a rate-enhancing ability to $CrCl^+$ over Cr^{2+}; evidence pertinent to the magnitude of such nonbridging ligand effects is available.[20] Reaction 8, the outer-sphere reduction of $CrNH_2^{3+}$ by Cr^{2+}, is not absolutely necessary to explain the data. An alternative scheme would involve reaction of $CrNH_2^{3+}$ with solvent to give $CrNH_3^{3+}$ + OH. Such reaction is thermodynamically unfavorable when NH_2 is free in solution (or as NH_3^+),[21,22] although coordination to Cr(III) may increase the oxidizing power. Nevertheless, the data argue against oxidation of solvent. Entry 3 compared to entries 4 and 5 in Table I show that a fourfold increase in the concentration of Cr(II) does not affect the quantity of dimer formed. This result implies that Cr^{3+} and $(Cr_2NH_2)^{5+}$ arise from reaction paths of the same order in Cr^{2+}. Thus reactions 7–9 adequately account for all the observed data.

The mechanism discussed above is usefully contrasted with that found for the Cr^{2+} reduction of NH_3OH^+.[23] In this case the Cr^{2+} attacks the oxygen atom forming Cr^{3+} and NH_3^+; the latter does not yield $CrNH_3^{3+}$ as a product but reacts with Cr^{2+} by an outer-sphere path. This result is consistent with the formation of a chromium–nitrogen bond in the first step of the reductions of HN_3 by Cr^{2+}. A comparison can also be made between the reactivities of NH_3^+ and $CrNH_2^{3+}$ by comparing the NH_3OH^+ and HN_3 oxidation of Cr^{2+}. In the former, added Cl^- has no effect and added Br^- leads to only a less than stoichiometric amount of $CrBr^{2+}$ as product.[23] This is to be contrasted to the Cr^{2+} reduction of HN_3 which produces $CrCl^{2+}$ quantitatively. This result is understood on the basis of increased oxidizing power of $CrNH_2^{3+}$ compared to NH_3^+.

The mechanism of the V^{2+} reduction of HN_3 cannot be specified as easily. The rate of this reaction is slower by a factor if almost 10^3 than the substitution-limiting rate of oxidation of V^{2+}.[24,25] Either an inner-sphere or outer-sphere mechanism is compatible with this result. It is possible to make some indirect rate comparisons to argue about mechanism, but it seems more advisable to await more rigorous means of assigning mechanism.

The entropy of activation of the V^{2+} and Cr^{2+} reductions of HN_3 are usefully compared to other activation entropies. Newton and Rabideau[26] first noted a parallel between the formal absolute entropy of an activated complex and its charge; this correlation was extended to many reactions of the actinides[27] and has been applied to other systems as well.[28] Table IV[29–33] lists values for several reactions of V^{2+} and Cr^{2+} that generate transition states with dipositive charges. All of these values fall within the range of −20 to +10 cal mol^{-1} deg^{-1} quoted by Newton and Baker[27] as appropriate for dipositive transition states. It would appear that charge effects are as predominant in determining $\Delta S^{\ddagger}$ for these reactions as they are for reactions between two metal ions.

TABLE IV

FORMAL IONIC ENTROPIES OF ACTIVATED COMPLEXES

Net activation process	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	$S^{\ddagger}$,[a] cal mol^{-1} deg^{-1}	Ref
$V^{2+} + Br_2 = [VBr_2^{2+}]^{\ddagger}$	−26	−20	32
$V^{2+} + I_2 = [VI_2^{2+}]^{\ddagger}$	−21	−12	32
$V^{2+} + HN_3 = [VN_3H^{2+}]^{\ddagger}$	−17	+8	This work
$Cr^{2+} + HN_3 = [CrN_3H^{2+}]^{\ddagger}$	−29	+9	This work
$Cr^{2+} + ClO_3^- + H^+ = [CrClO_3H^{2+}]^{\ddagger}$	−17	+9	33

[a] Entropies of the species taken from Latimer[29] except for V^{2+} = −23 cal mol^{-1} deg^{-1} [30] and Cr^{2+}, estimated as −13 cal mol^{-1} deg^{-1} from the Powell–Latimer equation.[31]

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