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Reduction of Azidochromium(III) Complexes by Vanadium(II)

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Received September 22, 1975 AIC50699B

The kinetics of the reduction of $(H_2O)_5CrN_3^{2+}$, *cis*-$(H_2O)_4Cr(N_3)_2^+$, and $(H_2O)_3Cr(N_3)_3$ by V^{2+} have been measured. The respective activation parameters at 25 °C, $I = 0.97$ M ($LiClO_4$), are as follows [ΔH^* (kcal/mol), ΔS^* (cal/(deg mol))]: 12.9, −13.0; 12.4, −12.9; 14.1, −6.5. These results and data from experiments with added Cr^{2+} are consistent with an inner-sphere pathway with electron transfer through a single azide bridge to the Cr(III) center for all three systems. The rate of reduction of VN_3^{2+} by Cr^{2+} was determined indirectly; $\Delta H^* = 3.85$ kcal/mol and $\Delta S^* = -27.3$ cal/(deg mol). Cr^{2+} was concluded to reduce $(H_2O)_3Cr(N_3)_3$ via a doubled-bridged activated complex; the rate constant is 112 ± 7 M^{-1} s^{-1} at 4.8 °C. The implications of these kinetic results are discussed and reaction schemes are proposed.

Introduction

Hydrazoic acid has been used in a number of kinetic studies both as an oxidant and as a reductant, and the results have revealed a rich chemistry.[1] Attempts to investigate the redox properties of the azide ion when coordinated to a substitution-inert metal ion center, however, have met with difficulty. Nitrous acid is the most notable exception; it reacts with many azido complexes and hydrazoic acid with analogous stoichiometry and similar rates.[2] Generally, though, the coordinated azide ion serves as an effective bridging ligand and either undergoes no net oxidation or reduction or does so in a subsequent step after the primary electron-transfer process. For example, although chromium(II) reduces hydrazoic acid rapidly,[1g] the only detectable reaction in the chromium(II)–azidochromium(III)[3] system is isotopic exchange.[4] When azidopentaamminecobalt(III) is treated with excess vanadium(II), an inner-sphere reaction occurs producing cobalt(II) and azidovanadium(III);[5] the latter species aquates rapidly in acidic solution,[6] and the hydrazoic acid released is reduced by the excess vanadium(II). Since vanadium(II) reduces hydrazoic acid at a moderate rate[1g] but reacts very slowly with chromium(III),[7] we thought it was conceivable that vanadium(II) would directly reduce the ligand when allowed to react with azidochromium(III) complexes. This does not occur; in every case the reaction proceeds via an inner-sphere pathway with electron transfer through a single azide bridge to the chromium(III) center. The results of our kinetic studies of these systems are presented in this article.

Experimental Section

Reagents. Azidochromium(III) solutions were isolated by ion-exchange separation at 5 °C of an equilibrated chromium(III)–hydrazoic acid, azide buffer mixture.[8] A minor modification utilized potassium azide instead of sodium azide in the equilibrium solution; the precipitation and separation of potassium perchlorate significantly lowered the electrolyte concentration and minimized smearing in the ion-exchange procedure. *cis*-Diazidochromium(III) solutions were purified by ion-exchange methods at 5 °C after allowing *excess* *cis*-diazidobis(ethylenediamine)cobalt(III) to react with chromium(II).[9] Triazidochromium(III) solutions were isolated from equilibrated chromium(III)–azide solutions by ion-exchange procedures at 5 °C after first removing excess hydrazoic acid by acidification, extraction with cold ether, and aeration. Diazidochromium(III) was retained by the long column of Dowex 50W-X12 resin used in the separation provided the potassium azide procedure was used in preparing the equilibrated solution. All of the separated azidochromium(III) solutions were stored at −78 °C. Triazidochromium(III) aquates rather rapidly; in the kinetic experiments individual aliquots were thawed just prior to initiation of the reaction.

A number of procedures were used in an attempt to prepare a diazidochromium(III) solution containing appreciable amounts of the trans isomer.

Method A. The middle fraction of diazidochromium(III) in an equilibrated chromium(III)–azide solution was collected.

Method B. The first 30% of the diazidochromium(III) fraction was collected following a slow elution (4 h) with 0.2 M $HClO_4$ or 0.2 M $NaClO_4$–10^{-3} M $HClO_4$ at 5 °C. Longer elution times (24 h) as used previously[10] to separate *cis*- and *trans*-dichlorochromium(III) were unsuccessful due to aquation of diazidochromium(III), even at 5 °C.

Method C. The final 30% of the diazidochromium(III) fraction described in method B was collected.

Method D. A solution of triazidochromium(III) was allowed to aquate, and the predominantly diazidochromium(III) product was isolated by ion exchange.

Method E. Chromium(II) was oxidized with excess hydrazoic acid–azide buffer and the diazidochromium(III) product was separated by ion exchange.[11] The first 30% was collected.

Method F. The last 30% of the diazidochromium(III) fraction described in method E was collected.

Method G. An equilibrated chromium(III)–azide solution was slowly (ca. 4 h) eluted, and the first 40% of the diazidochromium(II) fraction was collected. This eluent was allowed to react with half of its concentration of nitrous acid, and the remaining diazidochromium(III) was separated from the predominantly azidochromium(III) product by ion exchange (first 40% collected). It is not clear that any of these procedures resulted in a diazidochromium(III) solution containing an appreciable amount of the trans isomer (vide infra).

Vanadium(II) and chromium(II) solutions were prepared at 0 °C in the absence of oxygen by reduction of oxovanadium(IV) perchlorate and chromium(III) perchlorate, respectively, over a pool of mercury containing dissolved granulated zinc. These solutions were prepared freshly just prior to a series of kinetic or stoichiometric experiments. Total vanadium in the reaction mixtures were determined spectrophotometrically as vanadium(V) after addition of excess bromate ion.[12] Total chromium was determined as chromate ion.[13]

Stoichiometric Studies. When azidochromium(III) and excess vanadium(II) are allowed to react completely, 94–97% of the chromium(III) originally present in the complex ion is converted to amminechromium(III). For example, a solution originally containing 0.239 mmol of CrN_3^{2+} and 0.78 mmol of V^{2+} in 25 ml of 2 M $HClO_4$ was allowed to react for 40 min in the absence of oxygen at 25 °C. The ion-exchange separation of the reaction products, after addition of excess chlorate ion to convert the vanadium to a mixture of VO^{2+} and VO_2^+, yielded 0.226 mmol of $CrNH_3^{3+}$. Similarly, a solution originally containing 0.257 mmol of CrN_3^{2+}, 0.737 mmol of V^{2+}, and 6.80 mmol Cr^{2+} in 25 ml of 2 M $HClO_4$ yielded 0.250 mmol of $CrNH_3^{3+}$. Blank experiments showed negligible net chemical reaction between CrN_3^{2+} and Cr^{2+} under these conditions.

$CrNH_3^{3+}$ is produced in 94–98% yield when *cis*-$Cr(N_3)_2^+$ is allowed to react completely with excess V^{2+}. For example, 0.271 mmol of *cis*-$Cr(N_3)_2^+$ and 1.40 mmol of V^{2+} in 32 ml of $HClO_4$ were allowed to react for 35 min at room temperature in the absence of oxygen; 0.264 mmol of $CrNH_3^{3+}$ was separated (NH_3:Cr = 1.02).

Kinetic Studies. The kinetic experiments were monitored spectrophotometrically with a Zeiss PMQ-11 instrument equipped with a thermostated (±0.1 °C) sample compartment. The reactants were rapidly mixed (<1 s) by means of a magnetic stirring device. Oxygen was removed by continuously flushing the entire sample compartment with tank CO_2 and the reaction cuvette with CO_2 that had passed through a chromium(II) trap. Wavelengths and pertinent molar absorptivities (M^{-1} cm^{-1}) determined in this study were as follows: 2710 Å, $\epsilon(CrN_3^{2+})$ 3740, $\epsilon(V^{2+})$ 58; 2770 Å, $\epsilon(CrN_3^{2+})$ 3590, ϵ(*cis*-$Cr(N_3)_2^+$) 5940, $\epsilon(Cr(N_3)_3)$ ca. 7315, $\epsilon(V^{2+})$ 53. The molar absorptivity for *cis*-$Cr(N_3)_2^+$ is in good agreement with that reported by Haim[9] but is higher than the value of 5450 M^{-1} cm^{-1} reported by Swaddle and King.[8] In the experiments with chromium(II) a small contribution to the absorbance was made by the chromium(II) and traces of its air-oxidized product. Vanadium(III) is essentially transparent at these wavelengths.[14] In all cases the absorbance change in the kinetic experiments was due predominantly to disappearance of the azidochromium(III) reactant and, occasionally, to the appearance of an azidochromium(III) product. All of the reactions utilized large excesses of the reductant. This approach essentially eliminated interference from the subsequent reduction of hydrazoic acid produced in all the systems; this reaction did not sensibly alter the reductant concentration nor the observed absorbance changes.

The stopped-flow experiments designed to detect an azidovanadium(III) intermediate were performed with a Durrum D-110 instrument.

Calculations. The kinetic behavior of the *cis*-$Cr(N_3)_2^+$–V^{2+} reaction in the presence of added Cr^{2+} is complex. A reaction scheme is proposed in the Discussion that is consistent with the data. The analysis of the kinetic data must accommodate non-steady-state production of CrN_3^{2+} (the absorbance of this ion is appreciable at 2770 Å). If the steady-state approximation is applied to $[VN_3^{2+}]$, the instantaneous concentrations of *cis*-$Cr(N_3)_2^+$ and CrN_3^{2+} can be derived according to the reaction scheme. The derivation of [*cis*-$Cr(N_3)_2^+$] is straightforward but is more complicated for $[CrN_3^{2+}]$. The procedure involves obtaining the differential rate expressions for the two azidochromium(III) species, elimination of time as an independent variable, and integration, i.e.

$$[cis\text{-}Cr(N_3)_2^+] = [cis\text{-}Cr(N_3)_2^+]_0 e^{-at} \qquad (A)$$

where

$$a = k_4[V^{2+}]_0 + k_5[Cr^{2+}]_0 \qquad (B)$$

$$[CrN_3^{2+}] = \frac{\alpha[cis\text{-}Cr(N_3)_2^+]}{\beta}\left(\left[\frac{[cis\text{-}Cr(N_3)_2^+]}{[cis\text{-}Cr(N_3)_2^+]_0}\right]^{\beta} - 1\right) \qquad (C)$$

where

$$\alpha = \frac{-k_2k_4[V^{2+}]_0[Cr^{2+}]_0 - k_3k_5[Cr^{2+}]_0 - k_2k_5[Cr^{2+}]_0^2}{a[k_2[Cr^{2+}]_0 + k_3]} \qquad (D)$$

$$\beta = \frac{k_1k_3[V^{2+}]_0}{a[k_2[Cr^{2+}]_0 + k_3]} - 1 \qquad (E)$$

Thus, for each kinetic experiment the calculated absorbance of *cis*-$Cr(N_3)_2^+$ plus CrN_3^{2+} as a function of time can be compared to the observed values. The values of the rate constants used in the calculation (appropriate to the experimental conditions) were k_1 = 2.06 M^{-1} s^{-1}, k_2 = 9.35 × 10^3 M^{-1} s^{-1}, k_3 = 6.27 s^{-1}, k_4 = 4.91 M^{-1} s^{-1}, and k_5 = 7.40 M^{-1} s^{-1} (determined independently in the present work).

Results

Reduction of Azidochromium(III) by Excess Vanadium(II). The nearly quantitative production of $CrNH_3^{3+}$ and the stoichiometry of the HN_3–V^{2+} reaction[1g] strongly suggest that reaction 1 is operative.

$$2V^{2+} + CrN_3^{2+} + 3H^+ = 2V^{3+} + CrNH_3^{3+} + N_2 \qquad (1)$$

Table I. Kinetic Results for the Vanadium(II)–Azidochromium(III) Reaction[a]

$[HClO_4]$, M	I, M	k_1, M^{-1} s^{-1}	$[HClO_4]$, M	I, M	k_1, M^{-1} s^{-1}
0.0735	0.969	1.95 ± 0.01	0.960	0.969	1.27 ± 0.02[d]
0.120	0.969	1.93 ± 0.01	0.960	0.969	4.10 ± 0.03[e]
0.212	0.969	2.06 ± 0.01	0.120	0.130	0.801 ± 0.009
0.401	0.969	2.03 ± 0.04	0.120	0.269	1.08 ± 0.02
0.680	0.969	2.12 ± 0.01	0.120	0.501	1.49 ± 0.02
0.960	0.969	2.12 ± 0.01	0.120	1.90	3.59 ± 0.03
0.960	0.969	2.23 ± 0.01[b]	0.120	2.82	5.55 ± 0.02
0.960	0.969	2.18 ± 0.05[c]			

[a] Ionic strength maintained with $LiClO_4$. T = 20.0 °C, $[CrN_3^{2+}]_0$ = (4.00–6.52) × 10^{-5} M, and $[V^{2+}]_0$ = ca. 3.0 × 10^{-3} M unless otherwise indicated. Uncertainties are average deviations of two to four determinations. [b] $[V^{2+}]_0$ = 2.24 × 10^{-3} M. [c] $[V^{2+}]_0$ = 5.75 × 10^{-3} M. [d] T = 13.15 °C. [e] T = 28.1 °C.

The kinetics of the V^{2+}–CrN_3^{2+} reaction were monitored at 2710 Å (an absorption maximum for CrN_3^{2+}) with large excesses of V^{2+}. Nearly all of the absorbance change was due to loss of CrN_3^{2+}. Very good pseudo-first-order kinetic data were obtained; varying the $[V^{2+}]$ indicated that the empirical rate law (2) governs this reaction. Values of the second-order

$$-d[CrN_3^{2+}]/dt = k_1[CrN_3^{2+}][V^{2+}] \qquad (2)$$

rate parameter k_1 were calculated by dividing the pseudo-first-order rate constants obtained by a least-squares analysis of the kinetic data (the plots were linear for at least 85% reaction with standard deviations ≤0.5%) by the initial $[V^{2+}]$. The results of these experiments are summarized in Table I. The values of the rate parameter k_1 are essentially independent of $[H^+]$ over the range 0.0735–0.960 M.

The effect of ionic strength on the rate parameter k_1 is consistent with an extended form of the Debye–Hückel equation[15]

$$\log k_1 = \log k_0 + \Delta Z^2 \alpha I^{1/2}/(1 + \beta I^{1/2}) + \gamma I \qquad (3)$$

The least-squares values of the parameters (with α = 0.5046 and ΔZ^2 = 8) were k_0 = 0.176 ± 0.027 M^{-1} s^{-1}, β = 3.56 ± 0.52 Å, and γ = 0.187 ± 0.025 M^{-1}. These parameters reproduce the experimental data with an average deviation of 2.4% and a maximum deviation of 5.7%.

Pseudo-first-order kinetic behavior is also observed under similar experimental conditions but with added Cr^{2+} present. The results of these experiments are summarized in Tables II and III; values of k^1 were obtained by dividing the pseudo-first-order rate constant by the initial $[V^{2+}]$. However, the value of the second-order rate parameter k^1 decreases as $[Cr^{2+}]_0$ increases at a given $[H^+]$. Equation 4 adequately

$$k^1 = (B(1))/[B(2)[Cr^{2+}]_0 + 1] \qquad (4)$$

correlated the variation of k^1 with $[Cr^{2+}]_0$ at a given $[H^+]$. The values of k^1_{calcd} listed in the fourth columns of Tables II and III were calculated from the best fit parameters $B(1)$ and $B(2)$. The values of $B(1)$ are essentially equal to the k_1 values

Table II. Kinetic Results with Added Chromium(II)[a]

$[HClO_4]$, M	10^3-$[Cr(II)]$, M	k^1, M^{-1} s^{-1}	k^1_{calcd}, M^{-1} s^{-1}	
			b	*c*
0.0735	0	1.95 ± 0.01	1.94	2.04
	0.239	1.20 ± 0.03	1.24	1.27
	0.490	0.927 ± 0.017	0.899	0.912
	0.824	0.668 ± 0.010	0.658	0.662
	1.17	0.536 ± 0.069	0.515	0.515
	1.71	0.360 ± 0.014	0.385	0.383
0.120	0	1.93 ± 0.01	1.95	2.04
	0.239	1.35 ± 0.03	1.33	1.37
	0.485	1.05 ± 0.06	1.00	1.02
	0.808	0.702 ± 0.012	0.755	0.768
	1.19	0.581 ± 0.002	0.588	0.595
	1.80	0.405 ± 0.005	0.431	0.435
0.212	0	2.06 ± 0.01	2.07	2.04
	0.256	1.50 ± 0.01	1.49	1.48
	0.489	1.24 ± 0.07	1.18	1.18
	0.792	0.869 ± 0.010	0.937	0.937
	1.16	0.769 ± 0.014	0.747	0.749
	1.71	0.552 ± 0.006	0.573	0.575
0.401	0	2.03 ± 0.04	2.01	2.04
	0.507	1.32 ± 0.01	1.36	1.38
	0.779	1.11 ± 0.01	1.16	1.17
	1.20	1.01 ± 0.01	0.947	0.954
	2.50	0.656 ± 0.071	0.600	0.603
	3.11	0.487 ± 0.007	0.512	0.514
	4.02	0.407 ± 0.007	0.420	0.422
0.680	0	2.12 ± 0.01	2.10	2.04
	0.495	1.54 ± 0.01	1.59	1.56
	0.780	1.35 ± 0.03	1.39	1.37
	1.07	1.34 ± 0.01	1.24	1.23
	2.49	0.763 ± 0.014	0.801	0.801
	3.07	0.728 ± 0.003	0.700	0.701
	3.94	0.573 ± 0.004	0.588	0.590
0.960	0	2.12 ± 0.01	2.14	2.04
	0.501	1.73 ± 0.01	1.72	1.66
	0.806	1.58 ± 0.06	1.53	1.49
	1.22	1.35 ± 0.10	1.34	1.31
	2.49	0.932 ± 0.016	0.962	0.950
	3.09	0.852 ± 0.001	0.847	0.840
	3.78	0.720 ± 0.005	0.747	0.743

[a] Conditions: $T = 20.0$ °C, $I = 0.969$ M ($LiClO_4$), $[CrN_3^{2+}]_0$ = ca. 6.4×10^{-5} M, and $[V^{2+}]_0$ = ca. 3.0×10^{-3} M. Uncertainties are average deviations of two to four determinations. [b] Calculated from best fit of data to eq 4, using individual $[H^+]$ sets. [c] Calculated from best fit of data to eq 6, using all entries.

Table III. Kinetic Results with Added Chromium(II) at Other Temperatures[a]

T, °C	$10^3[Cr(II)]_0$, M	k^1, M^{-1} s^{-1}	k^1_{calcd},[b] M^{-1} s^{-1}
13.15	0	1.27 ± 0.02	1.28
	0.490	0.999 ± 0.067	0.982
	0.970	0.830 ± 0.071	0.799
	1.47	0.673 ± 0.056	0.669
	2.12	0.512 ± 0.006	0.552
	3.01	0.439 ± 0.029	0.446
28.1	0	4.10 ± 0.03	4.09
	0.455	3.46 ± 0.06	3.54
	1.06	3.16 ± 0.12	3.01
	1.56	2.62 ± 0.11	2.67
	2.25	2.28 ± 0.06	2.32
	3.01	2.02 ± 0.03	2.02

[a] Conditions: $[HClO_4]_0 = 0.960$ M, $I = 0.969$ M ($LiClO_4$), $[CrN_3^{2+}]_0$ = ca. 6.4×10^{-5} M, and $[V^{2+}]_0$ = ca. 3.0×10^{-3} M. Uncertainties are average deviations of triplicate determinations. [b] Calculated from best fit of data to eq 6.

Table IV. Kinetic Results for the Vanadium(II)–*cis*-Diazidochromium(III) Reaction[a]

$[HClO_4]$, M	*I*, M	k_4, M^{-1} s^{-1}	$[HClO_4]$, M	*I*, M	k_4, M^{-1} s^{-1}
0.960	0.969	5.03 ± 0.03	0.120	0.130	2.91 ± 0.02
0.960	0.969	5.24 ± 0.03[b]	0.120	0.269	3.37 ± 0.08
0.960	0.969	5.03 ± 0.06[c]	0.120	0.501	4.11 ± 0.03
0.212	0.969	4.91 ± 0.05	0.120	0.969	4.97 ± 0.06
0.0735	0.969	4.59 ± 0.08	0.120	1.90	7.40 ± 0.10
0.960	0.969	2.96 ± 0.03[d]	0.120	2.82	10.4 ± 0.10
0.960	0.969	1.64 ± 0.01[e]			

[a] Ionic strength maintained with $LiClO_4$. $T = 20.0$ °C, $[cis\text{-}Cr(N_3)_2^+]_0$ = ca. 5.0×10^{-5} M, and $[V^{2+}]_0$ = ca. 3.4×10^{-3} M unless otherwise indicated. Uncertainties are average deviations of two or three determinations. [b] $[V^{2+}]_0 = 2.34 \times 10^{-3}$ M. [c] $[V^{2+}]_0 = 4.84 \times 10^{-3}$ M. [d] $T = 12.6$ °C. [e] $T = 5.8$ °C.

observed in the rate studies without added Cr^{2+} at each $[H^+]$. The variation of $B(2)$ with $[H^+]$ is reproduced satisfactorily by the functional form

$$B(2) = c/(a + b[H^+]) = B(3)/(1 + (B(4))[H^+]) \qquad (5)$$

Accordingly, all of the kinetic data for the CrN_3^{2+}–V^{2+} reaction in the presence of added Cr^{2+} were recalculated at a given temperature according to expression 6. The values

$$k^1 = (B(5))/([(B(6))[Cr^{2+}]_0/(a + b[H^+])] + 1) \qquad (6)$$

of k^1_{calcd} using the determined parameters $B(5)$ and $B(6)$ are presented in the last columns of Tables II and III. The agreement with the observed k^1 values is adequate.

The values of *a* and *b* used in this calculation are those reported[6] for the aquation of VN_3^{2+} in acid solution at I = 1.00 M (eq 7). Justification for this procedure and the

$$-d \ln [VN_3^{2+}]/dt = a + b[H^+] \qquad (7)$$

significance of the empirical parameters $B(5)$ and $B(6)$ will be presented later.[16]

Values of $B(6)$ were $(1.17 \pm 0.10) \times 10^4$, $(9.35 \pm 0.28) \times 10^3$, $(7.92 \pm 0.58) \times 10^3$ M^{-1} s^{-1} at 28.1, 20.0, and 13.2 °C, respectively.

Reduction of *cis*-Diazidochromium(III) by Excess Vanadium(II). Equation 8 is consistent with the nearly stoichiometric production of $CrNH_3^{3+}$ and the stoichiometry of the HN_3–V^{2+} reaction.[1g] Subsequent reduction of HN_3 by excess V^{2+} is slow relative to reaction 8 and does not affect the kinetic results.

$$2V^{2+} + cis\text{-}Cr(N_3)_2^+ + 4H^+ = 2V^{3+} + CrNH_3^{3+} + HN_3 + N_2 \qquad (8)$$

The kinetics of the reaction with excess vanadium(II) were monitored at 2770 Å, an absorption maximum for the cis complex. The data were consistent with the empirical rate expression

$$-d[cis\text{-}Cr(N_3)_2^+]/dt = k_4[cis\text{-}Cr(N_3)_2^+][V^{2+}] \qquad (9)$$

The pseudo-first-order plots were linear to 80–90% reaction, with standard deviations ≤0.7%. Values of the rate parameter k_4 are summarized in Table IV. Again, there is very little variation in the value of k_4 with $[H^+]$, although there is a minor change at the lowest $[H^+]$ used.

The effect of ionic strength on the rate parameter k_4 is consistent with the extended form of the Debye–Hückel equation. Values of $k_0 = 1.36 \pm 0.09$ M^{-1} s^{-1}, $\beta = 3.68 \pm 0.47$ Å, and $\gamma = 0.146 \pm 0.011$ M^{-1} reproduce the pertinent experimental data in Table IV with an average deviation of 0.56% and a maximum deviation of 1.8%.

The kinetic behavior is altered markedly by the presence of added $[Cr^{2+}]$. The calculated absorbance as a function of time can be computed for a reaction scheme proposed later according to the analysis outlined in the Experimental Section. Two sets of kinetic experiments, each in triplicate and differing primarily in $[Cr^{2+}]_0$, were analyzed. The results of these calculations are presented in Tables V and VI; for each set,

Table V. Kinetic Results for the Vanadium(II)–*cis*-Diazidochromium(III) Reaction in the Presence of Added Chromium(II) (Experiment 31)[a]

Time, s	A_{obsd}	A_{calcd}[b]	10^5-[cis],[b] M	10^5-[CrN_3^{2+}],[b] M
0	0.608	0.608	5.12	0
12	0.518	0.519	4.02	0.58
17	0.485	0.488	3.64	0.77
22	0.455	0.459	3.29	0.95
27	0.430	0.432	2.97	1.10
32	0.405	0.408	2.69	1.23
37	0.386	0.385	2.43	1.34
42	0.363	0.365	2.20	1.44
47	0.346	0.346	1.99	1.52
52	0.329	0.328	1.80	1.60
57	0.312	0.312	1.63	1.66
62	0.299	0.298	1.47	1.71
67	0.285	0.284	1.33	1.75
72	0.273	0.271	1.20	1.79
82	0.251	0.249	0.98	1.84
92	0.233	0.229	0.80	1.86
102	0.217	0.212	0.66	1.87
112	0.202	0.197	0.54	1.86
122	0.189	0.184	0.44	1.84
137	0.171	0.168	0.33	1.80
152	0.159	0.154	0.24	1.74
167	0.144	0.141	0.18	1.67
187	0.128	0.128	0.12	1.58
207	0.116	0.116	0.08	1.48
232	0.102	0.104	0.05	1.36
262	0.087	0.091	0.03	1.22

[a] Conditions: $[V^{2+}]_0 = 3.32 \times 10^{-3}$ M, $[Cr^{2+}]_0 = 5.13 \times 10^{-4}$ M, $[H^+] = 0.21$ M, $I = 0.969$ M ($LiClO_4$), $T = 20.0$ °C, λ 2770 Å; path length 2.0 cm. $2\epsilon(cis\text{-}Cr(N_3)_2^+) = 1.188 \times 10^4$ M^{-1} cm^{-1} and $2\epsilon(CrN_3^{2+}) = 7.179 \times 10^3$ M^{-1} cm^{-1}. [b] Calculated values as described in the text. The calculations were performed by a computer; any slight discrepancies between A_{calcd} and that obtained using the concentrations of azidochromium(III) complexes presented arise from rounding errors.

Table VI. Kinetic Results for the Vanadium(II)–*cis*-Diazidochromium(III) Reaction in the Presence of Added Chromium(II) (Experiment 33)[a]

Time, s	A_{obsd}	A_{calcd}[b]	10^5-[cis], M	10^5-[CrN_3^{2+}], M
0	0.618	0.618	5.20	0
6	0.569	0.573	4.50	0.53
11	0.538	0.539	3.98	0.92
16	0.507	0.509	3.53	1.25
21	0.479	0.483	3.13	1.55
26	0.458	0.458	2.77	1.80
31	0.435	0.437	2.45	2.02
36	0.414	0.417	2.18	2.21
41	0.396	0.399	1.93	2.37
46	0.382	0.383	1.71	2.51
51	0.367	0.369	1.51	2.63
56	0.351	0.355	1.34	2.73
61	0.340	0.343	1.19	2.81
66	0.327	0.332	1.05	2.88
76	0.308	0.313	0.83	2.99
86	0.291	0.296	0.65	3.05
96	0.275	0.282	0.51	3.09
106	0.263	0.270	0.40	3.10
116	0.250	0.259	0.31	3.09
126	0.241	0.250	0.25	3.07
141	0.228	0.237	0.17	3.02
156	0.214	0.226	0.12	2.95
171	0.206	0.216	0.08	2.88
186	0.195	0.207	0.06	2.79
206	0.184	0.197	0.04	2.68
226	0.173	0.187	0.02	2.57

[a] Conditions: $[V^{2+}]_0 = 3.16 \times 10^{-3}$ M, $[Cr^{2+}]_0 = 1.17 \times 10^{-3}$ M, $[H^+] = 0.212$ M, $I = 0.969$ M ($LiClO_4$), $T = 20.0$ °C, λ 2770 Å, path length 2.0 cm. [b] Calculated values as described in the text.

Table VII. Kinetic Results for the V(II) and Cr(II) Reactions with Various Diazidochromium(III) Preparations

Diazidochromium(III) species	k_4,[a] M^{-1} s^{-1}	k_5,[b] M^{-1} s^{-1}
Cis isomer	5.10 ± 0.07	7.40 ± 0.10
Method A	5.19 ± 0.09	7.26 ± 0.06
Method B	5.03 ± 0.01	6.96 ± 0.08
Method C	5.24 ± 0.13	
Method D	5.24 ± 0.01	7.31 ± 0.05
Method E	5.10 ± 0.05	7.15 ± 0.03
Method F	5.08 ± 0.15	

[a] $T = 20.0$ °C, $[H^+] = 0.960$ M, $I = 0.969$ M ($LiClO_4$), $[Cr(N_3)^+]_0$ = ca. 5.0×10^{-5} M, and $[V^{2+}]_0$ = ca. 3.4×10^{-3} M. [b] $T = 20.0$ °C, $[H^+] = 0.212$ M, $I = 0.969$ M ($LiClO_4$), $[Cr(N_3)_2]_0$ = ca. 5.0×10^{-5} M, and $[Cr^{2+}]_0$ = ca. 3.1×10^{-3} M. Uncertainties are average deviations of two or three determinations. The values of k_5 refer to the single-bridge path.

the intermediate "best fit" experiment is included.

Reduction of Other Diazidochromium(III) Preparations by Excess Vanadium(II) and Chromium(II). Numerous attempts were made to produce diazidochromium(III) solutions containing an appreciable fraction of the trans isomer (see Experimental Section). It is assumed that cis–trans isomerization of $Cr(N_3)_2^+$ is not rapid at 5 °C. Equilibrium mixtures of several disubstituted chromium(III) complexes have been shown to contain approximately equal amounts of the cis and trans isomers.[10,18,19] Slow ion-exchange separations of the isomers have been achieved, and the ratio of the absorbances at the two visible maxima has provided a convenient method of distinguishing the isomers.[10] Therefore, a number of experiments were performed using equilibrated chromium(III)–azide solutions, but none resulted in solutions of $Cr(N_3)_2^+$ with detectable spectral differences. Several of these preparations were allowed to react with excess V^{2+}; the kinetic behavior is identical with that shown by the cis isomer (see Table VII, first four entries). These results do not establish that the cis isomer predominates in the equilibrated solutions; it is possible that the spectra and rate behavior toward V^{2+} are very similar for the two isomers. Therefore, another reducing agent, the very labile Cr^{2+} ion, was used. The rate constants reported in Table VII refer to the single-bridge path producing CrN_3^{2+} and HN_3. The results do not indicate appreciable rate differences for these preparations compared to that exhibited by the cis isomer. Alternative nonequilibrium preparations gave the same results. These methods included aquation of an equilibrated $Cr(N_3)_3$ solution, the reduction of a HN_3–N_3^- buffer solution by Cr^{2+}, and the use of nitrous acid which would be expected to react more rapidly with the cis isomer. We tentatively conclude that we have succeeded only in preparing predominantly the cis isomer by a number of routes. If correct, this result implies a preferred stability for the cis configuration by diazidochromium(III) not shown by dichloro- and dithiocyanatochromium(III)[10,18,19] nor by a number of disubstituted amminecobalt(III) complexes.[20–22] The alternative is that *cis*- and *trans*-$Cr(N_3)_2^+$ have very similar spectra and reaction rates toward both V^{2+} and Cr^{2+}.

Reduction of Triazidochromium(III) by Excess Vanadium(II) and Chromium(II). The $Cr(N_3)_3$ solutions were obtained by an ion-exchange procedure that retained all cationic species other than H^+ present in an equilibrated chromium(III)–azide solution (excess HN_3 and N_3^- were removed just prior to use). The absence of detectable $Cr(N_3)_4^-$ impurity was demonstrated by lack of retention on an anion-exchange column. The reaction of $Cr(N_3)_3$ with excess V^{2+} obeyed pseudo-first-order kinetics, and drawing inference from the CrN_3^{2+} and *cis*-$Cr(N_3)_2^+$ systems, we assume reaction 10 is responsible for the absorbance changes. Values of the apparent

Table VIII. Kinetic Results for the V(II) and Cr(II) Reactions with Triazidochromium(III)

T, °C	k_6,[a] $M^{-1}\,s^{-1}$	k_7,[b] $M^{-1}\,s^{-1}$	T, °C	k_6,[a] $M^{-1}\,s^{-1}$	k_7,[b] $M^{-1}\,s^{-1}$
20.0	7.59 ± 0.05		12.2	3.20 ± 0.02[c]	
12.2	3.94 ± 0.02	136 ± 6	4.8	1.92 ± 0.03	112 ± 7

[a] $[H^+] = 0.960$ M, $I = 0.968$ M, $[Cr(N_3)_3]_0 =$ ca. 4.0×10^{-5} M, and $[V^{2+}]_0 =$ ca. 3.4×10^{-3} M unless otherwise indicated. Uncertainties are average deviations of two or three determinations. [b] $[H^+] = 0.960$ M, $I = 0.969$ M, $[Cr(N_3)_3]_0 = (2.74\text{–}4.04) \times 10^{-5}$ M, and $[Cr^{2+}]_0 = (1.70\text{–}3.88) \times 10^{-4}$ M. [c] $[H^+] = 0.212$ M.

$$Cr(N_3)_3 + V^{2+} \underset{k_6}{\overset{H^+}{=}} VN_3{}^{2+} + 2HN_3 + Cr^{2+} \tag{10}$$

second-order rate constant k_6 are presented in Table VIII. The oxidant solutions presumably contain a mixture of *fac–mer* isomers, but we cannot detect any kinetic evidence for this. The limited data do suggest the presence of a protonated pathway.

The reduction of $Cr(N_3)_3$ by Cr^{2+} is consistent with reaction 11. The values of the rate parameter k_7, listed in Table VIII,

$$Cr(N_3)_3 + Cr^{2+} \underset{k_7}{\overset{H^+}{=}} cis\text{-}Cr(N_3)_2{}^+ + HN_3 + Cr^{2+} \tag{11}$$

are rather imprecise for two reasons. First, the observed absorbance change was small due to similar spectral properties of $Cr(N_3)_3$ and *cis*-$Cr(N_3)_2{}^+$. Second, the infinite absorbance reading (A_∞) was somewhat uncertain due to the onset of the *cis*-$Cr(N_3)_2{}^+$–Cr^{2+} reaction. This latter problem led to allowing A_∞ to be an adjustable parameter in the computer analysis. The agreement between the calculated and estimated values was satisfactory and is consistent with the stoichiometry shown in eq 11.

Discussion

Reduction of Azidochromium(III) by Excess Vanadium(II). Reaction Scheme I is consistent with the data presented. In the absence of added Cr^{2+}, reaction 13, the reverse of reaction 12, must be negligible to account for the pseudo-first-order kinetics. The nearly quantitative production of $CrNH_3{}^{3+}$ in the stoichiometry studies requires that the Cr^{2+} produced in step 12 compete very favorably with V^{2+} for the HN_3 produced in step 14. The results of Linck[1g] give $k_{Cr} = 625k_V$ at 25 °C and also establish the stoichiometric production of $CrNH_3{}^{3+}$ in the HN_3–Cr^{2+} reaction. The kinetic experiments utilized large excesses of V^{2+}; under these conditions the yield of $CrNH_3{}^{3+}$ is presumably diminished. The reactions occurring after step 14 do not affect the present kinetic results.

Scheme I

$$CrN_3{}^{2+} + V^{2+} \overset{k_1}{=} Cr^{2+} + VN_3{}^{2+} \tag{12}$$

$$VN_3{}^{2+} + Cr^{2+} \overset{k_2}{=} V^{2+} + CrN_3{}^{2+} \tag{13}$$

$$VN_3{}^{2+} + H^+ \overset{k_3}{=} V^{3+} + HN_3 \tag{14}$$

The justification for the mechanistic features implied by Scheme I lies largely on the kinetic results with added Cr^{2+}. The scheme requires that competition between Cr^{2+} reduction and aquation of the $VN_3{}^{2+}$ intermediate occur. The kinetic parameters for reaction 14 have been determined independently by Espenson and Pladziewicz.[6] Equation 15 can be

$$\begin{aligned}(-d[CrN_3{}^{2+}]/dt)/[CrN_3{}^{2+}][V^{2+}] &= k^1 \\ &= k_1/\{[k_2[Cr^{2+}]_0/(a + b[H^+])] + 1\}\end{aligned} \tag{15}$$

derived using their results and applying the steady-state approximation for the $VN_3{}^{2+}$ intermediate. This expression is equivalent to the empirical eq 6 and identifies the parameters $B(5)$ and $B(6)$ as k_1 and k_2, respectively.

The $B(4)$ parameter in eq 5 was determined to be 6.25 ± 0.29 M^{-1} at 20.0 °C and $I = 0.97$ M. This parameter is equal to b/a according to Scheme I; Espenson and Pladziewicz[6] reported a value of 8.0 M^{-1} under the same experimental conditions. We consider this agreement satisfactory in view of the indirectness of the present results and the experimental difficulties encountered in the direct studies.

Values of $\Delta H^* = 3.85 \pm 0.20$ kcal/mol and $\Delta S^* = -27.3 \pm 0.7$ cal/(deg mol) were determined at 25 °C for the net activation process 16, by use of expression 17[23] where $\Delta H^* = \Delta E - RT$. This system would be very difficult to study directly.

$$VN_3{}^{2+} + Cr^{2+} = [VN_3Cr^{4+}]^{\pm} \tag{16}$$

$$k = (ekT/h)\exp(-\Delta E/RT)\exp(\Delta S^*/R) \tag{17}$$

The present data allow a determination of the equilibrium constant for the process

$$CrN_3{}^{2+} + V^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} VN_3{}^{2+} + Cr^{2+} \tag{18}$$

The calculated value is 2.2×10^{-4} at 20.0 °C. In spite of this unfavorable equilibrium constant, the reaction is driven to completion in our studies both by the excess V^{2+} and by the essentially irreversible aquation of $VN_3{}^{2+}$. It should be noted that the system is one of the few nonisotopic exchange reactions where the initial inner-sphere attack is reversible.

It is surprising to us that the reaction proceeds by reduction of the chromium(III) center rather than direct reduction of the azide ligand. Apparently the bridging ability of the azide group is the deciding factor in this system.

Values of $\Delta H^* = 12.9 \pm 0.5$ kcal/mol and $\Delta S^* = -13.0 \pm 1.7$ cal/(deg mol) were calculated for the net activation process

$$CrN_3{}^{2+} + V^{2+} = [CrN_3V^{4+}]^{\pm} \tag{19}$$

These results furnish additional support for the proposed reaction scheme. The values of the activation parameters are characteristic of substitution-limited inner-sphere reactions of vanadium(II),[24-26] a feature that is consistent with reaction 12.

An intermediate identified as $VN_3{}^{2+}$ has been observed in the *cis*-$(en)_2Co(N_3)_2{}^+$–V^{2+} and $(NH_3)_5CoN_3{}^{2+}$–V^{2+} systems.[5,27] Stopped-flow instrumentation was used with a large initial $[V^{2+}]$ and low $[H^+]$ to maximize the nonequilibrium production of the intermediate. The same procedure should be applicable to the present reactions, but there are complications. First, the value of the rate parameter for the V^{2+} reduction of $CrN_3{}^{2+}$ is lower than those for the cobalt(III) complexes, resulting in lower $[VN_3{}^{2+}]$. Second, in order to generate detectable concentrations of the intermediate, larger $[CrN_3{}^{2+}]$ are required than utilized in the conventional kinetic studies. Unfortunately, larger $[Cr^{2+}]$ are produced concomitantly with $VN_3{}^{2+}$, resulting in several competing reactions as listed in Scheme I. Nevertheless, direct observation of an intermediate in these reactions would increase confidence in the conclusions drawn from indirect studies.

The experimental conditions for the $CrN_3{}^{2+}$–V^{2+} reaction were $[CrN_3{}^{2+}]_0 = 5.60 \times 10^{-4}$ M, $[V^{2+}]_0 = 0.109$ M, $[H^+] = 0.20$ M, $I = 1.0$ M ($LiClO_4$, $Zn(ClO_4)_2$), $T = 20.0$ °C, and λ 3550 Å (an absorption maximum for $VN_3{}^{2+}$, with ε 1.9×10^3).[6] If only reactions 12 and 14 are operative, the calculated maximum $[VN_3{}^{2+}]$ is 1.83×10^{-5} M (occurring at 0.50 s); the observed value was 1.76×10^{-5} M at 0.60 s. The calculated rate of the VN_3^{2+}–Cr^{2+} reaction (eq 13) is ca. 10% that of reaction 14 at 0.50 s.

A rough estimate of the formation constant of CrN_3^{2+} can be made using expression 20, where K_1 is the formation

$$K_f = [H^+][CrN_3^{2+}]/([HN_3][Cr^{3+}]) = K_1/(K_2K_{18}) \qquad (20)$$

constant of VN_3^{2+} (0.0155 at 25 °C, I = 1.0 M),[6] K_2 is the equilibrium constant for the Cr^{2+}–V^{3+} reaction (506 at 25 °C, I = 1.0 M, using standard electrode potentials[28]), and K_{18} is the equilibrium constant for process 18 (3.00×10^{-4} at 25 °C, I = 0.97 M). The calculated value of K_f is 0.10, a value intermediate between that reported for VN_3^{2+} and FeN_3^{2+} (0.51).[29] This trend is consistent with previous rationalizations.[6,30]

Available data suggest that the sulfur-bonded thiocyanato complexes frequently react faster with a common reductant than the corresponding azido complex.[31] This is the case also when the $CrSCN^{2+}$–V^{2+} system (k = 8.0 M^{-1} s^{-1} at 25 °C, I = 1.0 M, for the hydrogen ion independent path[32]) is compared with the CrN_3^{2+}–V^{2+} reaction (k = 3.2 M^{-1} s^{-1} at 25 °C, I = 1.0 M).

Reduction of *cis*-Diazidochromium(III) by Excess Vanadium(II). Since the CrN_3^{2+}–V^{2+} reaction was concluded to proceed via an inner-sphere path with reduction of the chromium(III) center, we will assume the same mechanistic feature for the *cis*-$Cr(N_3)_2^+$–V^{2+} system. This assumption is fortified by the temperature-dependence data. Values of ΔH^* = 12.4 ± 0.5 kcal/mol and ΔS^* = −12.9 ± 1.6 cal/(deg mol) were determined for the net activation process

$$cis\text{-}Cr(N_3)_2^+ + V^{2+} = [Cr(N_3)_2V^{3+}]^{\pm} \qquad (21)$$

These values are again characteristic of a substitution-limited inner-sphere reaction of V^{2+},[24-26] as was the case for the CrN_3^{2+}–V^{2+} system.

The question arises as to whether a single- or double-bridging mechanism is operative. The first demonstration of a double-bridging mechanism empolyed the *cis*-$Cr(N_3)_2^+$–Cr^{2+} system,[11] although it was later found that this reaction also proceeds by a slower single-bridging path leading to net chemical change.[9] The *cis*-$Co(en)_2(N_3)_2^+$–V^{2+} reaction has been demonstrated to proceed with formation of an azidovanadium(III) intermediate, although a double-bridging mechanism could not be ruled out.[5,27] In the present study, there is a method available to test the single-bridging mechanism (Scheme II), where again Cr^{2+} is added to the reaction solution.

Scheme II

$$cis\text{-}Cr(N_3)_2^+ + V^{2+} \overset{k_4}{=} VN_3^{2+} + Cr^{2+} + N_3^- \qquad (22)$$

$$VN_3^{2+} + Cr^{2+} \overset{k_2}{=} CrN_3^{2+} + V^{2+} \qquad (23)$$

$$VN_3^{2+} + H^+ \overset{k_3}{=} V^{3+} + HN_3 \qquad (24)$$

$$CrN_3^{2+} + V^{2+} \overset{k_1}{=} VN_3^{2+} + Cr^{2+} \qquad (25)$$

$$cis\text{-}Cr(N_3)_2^+ + Cr^{2+} \overset{k_5}{=} CrN_3^{2+} + Cr^{2+} + N_3^- \qquad (26)$$

A double-bridging mechanism would produce a *cis*-$V(N_3)_2^+$ intermediate in the first step. If this intermediate only aquates to VN_3^{2+}, then the present method will not distinguish between the two pathways. However, in the presence of added Cr^{2+} reaction 27 would be very likely to compete for *cis*-$V(N_3)_2^+$.

$$cis\text{-}V(N_3)_2^+ + Cr^{2+} = cis\text{-}Cr(N_3)_2^+ + V^{2+} \qquad (27)$$

The consequence of this reaction would be different kinetic behavior than predicted by Scheme II. Aside from the results of the CrN_3^{2+}–V^{2+} reaction, support for the occurrence of reaction 27 *if* a double-bridging mechanism were operative comes from a consideration of the chromium(III) system. The double bridging reaction between *cis*-$Cr(N_3)_2^+$ and Cr^{2+} is considerably faster (ca. 46 times) than the single-bridging reaction of CrN_3^{2+} and Cr^{2+}.[11] The relevant data necessary to compare the aquation rates of *cis*-$Cr(N_3)_2^+$ and CrN_3^{2+} are not available, but a factor of ca. 49 is observed for the corresponding chloride system.[33]

The treatment of the kinetic data to test the single-bridging Scheme II is outlined in the Experimental Section, and the results are summarized in Tables V and VI. We consider the agreement between the calculated and observed absorbances (±0.002 in Experiment 31 and ±0.006 in Experiment 33) to be satisfactory in view of the complexity of the system and the large number of rate parameters used. The reactions were monitored until virtual depletion of the cis complex. During this time the $[CrN_3^{2+}]$ builds up to a maximum and then decreases. This maximum concentration is larger in Experiment 33 with a greater $[Cr^{2+}]_0$ due to the increased importance of reactions 23 and 26.

It is important to note that none of the terms in eq A–E (see Experimental Section) can be neglected. An indication of the sensitivity of the calculated absorbances to the values of the rate constants was made by repeating the calculations with the imput rate parameters varied individually ±5%. The range of ΔA_{calcd} was 0.001–0.007 and 0.001–0.013 absorbance units for Experiments 31 and 33, respectively. This sets a reasonable although arbitrary error limit, and the fit of the data is nearly within this range.

We conclude that the data are consistent with a single-bridging mechanism. Another point to consider is that the rate of the *cis*-$Cr(N_3)_2^+$–V^{2+} reaction is limited by substitution on the reductant. It seems unlikely to us that a double-bridging mechanism will be favored in this situation. Although Cr^{2+} attacks *cis*-$Cr(N_3)_2^+$ more rapidly via the double bridge,[9] the rate of electron transfer is most certainly not limited by substitution on the reductant.[34]

Price and Taube[24] have established that the $(NH_3)_5Co(C_2O_4)^+$–V^{2+} reaction proceeds by an inner-sphere mechanism at a rate probably limited by substitution on V^{2+}. However, chelation in the activated complex was not demonstrated, and it is possible that a single-bridge mechanism is operative, with ring closure occurring after the electron-transfer reaction.

An intermediate was detected in the *cis*-$Cr(N_3)_2^+$–V^{2+} reaction. The experimental conditions were $[cis\text{-}Cr(N_3)_2^+]_0$ = 6.08×10^{-4} M, $[V^{2+}]_0$ = 0.109 M, $[H^+]$ = 0.20 M, I = 1.0 M, T = 20.0 °C, and λ 3550 Å. If only reactions 22 and 24 were operative, the calculated maximum $[VN_3^{2+}]$ is 4.39×10^{-5} M at 0.41 s; the observed value was 3.52×10^{-5} at 0.40 s. The calculated rate of reaction 23 is ca. 19% that of reaction 24 at 0.41 s.

The rate constants k_1 and k_4 illustrate a similarity that has been ascribed to a quenching of nonbridging ligand effects by substitution-limited reactions of V^{2+},[5] although in the present comparison the cis nonbridging ligand effects of water and azide ion are probably not very different.[9] This rate comparison is complicated by a difference in ΔZ^2 for processes 19 and 21. However, the effect of ionic strength on both rate parameters was consistent with the extended form of the Debye–Hückel equation. Therefore, the ratio k_4/k_1 can be calculated at any ionic strength of interest. At 20 °C the ratio k_4/k_1 is 7.72, 2.58, and 1.00 at I = 0, 0.97, and 8.7 M ($LiClO_4$), respectively.

Reduction of Triazidochromium(III) by Vanadium(II) and Chromium(II). Values of ΔH^* = 14.1 ± 0.4 kcal/mol and ΔS^* = −6.5 ± 1.4 cal/(deg mol) were calculated for the net activation process

$$Cr(N_3)_3 + V^{2+} = [Cr(N_3)_3V^{2+}]^{\pm} \qquad (28)$$

These values are marginally consistent with a substitution-limited rate on V^{2+} for this reaction also.[24-26]

The $Cr(N_3)_3$–Cr^{2+} reaction appears to proceed by a double-bridged activated complex, with a second-order rate constant of ca. 98 $M^{-1}\ s^{-1}$ at 0 °C. The value of the rate constant for the double-bridge pathway in the isotopic exchange reaction between *cis*-$Cr(N_3)_2^+$ and Cr^{2+} is 60 $M^{-1}\ s^{-1}$ at 0 °C.[11] Thus, the two double-bridged reactions proceed with similar rates, as do the single-bridged pathways[9] in the Cr^{2+} reactions with CrN_3^{2+} and *cis*-$Cr(N_3)_2^+$. Again, this feature can be interpreted as an indication of similar cis nonbridging ligand effects of azide and water. The same feature is illustrated in the single-bridging rates of the V^{2+} reductions of the azidochromium(III) complexes, although these systems appear to be limited by substitution on V^{2+}.

Registry No. $(H_2O)_5CrN_3^{2+}$, 18517-09-4; *cis*-$(H_2O)_4Cr(N_3)_2^+$, 53023-12-4; $(H_2O)_3Cr(N_3)_3$, 58512-47-3; $(H_2O)_5VN_3^{2+}$, 58512-48-4; Cr, 7440-47-3; V, 7440-62-2.

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Partial Photoresolution. V. Substituted β-Diketonate Complexes of Chromium(III)[1,2]

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Received October 26, 1975 AIC507662

The partial photoresolution at 5461 Å in chlorobenzene solution of tris-chelate complexes of chromium(III) with propanedialato, 1,3-diphenylpropanedionato, 3-chloro-2,4-pentanedionato, 3-bromo-2,4-pentanedionato, 3-iodo-2,4-pentanedionato, and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato ligands is reported. The quantum yield results are very similar to those obtained previously for tris(2,4-pentanedionato)chromium(III), except in the cases of tris(propanedialato)chromium(III), and tris(1,3-diphenylpropanedionato)chromium(III), which have quantum yields 3 times and 0.03 times that for $Cr(acac)_3$, respectively. The circular dichroism spectra for these compounds are reported. Only the hexafluoro diketonate exhibited any noticeable thermal racemization at 34 °C.

Introduction

The partial resolution of a number of the β-diketonate–chromium(III) complexes has been reported using gas chromatography[3] and liquid chromatography.[4,5] The use of circularly polarized light as a partial resolving agent has been employed for several Cr complexes in aqueous solution[2a,b,6-8] as well as for β-diketonate complexes[2c,d,9] in organic solvents. An advantage of the latter technique is that the degree of resolution at the photostationary state is the result of the dissymmetry factor, $(\epsilon_l - \epsilon_r)/\epsilon$, at the irradiating wavelength, and hence the molar circular dichroism spectra can be obtained from a partially resolved system. This is particularly useful for determining CD spectra of compounds which are not charged and are therefore difficult to resolve chemically.

In addition, if the photokinetics are studied, the quantum yields for photolytic inversion of enantiomers are obtained. The two previous papers on $Cr(acac)_3$[2c] and $Cr(tfa)_3$[2d] have established that the quantum efficiency of photolytic inversion is essentially wavelength independent and slightly temperature and solvent dependent and that the mechanisms for inversion include both twisting and bond-rupture processes.

The purpose of this report is to determine what effects substituent groups on the β-diketone ligand have on optical activity and quantum efficiency parameters. Accordingly, Table II lists those complexes which have been subjected to photoresolution attempts as reported in this paper and the two preceding articles.[2c,d]

Experimental Section

Most of the compounds were prepared according to the established procedures referred to in Table I. The percentage compositions of the purified samples are also given in this table. $Cr(hfa)_3$ was obtained from Apache Chemicals, Seward, Ill., and was purified by recrystallization from CCl_4.

Solutions of the desired concentrations were prepared in reagent grade chlorobenzene. Irradiations in circularly polarized light at 5461 Å were carried out in an optical system described previously.[2] Both