the other hand, the magnitude of K_3 for this system (0.85 at 50°) is only greater by a factor of about 6 than the theoretical value.[24] This is the same order of magnitude as exists between the comparable observed and calculated association constant values for the $Co(en)_2(H_2O)_2^{3+}$–$HC_2O_4^-$ system, as was indicated above.

The experiments listed in Table II show that k_0 is only moderately sensitive to ionic strength, as was found for the corresponding rate constant for water dissociation from the $Cr(C_2O_4)_2(H_2O)_2^-$ ion.[6] In fact, a plot of the variation of k_0 with ionic strength (Figure 3) resembles very closely the similar plot (Figure 6) in ref 6. It is observed that an essentially linear relationship occurs in both instances. The change in k_0 is approximately a factor of 4 in going from $I = 0$ to $I = 3$ in both sets of data in this work and in the chromioxalate study. There is no clear-cut evidence, either in this or in the previous study,[6] that the inert-salt influence is other than a nonspecific ionic strength effect, for which there is no suitable theoretical interpretation under the conditions of the studies. However, it is also reasonable to conceive of the nonsubstituting nitrate ion as facilitating metal ion–water ligand bond fission through specific attack on the coordinated water molecule which is not associated with oxalate. Consequent labilization of this water would catalyze the entry of the free end of the oxalate, as conceived for the oxalate substitution mechanism above. Such a concept would require a linear relationship between rate constant and nitrate concentration which is also evident from Figure 3.[25]

The preliminary study of the reaction in solutions of low acidity gave results which are within expectation. The pK for the first acid dissociation of $Co(en)_2(H_2O)_2^{3+}$ is about 5.8.[12] Thus, at pH 5.5, a large fraction of the complex is in the form $Co(en)_2(H_2O)(OH)^{2+}$. Water exchange with this ion is some 60 times more rapid than with the diaquo species,[20] undoubtedly owing to the well-known labilizing influence of hydroxide adjacent to the water ligand. The tendency in this case will therefore be for a reaction scheme of the form[26]

$$Co(en)_2(H_2O)(OH)^{2+}\cdot C_2O_4^{2-} \xrightarrow{k_0} Co(en)_2(OH)(C_2O_4) + H_2O \quad (11)$$

$$Co(en)_2(OH)(C_2O_4) \xrightarrow{k_1} Co(en)_2C_2O_4^{2+} + OH^- \quad (12)$$

Since in general hydroxide is a difficult ligand to dislodge as compared to water, k_1 should share the rate determination with k_0, and $Co(en)_2(OH)(C_2O_4)$ must appear as an intermediate.[27] The spectrum observed for the intermediate supports this view in that it differs little from the spectrum of the related monodentate oxalato complex, $Co(NH_3)_5C_2O_4$, as shown in Figure 1.[28]

Acknowledgment. Support of this research through Contract No. AR(30-1)-1578 with the U. S. Atomic Energy Commission is gratefully acknowledged.

(24) Using the equations of ref 17, one calculates $K_3 = 0.15$ at 50°, assuming $a = 6$ Å.

(25) The contribution to the ionic strength made by compounds other than nitrates is only 0.02 M, so $I \simeq$ (nitrate).

(26) Since the pK of $HC_2O_4^-$ is 4.3,[16] nearly all of the oxalate will be in the form of $C_2O_4^{2-}$ at pH 5.5. This should associate strongly with $Co(en)_2(H_2O)(OH)^{2+}$, to produce the reactive ion pair of reaction 11, with an equilibrium constant perhaps in excess of 100.

(27) This intermediate has been invoked[5] in explaining the kinetics of the base hydrolysis of $Co(en)_2C_2O_4^+$. Unfortunately, no conclusions concerning its rate of further hydrolysis under the conditions of the present study can be derived from the data of the earlier work. It is perhaps of interest, however, that the pseudo-first-order rate constant at 71° for base hydrolysis of $Co(en)_2C_2O_4^+$ at unit (OH^-) is 3×10^{-2} sec^{-1}, not drastically divergent from that for $HC_2O_4^-$ attack on $Co(en)_2(H_2O)_2^{3+}$ at unit concentration of the oxalate ion, $\sim 2 \times 10^{-3}$ sec^{-1}. (This is predicted by assuming pH $\sim$3, where $HC_2O_4^-$ is the predominant oxalate species. Then, as seen from eq 4, $k = k_0$, and k_0 is easily extrapolated to 71° from the data of Table III.) Similarity between these rate constants should occur if cobalt–oxygen bond fission is the rate-limiting process in both instances (to bioxalate in one case and to water in the other).

(28) The spectrum is as given in ref 13. Data obtained by these authors on the reaction of $Co(NH_3)_4(H_2O)_2^{3+}$ ion with oxalic acid at 25° and pH $\sim$3 suggest the formation of an intermediate of the type $Co(NH_3)_4(OH_2)(C_2O_4)^+$, with ring closure becoming observable at higher temperatures.

Contribution from the Department of Chemistry, Argonne National Laboratory, Argonne, Illinois

A Kinetic Study of the Reduction of Cobalt(III) by Hydrazoic Acid in Aqueous Perchlorate Media[1]

By R. Kent Murmann,[2] James C. Sullivan, and R. C. Thompson[2]

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The reaction of Co(III) with HN_3 in acid perchlorate media yields primarily, if not solely, Co(II) and N_2. The empirical form of the rate law is: $-d[Co(III)]/dt = k'[HN_3][Co(III)]$, where $\log k' = n \log [H^+] + \text{constant}$. At 25°, $\mu = 2.0$ ($LiClO_4$), $n = -0.973 \pm 0.026$, and $k' = 17.5 \pm 2$ M^{-1} sec^{-1} at 2.00 M $HClO_4$. The apparent activation energy of k' is 25.4 kcal/mol. The results of ^{15}N tracer studies are: $Co(III) + HN^*\text{-}N\text{-}N^* \rightarrow N^*\text{-}N + 0.5N^*\text{-}N^* + Co(II) + H^+$. Plausible mechanisms for this reaction are discussed.

The variety of products that result when HN_3 is oxidized by metal ions in aqueous solutions reaffirms the statement by Audrieth:[3] "From whatever point of view hydrazoic acid be considered, it is bound to excite and stimulate curiosity, if not wonderment and amazement."

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Department of Chemistry, University of Missouri, Columbia, Mo. 65201.

(3) L. F. Audrieth, *Chem. Rev.*, **15**, 169 (1934).

The only 1-equiv oxidant previously described that reacts with HN_3 to produce the stoichiometric quantity of N_2 is Ce(IV). In this communication we present evidence for the stoichiometry of the reaction

$$\mathrm{Co(III)} + \mathrm{HN_3} \longrightarrow \mathrm{Co(II)} + 1.5\mathrm{N_2} + \mathrm{H^+} \quad (1)$$

and a detailed study of its kinetics. The isotopic composition of the product N_2 has been determined from redox reactions with the labeled $^{15}N-N-^{15}N^-$ ion.

The primary concern that motivated this study was to provide a basis for the comparative redox kinetic behavior when the azide ion is associated with cations other than hydrogen. To this end stoichiometric and kinetic studies of the reaction between $Co(NH_3)_5N_3^{2+}$ and Co(III) are in progress.

Experimental Section

Reagents.—The preparation and standardization of the perchloric acid, lithium perchlorate, and cobaltous and cobaltic perchlorates have been described in a previous publication.[4] Commercial NaN_3 was recrystallized twice using previously described procedures.[5] This was followed by a recrystallization form triply distilled water and the final product was dried in a vacuum oven at *ca.* 100° for several hours. A second source of NaN_3 was prepared by the same method as to be described for the isotopically labeled compound. Solutions of NaN_3 were analyzed by the cerate procedure.[6]

The sodium azide, $Na^{15}N-N-^{15}N$, was prepared from potassium nitrate (98.5% ^{15}N) by the methods of Maimind and Thiele as outlined by Herber.[7] Analysis for the ^{15}N content in the center and terminal atoms was carried out by reaction with nitrite ion at a pH of 3.0–3.5. In this reaction

$$\mathrm{H^+} + {}^{15}\mathrm{N{-}N{-}}^{15}\mathrm{N^-} + \mathrm{NO_2^-} \longrightarrow {}^{15}\mathrm{N{-}N} + {}^{15}\mathrm{N{-}N{-}O} + \mathrm{OH^-} \quad (2)$$

The N_2 and N_2O produced were separated, purified, and analyzed for ^{15}N content using a Nuclide RMS-16 mass spectrometer. Since the enrichments were high, the *m/e* 28, 29, 30, 44, 45, and 46 peaks were scanned repeatedly rather than using the dual collector system. Two preparations of enriched NaN_3 were used and both had the same ^{15}N enrichment within the precision of the measurements. Analysis for ^{15}N content using N_2 compared well with that obtained using N_2O. The latter values were used to eliminate the possibility of low values from atmospheric nitrogen contamination.

Procedures.—Aliquots of the standardized NaN_3 solutions were pipetted into solutions containing excess Co(III). The amount of Co(III) consumed was determined spectrophotometrically at 6020 Å. The previously determined value[4] of $34.5 \pm 0.1\ M^{-1}\ \mathrm{cm}^{-1}$ was used for the molar extinction coefficient of the Co(III).

For the kinetic experiments all of the reagents, except the NaN_3, were pipetted into 2- or 5-cm absorption cells. The cell was placed in the thermostated compartment of a Cary Model 14 MR spectrophotometer and an aliquot of the NaN_3—from a stock solution thermostated at the working temperature—was introduced into the cell. The absorptivity of the Co(III) was recorded as a function of time at 6020 Å, 4020 Å (ϵ 39.6 $\pm$ 0.2 $M^{-1}\ \mathrm{cm}^{-1}$), or 2800 Å. The values for the molar absorptivities at 6020 and 4020 Å were not sensitive to temperature variation over the range covered in this work. The values determined at 2800 Å were $285 \pm 8\ M^{-1}\ \mathrm{cm}^{-1}$ at 25° and $265 \pm 5\ M^{-1}\ \mathrm{cm}^{-1}$ at 10°. The [H^+] of the reaction mixture was determined by titration of an aliquot after completion of the reaction.

The first observation was generally made within 10 sec after mixing and the reaction was followed to $\geq$95% completion. Values reported for k' were obtained by a least-squares adjustment of the data (25–35 OD, *t* data points per experiment) in terms of the functional form previously described.[8]

In the isotope studies the reaction of Ce(IV) or Co(III) with $^{15}N-N-^{15}N^-$ was carried out in a two-tube mixing container which could be evacuated to better than 10^{-5} mm. One tube contained the oxidant in acid solution and the other sodium azide either as a solid or in aqueous solution. The reactant solutions were degassed 4–6 times to remove atmospheric N_2 and then mixed at a temperature of 0–10°. The nitrogen released was collected over liquid air using a Toepler pump and the *m/e* 28, 29, and 30 peaks were measured.

Results

Stoichiometry.—The gaseous product of the reduction of Co(III) and Ce(IV) by azide was found to be solely N_2 (no N_2O, NO, or NO_2) by mass spectrometric analysis. Identical results were obtained with either Co(III) or NaN_3 in excess and for at least two different preparations of each of the reactants.

The ratio of Co(III) consumed/N_3^- consumed = 1.007 $\pm$ 0.010 where the uncertainty is the standard deviation from the mean of five independent determinations using NaN_3 prepared by the first method. With NaN_3 prepared by the second method, a value of 1.002 $\pm$ 0.007 was obtained for this ratio from four independent determinations.

Kinetics.—The observed OD,*t* data points were reproduced by the two parameters associated with the integrated form of the bimolecular rate law to $\leq$0.003 OD unit. The precision indices assigned to the rate parameter k' ranged from 0.3 to 1%. The reproducibility of replicate determinations was between 1 and 6%.

At 5°, [H^+] = 0.25 M (which defines the ionic strength), and the initial concentrations [Co(III)] = $5.4 \times 10^{-3}\ M$ and [NaN_3] = $4.2 \times 10^{-3}\ M$, the average value computed for $k' = 8.80 \pm 0.32\ M^{-1}\ \mathrm{sec}^{-1}$ with the first preparation of the azide salt. The value calculated under the same experimental constraints using the second preparation was $8.66 \pm 0.06\ M^{-1}\ \mathrm{sec}^{-1}$.

At 10°, [H^+] = 0.78 M, μ = 2.0 (maintained with $LiClO_4$), and initial concentrations of Co(III) and NaN_3 as above, values computed for k' ($M^{-1}\ \mathrm{sec}^{-1}$) were 4.25 $\pm$ 0.04 and 4.33 $\pm$ 0.07, when the reaction was followed at 6020 and 4020 Å, respectively. At 17°, [H^+] = 0.52 M, and with ionic strength and initial concentrations of the reactants as above, values computed for k' ($M^{-1}\ \mathrm{sec}^{-1}$) were 18.9 $\pm$ 0.5 and 18.1 $\pm$ 0.1 when the reaction was followed at 6020 and 2800 Å, respectively.

The following comparison demonstrates the invariance of the rate parameter with initial concentrations of Co(II). At 17°, [H^+] = 1.04 M, μ = 2.0, $[\mathrm{Co(III)}]_0 = 6.0 \times 10^{-3}\ M$, and $[\mathrm{NaN_3}]_0 = 4.4 \times 10^{-3}\ M$, values computed for k' ($M^{-1}\ \mathrm{sec}^{-1}$) were 9.62 $\pm$ 0.03 and 9.75 $\pm$ 0.05 for reaction systems with the initial concentrations $[\mathrm{Co(II)}]_0 = 5 \times 10^{-4}$ and $5 \times 10^{-2}\ M$, respectively.

At 5° and with the other experimental conditions as

(4) R. C. Thompson and J. C. Sullivan, *Inorg. Chem.*, **6**, 1795 (1967).
(5) A. W. Browne, *Inorg. Syn.*, **1**, 79 (1939).
(6) J. W. Arnold, *Ind. Eng. Chem.*, **17**, 215 (1945).
(7) R. H. Herber, Ed., "Inorganic Isotopic Synthesis," W. A. Benjamin, Inc., New York, N. Y., p 99, 117.
(8) R. C. Thompson and J. C. Sullivan, *J. Am. Chem. Soc.*, **89**, 1096 (1967).

Table I

$[H^+]$ and Temperature Dependencies of k'[a]

5°		10°		17°		25°	
$[H^+]$, M	k', M^{-1} sec^{-1}	$[H^+]$, M	k', M^{-1} sec^{-1}	$[H^+]$, M	k', M^{-1} sec^{-1}	$[H^+]$, M	k', M^{-1} sec^{-1}
2.00	0.658 ± 0.033	2.00	1.53 ± 0.03	2.00	4.79 ± 0.04	2.00[d]	17.5 ± 0.2
1.76	0.722 ± 0.010	1.76	1.76 ± 0.03	1.78	5.57 ± 0.03	1.78	18.8 ± 0.2
1.52	0.856 ± 0.034	1.53	2.02 ± 0.03	1.55	6.36 ± 0.07	1.53	22.2 ± 0.3
1.26	1.04 ± 0.04	1.27	2.48 ± 0.04	1.29	8.01 ± 0.05	1.26	26.3 ± 0.4
1.01	1.36 ± 0.06	1.02	3.17 ± 0.07	1.09	9.29 ± 0.05	1.13	29.3 ± 0.7
0.756	1.86 ± 0.03	0.781[b]	4.29 ± 0.04	0.779	12.8 ± 0.2	0.874	40.0 ± 0.4
0.512	2.80 ± 0.11	0.764	4.34 ± 0.03	0.519[c]	18.1 ± 0.2	0.518	66.7 ± 3.2
0.254	5.78 ± 0.08	0.509	6.58 ± 0.11	0.261[c]	36.6 ± 0.4		
		0.258	13.2 ± 0.4				

[a] $\mu = 2.00$ (maintained with $LiClO_4$). Each entry is the average of two to five independent observations. Uncertainties are standard deviations from the mean. Measured at 6020 Å unless otherwise noted. Initial concentrations: $[Co(III)]_0 = (6.3–0.89) \times 10^{-3}\ M$ and $[NaN_3]_0 = (5.3–0.67) \times 10^{-3}\ M$. [b] At 4020 Å. [c] At 2800 Å. [d] At 6020 Å; all the other measurements at 25° at 2800 Å.

outlined above at the same temperature, except that the ionic strength was maintained at 2.0, the average value computed for k' was $5.78 \pm 0.08\ M^{-1}$ sec^{-1}. The effect of solution composition variation on the rate parameter is even smaller if we compare the values determined at the same temperature for $[H^+] = 1.03\ M$. At $\mu = 1.03$, $k' = 1.62 \pm 0.04\ M^{-1}$ sec^{-1} while at the same $[H^+]$ and $\mu = 2.00$, $k' = 1.39 \pm 0.06\ M^{-1}$ sec^{-1}. The variation of the rate parameter with change in $[H^+]$ and temperature is summarized in Table I.

Mass Spectrometry.—The isotopic composition that was determined for the N_2O prepared from the reaction of the enriched sodium azide with normal sodium nitrite is presented in Table II.

Table II

Isotopic Composition of N_2O

Prepn	45/44	46/44
1	0.983	<0.0004
2	0.985	<0.0003
2[a]	0.982	<0.0003

[a] The same preparation after an additional recrystallization.

On this instrument the mole fraction of ^{15}N in normal nitrogen is $(3.80 \pm 0.05) \times 10^{-3}$. Assuming the ^{17}O contribution to be negligible, the composition of the azide ion written as an average over the two outer nitrogen atoms can be calculated in the usual fashion. The results of such a computation for the azide ion used in this investigation are

$$N^{15}/_{14} = (\text{fraction } {}^{15}N/\text{fraction } {}^{14}N) = [N^{0.4920}/_{0.5080}\text{—}N^{0.0038}/_{0.9962}\text{—}N^{0.4920}/_{0.5080}]^-$$

The isotopic compositions of the N_2 produced from the oxidation of the labeled azide are given in Table III.

Discussion

The empirical dependence of the rate parameter with variation in hydrogen ion concentration, expressed in the usual manner, is

$$\log k' = \log k - n \log [H^+] \qquad (3)$$

At 5, 10, 17, and 25°, respectively, values computed for n were -1.08 ± 0.02, -1.06 ± 0.01, -0.987 ± 0.016, and -0.973 ± 0.026.[9] The empirical composition of

(9) Values of n were calculated by a least-squares adjustment of 16–21 k',$[H^+]$ data points. Weights were assigned based on the precision indices previously computed for k', after taking cognizance of the functional form equation (eq 3).

Table III

Isotopic Composition of N_2 from the Oxidation of N_3^{*-} (2–4 M H^+)

Oxidant		29/28	30/28
Ce^{4+}		1.146	0.185[a]
		1.149	0.188[b]
	Av	1.148	0.187
Co^{3+}		1.166	0.187[c]
		1.171	0.189[c]
		1.167	0.165[d]
		1.154	0.189[d]
		1.154	0.185[d]
		1.110	0.181[e,f]
		1.166	0.186[c,e]
	Av	1.155 ± 0.021	0.183 ± 0.008

For Co^{3+} av %: 28, 42.77; 29, 49.40; 30, 7.83

[a] Excess Ce^{4+}. [b] Excess N_3^-. [c] Excess Co^{3+}. [d] Excess N_3^-. [e] Recrystallized N_3^-. [f] $[Co^{3+}] = [N_3^-]$.

the activated complex (uncertain as to the number of molecules of water present) is therefore defined as one molecule of Co(III) and one molecule of HN_3[10] with one less than the usual number of hydrogen ions associated with these species.[11]

Values computed for the rate parameter k from a least-squares adjustment of the data in terms of

$$k' = \alpha + (k/[H^+]) \qquad (4)^{12}$$

are 1.48 ± 0.03, 3.45 ± 0.04, 10.0 ± 0.2, and 32.9 ± 1.2 sec^{-1} at 5, 10, 17, and 25°, respectively. At the same temperatures the values of α are -0.91 ± 0.03, -0.20 ± 0.04, -0.010 ± 0.14, and $0.99 \pm 0.66\ M^{-1}$ sec^{-1}, where the uncertainties are the computed standard deviations of the parameters based on external consistency.

The apparent energy of activation calculated from these rate parameters is 25.4 ± 0.3 kcal/mol. The internal consistency of the rate parameter k (sec^{-1}) as calculated from H^+ dependence and from temperature de-

(10) HN_3 is the predominant species in the acid range under consideration. The ionization constant for $HN_3 = H^+ + N_3^-$ is $K = 1.8 \times 10^{-5}\ M$. See W. L. Jolly, "The Inorganic Chemistry of Nitrogen," 1st ed, W. A. Benjamin, Inc., New York, N. Y., 1964, p 62.

(11) This statement is not meant to imply any mechanistic inferences. The empirical hydrogen ion dependence can be accounted for in a formalism that postulates preequilibria of either hydrazoic acid ionization or cobalt(III) hydrolysis.

(12) The parameter α is used in the adjustment of the data to allow for small variations in the pertinent activity coefficient ratios of reactants and the activated complex with change in solution composition.

pendence at 5, 10, 17, and 25°, respectively, is as follows: (1.48 ± 0.03, 1.51), (3.45 ± 0.04, 3.40), (10.0 ± 0.2, 10.1), and (32.9 ± 1.2, 33.1).

A postulated reaction scheme for this system is

$$Co(OH_2)_6^{3+} \underset{}{\overset{K}{\rightleftharpoons}} Co(OH_2)_5OH^{2+} + H^+ \quad (5)$$

$$Co(OH_2)_5OH^{2+} + HN_3 \overset{K'}{\rightleftharpoons} [X^{2+}]^*$$

$$[X^{2+}]^* \xrightarrow{k^0} Co(II) + N_3^0 \quad (6)$$

$$2N_3^0 \longrightarrow 3N_2 \text{ (rapid)} \quad (7)$$

At the acidities used in this investigation, hydrazoic acid is essentially completely associated whereas the hydrolysis (eq 5) occurs to a finite extent. A quantitative value for the extent of this hydrolysis is not unambiguous since values reported for K differ by a factor of *ca.* 10.[13]

A detailed representation of the activated complex is not presented because of a paucity of relevant information. For example, a value of $k \approx 3 \times 10^3$ sec^{-1} has been estimated for the exchange of solvent water with $Co(OH_2)_5OH^{2+}$.[13b] The rate of ligand exchange would therefore not prevent formation of an inner-sphere activated complex. There is, however, no compelling evidence from the other available data, in particular the invariance of the rate constant with wavelength, that would provide a basis for the description of the activated complex as either inner or outer sphere.

The stoichiometry plus the empirical composition of the activated complex, subject to the condition of restraint of integral numbers for the products at the molecular level, necessitates a rapid reaction (or reactions) of nitrogen intermediates after the rate-determining step. A comparison of the isotopic composition of the molecular nitrogen with that calculated on the basis of models provides evidence consistent with the postulated reaction scheme.

For random mixing of all six N atoms to produce the three molecules of N_2, values calculated for the per cent of isotopes 28, 29, and 30 are 44.98, 44.17, and 10.48, respectively. With the ^{15}N-enriched N atoms designated as N*, the per cent of isotopes 28, 29, and 30 calculated for two other combinations are: 2N*–N* + N–N, 50.28, 33.58, and 16.14; 2N*–N + N*–N*, 42.34, 49.45, and 8.21. The experimental composition determined for the product N_2 is in good agreement with that calculated for this last model.

It is of interest to note that, when Ce(IV) is the oxidant, the isotopic composition of the product N_2 is the same as when Co(III) is the oxidant. This is, however, not an invariant result. For example, with the multiequivalent oxidizing agent BrO_3^-, the products are N_2 and N_2O. For reactions carried out in dilute and 1 M $HClO_4$ the compositions determined are: for N_2: 29/28, 0.96; 30/28, <0.004; for N_2O: 45/44, 1.96; 46/44, 0.95. This agrees with values calculated for N*–N and N*–N*–O.

Two postulated reaction schemes that will produce the isotopic composition of the N_2 when Co(III) is the oxidant are: (a) Dissociation of free or metal ion associated N_3^0 to N_2 and a "nitrogen atom." This nitrogen atom may be still associated with the reduced metal ion. The following step is the reaction of two "nitrogen atoms" to produce the third molecule of N_2. (b) The formation of $(N–N–N\cdots N–N–N)^0$ which decomposes into three molecules of N_2.

Unimolecular decomposition of the azide radical is not a highly probable reaction step. The N atom is a reactive species, which has a very short half-life at temperatures above *ca.* −170°[14] and reacts with water to produce N_2O and other species. In addition, if the azide radical is formed in the ground state, the first allowed mode of decomposition is

$$N_3(^2\pi_g) \longrightarrow N(^2D) + N_2(^1\Sigma_g^+) \quad (8)$$

The bond dissociation energy for this process is, however, 62 kcal/mol.

The probability of a reaction path where bond rupture occurs, $Co^{II}N\text{-}N_2$ to produce the $Co^{II}N$ radical, cannot be assessed in thermochemical terms owing to lack of pertinent data.

Evidence consistent with the postulated eq 7 is provided by the following facts. (a) The reaction $2N_3(^2\pi_g) \rightarrow 3N_2(^1\Sigma_g^+)$ is not forbidden by spin conservation rules and is exothermic with $\Delta H = -210$ kcal/mol.[14] (b) In the electrolysis of potassium azide where the azide ion has the isotopic composition $^{14}N–^{15}N–^{14}N^-$, the nitrogen at the anode has the predominant isotopic composition $^{14}N–^{14}N + 2\,^{14}N–^{15}N$.[15] Since the amount of $^{15}N–^{15}N$ was *ca.* 35 times less than the statistical amount (values determined ranged from 0.0 to 0.4%), the authors concluded that a reaction equivalent to (7) could provide a dominant path. (c) In a recent study of the redox reaction between ethylenediaminetetraacetatomanganate(III) and azide[16] the stoichiometry and kinetic results are again consistent with the reaction postulated in eq 7.

Two plausible structures for the N_6 intermediate consistent with the isotopic composition of the nitrogen determined in this study and that by Clusius and Schumacher[15] are a linear pseudo-halogen $(N_3)_2$ type or a six-membered ring structure. In the absence of additional information (such as might be provided by epr studies) a choice cannot be made among these two and other possible structures.

(13) (a) L. H. Sutchiffe and J. R. Weber, *Trans. Faraday Soc.*, **52**, 1225 (1956); $K = 0.0175$ M; (b) T. J. Conocchioli, G. H. Nancollas, and N. Sutin, *Inorg. Chem.*, **5**, 1 (1966); $K = 0.22 \pm 0.05$ M.

(14) P. Gray, *Quart. Rev.* (London), **17**, 441 (1963).

(15) K. Clusius and H. Schumacher, *Helv. Chim. Acta*, **41**, 2264 (1958).

(16) M. A. Suwyn and R. E. Hamm, *Inorg. Chem.*, **6**, 2150 (1967).