

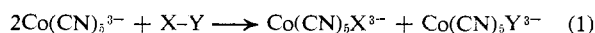
The Reactions of Pentacyanocobaltate(II) with Hydrogen Peroxide, Hydroxylamine, and Cyanogen Iodide¹

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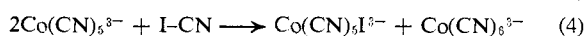
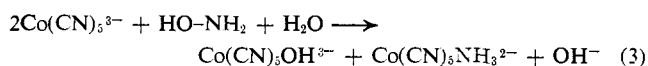
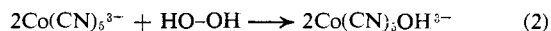
Abstract: The oxidation of pentacyanocobaltate(II) by several molecules, namely hydrogen peroxide, hydroxylamine, and cyanogen iodide, was examined in aqueous solution. The reaction in each case conforms to the stoichiometry $2\text{Co}(\text{CN})_5^{3-} + \text{X}-\text{Y} \rightarrow \text{Co}(\text{CN})_5\text{X}^{3-} + \text{Co}(\text{CN})_5\text{Y}^{3-}$, where $\text{X}-\text{Y} = \text{HO}-\text{OH}$, $\text{HO}-\text{NH}_2$, or $\text{I}-\text{CN}$. Each of the reactions exhibits second-order kinetics according to the rate law $-\text{d}[\text{X}-\text{Y}]/\text{d}t = k[\text{Co}(\text{CN})_5^{3-}][\text{X}-\text{Y}]$. The values of k at 25° ($M^{-1} \text{sec}^{-1}$), of ΔH^\ddagger (kcal/mole), and of ΔS^\ddagger (eu), respectively, were determined to be as follows: for $\text{HO}-\text{OH}$, 7.4×10^2 , 4.2, -31 ; for $\text{HO}-\text{NH}_2$, 5.3×10^{-3} , 10.3, -35 ; for $\text{I}-\text{CN}$, 9.5, 12.7, -12 . The results are interpreted in terms of free-radical mechanisms of the type: $\text{Co}(\text{CN})_5^{3-} + \text{X}-\text{Y} \rightarrow \text{Co}(\text{CN})_5\text{X}^{3-} + \text{Y}\cdot$ (rate determining); $\text{Co}(\text{CN})_5^{3-} + \text{Y}\cdot \rightarrow \text{Co}(\text{CN})_5\text{Y}^{3-}$. Added I^- interferes with the reaction between $\text{Co}(\text{CN})_5^{3-}$ and H_2O_2 by reacting with the OH radical intermediate according to $\text{I}^- + \text{OH}\cdot \rightarrow \text{I}\cdot + \text{OH}^-$, with subsequent capture of the I atom by $\text{Co}(\text{CN})_5^{3-}$ to form $\text{Co}(\text{CN})_5\text{I}^{3-}$. In the presence of added I^- the stoichiometry thus becomes $2\text{Co}(\text{CN})_5^{3-} + \text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{Co}(\text{CN})_5\text{OH}^{3-} + \text{Co}(\text{CN})_5\text{I}^{3-} + \text{OH}^-$.

Among the reactions which pentacyanocobaltate(II) has been reported to undergo are a number of reactions involving the reductive cleavage of covalent molecules, the general stoichiometry of which conforms to eq 1. The molecules which have been shown to react

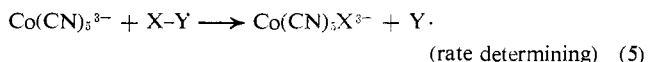


with $\text{Co}(\text{CN})_5^{3-}$ in this way include H_2 ,²⁻⁶ H_2O ,³ Br_2 ,⁷ I_2 ,⁷ $\text{HO}-\text{OH}$,⁸ CH_3-I , and various other organic halides.⁹⁻¹¹

In this paper we describe kinetic studies on several such reactions, namely



In each case the results are interpreted in terms of a free-radical mechanism depicted by eq 5 and 6, analogous to that previously proposed for the reaction of $\text{Co}(\text{CN})_5^{3-}$ with organic halides.^{10,11}



Recently we have also shown¹² that other low-spin cobalt(II) complexes, such as pyridinatosbis(dimethylglyoximate)cobalt(II), react similarly, although more slowly than $\text{Co}(\text{CN})_5^{3-}$, with organic halides.

(1) Support of this work through grants from the National Science Foundation and the Advanced Research Projects Agency is gratefully acknowledged.

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(10) J. Halpern and J. P. Maher, *ibid.*, **87**, 5361 (1965).

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Experimental Section

Materials. Cyanogen iodide (ICN) was prepared by the method of Bak and Hillebert¹³ and recrystallized twice from boiling chloroform. Sodium perchlorate was prepared by neutralizing reagent grade sodium carbonate with perchloric acid, followed by recrystallization twice from distilled water. Hydrogen peroxide, hydroxylamine hydrochloride, sodium and potassium cyanides, potassium chloride, and potassium hydroxide were all AR grade reagents. Distilled water was used for the preparation of all solutions.

Preparation of $\text{K}_2\text{Co}(\text{CN})_5\text{NH}_3$.¹⁴ An authentic sample of this compound, the only product whose spectrum was not already fully characterized, was prepared by adding 50 ml of a 5 M solution of hydroxylamine to 200 ml of a 0.05 M $\text{Co}(\text{CN})_5^{3-}$ solution also containing 0.25 M KCN. Successive concentration of the resulting yellow solution by room temperature evaporation yielded, first, $\text{K}_3\text{Co}(\text{CN})_5$ (2 g), followed by several successive fractions of mixed products. Finally, addition of ethanol to the last 5 ml of residual mother liquor yielded 0.3 g (~10% yield) of the pure product, $\text{K}_2[\text{Co}(\text{CN})_5\text{NH}_3] \cdot 2\text{H}_2\text{O}$. *Anal.* Calcd: C, 18.7; H, 2.2; N, 26.6; Co, 18.4; K, 24.4. Found: C, 18.9; H, 2.0; N, 26.1; Co, 18.3; K, 24.2. An aqueous solution of this compound exhibited the following spectral features: λ_{max} 346 m μ (ϵ_{max} 230); λ_{min} 295 m μ (ϵ_{min} 108).

Kinetic Measurements. The kinetics of each of the reactions were followed spectrophotometrically at a wavelength near the absorption maximum of $\text{Co}(\text{CN})_5^{3-}$ at 967 m μ (ϵ 298). In the case of the reaction with ICN, the rate of formation of the product $\text{Co}(\text{CN})_5\text{I}^{3-}$ (using the peak at 495 m μ (ϵ 117)), as well as of the consumption of $\text{Co}(\text{CN})_5^{3-}$, was measured and good agreement between the two measurements was obtained. The rate measurements on the reaction with NH_2OH were made in a Cary 14 spectrophotometer with a thermostated cell compartment. The reaction vessel was a nitrogen-purged, serum-capped quartz 1-cm spectrophotometer cell into which the reactant solutions were introduced with hypodermic syringes. The reactions with ICN and with H_2O_2 were too fast for conventional measurement, and their rates were therefore measured by the stopped-flow method using the procedure previously described¹¹ for measurement of the rates of reaction of $\text{Co}(\text{CN})_5^{3-}$ with organic halides. The same stopped-flow apparatus as in those experiments was used for the reaction with H_2O_2 , and a Durrum-Gibson stopped-flow spectrophotometer was used for the reaction with ICN. Because of the sensitivity of $\text{Co}(\text{CN})_5^{3-}$ to oxygen, the latter was rigorously excluded during the preparation of solutions and kinetic measurements. Temperature control both in the conventional and stopped-flow experiments was estimated to be better than $\pm 0.3^\circ$.

(13) B. Bak and A. Hillebert, *Org. Syn.*, **32**, 29 (1952).

(14) The formation of $\text{Co}(\text{CN})_5\text{NH}_3^{2-}$ in solution by the reaction $\text{Co}(\text{CN})_5\text{OH}^{3-} + \text{NH}_3 \rightleftharpoons \text{Co}(\text{CN})_5\text{NH}_3^{2-} + \text{H}_2\text{O}$ has previously been described by R. Barca, J. Ellis, M. Tsao, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 243 (1967).

Results and Discussion

Stoichiometry and Products. The stoichiometry for each of the reactions was established spectrophotometrically. In each case the spectrum of the reaction solution measured immediately following completion of the reaction was found to correspond quantitatively to that of the products predicted by eq 2-4, respectively. The spectrum of $\text{Co}(\text{CN})_5\text{NH}_3^{2-}$ needed for this purpose was determined, as described previously, by isolating a pure sample of the potassium salt from the reaction mixture.

Kinetics and Mechanism. At least under certain limiting conditions ($>0.01 M \text{CN}^-$ in the case of the reaction with ICN , and $\text{pH} < 10$ in the case of the reaction with H_2O_2), each of the reactions exhibited simple second-order kinetics, first order in each of the reactants, in accord with the rate law

$$-d[\text{Co}(\text{CN})_5^{3-}]/dt = -2d[\text{XY}]/dt = 2k[\text{Co}(\text{CN})_5^{3-}][\text{X-Y}] \quad (7)$$

where $\text{X-Y} = \text{H}_2\text{O}_2$, HONH_2 , or ICN . Under the conditions of the measurements, *i.e.*, with X-Y always in excess over $\text{Co}(\text{CN})_5^{3-}$, the observed kinetic behavior was pseudo-first order, *i.e.*

$$-d \ln [\text{Co}(\text{CN})_5^{3-}]/dt = k_{\text{obsd}} = 2k[\text{XY}] \quad (8)$$

Values of k_{obsd} were determined from the slopes of

Table I. Summary of Kinetic Data

X-Y	[X-Y], M	Temp, °C	k_{obsd} , sec ⁻¹	k , M ⁻¹ sec ⁻¹
HO-OH ^a	3.1×10^{-3}	25.0	4.44	7.2×10^2
	7.1×10^{-3}	25.0	10.8	7.6×10^2
	3.1×10^{-2}	25.0	47.1	7.5×10^2
	1.7×10^{-2}	14.9	20.0	5.9×10^2
	1.7×10^{-2}	17.9	21.4	6.3×10^2
HO-NH ₂ ^b	1.7×10^{-2}	31.0	30.8	9.1×10^2
	7.1×10^{-2}	25.0	8.6×10^{-4}	6.1×10^{-3} ^c
	1.37×10^{-1}	25.0	1.50×10^{-3}	5.5×10^{-3}
	1.68×10^{-1}	25.0	1.68×10^{-3}	5.0×10^{-3}
	1.91×10^{-1}	25.0	1.96×10^{-3}	5.1×10^{-3}
	2.35×10^{-1}	25.0	2.34×10^{-3}	5.0×10^{-3}
I-CN ^e	7.1×10^{-2}	35.0	1.54×10^{-3}	1.08×10^{-2} ^d
	7.1×10^{-2}	45.0	2.72×10^{-3}	1.91×10^{-2} ^d
	8.0×10^{-4}	25.0	1.7×10^{-2}	10.6
	1.6×10^{-3}	25.0	3.4×10^{-2}	10.6
	3.2×10^{-3}	25.0	5.7×10^{-2}	8.9
	4.8×10^{-3}	25.0	8.0×10^{-2}	8.4
	6.4×10^{-3}	25.0	1.2×10^{-1}	9.4
	7.5×10^{-3}	25.0	1.4×10^{-1}	9.3
	8.0×10^{-3}	25.0	1.5×10^{-1}	9.4
	1.0×10^{-2}	25.0	1.9×10^{-1}	9.5 ^f
	1.0×10^{-2}	15.2	8.7×10^{-2}	4.35
	1.0×10^{-2}	20.0	1.34×10^{-1}	6.7
1.0×10^{-2}	30.0	2.72×10^{-1}	13.6	

^a Conditions for H_2O_2 reactions, unless otherwise specified, are initial $[\text{Co}(\text{CN})_5^{3-}] \sim 5 \times 10^{-4} M$, $[\text{CN}^-] = 0.5$ to $1.5 \times 10^{-2} M$, ionic strength maintained at $0.5 M$ with NaClO_4 . pH dependence of rate is described in Figure 1 and text. ^b Conditions for NH_2OH reactions, unless otherwise specified, are initial $[\text{Co}(\text{CN})_5^{3-}] = 1.5 \times 10^{-3} M$, $\text{pH} \approx 8-9$, $[\text{CN}^-] = 0.1 M$, ionic strength maintained at $0.2 M$ with KCl . ^c This rate was unaffected by varying the pH from 8 to 12 and increased by about 20% when $0.13 M$ excess CN^- was added. ^d At pH 12. ^e Conditions for ICN reactions, unless otherwise specified, are initial $[\text{Co}(\text{CN})_5^{3-}] = 2 \times 10^{-4} M$, $[\text{CN}^-] = 0.1 M$, $[\text{OH}^-] = 5.0 \times 10^{-3} M$, ionic strength maintained at $1.0 M$ with NaClO_4 . ^f Unaffected by varying the initial $[\text{Co}(\text{CN})_5^{3-}]$ from 2×10^{-4} to $1 \times 10^{-3} M$, $[\text{OH}^-]$ from 1×10^{-3} to $8 \times 10^{-3} M$, and $[\text{CN}^-]$ from 0.01 to $0.1 M$. At lower $[\text{CN}^-]$ an increase in rate was noted which is discussed in the text.

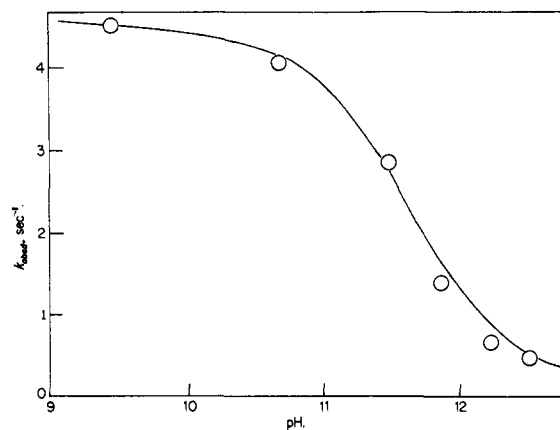


Figure 1. pH dependence of the rate of reaction of $\text{Co}(\text{CN})_5^{3-}$ with $3.08 \times 10^{-3} M \text{H}_2\text{O}_2$. The points represent experimental values of k_{obsd} . The curve is computed on the assumption that only H_2O_2 ($\text{p}K_a = 11.62$), and not HO_2^- , reacts with $\text{Co}(\text{CN})_5^{3-}$.

first-order plots and were generally reproducible to within $\pm 5\%$. These values, together with the values of k derived from them, are listed in Table I.

In addition to establishing the kinetic dependence on $\text{Co}(\text{CN})_5^{3-}$ and X-Y , the effect of the following variables was examined for each of the reactions: (i) temperature, (ii) pH, (iii) CN^- concentration, and (iv) the effect of added I^- on both the stoichiometry and rate of reaction. Under the limiting conditions defined in the last paragraph, no pH dependence or $[\text{CN}^-]$ dependence was observed. The activation parameters determined from the temperature dependence under these conditions (from the data in Table I) are listed in Table II. The dependence on pH and on the CN^-

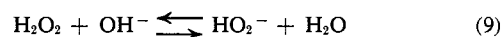
Table II. Summary of Activation Parameters

X-Y	k_{25° , M ⁻¹ sec ⁻¹	ΔH^\ddagger , kcal/mole ^a	ΔS^\ddagger , eu ^b
HO-OH	$(7.4 \pm 0.2) \times 10^2$	4.2	-31
HO-NH ₂	$(5.3 \pm 0.3) \times 10^{-3}$	10.3	-35
I-CN	9.5 ± 0.5	12.7	-12

^a ± 0.5 kcal/mole. ^b ± 2 eu.

concentration, under other conditions, as well as the effects of I^- are discussed separately below for each reaction.

H_2O_2 Reaction. Above pH 10, the rate of reaction of $\text{Co}(\text{CN})_5^{3-}$ with H_2O_2 exhibited an inverse pH dependence which is depicted in Figure 1. Using the $\text{p}K_a$ value¹⁵ of 11.62 for H_2O_2 , this dependence can be quantitatively accounted for in terms of the acid-base equilibrium

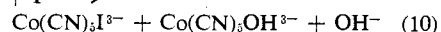


on the assumption that only H_2O_2 (and not HO_2^-) reacts with $\text{Co}(\text{CN})_5^{3-}$. The rate-pH profile, calculated on this basis, is shown in Figure 1 and is seen to be in agreement with the experimental data.

The addition of I^- ($\sim 0.1 M$) had no effect on the rate of reaction between $\text{Co}(\text{CN})_5^{3-}$ and H_2O_2 , but altered

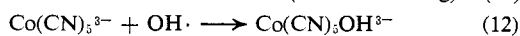
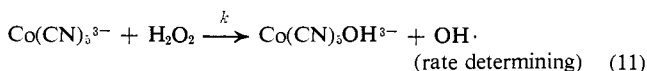
(15) W. L. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1952.

the stoichiometry of the reaction which, under these conditions, was shown spectrophotometrically to conform to eq 10. In this connection it should be noted

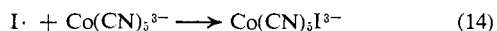
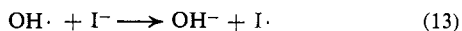


that the reaction between I^- and H_2O_2 to form IOH is slower by at least a factor of 1000 ($k = 0.69 \text{ M}^{-1} \text{ sec}^{-1}$)¹⁶ than the reaction between $\text{Co}(\text{CN})_5^{3-}$ and H_2O_2 . Since I^- and H_2O_2 were contained in the two separate solutions of the stopped-flow experiments, IOH formation occurred only after mixing of the solutions in the stopped-flow chamber and was negligible during the very short duration ($t_{0.5} \approx 0.1 \text{ sec}$) of the reaction between H_2O_2 and $\text{Co}(\text{CN})_5^{3-}$.

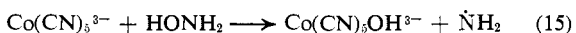
The above observations, particularly those relating to the effect of I^- on the reaction between $\text{Co}(\text{CN})_5^{3-}$ and H_2O_2 , are most readily accommodated by the mechanism depicted by eq 11 and 12, which is analogous to that previously proposed for the reactions of $\text{Co}(\text{CN})_5^{3-}$ with organic halides.



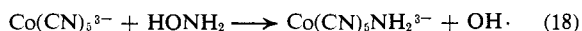
An explanation for the effect of added I^- is provided by reaction 13, which is known¹⁷ to occur in aqueous solution with a rate constant ($1.0 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$) approaching the diffusion-controlled limit. I^- , present in considerably higher concentration than $\text{Co}(\text{CN})_5^{3-}$, thus competes very effectively with the latter for reaction with the intermediate $\text{OH}\cdot$ radicals to form $\text{I}\cdot$ atoms which react rapidly with $\text{Co}(\text{CN})_5^{3-}$ to form $\text{Co}(\text{CN})_5\text{I}^{3-}$ according to eq 14.



HONH₂ Reaction. The second-order kinetics of this reaction imply that the mechanism in this case also is stepwise. The most probable mechanism is considered to be one similar to that advanced for H_2O_2 , *i.e.*



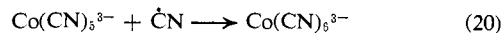
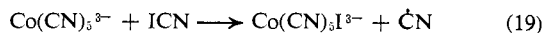
The alternative possibility involving the formation of an $\text{OH}\cdot$ radical in the rate-determining step according to eq 18 appears to be excluded by the absence of any effect of added I^- on the stoichiometry of the reaction. The conclusion that it is not $\text{NH}_2\cdot$, but rather $\text{OH}\cdot$, which is abstracted from HONH_2 by $\text{Co}(\text{CN})_5^{3-}$ is also consistent with our observation that reaction of $\text{Co}(\text{CN})_5^{3-}$ with H_2NNH_2 , if it occurs at all, is much slower than reaction with HONH_2 .



ICN Reaction. For this reaction also, at least under the limiting conditions cited earlier (*i.e.*, $>0.01 \text{ M CN}^-$), where the kinetics were first order each in $\text{Co}(\text{CN})_5^{3-}$ and ICN , and independent of the pH and CN^- concentration, a free-radical mechanism, depicted by eq 19 and 20, analogous to those proposed for the other two reactions appears likely.

(16) H. A. Liebhafsky and A. Mohammed, *J. Am. Chem. Soc.*, **55**, 3977 (1933).

(17) J. K. Thomas, *Trans. Faraday Soc.*, **61**, 702 (1955).



Two further observations concerning this reaction, as yet not fully examined, deserve mention.

1. Below 0.01 M CN^- , the rate of reaction exhibited a pronounced inverse $[\text{CN}^-]$ dependence. One possible explanation, for which there is however as yet no other supporting evidence, is that $\text{Co}(\text{CN})_4^{2-}$, small amounts of which may exist in equilibrium with $\text{Co}(\text{CN})_5^{3-}$ and CN^- , is responsible for the enhanced reactivity at low CN^- concentrations.

2. The addition of I^- resulted in a pronounced increase in the rate of reaction of $\text{Co}(\text{CN})_5^{3-}$. This rate enhancement appears to be associated with one or more additional reaction paths leading to the formation of $\text{Co}(\text{CN})_5\text{I}^{3-}$. Species which may result from the reaction of I^- with ICN , and which may possibly contribute to such additional reaction paths, are I_2CN^- and I_3^- .

Activation Parameters and Kinetic Trends. The reactivities of the three molecules studied toward $\text{Co}(\text{CN})_5^{3-}$ decrease in the order $\text{HOOH} > \text{ICN} > \text{HONH}_2$. The difference in k between HOOH and HONH_2 is about 10^{-5} and is reflected almost entirely in an increase of some 6 kcal/mole in ΔH^\ddagger , the values of ΔS^\ddagger (-31 and -35 eu , respectively) being nearly constant for the two reactions. These values of ΔS^\ddagger are unexpectedly negative for bimolecular reactions in which one of the reactants is a neutral molecule. ΔS^\ddagger ($= -12 \text{ eu}$) for ICN , on the other hand, is in the normal range for such reactions. For comparison, the values of ΔS^\ddagger previously reported¹⁹ for the reaction of $\text{Co}(\text{CN})_5^{3-}$ with neutral organic halides are in the range -20 to -27 eu . No convincing explanation can be offered at this time either for the very negative magnitudes of some of these ΔS^\ddagger values, or for the differences among the values.

For the reactions of $\text{Co}(\text{CN})_5^{3-}$ with organic halides, which have been shown to proceed by analogous mechanisms in which the rate-determining step is the abstraction of a halogen atom by $\text{Co}(\text{CN})_5^{3-}$, reactivity sequences have been observed (*i.e.*, $\text{RI} > \text{RBr} > \text{RCl}$, and $\text{PhCH}_2\text{X} > (\text{CH}_3)_3\text{CX} > (\text{CH}_3)_2\text{CHX} > \text{CH}_3\text{CH}_2\text{X} > \text{CH}_3\text{X}$)^{10,18} which can be correlated with an inverse dependence on the dissociation energy of the carbon-halogen bond. The available data¹⁹⁻²¹ for the bond dissociation energies of HO-OH ($51 \pm 1 \text{ kcal/mole}$), I-CN ($82 \pm 5 \text{ kcal/mole}$),²² and HO-NH_2 ($\sim 65 \text{ kcal/mole}$),²³ while subject to some uncertainty, suggest a similar correlation with the activation energies of the reactions of these molecules with $\text{Co}(\text{CN})_5^{3-}$. Because of differences in ΔS^\ddagger , however, this correlation does not extend to the values of the rate constant k .

(18) P. B. Chock, Ph.D. Dissertation, The University of Chicago, 1968.

(19) "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1964.

(20) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(21) T. L. Cottrell, "The Strength of Chemical Bonds," 2nd ed, Butterworth and Co., Ltd., London, 1958.

(22) This value was estimated from data in ref 19 where the value given for ΔH_f° of $\cdot\text{CN}$ is $111 \pm 5 \text{ kcal/mole}$. Other estimates of this value (see ref 21) are as low as 93 kcal/mole , leading to values of $D(\text{I-CN})$ as low as 64 kcal/mole .

(23) Estimated from data in ref 19 and 20 assuming a value of 10 kcal/mole for the heat of sublimation of solid NH_2OH .