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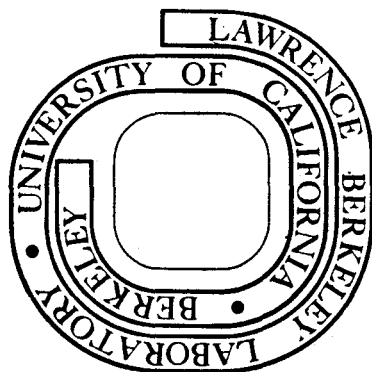
John D. Illige and William L. Jolly

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The Mechanism of the Thermal Decomposition
of Nitrosyl Cyanide

John D. Illige and William L. Jolly*

Since the recent first synthesis of nitrosyl cyanide,^{1,2} several physical chemical studies have been carried out on the compound,²⁻⁴ but relatively little is known about its chemical behavior. In this study we investigated the stoichiometry and mechanism of the spontaneous thermal decomposition of nitrosyl cyanide. The compound undergoes both photochemical and thermal decomposition, but we restricted our study to the thermal decomposition to avoid the complications of mixed reactions and possible photolysis of the products of the thermal reaction.

Experimental

Volatile materials were handled in a glass vacuum line with greaseless stopcocks and a manometer containing mercury under a 5-mm layer of Dow-Corning 704 silicone pump oil. Nitrosyl cyanide was prepared by the reaction of nitrosyl chloride (Matheson) with silver cyanide (J. T. Baker) in a 200-ml glass vessel equipped with a Teflon-covered magnetic stirring bar, a cap with an O-ring seal, and a greaseless stopcock. In a typical run, 6.0 mmol of nitrosyl chloride was condensed onto 1.6 mmol of powdered silver cyanide at -196° ; the closed vessel was then placed in a -45° bath, and stirring was commenced. At 10-min intervals during a total reaction time of 2 hr, the stopcock was briefly opened to allow the vapors in the vessel to condense in a train of traps at -95 , -130 , and -196° . Nitrosyl chloride collected in the -95 and -130° traps, and nitrosyl cyanide collected in the -196° trap. The crude nitrosyl cyanide was purified by fractional sublimation in a thermal gradient column of the type described by Dobson and Schaeffer.⁵ The product (0.9 mmol; 56% yield) was shown to be pure by mass spectrometry and by the analysis effectively provided by the quantitative determination of the decomposition products.

Nitrosyl cyanide with the terminal nitrogen atom labelled with ^{15}N was prepared by essentially the same procedure, using ^{15}N -labelled AgCN . The latter was prepared in a darkroom by adding aqueous KC^{15}N (Bio-Rad Laboratories, Richmond, Calif.) to excess aqueous AgNO_3 , filtering, washing, drying in vacuo, pulverizing, and, finally, vacuum drying at 50° for several hours. A portion of the KC^{15}N used in the synthesis was converted to hydrogen cyanide; mass spectral analysis showed that the nitrogen was 79.5% ^{15}N .

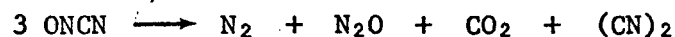
The thermal decompositions were carried out in all-glass vessels with break-seals, having volumes ranging from 75 to 400 ml. After distillation of a known amount of ONCN into a vessel, the vessel was sealed, wrapped in aluminum foil to exclude light, and placed in an oven at 75° . After 10 days the vessel was cooled to -196° , opened to the vacuum line, and the noncondensable gas was Toepler-pumped into a gas buret and measured. Mass spectral analysis generally showed the gas to be essentially pure N_2 ; only small amounts of NO or traces of CO were found. The condensable products were separated by fractional condensation in traps at -130° and -196° . The -130° trap collected cyanogen, which was measured and identified mass spectrometrically. The -196° trap collected N_2O and CO_2 . This mixture of gases and the N_2O remaining after treatment of the mixture with Ascarite (to remove CO_2) were measured; the amount of CO_2 was obtained by difference. Occasionally the $\text{CO}_2/\text{N}_2\text{O}$ ratio was determined from the ratio of the $m/e = 12$ and $m/e = 30$ peak heights in the mass spectrum of the mixture.

The mass spectra were obtained with a Finnigan Instruments quadrupole mass spectrometer. When the data were to be treated quantitatively, peak heights were corrected for background. In the analysis of the products of the decomposition of ^{15}N -labelled ONCN , the distribution of ^{15}N and ^{14}N in the N_2 , N_2O , and $(\text{CN})_2$ was determined directly from the appropriate m/e

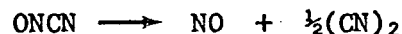
peaks. The heights of the peaks at m/e 30 and 46 ($^{15}\text{N}_2$ and $^{15}\text{N}_2\text{O}$, respectively) were always within experimental error of zero, and were assumed to be exactly zero in the calculations.

Results and Discussion

Preliminary experiments showed that nitrosyl cyanide decomposes at room temperature, but that about 6 weeks are required for complete reaction. All the experiments reported in this Note were carried out in the absence of light at 75° with reaction times of 10 days. These conditions apparently sufficed to give complete reaction, because longer reaction times at 75° did not give significantly different results. The amounts of the gaseous products formed in a series of experiments are listed in Table I. Except in the two highest pressure runs, the total amounts of oxygen, nitrogen, and carbon, calculated from the measured product gases, were in good agreement with the initial amounts of nitrosyl cyanide. The principal products were N_2 , N_2O , CO_2 , and $(\text{CN})_2$, generally formed in equimolar amounts according to the following equation:



In the two lowest pressure runs, a significant amount of NO and an equivalent extra amount of $(\text{CN})_2$ formed. Apparently at low pressures the following side reaction occurs to an important extent.



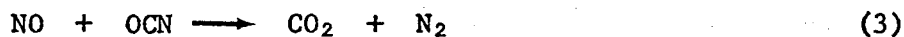
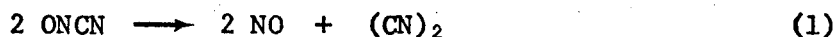
In the studies of the decomposition of ONCN having the terminal nitrogen atom labelled with ^{15}N , the distribution of ^{15}N among the nitrogen-containing products was determined mass spectrometrically. Because the

Table I. Product Yields in Decomposition of Nitrosyl Cyanide

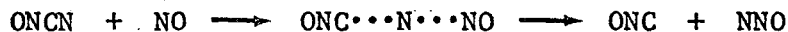
Pressure ONCN, torr	ONCN, mmol	Products, mmol						Fraction of element accounted for in products		
		N ₂	N ₂ O	CO ₂	(CN) ₂	NO	CO	O	N	C
1	0.027	0.008	0.006	0.007	0.010	0.006		.96	1.00	1.00
7	0.021	0.006	0.005	0.006	0.008	0.003		.95	.98	1.05
24	0.0611	0.0207	0.0205	0.0202	0.0201	trace		1.00	1.00	.99
27	0.080	0.029	0.027	0.027	0.027	trace	trace	1.01	1.04	1.01
33	0.098	0.033	0.032	0.032	0.034	trace	trace	.98	1.01	1.02
64	0.173	0.058	0.057	0.058	0.058	----	trace	1.00	1.00	1.01
156	0.464	0.167	0.166	0.165	0.170	----	trace	1.07	1.08	1.09
201	0.598	0.225	0.223	0.218	0.231	----	~0.002	1.11	1.14	1.14

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isotopic purity of our labelled ONCN was only 79.5%, we corrected, using simple probability theory, the observed ^{15}N values to the values corresponding to 100% labelling of the terminal nitrogen of the ONCN. These corrected data are presented in Table II. The data show that most of the labelled nitrogen ends up as the two nitrogen atoms of cyanogen and the terminal nitrogen atom of nitrous oxide. However small amounts of singly-labelled $(\text{CN})_2$ and N_2 form, and the amount of labelled N_2 is always greater than the amount of unlabelled N_2O . The data as a whole can be quantitatively accounted for in terms of two concurrent mechanisms. We propose the following principal mechanism:



Reaction 1 is quite reasonable as the initiation step in view of the very low C-N bond dissociation energy of nitrosyl cyanide. Reaction 2 can be envisaged as taking place in either of two ways. In the first way, the NO molecule essentially plucks off the terminal nitrogen atom from the ONCN molecule to form the fulminate radical, ONC:



This radical has been observed as a short-lived product of the photolysis of ozone-cyanogen mixtures.⁶ We assume that it rapidly rearranges to the more stable cyanate radical, OCN.⁷ When labelled ONCN is used, this first way leads to labelled N_2O and unlabelled OCN. In the second way, the NO and ONCN molecules react by a 4-center process:

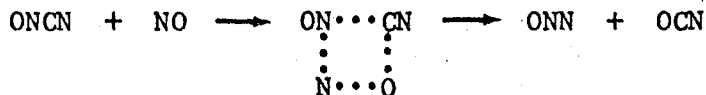


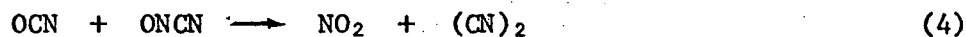
Table II. Distribution of ^{15}N in Each of the N-Containing Products, Calculated on the Basis of 100% Labelling of the Terminal Nitrogen of ONCN

Isotopic Species	Fraction of Compound as the Isotopic Species			
	Run 1	Run 2	Run 3	Run 4
* $\overset{*}{\text{N}}\text{CCN}$	0.85	0.95	0.93	0.93
* $\overset{*}{\text{N}}\text{CCN}$.12	.05	.08	.08
NCCN	.03	.00	-0.01 ^a	-0.01 ^a
* $\overset{*}{\text{N}}\text{N}$.32	.45	.30	.47
NN	.68	.55	.70	.53
* $\overset{*}{\text{N}}\text{NO}$.85	.82	.77	.86
NNO	.15	.18	.23	.14

^aNegative fractions are a consequence of our use of the binomial coefficients in the statistical calculations and our assumption of 79.5% isotopic purity of the ^{15}N .

When labelled ONCN is used, the second way yields unlabelled N_2O and labelled OCN. Reaction 3 is probably a 4-center process. The fact that NO does not abstract the nitrogen atom from OCN, giving CO and N_2O , is probably related to the fact that the latter products are less stable by 87 kcal/mol than the observed products CO_2 and N_2 .⁸

According to the first mechanism, the use of terminally-labelled ONCN should yield only doubly-labelled cyanogen, and the amount of labelled N_2 should equal the amount of unlabelled N_2O . To account for the fact that the observed data deviate from these predictions, we propose that the following mechanism occurs concurrently with, but to a lesser extent than, the first mechanism:



This mechanism consists of three chainpropagating steps, involving the chain carriers NO, OCN, and NO_2 . Reactions 1 and 3 can serve as the chain initiating and terminating steps, respectively, of this mechanism. It should be noted that the first step of the second mechanism (reaction 2) is the same as the second step of the first mechanism. The second step (reaction 4) is probably a 4-center process; it yields singly-labelled $(CN)_2$ when the OCN is unlabelled and the ONCN is labelled. The third step (reaction 5) may occur directly as a complicated multicenter process or may actually be a 2-step process, involving nitryl cyanide as an intermediate.

The fraction of the nitrous oxide which is formed in reaction 2 by the abstraction by nitric oxide of the terminal nitrogen atom of nitrosyl cyanide is equal to the fraction of labelled N_2O formed in the experiments with

labelled nitrosyl cyanide, $f(\overset{*}{\text{NNO}})$. The average value of this quantity in Runs 1-4 was $0.82 \pm .03$. The fraction of the nitrosyl cyanide which decomposed by the first mechanism, f_1 , can be calculated from two independent sets of data:

$$f_1 = f(\text{NN})/f(\overset{*}{\text{NNO}})$$

$$f_1 = [f(\overset{*}{\text{NNO}}) - f(\overset{*}{\text{NCCN}})]/f(\overset{*}{\text{NNO}})$$

The values of f_1 calculated in these ways for each of the four ^{15}N -labelled runs are given in Table III. The values calculated by the two different ways are in good agreement except in the case of runs 2 and 4. In spite of these discrepancies, all the data clearly indicate that the first mechanism (reactions 1-3) predominates in the thermal decomposition.

Acknowledgment

This work was supported by the U. S. Energy Research and Development Administration.

Table III. Fraction of ONCN Decomposed by First Mechanism, Calculated in Two Different Ways

	Run 1	Run 2	Run 3	Run 4
$\frac{f(NN)}{f^*(NNO)}$	0.80	0.67	0.91	0.62
$\frac{f^*(NNO) - f^*(NCCN)}{f^*(NNO)}$	0.86	0.94	0.90	0.91

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