Reaction Dynamics during Warm-Up of Matrix-Isolated Cyanogen Azide After Photolysis

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The photolysis products of NCN_3 in solid argon and nitrogen have been observed in the IR as well as UV-visible emission upon warm-up. Our IR data are consistent with earlier work on this system except for the observation of three additional bands with photolysis growth independent of each other: 339, 1232, and 1850 cm^{-1}. The warm-up emission is assigned to the CCN radical, C_2 (five Swan bands), N atoms ($^2D \rightarrow {}^4S$), and a strong emission at 6000 Å, yet unidentified. We report here the experimental evidence for a possible mechanism for the photolysis and subsequent warm-up in argon and nitrogen matrices.

Introduction

The chemistry of atomic carbon is made very difficult to study by the huge heat of formation, 172 kcal/mol, relative to graphite. This makes it hard to create atomic carbon in the laboratory; it accounts for very fast reaction rates, and it has forced observers merely to postulate reaction mechanisms with only sporadic experimental evidence. In the work reported here we have made use of two powerful experimental tools. First, the matrix isolation method confines the system to an inert gas matrix, here at 10–35 K, which slows down the reaction dynamics. Second, we have studied both infrared absorption and visible emission during slight warm-up. In our search for a carbon atom source, we have photolyzed cyanogen azide, NCN_3. This molecule was first synthesized by Marsh and Hermes in 1964.[1,2] The detailed structure of the angular NCN_3 molecule has been established by use of infrared and Raman spectroscopy,[3] microwave,[4] and the gas electron diffraction method.[5] The gas-phase photolysis has been investigated,[6,7] and as early as 1965 Milligan and Jacox[8,9] did matrix isolation studies of the photolysis of NCN_3 by observation of infrared and ultraviolet absorption spectra. They identified the free radical NCN in the primary photolysis of NCN_3[8] and in subsequent photolysis the radical CNN.[9] They even observed, although only qualitatively, the emission during warm-up as "a blue glow, shading into a deep rose color in the center of the sample...".[8]

We have taken this a step further by observation of infrared absorption spectra as well as visible emission spectra during warm-up using an optical multichannel analyzer (OMA). We have observed visible emission from CNN, C_2, and N atoms. In addition, emission from at least one additional species has been observed. In the infrared, absorptions from at least three as yet unidentified species have been observed.

Work is currently in progress using cyanogen azide as a carbon atom source. Here we report the experimental evidence for a possible mechanism for the photolysis and subsequent warm-up of NCN_3 in argon and nitrogen matrices.

Experimental Section

Cyanogen azide was synthesized from sodium azide and cyanogen chloride basically according to the procedure of Marsh.[2] Modifications were developed to eliminate the danger of violent detonations as well as to yield a very pure product.

About 115 g of NaN_3 was ground by mortar and pestle in the hood (use gloves!), packed in a column (Vigreux distillation column, 38 cm high, 2.5-cm o.d.), and held in place with pyrex glass wool. The column was attached at the top to a vacuum system, and at the bottom connected to the regulator and ClCN cylinder with flexible copper tubing. The freshly packed column was degassed by pumping with a 2-in. diffusion pump for at least 24 h. The column was then closed off to the vacuum system, charged with 100–200 torr of ClCN, and allowed to react for 8 h. The NCN_3 was then expanded into a 5.0-L Pyrex bulb (total pressure about 3 torr) and immediately diluted with argon (or nitrogen). The bulb was wrapped with aluminum foil and connected with the cryostat through a greaseless vacuum system. Under these conditions samples were stable and usable for about 1 week. *This way NCN_3 was never condensed*, and we have had no explosions. The synthesis was checked qualitatively with a gas-phase IR spectrum of 3–15 torr of pure NCN_3. The purity of the NCN_3 product was estimated to be no less than 98% based on comparison with IR matrix spectra of very dilute ClCN/Ar mixtures.

All chemicals were used without prior purification: NaN_3 (Aldrich, 99%), ClCN (Matheson, 97% minimum), argon (Matheson, UHP, 99.999%), nitrogen (Alabama Oxygen, 99.95%), and CH_4 (Matheson, research grade). In general, the following samples were used: $NCN_3/Ar = 1/100$ and $1/1000$, $NCN_3/N_2 = 1/100$, $CH_4/Ar = 1/100$ and $1/1000$. In all experiments to be described, the matrix samples were deposited on a polished CsI plate maintained at 8–10 K. With sample concentration 1/100 a total of 10–15 mmol was deposited over a period of 2 h; with sample concentration 1/1000 a total of 2–3 mmol was deposited over a period of 4 h. After deposition the samples were irradiated 4–6 h with a 200-W mercury lamp set at 4.5 A (Oriel No. 6283) through a 5-cm water filter. Both filter and cryostat were equipped with quartz windows. In the direction perpendicular to the photolysis, the cryostat was equipped with two CsI windows for the recording of IR spectra. The experimental setup has been described earlier[10] in detail. The matrix plate was cooled by a closed

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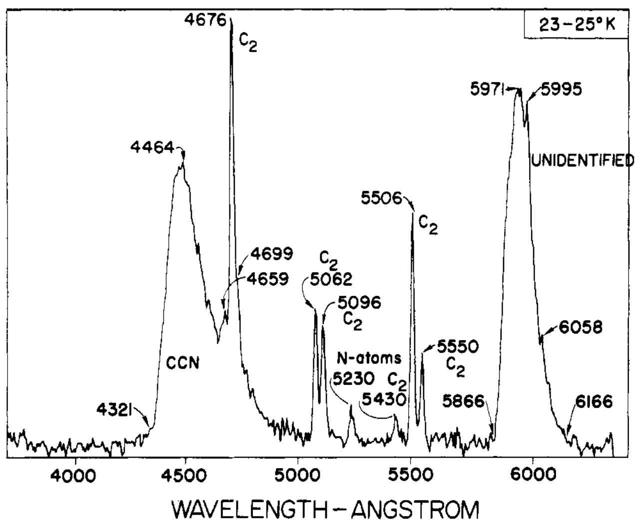

Figure 1. OMA spectrum of NCN_3, photolysis products after warm-up to about 24 K. Argon matrix with M/R = 100.

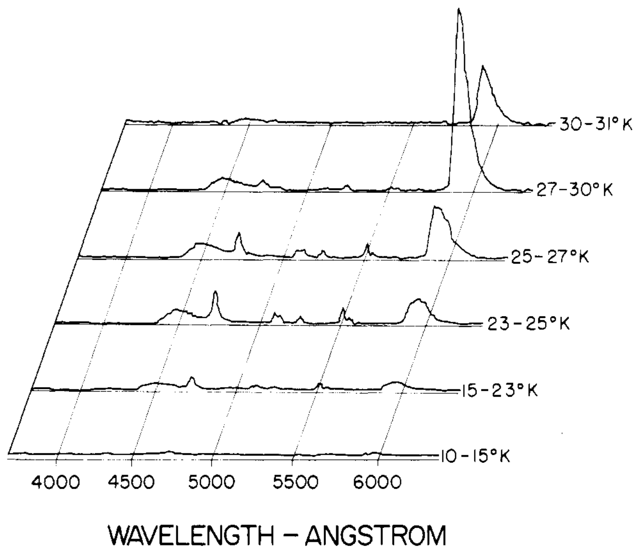

Figure 2. Three-dimensional plot of OMA spectra of NCN_3 photolysis products during warm-up. Argon matrix with M/R = 100. Figure 1 is the trace assigned to 23-25 K in this figure.

cycle refrigerator (Air Products CSA-202B) and pumped to a vacuum of 3×10^{-6} torr by a 4-in. diffusion pump through a liquid-nitrogen-cooled baffle. Emission is initiated by slight warm-up of the matrix and is detected through the quartz window with the mercury lamp now replaced by a 0.3-m Ebert monochromator. A silicon intensified target detector (SIT) is in place of the exit slit and is part of the optical multichannel analyzer (OMA II from Princeton Applied Research). This also includes a detector–controller, a computer with a floppy disk system, a console, and an X-Y recorder for hard copies. The sample spectra were calibrated before the experiment with lines from a mercury lamp, and from a hydrogen and a helium lamp. The spectra used in this work were recorded with a 147.5 gratings/mm grating, blazed at 500 nm, and with a spectral resolution of 0.55 nm/channel. The spectral range covered by this grating was 275 nm. We took our data at a rate of 140 ms/scan and used an average of 100 spectra before any storage. Time for storage resulted in a 13-s interval between our recordings. This was calibrated to correspond to 1–2 K during warm-up, which was initiated by turning off the compressor. Mobility of the cryostat allowed for recording of IR spectra (Perkin-Elmer 621 grating IR) of the matrix sample within minutes both before and after observation of the emission with the OMA system. The SIT detector is sensitive in the range 3300–8000 Å. Experiments were conducted with OMA scans outside the range shown in Figure 1 (3700–6400 Å). Scans in the range 3300–5700 Å showed no emission at wavelengths shorter than 4300 Å. Scans in the range 5300–8000 Å showed no emission at wavelengths longer than the unassigned peak at 5800–6100 Å. We were in all cases able to include already assigned emission in one or the other end of the scans to make sure that all equipment was working properly.

Results

The routine experimental procedure is that we record IR spectra to check the purity of the gas sample in a 10-cm gas cell, and take the matrix spectrum after initial deposition, midway during photolysis, and just before warm-up. In addition, we take the IR spectrum after warm-up and recooling to 10 K. During warm-up we capture the UV–visible emission with the OMA. Below we report all spectroscopic data relevant to each category of sample.

NCN_3/Ar Mixtures. We have not been able to eliminate completely small impurities like CO_2, H_2O, air, and hydrocarbons (diffusion pump oil from back streaming) as evidenced by IR spectra.

The IR spectra during photolysis followed closely the data obtained by Milligan and Jacox.[8] After about 2–3 h of unfiltered (except for the H_2O filter) photolysis with our 200-W mercury lamp, the growing peaks for the free radical NCN[8] at 423 (medium) and 1475 (strong) cm^{-1} reached maximum intensity. During the next 2–3 h of photolysis, the NCN bands would vanish while the three bands from the free radical CNN[9] at 390 (strong), 1238 (strong), and 2845 (strong) cm^{-1} grow in. After 4–6 h of photolysis, but before warm-up, the IR spectrum shows that usually 80–90% of the parent NCN_3 has been photolyzed, as has been the intermediate NCN. In addition to the three peaks from CNN, the IR spectrum showed the following absorptions (tentative assignments in parentheses; to be discussed in the following section): 2058 (strong), CN, 2162 (strong), $(CN)_2$, 2347 (strong, $(CN)_2$), 2047 (weak, C_3), and 2179 (weak, C_4) cm^{-1}, and three unassigned peaks at 339 (medium), 1232 (medium), and 1850 (weak) cm^{-1}.

The emission from a $NCN_3/Ar = 1/100$ (12 mmol of total deposit) sample is shown in Figure 1. The sample had been photolyzed about 6.5 h, and the emission occurred during warm-up from 10 to 40 K. Figure 1 shows the OMA spectrum at 24 ± 2 K, and Figure 2 a three-dimensional plot of the temporal behavior. The spectrum contains four independent features. One is a broad, unresolved band between 4300 and 4700 Å. A sharp emission is observed at 5230 Å (100-cm^{-1} fwhm), and a much broader band is centered at 5980 Å, 130 Å wide at half-height (370-cm^{-1} fwhm). It can be seen from Figure 2 that the latter emission grows independently of all other features in the spectrum. The same is true for the former two emissions as later results have shown. The remaining five features are assigned to the Swan system of C_2 and consist of one singlet and two resolved doublets at 4676, 5062, 5096, 5506, and 5550 Å which grew in concert. Sometimes associated with these five peaks were shoulders on either side of the first, very intense peak, at 4659 and 4699 Å and a weak and broad emission at 5430 Å.

NCN_3/Ar samples with M/R = 10, 50, 100, and 1000 all show qualitatively the same features. At M/R = 10000

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the H_2O impurity becomes dominant (see below).

NCN_3/N_2 Mixtures. The IR data are very similar to the argon matrix data. As NCN_3 is photolyzed, NCN is observed with no matrix shifts, and later CNN bands appear, now at 390, 1244, and 2845 cm^{-1}. One of the unassigned peaks moved from 1232 to 1241 cm^{-1}. The effect of the N_2 matrix was more dramatic in emission upon warm-up: all of the features (in argon) disappeared except for the unassigned band at 5897 Å. Its shape and line width are similar to those of the band at 5980 Å in solid argon.

NCN_3/Ar Mixtures Doped with H_2O. An experiment with double deposition of $NCN_3/Ar = 1/100$ and $H_2O/Ar = 1/10000$ showed no effect on either the IR observations or the visible emission. A second experiment, however, was drastically different: $NCN_3/Ar = 1/100$ and $H_2O/Ar = 1/1000$ showed only a single feature in emission, the N atom line, calibrated in that experiment to be at 5228 Å.

NCN_3/Ar Mixtures Doped with CH_4. We here only report the effects of adding hydrocarbons (with CH_4 as a prototype) on the assigned emission feature listed above. The additional features appearing upon doping with hydrocarbons will be reported and discussed in a later publication.

In the IR, CH_4 seemed to be unaffected by reaction with photolysis products from NCN_3, indicating a huge surplus of CH_4. The photolysis of NCN_3 in the argon matrix progressed in a normal manner through NCN to CNN, but the photolysis went much faster and the yield of CNN was significantly smaller. A typical photolysis lasted only 2–3 h as opposed to about 6 h without any added CH_4.

In emission the result was, in general, a very pronounced enhancement of the N atom emission and a strong suppression of the unassigned band at 6000 Å, as well as of the emission assigned to CCN. The following mixtures were tried in dual deposition: NCN_3/Ar, CH_4/Ar = 1/1000, 1/1000; 1/100, 1/100; 1/50, 1/50; 1/1000, 1/10. As the samples became more concentrated in CH_4, the suppression of both the CCN emission and the 6000-Å band becomes stronger, and in the last experiment, NCN_3/Ar, CH_4/Ar = 1/1000, 1/10, only traces are left. This same experiment is remarkable in the respect that the Swan bands of C_2 were observed all the way up to 36 K. During this warm-up, the N atom emission was observed to grow at the expense of the Swan bands, and above 36 K only emission from N atoms was seen.

Discussion

C_2 Emission. The thermoluminescence from C_2, $d^3\Pi_g \rightarrow a^3\Pi_u$, is readily assigned as Swan bands primarily because of the number of bands, five or most likely eight. This is in excellent agreement with the laser-induced emission from C_2, also in an argon matrix, observed by Bondybey in 1976,[11] as well as the recent observation of the Swan bands in thermoluminescence by van de Bult and Allamandola.[12] The five dominant peaks at 4676, 5062, 5096, 5506, and 5550 Å are assigned to $v' \rightarrow v''$: $2 \rightarrow 1$, $2 \rightarrow 2$, $1 \rightarrow 1$, $2 \rightarrow 3$, and $1 \rightarrow 2$, respectively. The three additional, less distinctive, features at 4659, 4699, and 5430 Å are assigned to $3 \rightarrow 2$, $1 \rightarrow 0$, and $4 \rightarrow 5$. Notice that all assigned Swan bands originate in vibrationally excited levels of the upper electronic state, $d^3\Pi_g$. This seems to be indicative of the short radiative lifetime of C_2 in this state and, possibly, inefficient energy transfer and deactivation of C_2 in the matrix environment. There is a general "blue shift" on our values compared to Bondybey's of 5 Å, corresponding to a single channel on the OMA.

CCN Emission. The assignment is tentative only because of the poor resolution with the present grating. However, it is the first observation of the thermoluminescence from the CCN free radical, and it is assigned to the $A^2\Delta_i \rightarrow X^2\Pi_i$ transition, based on the work by Bondybey and English[13] and on the flash photolysis work by Merer and Travis.[14] Since the intense blue emission dominates the thermoluminescence in the temperature range 10–15 K, we associate this with the mobility of C atoms and propose the reaction C + CNN as the origin, although other possibilities are feasible.

N Atom Emission. Recalling that one channel on the OMA covers 5 Å with the grating used here, the emission is at 5228 ± 5 Å and is assigned to the $^2D \rightarrow {}^4S$ transition for atomic nitrogen.[19] The origin of this emission could be the reaction mentioned above, C + CNN, which would produce N atoms in the ^2D state. Another possibility would be the reaction $CCN \rightarrow C_2 + N(^2D)$. The emission, however, is most prominent in the presence of H_2O or CH_4, both of which we regard as C atom scavengers. Since both of the above sources of $N(^2D)$ atoms require free or at least loosely bound C atoms, they would not appear to be the major contributions to the N atom emission.

Searching for a more reasonable source of $N(^2D)$ atoms, one should recall that ΔH_f of ^4S ground-state N atoms is 112.5 kcal/mol[20] and excitation to the ^2D level adds another 19 227 cm^{-1} or 55 kcal/mol[19] so that the total cost of $N(^2D)$ atoms will be 167.5 kcal/mol. It is tempting to look to the N_3 radical as a source of N atoms since we have IR evidence of CN radicals, and an alternative photolysis path for N_3CN has been shown[8] to form N_3 and CN. There is no IR assignment available for N_3, and the ΔH_f (+99 kcal/mol) is uncertain.[21]

The decomposition

$$N_3(X^2\Pi_g) \rightarrow N_2(X^1\Sigma_g^+) + N(^4S_{3/2})$$

then would be endothermic by 13 kcal and is in addition spin forbidden. The reaction

$$N_3(X^2\Pi_g) \rightarrow N_2(X^1\Sigma_g^+) + N(^2D_{5/2,3/2})$$

is spin allowed but would be endothermic by 68.5 kcal/mol.[25]

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[21] Values of ΔH_f of $N_3(g)$ ranging from 95.7 to 116.0 kcal/mol have been reported or may be calculated from reported data.[6,22-24] The data of Clark and Clyne[22] for ΔH of the reaction $N + N_3 \rightarrow N_2^* + N_2$ lead to a value of 95.7 kcal/mol for ΔH_f of $N_3(g)$. ΔH of the reaction $O + N_3 \rightarrow NO^* + N_2$ reported in the same work leads to a value of 101.2 kcal/mol for ΔH_f of $N_3(g)$. The data of Okabe and Mele[6] for the reaction $NCN_3 \rightarrow CN(B^2\Sigma) + N_3$ combined with JANAF data[23] lead to a ΔH_f value of 99.6 kcal/mol. We have accordingly chosen a value of ΔH_f of $N_3(g)$ of 99.0 ± 3.5 kcal/mol.

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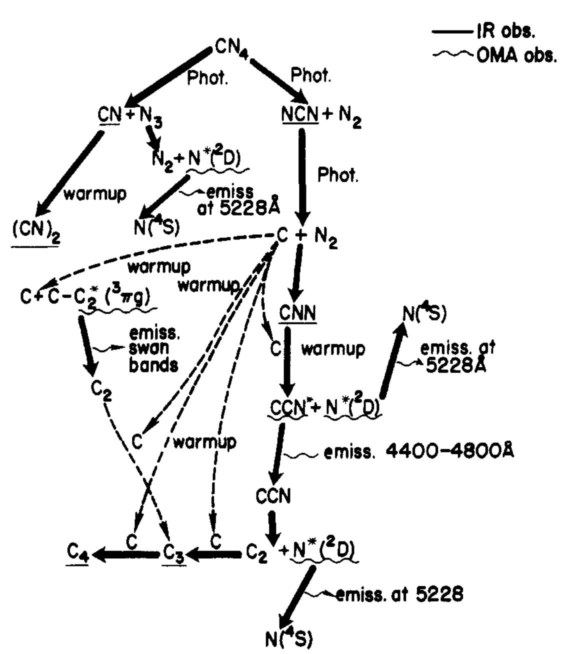

Figure 3. Reaction mechanism in argon matrix.

The energy required to produce $N(^2D)$ from N_3 could conceivably be provided by energy transfer from $C_2(d^3\Pi_g)$, but that would be inconsistent with increased N atom emission in the presence of H_2O/CH_4, which would scavenge C atoms. However, the necessary energy could easily be provided photolytically and stored until warm-up in the form of a metastable cyclic isomer of N_3. This would be analagous to the photolytic isomerization of the allyl radical to form a cyclopropyl radical. In the absence of H_2O/CH_4, the N_3 radical or its cyclic isomer would react with one of the numerous radicals in this system, and emission from $N(^2D)$ would be blocked. However, addition of H_2O/CH_4 would scavenge all identified radicals but the N_3. Even if we use an upper limit of 110 kcal/mol for ΔH_f of N_3, any reaction with H_2O/CH_4 would be endothermic. The much weaker $N(^2D)$ emission that we observe in the absence of added H_2O/CH_4 must then be due to our unavoidable H_2O impurity.

IR Data. In addition to the radicals NCN and CNN mentioned above, also the CN radical is observed at 2057 cm^{-1} as reported by Weltner et al.[15] The source could be from primary photolysis of the parent NCN_3 as well as reaction of C atoms with N_3 or N atoms. Not surprisingly, also $(CN)_2$ is observed. We observe the asymmetric stretch from C_3 at 2047 cm^{-1} as well as possibly C_4 at 2179 cm^{-1}. Both species have been observed by Weltner et al. in argon matrices.[16,17] We had expected to be able to observe the phosphorescence from the $^3\Pi_u \rightarrow {}^1\Sigma_g{}^+$ transition[16b] of C_3, which has recently been observed by van de Bult and Allamandola[12] in a completely different chemical system at 5905 Å (fwhm 20 Å). It is possible that this transition is part of our very broad unassigned emission between 5800 and 6100 Å.

Mechanism. The mechanism for photolysis of NCN_3 as well as the reactions during subsequent warm-up in an argon matrix are shown in Figure 3. Our IR data confirm the two photolysis routes postulated by Milligan et al.: either to CN and N_3 (and during warm-up formation of $(CN)_2$) or formation of NCN in primary photolysis and CNN in the secondary photolysis.[8] We can also confirm that C atoms react with N_2 at 10–15 K as found by Milligan and Jacox[9] as well as Moll and Thompson.[18] Thus, the thermoluminescence in a nitrogen matrix consists of only the unassigned emission at 6000 Å, whereas the matrix itself scavenges the C atoms (see Figure 3). The concept of C atom scavenging is also essential for the understanding of our results from adding H_2O or CH_4 to the system. The fact that the photolysis is much faster in the presence of CH_4 invites the assumption that there is an equilibrium between NCN and CNN *through* free or at least very accessible C atoms. The drain of C atoms by reaction with CH_4 accelerates the decomposition of NCN and minimizes the yield of CNN, as observed. The addition of H_2O/CH_4 makes the reaction between C atoms and H_2O/CH_4 much more probable than recombination of C atoms to form C_2, and the absence of the Swan bands is the result. Likewise, the absence of CCN emission supports our proposal that the formation of the free radical CCN is associated with mobile C atoms, most likely by the reaction C + CCN. The strong enhancement of the N atom emission also associated with H_2O/CH_4 doping negates two possibilities for production of N atoms in the ^2D state: N atoms from the reactions C + CNN and decomposition of CCN cannot be substantial contributions to the emission since the formation of CNN and CCN involve mobile C atoms. We propose that the major source is decomposition of the N_3 radical, where the Wigner–Witmer rule of conservation of spin angular momentum necessitates the formation of N atoms in the ^2D state. Addition of H_2O/CH_4 would simply scavenge all identified radicals but the N_3.

Our present data would not make a discussion of the unassigned emission at 6000 Å conclusive, and we will thus defer discussion of the emission as well as of the unassigned IR absorptions until more information in available.

Conclusions

The proposed reaction mechanism is based on IR observations of CN, $(CN)_2$, NCN, CNN, C_3, and possibly C_4 as well as the thermoluminescence upon warm-up from CCN, C_2 (five, possibly eight, Swan bands), and N atoms. Despite its surprising complexity, it is clear, that the photolysis of NCN_3 comprises a system involving a powerful source of C atoms. The technique of matrix isolation provides a controlled environment in which to study the chemistry of the carbon atom and immediately offers a number of unique and exciting experiments. Such work is currently in progress in this laboratory, and results from the reaction between C atoms and some hydrocarbons will be published shortly.

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(25) It should be noted that decomposition of N_3 to form N_2, but not N atoms, is exothermic, i.e., $2N_3 \rightarrow 3N_2$, $\Delta H = -198$ kcal, as well as two possible spin-allowed reactions $2N_3(X^2\Pi_g) \rightarrow N_2(A^3\Sigma_u{}^+) + 2N_2(X^1\Sigma_g{}^+)$, $\Delta H = -54.5$ kcal, and $2N_3(X_2\Pi_g) \rightarrow N_2(B^3\Pi_g) + 2N_2(X^1\Sigma_g{}^+)$, $\Delta H = -27.5$ kcal. An intermediate N_6 molecule has been postulated in the decomposition of N_3 to only N_2.[26-28]

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