(c 1.0), $\lambda_{\max}^{\text{EtOH}}$ 240 mμ (ϵ 13,300), $\lambda_{\max}^{\text{CHCl}_3}$ 6.02 and 6.25 μ. *Anal.* Calcd. for $C_{21}H_{32}O$: C, 83.94; H, 10.73. Found: C, 83.84; H, 10.80.

Introduction of deuterium was effected by heating 29 mg. of XXVI under reflux for 3 days with 5 ml. of deuteriomethanol which was saturated with a 20% solution of sodium deuterioxide in deuterium oxide. The 8β,11-d_2 analog XXVII (m.p. 132–134°) was isolated in nearly quantitative yield and according to mass spectrometry was of excellent isotopic purity (6% d_1, 94% d_2).

9α-d_1-5α-Pregnan-12-one (XXVIII). A suspension of 30 mg. of 10% palladized charcoal catalyst in 5 ml. of cyclohexane was stirred for 30 min. in an atmosphere of deuterium, followed by the addition of 14 mg. of $\Delta^{9(11)}$-5α-pregnen-12-one (XXVI) dissolved in 5 ml. of cyclohexane. After continued stirring for 2 hr., the total crude product was heated under reflux for 36 hr. with methanol containing a few drops of dilute sodium hydroxide solution in order to back exchange the 11-deuterium atom. Ether extraction and t.l.c. purification gave 9 mg. of 9α-d_1-5α-pregnan-12-one (XXVIII), m.p. 137–138° of 93% isotopic purity (see Table I).

8β-d_1-5α-Pregnan-12-one (XXIX). Catalytic hydrogenation in the usual manner (see preparation of XIII) of 27 mg. of 8β,11-d_2-$\Delta^{9(11)}$-5α-pregnen-12-one (XXVII) in methylcyclohexane solution followed by back exchange (10 hr. of reflux with methanolic sodium hydroxide solution) produced after t.l.c. purification and recrystallization from ethanol 19 mg. of XXIX, m.p. 140–141° (for isotopic purity see Table I).

5α-Androstan-12β-ol-17-one Acetate (XXXI). Δ^{16}-5α-Pregnen-12β-ol-20-one acetate (XII) was converted in 77% yield into the oxime XXX (m.p. 150–166° by direct crystallization from the diluted reaction mixture) by heating for 30 min. with hydroxylamine hydrochloride in ethanol–pyridine. The crude oxime (364 mg.) was subjected directly to Beckmann rearrangement[26,45] giving 266 mg. of the acetate XXXI with m.p. 137–140°. The analytical specimen crystallized from methanol and exhibited m.p. 142–143°, $[\alpha]^{23}$D +35° (c 1.0). *Anal.* Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.84; H, 9.48.

Saponification of the acetate XXXI with methanolic potassium hydroxide and recrystallization from methanol gave 5α-androstan-12β-ol-17-one (XXXVII), m.p. 156–157°, $\lambda_{\max}^{\text{CHCl}_3}$ 2.80 and 5.75 μ. *Anal.* Calcd. for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.18; H, 10.12.

5α-Androstan-12-one (XXXII). Wolff–Kishner reduction (see preparation of IV) of 5α-androstan-12β-ol-17-one acetate (XXXI) proceeded in 87% yield to afford 5α-androstan-12β-ol, m.p. 128–129°, $[\alpha]^{25}$D +3° (c 1.2) after recrystallization from methanol. *Anal.* Calcd. for $C_{19}H_{32}O$: C, 82.54; H, 11.66. Found: C, 82.27; H, 11.39.

Jones oxidation[43] of the 12-alcohol and recrystallization from ethanol give the required ketone XXXII, m.p. 107–108.5°, $[\alpha]^{24}$D +64° (c 1.0), $\lambda_{\max}^{\text{CHCl}_2}$ 5.88 μ, ORD in methanol (c 0.14) $[\phi]_{307}^{\text{peak}}$ +4160°, $[\phi]_{265}^{\text{trough}}$ −2240°. *Anal.* Calcd. for $C_{19}H_{30}O$: C, 83.15; H, 11.01. Found: C, 83.22; H, 10.89.

Base-catalyzed equilibration at C-11 was performed in the same manner as described for XVII to give 11,11-d_2-5α-androstan-12-one (XXXIII), m.p. 104–105°, of 92% isotopic purity (see Table II).

8β-d_1-5α-Androstan-12-one (XXXVI). The conversion of 5α-androstan-12-one (XXXII) into $\Delta^{9(11)}$-5α-androsten-12-one (XXXIV) was accomplished in 88% yield by base-catalyzed (pyridine in *t*-butyl alcohol) treatment[46] (10 days of reflux) with selenium dioxide. Recrystallization from methanol led to colorless leaflets of XXXIV possessing m.p. 115–116°, $\lambda_{\max}^{\text{EtOH}}$ 238 mμ (ϵ 12,500), $\lambda_{\max}^{\text{CHCl}_3}$ 6.00 and 6.25 μ. *Anal.* Calcd. for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.37; H, 10.15.

Deuterium was introduced into the 8β and 11 positions of XXXIV in the same manner as described above for the pregnene derivative XXVII and afforded 8β,11-d_2-$\Delta^{9(11)}$-5α-androsten-12-one (XXXV) consisting of 96% d_2 and 4% d_1 species. Catalytic hydrogenation with palladized charcoal catalyst and back exchange with methanolic sodium hydroxide as recorded above for the corresponding pregnane XXIX gave in 65% over-all yield the desired 8β-d_1-5α-androstan-12-one (XXXVI) (m.p. 103–104°) of 97% isotopic purity (see Table II).

17,17-d_2-5α-Androstan-12-one (XXXIX). The conversion of 5α-androstan-12β-ol-17-one (XXXVII) into the 17-ethylene mercaptal XXXVIII was accomplished in 83% yield by exactly the same procedure employed for the preparation of XV. After recrystallization from aqueous methanol, the mercaptal XXXVIII exhibited m.p. 119–120° and lacked carbonyl absorption in the infrared. *Anal.* Calcd. for $C_{21}H_{34}OS_2$: C, 68.79; H, 9.35. Found: C, 68.66; H, 9.11.

The desulfurization was performed in the same manner as described for the analogous transformation in the pregnane series (XV → XIX) and was also accompanied by extensive isotopic scrambling as shown in Table II for the ketone XXXIX (m.p. 105–106° after t.l.c. purification and recrystallization from methanol) which resulted from Jones oxidation[43] of the intermediate 5α-androstan-12β-ol.

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(45) See D. N. Kirk and V. Petrow, *J. Chem. Soc.*, 2091 (1961).

(46) A. Bowers, E. Denot, M. B. Sanchez, F. Neumann, and C. Djerassi, *ibid.*, 1859 (1961).

The Reactions of Triplet NH with Olefins

Douglas W. Cornell,[1a] R. Stephen Berry,[1b] and Walter Lwowski

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut.

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Abstract: Reactions of several hydrocarbons (ethylene, ethane, methane, butene-1, heptene-3, and 2,3-dimethylbutene-2) with triplet NH were studied. The NH was produced by both flash and steady photolysis of HN_3; DN_3 also was used. Both flash kinetic absorption spectroscopy and product analysis were used to establish the mechanism of the reaction of triplet NH with olefins. The principal nitrogen-containing product (aside from N_2 itself) was CN, then HCN when the reaction conditions were adiabatic, and HCN and alkylnitriles when the conditions were isothermal. In the latter case, the reaction apparently involves a vibrationally equilibrated alkylnitrene. A rough estimate of the rate constant for bimolecular addition of NH($^3\Sigma^-$) to C_2H_4 is 10^7 l./mole sec.

The reactions of NH with ethylene and other simple olefins offer a tantalizing means for the study of simple gas-phase reactions. This applies both to the specific study of imine and nitrene formation and to the more general problem of skeletal bond formation. The NH can be prepared readily by steady or flash photolysis. With the latter procedure, the absorption spectrum of NH itself becomes a convenient detection probe; conceivably one can also observe spectra of

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[1] (a) National Institutes of Health Predoctoral Fellow; (b) Alfred P. Sloan Fellow; Department of Chemistry and Institute for the Study of Metals, University of Chicago, Chicago, Ill. 60637.

subsequent species formed in a reacting mixture. Furthermore, with both methods of photolysis, the products of the reactions can be collected and analyzed. Finally, some of the intermediates can be produced by an alternative path, the photolytic decomposition of alkyl azides, so that individual steps in a proposed mechanism can be tested independently.

The work described here deals with the photolytic decomposition of hydrazoic acid, normal and deuterated, in the presence of a number of simple olefins, and also with one alternate route, the photolysis of ethylazide. These studies utilized both flash kinetic spectroscopy to determine the transient species and their time dependence, and also analysis of stable products, particularly by chromatographic and spectroscopic product determinations. Only stable-product analysis could be used for studying steady photolysis reactions because of the small steady-state concentrations of transients. Flash studies were carried out at low pressures, near (and on both sides of) the detonation limit of the reacting mixture, so that it was not always practical to carry out product analyses. The steady irradiations were essentially isothermal; the flash-initiated reactions were not.

Although the final products differ somewhat for the hot flash and isothermal steady photolysis conditions, the initial steps of both seem to be similar. The major products are invariably cyanides. From the evidence presented here, we infer that the primary reaction in the gas phase is addition of NH to the double bond, followed by a hydrogen migration and then by the breakage of two or three of the bonds to the α-carbon.

In the following sections, we shall describe the experiments and the immediate results. Then, in the final section, we shall examine our results and inferences in light of previous work on NH and try to compare and contrast the reactions of this species with those of CH_2.

Experimental Section

A. Materials and Reaction Conditions. A water solution of hydrazoic acid was prepared by dropwise addition of sulfuric acid to a sodium azide solution.[2] The HN_3 was removed in small, convenient quantities by bubbling nitrogen through the solution, drying the gas by passing it through a calcium chloride column, and then collecting the hydrazoic acid in a cold trap containing molecular sieve (Union Carbide 3A 1/6 in.), kept at liquid nitrogen temperature. The infrared spectrum of the HN_3 vapor showed no absorption due to water.

Ethyl azide (vapor chromatographic purity) was supplied by Dr. John Emmett. All hydrocarbons were commercial research grade.

The flash photolysis and spectrographic equipment were described previously, in connection with polyatomic nitrenes.[3] The steady photolyses were carried out in a Rayonet photochemical reactor (Southern New England Ultraviolet Co., Middletown, Conn.) with 16 RPR-2573A lamps and a reactor temperature of approximately 40°. The sample vessel was a clear, fused silica tube, 43 × 2 cm. Irradiations were carried out for approximately 6 hr with the lamp emitting 35 w of ultraviolet light. At the end of this time most of the hydrazoic acid had decomposed, as shown by the disappearance of its peak on a tris(cyanoethoxy)propane vapor chromatograph column.

Conditions for flash photolysis typically were: room temperature; $p(HN_3)$, 6 cm; p(hydrocarbon), 2–6 cm; flash energy, 750 joules; and flash time, 20 μsec. Sample tubes generally shattered whenever the HN_3 pressure was above 6 cm.

For slow irradiations, the HN_3 pressure was again 6 cm, and the hydrocarbon pressure range was 8–56 cm.

B. Identification of Products. Transient species NH, CH, C_2, and CN observed in the flash reactions were determined by their well-known band spectra.[4]

Photolysis products were identified primarily by vapor chromatography. Table I shows the columns used for these identifications.

Table I. Chromatograph Columns

Product	Columns
CH_4	(1) Activated charcoal[a]
	(2) Silica gel[b]
HCN	(1) Silicone[c]
	(2) Tris(cyanoethoxy)propane[d]
CH_3CN	(1) Same columns as for HCN
C_2H_5CN	(1) Same columns as for HCN
H_2	(1) Molecular sieve 5A[e]

[a] Matheson Coleman and Bell CX655. [b] Fisher 28–200 mesh. [c] 25-ft in ice–G.P. 58 (Analabs) on Anachrome ABS (Analabs). [d] 3% on Anachrome ABS. [e] Analabs.

The compositions of HN_3–DN_3 mixtures were determined from the infrared spectra of the vapors. The integral intensities of the NH and ND stretching modes were measured; the ratio of these intensities divided by the ratio of the two oscillator strengths (just $1/\sqrt{2}$) is an accurate enough measure of the concentration ratio for these experiments. In the two mixtures used $[DN_3]/[HN_3]$ was 0.46 and 0.56, with about 10% uncertainty.

The ratios of CH_3CN and CH_2DCN concentrations were measured by mass spectrographic analysis of the chromatographed methyl cyanide product. With an electron-accelerating voltage of 15 v, the ratio of intensities of the parent peaks, 41 and 42, afforded a concentration ratio with about 10% uncertainty.

Results

The discussion of the immediate results of our experiments is perhaps best divided into three parts. These cover in turn: the hot reactions studied by flash-initiated decomposition of HN_3, in which transient species were observed spectroscopically; isothermal reactions, which were studied only by product analyses as functions of initial conditions; and finally the results of the alternative path, the photolysis of ethyl azide. We shall try to point out some of the immediate conclusions one can draw as we discuss the results, but only in the next section will we try to integrate these lines and the work of others.

A. Flash Photolysis. Flash kinetic spectroscopy of HN_3–hydrocarbon mixtures was carried out with ethylene, ethane, methane, heptene-3, and 2,3-dimethylbutene-2. In all the spectra, the most prominent features in absorption are the bands due to the triplet ground state of NH ($A^3\Pi \leftarrow X^3\Sigma^-$) and to the violet bands of the CN radical ($B^2\Sigma^+ \leftarrow X^2\Sigma^+$). We detected no absorption spectrum of the short-lived $^1\Delta$ state of NH.[5] The ratio of the NH intensity to the CN intensity varies in time; in the interval 400–700 μsec after photolysis, the NH intensity decreases and at the same time the CN intensity increases. At times as early as 100 μsec after photolysis, the NH bands at 3360 and 3370 A are clearly visible but CN is almost indetectable. At 400 μsec, NH is still clearly visible

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(2) L. F. Audrieth and C. F. Gibbs, *Inorg. Syn.*, 1, 78 (1939).

(3) D. W. Cornell, R. S. Berry, and W. Lwowski, *J. Am. Chem. Soc.*, 87, 3626 (1965).

(4) R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1963.

(5) This spectrum is well known in emission but in absorption, it has been reported in a comment by G. Herzberg, "Energy Transfer in Gases," R. Stoops, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 167.

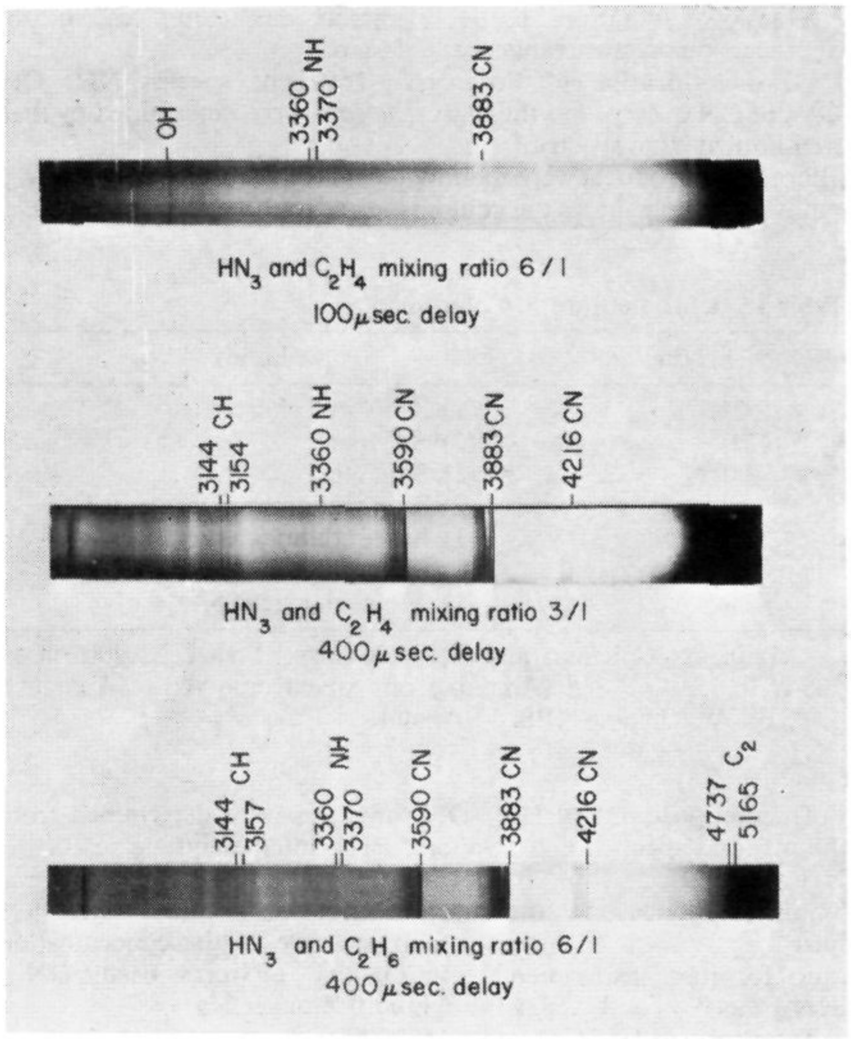


Figure 1. Typical spectra taken after photolysis of HN_3–ethylene mixtures.

and the CN bands have become quite intense. Typical spectra are shown in Figure 1. We infer that the reactions we observe are those of *triplet* NH.

The CN bands show considerable vibrational excitation; we generally observe band heads due to $v'' = 5$ and $v'' = 6$ states of the ground electronic state. Since ω_e is 2068 cm^{-1} for the ground state of CN,[6] we infer that over 30 kcal/mole can be given to CN as vibrational energy.

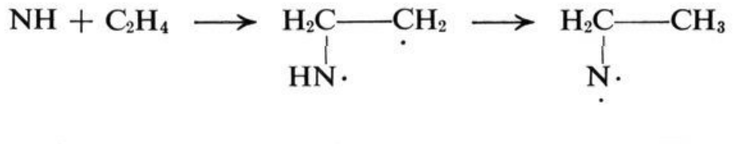
The principal nitrogen-containing products of all the flash-initiated reactions were N_2 and HCN. This was true in the photolysis with 2,3-dimethylbutene-2 (tetramethylethylene) as well as with the other hydrocarbons. In this reaction and in the reaction with heptene-3, HCN was the only cyanide compound; no alkyl cyanides could be detected. Presumably the HCN is formed by abstraction of hydrogen atoms by CN radicals.[7]

In addition to NH and CN bands, other absorption bands appear in the spectra of reaction mixtures of HN_3 with ethylene, ethane, and methane. In the ethylene and ethane examples, the C_2 Swan bands appear at about the same time as the CN bands. With all three of the light hydrocarbons, the CH bands in the 3143-A region appear as the triplet NH reacts.

B. Isothermal Photolyses. The flash experiments showed clearly that under adiabatic conditions, the *most important reaction of NH radicals with ethylene* involves highly excited products. As we shall see, these reactions cannot be very exothermic, so that the NH radicals are necessarily quite "hot" when they react.

To study the reaction of thermal NH with olefins, we investigated the products from continuous irradiation of HN_3 with ethylene, ethane, 2,3-dimethylbutene-2 and -butene-1, and of DN_3 irradiated with ethylene.

In the HN_3–ethylene system, the photolysis products are HCN, CH_3CN, CH_4, H_2, and an amorphous solid. The total cyanide yield represents about 10% of the HN_3 consumed. No explicit determination of NH_3 or NH_4N_3 was made. The ratio of amounts of HCN and CH_3CN is insensitive to ethylene pressure, over a range from 8 to 56 cm. Typical values at 8 and 56 cm are, respectively, 0.9 ± 0.15 and 0.7 ± 0.15. The large uncertainty is due to the overlap of the long tails of the HCN and ethylene peaks in the vapor chromatograph. We infer that these two products come from the same primary reaction, the attack of triplet NH on C_2H_4. The simplest reaction fitting this pattern is sequence 1: first, direct addition of NH to the double bond, followed by transfer of a hydrogen. The pattern of final products is governed by the next step, which can occur in either of two ways. In the isothermal reaction, products appear when any two of the bonds to C_α break; in the hot reaction, all three bonds to C_α break.



$$\mathrm{NH + C_2H_4 \longrightarrow \underset{\displaystyle HN\cdot}{H_2C}\!-\!\!\!-\!\underset{\cdot}{CH_2} \longrightarrow \underset{\displaystyle \underset{\cdot}{N}\cdot}{H_2C}\!-\!\!\!-\!CH_3} \qquad (1)$$

Products of the photolysis of HN_3 with 2,3-dimethylbutene-2 can be predicted from this reaction scheme. We expect to find acetonitrile but no HCN. This is indeed the case; CH_3CN is found but no HCN could be detected among the products of the HN + $(CH_3)_2C{=}C(CH_3)_2$ reaction. We infer that in the isothermal reaction, the atom or group R in RCN is attached to the CN when the addition compound of NH and $R_2C{=}CR_2$ actually breaks up. No free CN radicals are present.

The reaction of HN_3 with ethane produces only one-fourth as much cyanide as the HN_3–ethylene reaction. We attribute the difference to the rapid attack of the olefinic bond by NH, and take the amount of CH_3CN and HCN formed in this reaction to be an approximate measure of the amount of nonolefinic reaction of NH with gaseous hydrocarbons.

The reaction of HN_3 with butene-1 sheds some light on the lifetime of the intermediate addition product. The NH group can add in the 1- or 2-position of butene-1. Addition to the 1-position would give HCN or n-C_3H_7CN, according to scheme 1, but this path is not of immediate interest to us. Addition to the 2-position is more interesting: if the reaction scheme is followed, 2-addition will give CH_3CN and C_2H_5CN. If the lifetime of the intermediate is sufficiently long, the vibrational modes of the species will come into thermal equilibrium with each other or perhaps with the entire gaseous system. If this occurs, then the intermediate can usefully be described as a well-defined nitrene. Its CH_3–C_α bond and C_2H_5–C_α bond will be roughly equivalent; we would then expect that when the nitrene dissociates, the yields of CH_3CN and C_2H_5CN will be about the same. If, on the other hand, the intermediate dissociates rapidly, before the bonds to C_α become equivalent, we expect the yields of CH_3CN and C_2H_5CN to be very different. In the limit of complete equilibration, we cannot expect the

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[6] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand and Co., Inc., Princeton, N. J., 1950.

[7] C. A. Goy, D. H. Shaw, and H. O. Pritchard, *J. Phys. Chem.*, **69**, 1504 (1965).

CH_3CN/C_2H_5CN ratio to be unity because of mass and electronegativity differences and perhaps because of attack of NH on C_3, which could give CH_3CN but not C_2H_5CN. We can estimate the amounts of CH_3CN produced this way by taking the proportion of CH_3CN produced from ethane to that from ethylene. This value, as we said previously, is less than 25%. The raw result of the C_2H_5CN/CH_3CN ratio, uncorrected for the paraffinic reaction, gives an average of 0.63 ± 0.04. With the correction, the ratio is only 0.78 ± 0.07. This is so near to unity that we can suspect strongly that the intermediate is vibrationally stabilized. In other words the bonds between CH_3 and CN and between C_2H_5 and CN become roughly equivalent before the intermediate breaks up.

Reaction of $DN_3 + C_2H_4$ showed that the deuterium atom is sometimes incorporated into the methyl group of CH_3CN. Mass spectrometric analysis, at low ionizing voltage, of the chromatographically separated acetonitrile showed that approximately half the deuterium atoms appeared as CH_2DCN. That is, the intensity ratio CH_2DCH/CH_3CN in the mass spectrum was approximately 0.25, while the initial DN_3/HN_3 concentration ratio was 0.5.

C. Photolysis of $C_2H_5N_3$. If the hypothesis (1) were correct, and the transient C_2H_5N: were a stabilized intermediate in the NH–ethylene reaction, then the same transient should be produced by photolytic decomposition of ethyl azide, $CH_3CH_2N_3$.

Flash-initiated, rapid (unquenched) decomposition of $C_2H_5N_3$ yielded HCN, CH_3CN, H_2, and CH_4 as the principal gaseous products and also a film of white solid. The ratios of amounts of HCN and CH_3CN were approximately the same as that from $C_2H_4 + HN_3$.

Slow, isothermal photolysis of $C_2H_5N_3$ yielded CH_3CN, CH_4, H_2, and a gum which we have so far been unable to identify.

We can make the inference that HCN is produced by isothermal photolysis and then is consumed in a subsequent reaction, presumably involving the gum. When a mixture of $C_2H_5N_3$ and HCN was irradiated, the HCN did in fact disappear.

Neither ethylenimine nor ethylamine, the products of solution photolysis of $C_2H_5N_3$,[8,9] could be found among the products of other gas photolyses.

The results of photolysis of ethyl azide seem entirely consistent with the hypothesis of a stabilized nitrene intermediate CH_3CH_2N:, which decomposes to give HCN and CH_3CN. This is based on the product ratio HCN/CH_3CN from flash photolysis, and from the appearance of CH_3CN.

The results do not rule out completely other possibilities like the reaction of an excited $C_2H_5N_3$ with a ground state $C_2H_5N_3$, but under the conditions of our experiments, this is unlikely. With the pressures we used, $C_2H_5N_3{}^*$ would have to survive for 10^{-7} sec or more in order to participate in the most likely process, $C_2H_5N_3{}^* + C_2H_5N_3 \rightarrow C_2H_5N_4CH + N_2 + CH_4$. Possibly this lifetime could be achieved by an internal conversion. However the azide photolysis is more easily interpreted as proceeding through C_2H_5N, in the same way as C_2H_4 + NH, than as following a different path.

Discussion

From the results just described, we infer that (1) photolysis of gaseous HN_3 produces N_2 and a triplet NH, (2) that the NH attacks olefinic bonds more readily than aliphatic bonds, and (3) that a 1–3 transfer of a hydrogen from nitrogen to carbon produces a nitrene with a lifetime long enough for vibrational relaxation to occur.

The product analyses and transient identifications we have obtained seem fairly certain and unequivocal. We believe we have accounted for the volatile and some of the nonvolatile products. We ourselves have not, however, established a complete mass balance nor have we searched for all the conceivable products and transients. Therefore we must examine with some care the alternative explanations for our results and the possible parallel reactions that we have not considered explicitly. We must consider particularly the relationship of the results presented here to the several discussions of NH reactions already in the literature.[10-14]

A. Nitrogen Atoms. First we examine the flash photolysis results. The products of the reactions are rather similar to those obtained by Evans, Freeman, and Winkler,[15] who introduced active nitrogen into gaseous olefins and recovered up to 70% of the atomic nitrogen as HCN. Similar results were obtained with active nitrogen and methanol, by Sole and Gartagonis.[16] We must ask whether our system could involve the reaction of atomic nitrogen with olefin, rather than the reaction of NH. The energetics of the reaction do permit photolysis of HN_3 to $H + N + N_2$; the heat of formation of HN_3 is 71 kcal/mole,[17] the heat of formation of NH is 79 kcal, and the dissociation energy of NH is 78–97 kcal.[5] Thus the photon energy required to produce $H + N + N_2$ is about 95 kcal/mole. The energy in an einstein of 2537-A light is *ca.* 115 kcal, clearly enough to produce nitrogen atoms from HN_3.

Nevertheless we consider the nitrogen atom hypothesis very unlikely on two grounds. First, we observe no indication, either in emission or absorption, of the first positive bands of triplet nitrogen molecules, despite the general association of these intense bands with recombining nitrogen atoms. This, however, is only negative evidence. The other ground is the close correlation between the decay time of the NH absorption spectrum and the appearance time of the CN spectrum. This time, 400–600 μsec, is long enough that the NH could not be dissociating to give very reactive N atoms. The NH vibration must be nearly relaxed by this time, at pressures of several centimeters used in these experiments. Translations and rotations are obviously relaxed in this time, so that the NH radicals are at thermal equilibrium. (But note that the gas is heated by the exothermicity of the reaction, so band-intensity measurements are not quantitatively useful in any direct way.)

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(11) E. D. Miller, Ph.D. Dissertation, Catholic University of America, Catholic University of America Press, Washington, D. C., 1961.

(12) J. Y. P. Mui and R. A. Back, *Can. J. Chem.*, **41**, 826 (1963).

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(16) M. J. Sole and P. A. Gartagonis, *ibid.*, **41**, 1097 (1963).

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The similarity between the HN_3 olefin system and the active nitrogen–olefin system remains. One is tempted to ask whether the primary reaction in the active nitrogen system might either be (a) abstraction of a hydrogen by a nitrogen atom, followed by attack of NH on the olefin, or (b) addition of N to C_2H_4 to produce a dehydro analog of the product of reaction 1. The results of Avramenko and Krasnen'kov[18] and of Dubrin, Wolfgang, and McKay[19] make the latter particularly attractive.

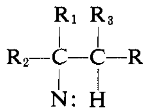
B. Singlet NH. The mechanism proposed here attributes the cyanide formation to the triplet ground state of NH. Just as in the case of the isoelectronic CH_2 species, one can inquire about the possibility that the singlet excited state is the reactive state. The energy separation of singlet and triplet is not known; thermal activation to the singlet could occur in principle. However the only reported observations of the singlet are in emission,[20,21] or during the duration of a photolysis flash in absorption.[5] We observe no spectrum of the singlet whatsoever, but see the triplet quite clearly. If the triplet were in equilibrium with the singlet and the singlet were responsible for CN formation, then in the flash experiments, the rate of CN formation should be much greater at early times when the singlet concentration is apparently highest. This is not the case at all. We infer then that singlet NH is not the reactive species in our system.

The photolysis of HN_3 in a low-temperature matrix containing ethylene was studied by Milligan and Jacox.[10] Under the conditions of low temperature and solid density, NH reacts with ethylene to produce ethylenimine, apparently exclusively. We have searched extensively for this material among our products, and have found no traces of it. We see only two reasonably possible ways of reconciling these two different results. Either the three-membered ring is formed when triplet NH adds to ethylene, and in the high-density matrix, the newly formed product both gives up its excess energy and converts to a singlet faster than a hydrogen moves from N to C, or the ethylenimine is a product of *singlet* NH adding to C_2H_4. The matrix experiments were carried out at 4°K, at which temperature migration of NH is supposed to be slow. This slow diffusion makes it hard to reconcile with the singlet hypothesis, so that the singlet hypothesis seems a little less attractive than the supposition of a triplet reaction with fast energy removal and fast internal conversion. Distinguishing between these two cannot be done with the present evidence. In either case, the conditions are so drastically different from the gas-phase conditions used in our work that we feel there is no real incompatibility in the two sets of results.

C. Diimide. The presence of diimide N_2H_2 has been reported by Foner and Hudson[22] and its formation has been inferred in more recent studies of NH reactions[12,14] to which we shall return. It is conceivable, at first sight, that the formation of cyanides somehow involves reaction of diimide with olefins. This, however, seems rather unlikely. Diimide is apparently rather stable. Its dissociation energy into 2NH is about 104 kcal/mole[21] so that the equilibrium concentration of N_2H_2 must be considerably greater than that of NH. If the rate of formation of N_2H_2 were high, the rate of disappearance of the NH spectrum would be controlled by this process; the disappearance of NH would not be correlated with the appearance of CN. But in fact, there seems to be a good correlation between the NH disappearance and the appearance of CN, implying that the rate of diimide formation is much less than the rate of the olefin–NH reaction. The NH concentration cannot be severely depleted by diimide formation. Two-body collisions of NH with each other might well be responsible for the rapid conversion of singlets to triplets, and only the infrequency of the stabilizing third-body collisions of transient NH–NH prevents the formation of considerable N_2H_2.

D. Free-Radical Chains. The possibility of free-radical chains in the flash reactions is real indeed. The reactions are near enough to the detonation limit that branching chains almost certainly occur. Moreover a variety of radical fragments is observed as transients and both methane and acetylene are recovered from reactions with ethylene. However, none of the highly fragmented species like C_2 or CH appear before CN or until the NH spectrum has begun to diminish in intensity. It seems unlikely that any free-radical chains occur except those initiated by attack of NH on olefin, and that these chains are all associated with CN formation in a primary step.

In the slow isothermal photolyses, no products are found which would indicate free-radical processes. Ethane, for example, does not appear. In fact we are led to suspect that when



$$R_2\text{—}\overset{\displaystyle R_1}{\underset{\displaystyle N:}{C}}\text{—}\overset{\displaystyle R_3}{\underset{\displaystyle H}{C}}\text{—}R$$

breaks up to give R_1CN, for example, there is never a significant amount of free $\cdot R_2$ or $\cdot CHR_3R_4$. We shall return briefly to this point in a discussion of energetics.

E. Different Reactions for Flash and Slow Photolyses. The discussion of the previous section postulated that the primary reaction of NH with olefins is the same for our flash and steady photolysis (*i.e.*, hot and isothermal) conditions, and that the nitrene intermediate in the case of ethylene is the same as that produced by ethyl azide photolysis. We have inferred the primary step in the flash-initiated reaction from the transient absorption spectra and have assumed from the similarity of products that the primary step in the isothermal reactions is the same, the addition of NH to the double bond, followed by an H-atom shift. The primary reaction in the isothermal NH and ethyl azide reaction could conceivably be different from the flash reaction. For example the isothermal reaction of NH with ethylene might conceivably proceed through excited ethylenimine, in some way parallel to the path of the reaction in a cold matrix. However the similarity of products from the isothermal NH–ethylene and ethyl azide reactions and of the corresponding flash-initiated reactions is a strong indication that in all cases the

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azide and NH–ethylene reactions pass through the same intermediate step, and that the differences in products are due only to the amount of energy removed by the surrounding gas and to the different reactivities of the products toward the different starting materials.

F. Other Reactions. We must ask whether cyanide formation is the only or even the most important reaction path for the NH–olefin and the ethyl azide systems. At this point we can look in some detail at the work of Miller and Rice.[11] This was a study of the mass balance in the reactions of NH with aliphatic hydrocarbons and with ethylene. The NH was produced by slow photolysis of HN_3 vapor in the presence of gaseous hydrocarbon. The products were collected and measured—amines and ammonia by titration (with the assumption that the solid products were two-component mixtures of NH_4N_3 and amine salts), and noncondensables by mass spectrometry and vapor chromatography. The major product was NH_4N_3 from reactions of aliphatics. In the ethylene reaction, considerable amounts of ethane and HCN were found, comparable to the amount of ammonium azide, and there was much less H_2 than in the aliphatic systems. Miller also reports finding a trace of CH_3CN. No trace was found of ethylenimine or of products due to ethylenimine reactions. Although our results differ from Miller's in regard to the relative amounts of HCN and CH_3CN, the two sets of results are reasonably consistent. We did not search for ammonium azide, but only for carbon-containing products. We simply use Miller's results to tell us the relative amounts of reactions 1 and 2. The CH_3CN discrepancy may be associated with the consistent nitrogen deficiency of 1–5% in Miller's mass balance; CH_3CN may react with HN_3 to form 5-methyltetrazole, very possibly the yellow material he says deposited on the walls of his photolysis bulb. (However, see the discussion of ethyltetrazole below.)

$$\begin{array}{l} NH + 2C_2H_4 \longrightarrow NH_3 + 2C_2H_5 \text{ (or other H source)} \\ \qquad\qquad\qquad\quad + \\ \qquad\qquad\qquad HN_3 \longrightarrow NH_4N_3 \end{array} \qquad (2)$$

The results of the mass balance determination is neatly complementary to our results: we conclude that the only important reaction path neglected in our work is the one leading to NH_4N_3 formation. This product occurs with alkanes and alkenes alike, by H abstraction and subsequent reaction of NH_3 with HN_3; the NH_4N_3 product is apparently not associated with a double bond.

G. Comparison of HN_3 and HNCO. On eset of experimental results is particularly pertinent to the work described in this report; this is the analysis of flash and steady photolysis of gaseous HNCO in the presence of ethylene, carried out by Mui and Back[12] and extended by Back.[13] It would seem that photolyses of HNCO and HN_3 should bear a relationship to each other similar to that of the well-known ketene and diazomethane photolyses.[23] In these latter two systems, it appears that methylene is produced from both, and that the methylenes from the two sources are qualitatively similar but lead to rather different product distributions. The inference has been made that CH_2 groups from the two sources differ substantially in their initial translational and vibrational energy. Diazomethane apparently supplies excess energy in both sorts of degrees of freedom, and the amount of translational excess energy is a function of the wavelength of the photolysis radiation.

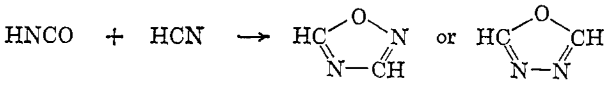
The relationship of our results to those of Mui and Back is not as simple as that of CH_2N_2 and CH_2CO photolyses. Mui and Back observe no HCN at all, despite a search for it and other possible gaseous products. They measured the yield of N_2, CO, and small amounts of hydrogen, both for pure HNCO photolyses and for mixtures of HNCO with hydrogen and ethylene, and with propane in flash reactions only. The presence of either hydrocarbon reduced the yield of CO to 2/5 of $(CO)_0$, the yield in pure HNCO, when the partial pressure of HNCO was about twice that of hydrocarbon. As the hydrocarbon pressure was increased, the yield of CO dropped slowly to about 0.1 $(CO)_0$ with ethylene and about $0.2(CO)_0$ with propane. Moreover both hydrocarbons reduced the ratio of N_2/CO in addition to the reduction in CO itself. Back has interpreted this in terms of a mechanism involving the formation of diimide from 2NH, followed either by decomposition to $N_2 + H_2$ or, if hydrocarbon is present, by some mechanism preventing formation of N_2 from N_2H_2.

In view of the cyanides found both in Miller's work and ours on HN_3, and of the relationship between NH and CN in our transient studies, we are encouraged to give our own interpretation of the results from the HNCO photolyses. We offer two alternatives, not mutually exclusive, which are both amenable to experimental verification.

The first possibility follows the interpretation of Mui and Back in assuming the primary process is

$$HNCO + h\nu \longrightarrow NH + CO$$

but in the presence of ethylene we now suppose that HCN is formed. What becomes of the HCN (or the CH_3CN in the steady photolyses) so that it is not observed? In the slow irradiation of $C_2H_5N_3$, we observed that no HCN was produced, and that added HCN actually disappeared during the irradiation. The simplest reaction one might postulate, the formation of either ethyltetrazole isomer by direct addition of HCN to $C_2H_5N_3$, does not occur, or is followed by other reactions that destroy the tetrazole; at least we have been unable to find ethyltetrazole in the gum. Nevertheless the HCN does disappear, and is presumably a constituent of the unidentified product. This leads us to make the suggestion that HCN may react with HNCO. Such a reaction would account for the negative result of Back's search for HCN. One possible reaction that could be responsible might be formation of either 1,2,4-oxadiazole or 1,3,4-oxadiazole. This would be analogous to the known 1,3-dipolar cycloadditions of cyanates and nitriles,[24,25] but the isocyanate–nitrile reaction would require a hydrogen shift from N to an adjacent C.



[23] For a review and extensive bibliography, *cf.* W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, Chapters 2, 11, and 12.

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[24] R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565, 633 (1963).

[25] G. Leandri and M. Pallotti, *Ann. Chim.* (Rome), **47**, 376 (1957).

Any oxadiazole would have missed detection in the HNCO experiments since no systematic analysis of condensable products was made. It would be entirely feasible to carry out the HNCO–ethylene and HNCO–propane experiments again and search for oxadiazoles among the condensables. It is also possible that polymeric material is produced in an addition process.

If the foregoing explanation were correct, then the quantum yield of CO would be much lower in the presence of hydrocarbon than with HNCO alone. If the reaction of NH with HNCO were completely suppressed, the yield would drop from 3 to 1. Moreover the quantum yield of N_2 would be zero if there were no reactions of NH except with hydrocarbon and if no other reactions of HNCO took place. Qualitatively, this is in accord with the observations. However the reduction in the CO yield is apparently too great to be accounted for entirely by this scheme. At the same time the nitrogen yield seems to drop slowly enough as a function of $p(C_2H_4)$ to be consistent with the scheme, but not with the very large observed drop in the CO production. There must be some mechanism that consumes both N_2 and CO.

The second possible interpretation for reconciling the results of the HN_3 and HNCO experiments does account for consumption of both nitrogen and CO. It diverges at the outset from the interpretation of Mui and Back. From the studies of the NCO spectrum, it is known that the *transient* absorption spectrum taken after photolysis of HNCO shows NH, NH_2, and NCO. It is apparently not known whether NH and NCO are produced by alternative primary steps, or whether only one is the primary transient and the other a product of an abstraction of H by NH from HNCO. Let us suppose that some NCO is produced in the primary step, or that NCO (produced by abstraction) reacts with C_2H_4 at a rate roughly equal to (or perhaps much faster than) the rate at which it reacts with another NCO. Then we can expect

$$NCO + H_2C{=}CH_2 \longrightarrow O{=}C{=}N{-}CH_2{-}CH_2$$

and this radical may abstract a hydrogen atom to form ethyl isocyanate, which would have escaped detection and which might be found among the condensables. The question of whether NCO is a primary product is an interesting one and is probably amenable to study by conventional flash kinetic spectroscopy. It is not absolutely crucial to the question of the consumption of nitrogen and CO *via* the formation of ethyl isocyanate since it is conceivable that excited HNCO could also explain the result. If NH and CO were at least partially produced by dissociation of a long-lived excited HCNO, and if this excited HCNO reacted with C_2H_4 to give ethyl isocyanate faster than it dissociated, the observed quantum yields could be rationalized.

Summary

The photolysis of HN_3 in the presence of ethylene and other olefins has led to the following inferences.

(1) The principal reactive species generated by photolysis is NH in its $^3\Sigma^-$ ground state. This follows from the time dependence of the absorption spectrum and the similarity of products from adiabatic flash-initiated reactions and isothermal continuous photolyses.

(2) The NH radical adds directly to the double bond. In the absence of thermal quenching, time-resolved spectra show that CN radicals are the first product of this attack. If quenching occurs, a hydrogen atom shifts, probably in a 1,3-shift, to produce an alkyl nitrene. The nitrene is more likely a triplet than a singlet.

(3) The nitrene intermediate, in the isothermal systems, achieves a considerable measure of vibrational relaxation, enough that all the bonds to the nitrile carbon are approximately equivalent.

(4) The nitrene eventually decomposes to give a nitrile or HCN. The other products could be two radicals, but, much more likely, are hydrocarbon or hydrogen molecules. This is easily inferred from an estimate of the heats of reaction.[6,26]

$$NH + C_2H_4 \longrightarrow CH_3CN + H_2 + 44 \text{ kcal/mole}$$
$$NH + C_2H_4 \longrightarrow HCN + CH_4 + 57 \text{ kcal/mole}$$

Neither of these is exothermic enough to give 2H from H_2, or $CH_3 + H$ from CH_4. Moreover in the several hundred microseconds between photolysis and reaction and at the pressures used in this work, an NH must essentially reach thermal equilibrium with its environments; it cannot retain much of the excess energy of the photodissociating HN_3 molecule.

(5) In light of the mass balance studied by Miller,[11] the results presented here imply that cyanide formation is the only important reaction of NH with olefins in the gas phase, other than abstraction of hydrogen, when the NH is produced by photolysis of HN_3.

(6) Presumably the NH from HN_3 and HNCO bears some relationship to the CH_2 produced from CH_2N_2 and CH_2CO. It is not possible to establish this relationship with the existing evidence, but certain paths look particularly fruitful, namely a study of the time dependence of the absorption spectrum in HNCO–olefin photolyses and a search for products of reactions of nitriles with both sorts of starting materials.

From the rate of disappearance of NH, we can make an estimate of the rate constant for the proposed bimolecular addition reaction. This value is $10^7 \times$ l./mole sec or 10^{-14} cm^3/sec, corresponding to a cross section of about 10^{-18} cm^2. We can claim an uncertainty of, perhaps, about a factor of 5. However, crude as the numbers are, they tell us immediately that the NH triplet is a much less reactive species in the gas phase than methylene.

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[26] K. S. Pitzer, "Quantum Mechanics," Prentice-Hall Co., Inc., Englewood Cliffs, N. J., 1953, p 170.