

[CONTRIBUTION FROM MELLON INSTITUTE, PITTSBURGH 13, PENNA.]

Infrared Study of the Reactions of CH<sub>2</sub> and NH with C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> in Solid Argon<sup>1</sup>

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As part of a systematic study of the reactions of NH and CH<sub>2</sub> with simple unsaturated molecules in an inert matrix, infrared spectral observations have been made on the photolysis products of dilute solid solutions of C<sub>2</sub>H<sub>4</sub> + HN<sub>3</sub>, C<sub>2</sub>H<sub>2</sub> + CH<sub>2</sub>N<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub> + HN<sub>3</sub> in argon at 4°K. The cyclic species ethylenimine is the product of the first reaction. However, radical attack on a triple bond does not appear to lead to a stable cyclic species. Allene is produced by the attack of CH<sub>2</sub> on C<sub>2</sub>H<sub>2</sub>. Evidence also suggests the production of ketenimine by the analogous reaction of NH with C<sub>2</sub>H<sub>2</sub>. Possible mechanisms for these reactions are discussed. These mechanisms suggest that at least part of the CH<sub>2</sub> and NH may undergo matrix deactivation to the ground triplet state before reaction.

## Introduction

The application of the matrix isolation technique to the study of free radical reactions opens a field of considerable potential for the observation of unorthodox and highly reactive species. The conditions prevailing in an inert solid matrix should be ideally suited for the stabilization of the primary products of the reactions of free radicals with other species.

The method was first applied to the study of reactions between two different species by DeMore, Pritchard and Davidson,<sup>2</sup> who studied the reactions of methylene with various molecular species suspended in a nitrogen matrix at 20°K. Particular evidence of the power of this technique was given by their study of the reaction of methylene with ketene. This experiment yielded two infrared absorptions which they assigned to cyclopropanone, previously observed only in a hydrated form. The attack of NH on O<sub>2</sub> suspended in a nitrogen matrix was studied by Baldeschwieler and Pimentel,<sup>3</sup> who reported the formation of HONO in this system. More recently, the reactions of CH<sub>2</sub> and of NH with CO<sub>2</sub> have been studied in this Laboratory and at the University of California.<sup>4a, b</sup> Evidence has been obtained for the production of a cyclic species by the attack of either of these radicals on a C=O bond in CO<sub>2</sub>. The reaction of the isoelectronic united atom counterpart of CH<sub>2</sub> and NH, O(<sup>3</sup>P), with C<sub>2</sub>H<sub>2</sub> in an argon matrix at 20°K., producing ketene, has been studied by Haller and Pimentel.<sup>5</sup>

As part of a systematic study of the reactions of NH and CH<sub>2</sub> with various other simple species, the present studies of their reactions with the simplest unsaturated hydrocarbons, ethylene and acetylene, were undertaken.

## Experimental Details

CH<sub>2</sub>N<sub>2</sub> and CD<sub>2</sub>N<sub>2</sub> were prepared by the hydrolysis of N-nitrosomethylurea (or its d<sub>2</sub> counterpart) in 70% aqueous KOH (KOD). Water was removed by passing the product through several traps cooled by a Dry Ice-acetone mixture, and non-condensables were removed by pumping on the sample after freezing with liquid nitrogen. Finally, traces of C<sub>2</sub>H<sub>4</sub> were removed by condensing the material at 140°K. and pumping. Only traces of CHDN<sub>2</sub> were observed in the CD<sub>2</sub>N<sub>2</sub> samples.

HN<sub>3</sub> (DN<sub>3</sub>) was prepared by the reaction of a concentrated aqueous (or D<sub>2</sub>O) solution of NaN<sub>3</sub> with concentrated H<sub>3</sub>PO<sub>4</sub> (or D<sub>3</sub>PO<sub>4</sub>). The product was freed of non-condensable gases by freezing with liquid nitrogen and pumping, and the degassed samples were dried by passing through a column packed with P<sub>2</sub>O<sub>5</sub>. A small amount of HN<sub>3</sub> appeared in the DN<sub>3</sub> samples

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(2) W. B. DeMore, H. O. Pritchard and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959).

(3) J. D. Baldeschwieler and G. C. Pimentel, *J. Chem. Phys.*, **33**, 1008 (1960).

(4) (a) D. E. Milligan and M. E. Jacox, *ibid.*, **36**, 2911 (1962); (b) D. E. Milligan, M. E. Jacox, S. W. Charles and G. C. Pimentel, *ibid.*, **37**, 2302 (1962).

(5) I. Haller and G. C. Pimentel, *J. Am. Chem. Soc.*, **84**, 2855 (1962).

because of exchange with adsorbed water in the deposition line. Its contribution to the product spectrum, known from the corresponding HN<sub>3</sub> experiment, could be subtracted out in interpreting the results.

C<sub>2</sub>H<sub>4</sub> (Matheson Co.) was subjected only to the removal of materials not condensed at 77°K.

C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>D<sub>2</sub> were prepared by the reaction of H<sub>2</sub>O (D<sub>2</sub>O) on CaC<sub>2</sub> (Fisher Electrolyte). Samples were dried by passage through P<sub>2</sub>O<sub>5</sub> and were degassed by repeated condensation with liquid nitrogen. C<sub>2</sub>D<sub>2</sub> prepared by this technique contained appreciable amounts of HCCD. Nevertheless, the predominant spectral absorptions were those of the fully deuterated compound.

Argon (Air Reduction Co.) was used without further purification. Samples were prepared by standard manometric procedures.

The cell used for these observations has been described previously.<sup>6</sup> Sample depositions onto a CsBr window were carried out at temperatures approaching 4°K., with liquid helium used as coolant. In some experiments it was necessary to prepare separate mixtures of argon with the two active species. Twin jets, oriented approximately at angles of 45° and 135° with respect to the CsBr window, were used for simultaneous deposition of the two samples at approximately equal rates. Initial infrared spectra of these sample deposits indicate that mixing is adequate in the solid sample and that deuterium exchange (*e.g.*, between CD<sub>2</sub>-N<sub>2</sub> or DN<sub>3</sub> and C<sub>2</sub>H<sub>2</sub>) or chemical reaction (*e.g.*, between CH<sub>2</sub>N<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>) does not occur to an extent sufficient for spectral observation.

Sample irradiations were carried out using a General Electric AH-4 medium pressure mercury arc. The sample irradiation window used for these experiments was of KBr, with an estimated cutoff near 2200 Å.

All spectra were recorded on a Beckman IR-7 spectrometer, estimated to have a resolution and frequency accuracy of ±2 cm.<sup>-1</sup> in the range 650-4000 cm.<sup>-1</sup> under the conditions of the experiments here reported.

## Observations

The reaction of CH<sub>2</sub> with C<sub>2</sub>H<sub>4</sub> in an inert solid matrix has been shown by DeMore, Pritchard and Davidson<sup>2</sup> to yield cyclopropane. Further studies of this system were not undertaken. However, the corresponding reaction of NH with C<sub>2</sub>H<sub>4</sub> was observed. A summary of the absorption frequencies appearing after photolysis is given in Table I, together with the bands of medium or greater intensity reported by Hoffman, Evans and Glockler<sup>7</sup> for gaseous ethylenimine. The excellent correspondence leaves little doubt that ethylenimine is the sole product of the reaction of NH with C<sub>2</sub>H<sub>4</sub> in the argon matrix.

The absorption frequencies appearing after photolysis of Ar:C<sub>2</sub>H<sub>2</sub> (C<sub>2</sub>D<sub>2</sub>):CH<sub>2</sub>N<sub>2</sub> (CD<sub>2</sub>N<sub>2</sub>) deposits are summarized in Table II. Comparison with the spectral data published for allene and allene-*d*<sub>4</sub> by Lord and Venkateswarlu<sup>8</sup> and for allene-1,1-*d*<sub>2</sub> by Evans, Wilms-hurst and Bernstein<sup>9</sup> indicates that the reaction between methylene and acetylene in the argon matrix leads predominantly to the production of allene. There is no spectral evidence for the presence of either

(6) D. E. Milligan, *J. Chem. Phys.*, **35**, 1491 (1961).

(7) H. T. Hoffman, Jr., G. E. Evans and G. Glockler, *J. Am. Chem. Soc.*, **73**, 3028 (1951).

(8) R. C. Lord and P. Venkateswarlu, *J. Chem. Phys.*, **20**, 1237 (1952).

(9) J. C. Evans, J. K. Wilms-hurst and H. J. Bernstein, *Can. J. Chem.*, **34**, 1139 (1956).

TABLE I

ABSORPTIONS IN CM.<sup>-1</sup> APPEARING ON PHOTOLYSIS OF Ar:C<sub>2</sub>H<sub>2</sub>:HN<sub>3</sub> MIXTURES AT 4°K.

Methylenimine	<sup>o</sup> bsd	Methylenimine	<sup>o</sup> bsd
752	..	1215	1212
777	779	1237	1233
838 <sup>a</sup>	..	..	1240
857	857	1269	..
878 <sup>a</sup>	..	..	1359w
922	Obscured	..	1397w
994	Obscured	1486	1470
1001	1006w	1654	1653
1017	..	2032	..
..	1047	3015	3006
1070	1088	3035	..
..	1097	3079	..
1103	1108	3110	..
1132	1132	3341	3322

<sup>a</sup> Not observed in spectrum of liquid.

cyclopropene<sup>10</sup> or methylacetylene,<sup>11</sup> although they might have been expected to be important products of the reaction. Comparison of the product spectrum with that of a dilute solid solution of allene in argon indicates satisfactory agreement of both frequencies and relative intensities.

TABLE II

ABSORPTIONS IN CM.<sup>-1</sup> APPEARING ON PHOTOLYSIS OF SOLID SOLUTIONS OF ACETYLENE AND DIAZOMETHANE IN ARGON AT 4°K.

Ar:C <sub>2</sub> H <sub>2</sub> = 50; Ar:CH <sub>2</sub> N <sub>2</sub> = 50	Ar:C <sub>2</sub> D <sub>2</sub> = 50; Ar:CH <sub>2</sub> N <sub>2</sub> = 50	Ar:C <sub>2</sub> D <sub>2</sub> = 50; Ar:CD <sub>2</sub> N <sub>2</sub> = 50
631	841	641
840	953 <sup>a</sup>	665
953 <sup>a</sup>	1938	724
1015(?)	1953w	818w
1115	1975w	824w
1263(?)	2346	884
1393w	2607	1044
1420	2950	1547(?)
1956	..	1582(?)
2987	..	1845
3022	..	1918
3102	..	1930
3325	..	1937w
..	..	2137
..	..	2200w
..	..	2256w
..	..	2345
..	..	2496w
..	..	2582w
..	..	2606

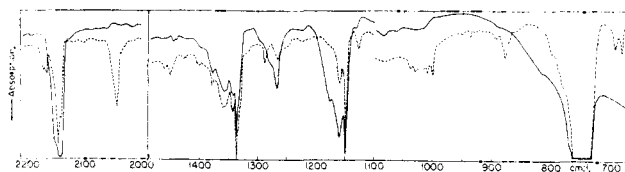
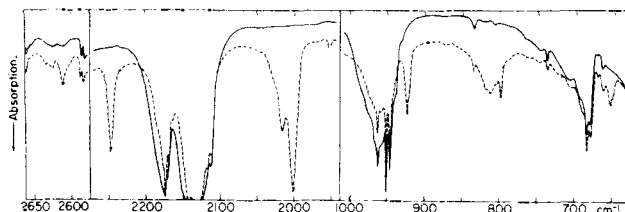
<sup>a</sup> C<sub>2</sub>H<sub>4</sub> absorption.

It should be noted that at 4°K. the argon matrix is sufficiently rigid to prevent gross migration of methylene from the site of its production, as evidenced by the appearance of only small amounts of ethylene. In a typical experiment, utilizing 80 to 100 μmoles each of diazomethane and acetylene, each present to the extent of about 1% in the argon matrix, the most intense allene absorption (1953 cm.<sup>-1</sup>) is about 40%. The intensities of the acetylene absorptions change very little during photolysis.

The photolysis of dilute solid solutions of HN<sub>3</sub> (DN<sub>3</sub>) and C<sub>2</sub>H<sub>2</sub> (C<sub>2</sub>D<sub>2</sub>) in argon yields infrared absorptions at the frequencies given in Table III. Typical spectra for Ar:C<sub>2</sub>H<sub>2</sub>:HN<sub>3</sub> and Ar:C<sub>2</sub>D<sub>2</sub>:DN<sub>3</sub> experi-

(10) D. F. Eggers, Jr., private communication.

(11) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 338.

Fig. 1.—Ar:C<sub>2</sub>H<sub>2</sub>:HN<sub>3</sub> = 70:1:1: —, before irradiation; --, 10-min. photolysis.Fig. 2.—Ar:C<sub>2</sub>D<sub>2</sub>:DN<sub>3</sub> = 100:1:1: —, before irradiation; --, 12-min. photolysis.

ments are shown in Fig. 1 and 2. Upon prolonged photolysis most of the new features tend to diminish in intensity. The acetylene spectrum is sufficiently simple to permit observations of the reaction of NH (ND) with a matrix of C<sub>2</sub>H<sub>2</sub> (C<sub>2</sub>D<sub>2</sub>) at 53°K. A similar pattern of absorptions was observed, allowing for small matrix shifts. In addition, a shoulder appeared after photolysis at 2430 cm.<sup>-1</sup>, on the high frequency side of the C<sub>2</sub>D<sub>2</sub> absorption.

TABLE III

ABSORPTIONS IN CM.<sup>-1</sup> APPEARING ON PHOTOLYSIS OF SOLID SOLUTIONS OF ACETYLENE AND HYDRAZOIC ACID IN ARGON AT 4°K.

Ar:C <sub>2</sub> H <sub>2</sub> :HN <sub>3</sub>	Ar:C <sub>2</sub> H <sub>2</sub> :DN <sub>3</sub>	Ar:C <sub>2</sub> D <sub>2</sub> :HN <sub>3</sub>	Ar:C <sub>2</sub> D <sub>2</sub> :DN <sub>3</sub>
686	693	810	654
697	817(?)	815	723w
878	878	998	798
894w	1120	1012	812
937w <sup>a</sup>	1127sh	1123(?)	872w
1002	1573w	1288	923
1011	2028vvs	1320	1953
1029	2040	1627w	2002vvs
1038 <sup>a</sup>	2163	2002	2015
1129	2777(?)	2020vs	2247
1286	..	2162	2430 <sup>b</sup>
1318	..	2249	2610
1424w <sup>a</sup>	..	2609	..
1447 <sup>a</sup>	..	..	..
1460w	..	..	..
2035sh	..	..	..
2042vvs <sup>a</sup>	..	..	..
2164 <sup>a</sup>	..	..	..
2170w	..	..	..
3045w	..	..	..
3137 <sup>a</sup>	..	..	..
3286 <sup>b</sup>	..	..	..
3337w	..	..	..

<sup>a</sup> Grows on prolonged photolysis. <sup>b</sup> Appears in acetylene matrix experiments at 53°K.

Particularly in experiments involving a relatively high concentration of HN<sub>3</sub>, weak absorptions were observed at 1286 and 1318 cm.<sup>-1</sup>. Becker, Pimentel and Van Thiel<sup>12,13</sup> have observed these absorptions in the photolysis of HN<sub>3</sub> in inert matrices and have assigned them to incompletely characterized species (NH)<sub>x</sub>. The corresponding absorption at 950 cm.<sup>-1</sup> in their deuterated system was not observed. While

(12) E. D. Becker, G. C. Pimentel and M. Van Thiel, *J. Chem. Phys.*, **26**, 145 (1957).(13) M. Van Thiel and G. C. Pimentel, *ibid.*, **32**, 133 (1960).

$\text{NH}_4\text{N}_3$  may contribute to the intense absorption appearing at  $2042\text{ cm}^{-1}$ , our failure to observe other  $\text{NH}_4\text{N}_3$  absorptions suggests that most of this absorption must be contributed by some other species. The assignment of the  $2042\text{ cm}^{-1}$  absorption to the intermediate, rather than to  $\text{NH}_4\text{N}_3$ , receives further support from the failure to observe appreciable enhancement of this peak relative to other absorptions of the intermediate when mixtures of high  $\text{HN}_3$  concentration are photolyzed.

### Interpretation

The literature on the gas phase photolysis of  $\text{CH}_2\text{N}_2$  has been reviewed by Steacie<sup>14</sup> and by Oliveri-Mandalà and Caronna.<sup>15</sup> It is well established that the primary process in the gas phase photolytic decomposition of  $\text{CH}_2\text{N}_2$  involves the formation of  $\text{CH}_2$  and  $\text{N}_2$ . The studies of Milligan and Pimentel<sup>16</sup> indicate that this primary process is also important when  $\text{CH}_2\text{N}_2$  is photolyzed in an inert matrix. Spin conservation requires that  $\text{CH}_2$  be initially produced in a singlet state. However, the experiments of Herzberg<sup>17</sup> have demonstrated that the ground state of  $\text{CH}_2$  is a triplet. His spectral observations on the products of the flash photolysis of dilute gaseous mixtures of diazomethane in argon have indicated that in this system both singlet and triplet methylene are produced. Methylene, formed in an excited singlet state, undergoes collisional deactivation to the lowest singlet state and to the ground triplet state. Approximately ten times as many collisions are required for deactivation to the ground triplet state as for the appearance of the lowest singlet state.

It is not known whether singlet or triplet methylene is the predominant form in inert matrices. However, significant gas-phase studies have been conducted by Kistiakowsky and co-workers,<sup>18-20</sup> who have carefully investigated the kinetics of the reaction of methylene produced by the photolytic decomposition of ketene with, for example, ethylene, propane, cyclopropane, propene, carbon dioxide and ketene. Two types of reaction characterize the methylene produced in their experiments—"insertion" in a C-H bond, with some preference for secondary hydrogens, and attack on a double bond to form a cyclic structure. Their work indicated consistently that the methylene produced by the photolytic decomposition of ketene is present in an excited singlet state and undergoes reaction before deactivation. Later collisional deactivation of the initially formed cyclic species may lead to its stabilization, rearrangement or rupture.

Frey,<sup>21</sup> studying the reaction of methylene with *cis*-butene-2 in a large excess of argon, has obtained some chemical evidence for the production of triplet methylene by collisional deactivation. Like singlet methylene, triplet methylene attacks double bonds, but with randomization of the steric configuration of substituents on the bond carbon atoms. Frey has not obtained evidence for the participation of triplet methylene in "insertion" reactions with C-H bonds.

It is also to be anticipated that the photolytic decomposition of  $\text{HN}_3$  in the argon matrix should produce as primary products singlet NH and  $\text{N}_2$ . The production of NH by the photolysis of gaseous  $\text{HN}_3$  was estab-

lished by Beckman and Dickinson.<sup>22</sup> Subsequent studies<sup>12,13</sup> of the photolysis of  $\text{HN}_3$  in inert solid matrices have confirmed the photolytic production of  $\text{NH} + \text{N}_2$  in this environment. That the ground state of NH is also a triplet has long been established.<sup>23</sup> Hence, there appears to be considerable justification for a parallel consideration of the isoelectronic species  $\text{CH}_2$  and NH.

The possibility that electronically excited acetylene is of importance in the system under study appears to be very remote, since the inefficiency imposed by the nearest-neighbor requirement would be multiplied by the relatively low transition probability for acetylene absorption in the range between 2500 and 2200 Å.

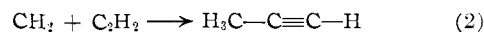
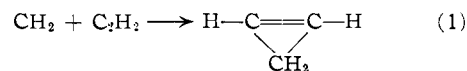
The reactions of  $\text{CH}_2$  and NH with double-bonded species heretofore studied<sup>2,4a,b</sup> give considerable evidence for the stabilization of cyclic species in the matrix. Hence the appearance of ethylenimine in the matrix reaction of NH with  $\text{C}_2\text{H}_4$  confirms the anticipated result.

The identification of allene as the major and possibly as the sole product of the reaction of methylene with acetylene in an argon matrix is rather surprising. By analogy with the reactions of methylene with double-bonded species, cyclopropane would have been expected to be the most likely product. Since this molecule is sufficiently stable to have yielded to infrared spectral observation in both the gas and solid states,<sup>10</sup> if excited cyclopropane is an intermediate in the reaction under study, one might expect ready stabilization of this species by matrix collisions.

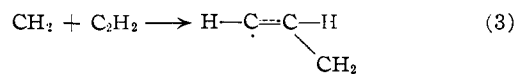
Methylacetylene would certainly be expected to be observed if the "insertion" reaction, characteristic of singlet methylene, occurs to an appreciable extent. It might also be predicted to be a likely product in the rearrangement of the intermediate, since at low temperatures it is thermodynamically more stable than allene.<sup>8</sup>

The closest analog to the present matrix study appears to be that of Haller and Pimentel<sup>5</sup> on the isoelectronic reaction between  $\text{C}_2\text{H}_2$  and  $\text{O}(^3\text{P})$  to produce ketene. Although their system does not offer the possibility of producing alternate thermodynamically stable structures, it appears possible to consider parallel primary reactions for the reaction of  $\text{CH}_2$  (or NH) with  $\text{C}_2\text{H}_2$ .

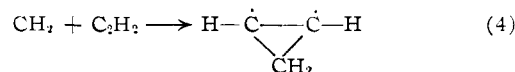
Singlet  $\text{CH}_2$  might be expected to undergo reaction either with the  $\text{C}\equiv\text{C}$  bond or with the C-H bond of  $\text{C}_2\text{H}_2$



On the other hand, triplet  $\text{CH}_2$  might undergo primary reaction with  $\text{C}_2\text{H}_2$  in either of the ways



or



The cyclopropane formed in 1 and the methylacetylene formed in 2 would initially be in excited states. However, there would be an excellent chance of their stabilization by collisional deactivation in the matrix. The species produced by reaction 3 or 4 can easily be envisioned to undergo further isomerization. Al-

(14) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954.

(15) E. Oliveri-Mandalà and G. Caronna, *Gazz. chim. ital.*, **81**, 523 (1951).

(16) D. E. Milligan and G. C. Pimentel, *J. Chem. Phys.*, **29**, 1405 (1958).

(17) G. Herzberg, *Proc. Roy. Soc. (London)*, **A262**, 291 (1961).

(18) H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 5373 (1957).

(19) G. B. Kistiakowsky and K. Sauer, *ibid.*, **80**, 1066 (1958).

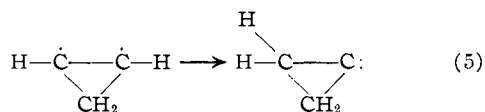
(20) J. N. Butler and G. B. Kistiakowsky, *ibid.*, **82**, 759 (1960).

(21) H. M. Frey, *ibid.*, **82**, 5947 (1960).

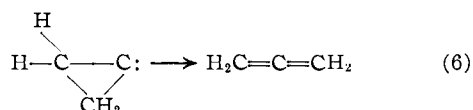
(22) A. O. Beckman and R. G. Dickinson, *ibid.*, **50**, 1870 (1928); **52**, 124 (1930).

(23) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2d Edition, D. Van Nostrand Co., Inc., Princeton, N. J., 1950, pp. 369-370.

though the spectra of partially deuterated allenes other than allene-1,1-*d*<sub>2</sub> have not been reported, the evidence presented in Table II gives reasonable indication that the hydrogens of CH<sub>2</sub> do not "scramble" with the deuterium atoms in C<sub>2</sub>D<sub>2</sub>. Matrix deactivation of 3, involving a migration of the hydrogen atom from the central carbon, might yield either allene or methylacetylene. A possible mechanism for the rearrangement of the product of reaction 4 might be



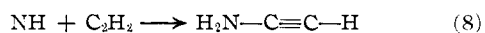
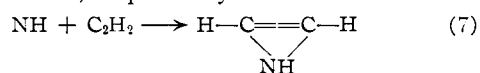
followed by



MacKay and co-workers<sup>24</sup> have postulated reaction 6 as occurring in the rearrangement of the intermediate formed by the reaction of atomic carbon with ethylene; C<sup>11</sup> is found to occupy the central position in the resulting allene.

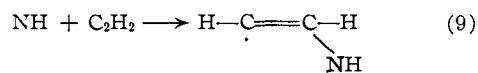
The present studies do not offer conclusive evidence supporting any of the above mechanisms. However, spectral observation of allene as the predominant product of the matrix reaction gives considerable support for the mechanism outlined by reactions 4, 5 and 6. Presumably allene formed by reaction 6 undergoes further deactivation by collisions in the matrix.

A parallel reaction sequence may be envisioned for the attack of NH on C<sub>2</sub>H<sub>2</sub>. Thus, singlet NH might yield energetic forms of acetylenimine or aminoacetylene by reactions 7 or 8, respectively. Matrix deactivation

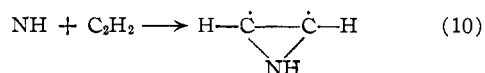


might lead to the stabilization of such species, not previously observed, at very low temperatures. Secondary rearrangement may lead to the stable species methyl cyanide or methyl isocyanide or to other species not previously reported.

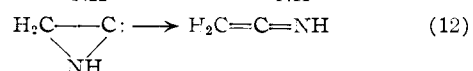
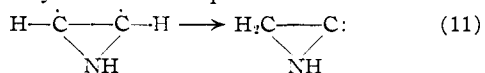
The primary reactions to be anticipated for triplet NH and C<sub>2</sub>H<sub>2</sub> are



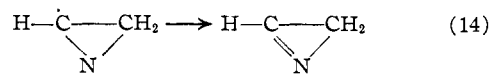
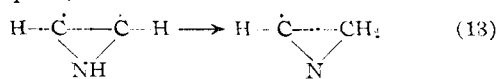
and



It is also possible to envision the parallel of reactions 5 and 6, in which the product of reaction 10 rearranges to the previously unobserved species ketenimine.



An alternate possibility for rearrangement of the cyclic species produced in reaction 10, as well as for that of reaction 7, would lead to the formation of azacyclopropene, as



Smolinsky<sup>25</sup> has reported the formation of 2-phenylazirine, the monophenyl derivative of azacyclopropene, as a decomposition product of  $\alpha$ -azidostyrene. Presumably the phenyl group permits sufficient energy delocalization to stabilize the ring. It is conceivable that the matrix may play a similar energy dissipation role in the present experiments.

Of the possible products, aminoacetylene and azacyclopropene are easily excluded. Characteristic absorptions should occur for the first of these near 2100 and 1600 cm.<sup>-1</sup>, the usual C $\equiv$ C stretching and NH<sub>2</sub> deformation frequencies, respectively. Neither absorption is observed. Smolinsky characterized 2-phenylazirine with the aid of a strong C=N absorption near 1740 cm.<sup>-1</sup>. This, too, is missing from the present experiments.

It would be difficult to predict the absorption frequencies to be expected from acetylenimine. However, since it appears to be even less stable than cyclopropene, which was not stabilized in the CH<sub>2</sub>:C<sub>2</sub>H<sub>2</sub> experiments, the production of acetylenimine by the attack of NH on C<sub>2</sub>H<sub>2</sub> appears to be relatively unlikely.

It is not possible completely to exclude methyl cyanide or methyl isocyanide. Several of the absorptions in Table III coincide rather closely with the fundamental absorption frequencies of these two species.<sup>26</sup> Moreover, the 2250 cm.<sup>-1</sup> absorption which is so intense in the ND + C<sub>2</sub>D<sub>2</sub> experiment coincides very well with the most intense feature of the CD<sub>3</sub>CN spectrum.<sup>27</sup> Its intensity is, however, too great to be attributed wholly to CD<sub>3</sub>CN.

Nevertheless, several absorptions shown in Table III cannot be assigned to methyl cyanide or to methyl isocyanide. Notable among these is the most intense absorption in these observations, that appearing between 2000 and 2045 cm.<sup>-1</sup>. This absorption may yield an important clue to the nature of the NH:C<sub>2</sub>H<sub>2</sub> intermediate. A characteristic feature of allene-like compounds, exhibited by a wide range of species, including CO<sub>2</sub>, azides, isocyanates, ketene, diazomethane and, of course, allene, is an intense skeletal asymmetric stretching vibration between about 1950 and 2350 cm.<sup>-1</sup>. As shown in Table III, systematic deuterium substitution affects this absorption frequency relatively little, with a slight lowering of the frequency for each deuterium atom added. The parallel to the corresponding mode of allene, near 1950 cm.<sup>-1</sup>, is striking.

While a detailed assignment of the absorptions of this intermediate will not be attempted, the other absorptions observed seem to be consistent with those expected for NH and CH<sub>2</sub> motions. The broad band observed at about 1030 cm.<sup>-1</sup> in the NH:C<sub>2</sub>H<sub>2</sub> compound (815 cm.<sup>-1</sup> in ND:C<sub>2</sub>D<sub>2</sub>) appears to be contributed by several modes. The 1129 cm.<sup>-1</sup> absorption in NH:C<sub>2</sub>H<sub>2</sub> also resembles in shape and relative intensity that at 923 cm.<sup>-1</sup> in ND:C<sub>2</sub>D<sub>2</sub>. Unfortunately, CH<sub>2</sub> absorptions to be expected near 3000 cm.<sup>-1</sup> appear only tentatively; the very intense  $\nu_3$  C<sub>2</sub>H<sub>2</sub> absorption has a broad low frequency "tail" that tends to mask other absorptions as low as 3000 cm.<sup>-1</sup>. The 3286-2430 cm.<sup>-1</sup> absorptions seen in the acetylene matrix experiments at 53°K. may also correspond. Since instrumentation for the low frequency infrared region was not available for the present experiments, information regarding the torsion mode and the two C=C=N

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bending modes expected for ketenimine is incomplete. Hence, the spectral identification of ketenimine, despite considerable support, must remain inconclusive.

### Conclusions

The attack of the isoelectronic species  $\text{CH}_2$  and  $\text{NH}$  on the  $\text{C}=\text{C}$  bond of  $\text{C}_2\text{H}_4$  in an inert matrix leads to the complete stabilization of the corresponding cyclic species. However, the principal product of the  $\text{CH}_2$

+  $\text{C}_2\text{H}_2$  reaction in the matrix is the linear species allene. Considerable evidence also supports the stabilization of the previously unobserved species ketenimine in the corresponding reaction of  $\text{NH}$  with  $\text{C}_2\text{H}_2$ . A consideration of possible mechanisms for the formation of these species suggests that at least some of the  $\text{CH}_2$  and  $\text{NH}$ , initially in an excited singlet state, may be deactivated by the matrix to the ground triplet state before reaction with  $\text{C}_2\text{H}_2$ .

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PA.]

## Compressibility of Gases. IV. The Burnett Method Applied to Gas Mixtures at Higher Temperatures. The Second Virial Coefficients of the Helium-Nitrogen System from 175° to 475°<sup>1</sup>

BY ROBERT J. WITONSKY AND JOHN G. MILLER

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The Burnett method of determining the compressibility factor of gases has been tested for the study of gaseous mixtures over a range of higher temperatures. Mixtures of helium and nitrogen were used at 175°, 250°, 325°, 400° and 475° and up to pressures slightly above 100 atmospheres. At each temperature, seven or more mixtures evenly spaced over the whole range of composition were measured. The results demonstrate the advantages of the method as judged by the values obtained for the second virial interaction coefficient,  $B_{12}$ , which is the quantity of central interest for mixtures. In addition to the rarity of such data in general, these values have especial interest because they lie on the high-temperature side of the maximum in  $B_{12}$  and their variation with temperature is not explained adequately by the existing theory of intermolecular interactions.

### Introduction

Previous experiments at this Laboratory<sup>2-4</sup> have revealed the advantages of the Burnett<sup>5</sup> method for obtaining compressibility data for gaseous mixtures. Those studies were limited to measurements at a single temperature (30°) and for that reason did not provide sufficient information for testing the agreement between second virial interaction coefficients determined from the compressibility data and those calculated from the intermolecular potential functions. The work reported here was undertaken to examine the potentialities of the Burnett method over a temperature range sufficiently wide to allow this comparison.

The helium-nitrogen system was chosen for the test. Despite the low magnitude of the molecular interactions in this system, the method has produced accurate data for it which are sufficiently fine-grained and extensive to call for refinement of the existing theory of the interaction of such non-polar molecules.

### Experimental

The two Burnett chambers had volumes of 100 and 300 ml. and were constructed of 19-9 DL stainless steel by the High Pressure Instrument Co. of Erie, Penna. Packless bellows valves especially designed for our work by Hoke Inc., were used successfully while immersed in the bath at 175°, but failed at higher temperatures. For the higher temperatures the system was altered so that the valves were external to the bath. For this purpose midjet needle valves with Teflon packing were employed. This modification did not significantly increase the unavoidable small (ca. 1% of total) unthermostated volume associated with the line from the thermostated chambers to the pressure measuring equipment.

The thermostat was a 28 gallon salt-bath kept at constant temperature by a Wheelco model 407 Capacitrol and model 610 magnetic pilot amplifier which controlled the saturable core reactor employed to regulate the power supply to the heaters. The Capacitrol picked up its signal from a Chromel-Alumel thermocouple located in the bath. Fine control was obtained manually with a Variac placed in the voltage supply to the magnetic am-

plifier. To guide this manual control and to determine the absolute value of the temperature, a platinum resistance thermometer placed in the bath between the chambers was used with a Leeds and Northrup G-2 Mueller bridge, the operator being guided by the bridge balance. The platinum resistance thermometer and the precision resistor used to calibrate the bridge were both calibrated by the National Bureau of Standards. With this arrangement the temperature was maintained within  $\pm 0.01^\circ$  at 175° and 250° and  $\pm 0.02^\circ$  at the other temperatures.

All pressures were measured with the same dead-weight piston gage as used in the earlier studies.<sup>3,4</sup> A Ruska Instrument Co. model 2406 pressure differential diaphragm indicator was used as the null device. The sensitivity of the indicator was 0.001 atmosphere when determined at one atmosphere. Flexing of the diaphragm was used to exchange gas in the indicator and the line connecting it to the first chamber with the gas in that chamber; this also enhanced the mixing.

The effective area of the piston was obtained by balancing the gage against the ice-point vapor pressure of carbon dioxide, taken as 34.4009 atmospheres.<sup>6</sup>

The helium and nitrogen used in this study were analyzed with a mass spectrometer. Both were better than 99.8% pure and were used without further purification. The carbon dioxide was known to contain 0.16% water and traces of hydrocarbons. These impurities were removed by passing the gas into an evacuated high pressure cylinder containing magnesium perchlorate at 200°.

The starting pressure in each run was close to 100 atmospheres. The volumes of the chambers given above were such that ten or more expansions could be obtained before the pressure became too low. The high pressure readings were reproducible to 1 part in 20,000; however, there was greater variation for pressures below 20 atmospheres because of the 0.001 atmosphere limiting sensitivity of the diaphragm indicator.

### Results

In earlier articles<sup>2-4</sup> methods have been given for treating the series of pressure readings,  $p_0, p_1, p_2, \dots, p_r, p_{r+1}, \dots$ , obtained in the Burnett expansions. These methods all employ the fundamental relationship which exists for any pair of the readings and the corresponding values of  $Z$ , the compressibility factor

$$p_r/p_{r+1} = N(Z_r/Z_{r+1}) \quad (1)$$

where  $N$  is the ratio of the volume after expansion to that before. In particular, those articles have dealt with the evaluation of the virial coefficients,  $B, C, D, \dots$ , in the equation of state

$$Z_r = 1 + Bp_r + Cp_r^2 + Dp_r^3 + \dots$$

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