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A SPECTROSCOPIC STUDY OF THE PHOTODECOMPOSITION OF DIAZOMETHANE

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Abstract—The decomposition of diazomethane by photolytic means has been studied both in inert gas matrices near 4°K and in the gas phase near 295°K. The direct detection of the diazomethyl radical, HCNN and DCNN, and evidence for the participation of methanal azine, $H_2C{=}N{-}N{=}CH_2$, by vibrational spectroscopy proved that both species play a significant role in the decomposition schemes under the conditions of investigation. The present results make possible the reinterpretation of the data from earlier published experiments to conform to these schemes. The isomerisation of diazomethane is also discussed, and evidence is presented for the production of both diazirine and isodiazomethane under certain photolytic conditions, the former by an intramolecular process and the latter by the recombination of the diazomethyl radical with a hydrogen atom. The vibronic absorption spectra of gaseous diazomethane at 295°K are presented, and deductions concerning photochemical processes are drawn.

1. INTRODUCTION

DIAZOMETHANE has had extensive use as a parent species of the methylene radical. Analysing chemically by classical methods, Kirkbride and Norrish[1] established that a primary photochemical process of diazomethane involved dissociation to methylene and molecular nitrogen. Before a further attempt to obtain a vibrational spectrum of the methylene radical, following photolysis of diazomethane at cryogenic temperatures, the prerequisite of estimated vibration frequencies was recognized. At the time that Milligan and Pimentel[2] mentioned their expected frequencies, the structure of the radical was not determined. After Herzberg's work[3], the ground state is believed to be (linear) $^3\Sigma_g^-$ the CH bond length being extraordinarily small, 1·03 Å. From spectra-structure correlations[4, 5] and a calculation of the bending force constant[6], the fundamental frequencies can be estimated from Herzberg's equations [7(b)] to be ν_1 (i.r. inactive) = 3300 cm^{-1}, $\nu_2 = 747$ cm^{-1} and $\nu_3 = 3930$ cm^{-1} (both i.r. active). By comparison with a similar calculation[6] for ν_2 for the (linear) $^2A_1\pi_u$ state of NH_2, that bending frequency may be a considerable overestimate. Thus the predicted frequencies lie outside the spectral region previously searched for them (at the time the present experiments were commenced), and this recognition raised hope for success in the objective.

However, even after the present experiments, it is still true that positive spectroscopic detection of methylene (among several other radicals produced after flash photolysis of diazomethane) has been achieved only in the gas phase[3]. Although the spectroscopic data from the cryogenic experiments of Milligan and Pimentel[2] and of DeMore, Pritchard and Davidson[8] are similar, the conclusions of these groups contrasted: the former workers suggested that possible bending frequencies of the methylene radical had been detected, whereas the latter group concluded that convincing evidence for the isolation of methylene was not present. Moreover, despite some directly comparable experiments, the data of Robinson and McCarty [9] differ considerably from those of Goldfarb and Pimentel [10]. As a result of these cryogenic investigations, there have been several tentative assignments of ultra-violet and infra-red absorptions to radicals and isomers which have not been unambiguously confirmed. The argument that, because diazomethane has been decomposed, methylene radicals are formed and trapped, has on occasion been implied without justification.

Therefore, the re-examination of the photochemistry of diazomethane which has been made under both cryogenic and gaseous conditions has yielded definite conclusions concerning processes in this system. First of all, the vibronic absorption, between 14,000 and 52,500 cm^{-1}, has been quantitatively obtained as a basis for the discussion of photochemical processes. Then from the cryogenic and gas phase results, two new decomposition schemes were discovered; the first path involved the diazomethyl radical [11]:

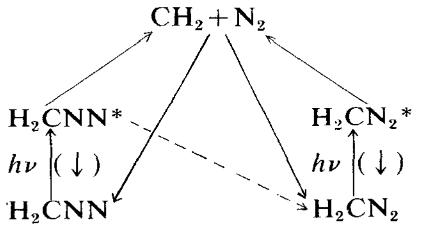
$$\begin{aligned} H_2CNN + h\nu &\rightarrow HCNN + H \\ HCNN + h\nu &\rightarrow CH + N_2 \\ 2CH &\rightarrow HCCH \end{aligned}$$

$$\left.\begin{aligned} CH_2 + H_2CNN &\rightarrow CH_3 + HCNN \\ \text{or} \qquad H + H_2CNN &\rightarrow CH_3 + N_2 \end{aligned}\right\}$$

whilst the second involved the intermediacy of methanal azine [12]:

$$\begin{aligned} CH_2 + NNCH_2 &\rightarrow H_2CNNCH_2 \\ H_2CNNCH_2 + h\nu &\rightarrow 2H_2CN \\ 2H_2CN &\rightarrow HCN + H_2CNH \\ 6H_2CNH &\rightarrow (CH_2)_6N_4 + 2NH_3. \end{aligned}$$

Also evidence will be briefly presented for some diazomethane (designated H_2CNN) isomers being formed in the matrix experiments; diazirine (H_2CN_2) and isodiazomethane (HCNNH) are discussed. The equations are:



and

$$H + HCNN \rightarrow HCNNH.$$

Much of the previously published data is referred to, and is in some cases re-interpreted. These topics are treated in the following sections.

2. EXPERIMENTAL

The apparatus employed in this study had three functions, cryogenic, spectroscopic or photochemical. The site of the reactions at temperatures near zero was the surface of a caesium bromide crystal maintained at the desired temperature by indirect thermal contact with the appropriate refrigerant contained in a modified cryostat of the type devised by Deurig and Mador[13]. The refrigerants used were liquid helium at its normal boiling point, or solid nitrogen at 45–47°K, surrounded by a vessel containing liquid nitrogen serving as a radiation shield. The cryostat was mounted in the sample compartment of a Unicam SP100 spectrophotometer[14] which could scan from 370 to 5000 cm^{-1} with spectral slit widths generally less than 3 cm^{-1}[15]. This apparatus has been previously described[16] and illustrated[11]. Other spectrometers used for gaseous samples were Unicam SP800C, Perkin–Elmer 137UV and Cary 14 instruments for vibronic spectra, and Perkin–Elmer 137 and 521 for vibration-rotation spectra.

Three sources of u.v. radiation for photolytic purposes were employed. For gaseous samples only, the light from a 1 kW. A.E.I. Mazda ME/D mercury arc operating at 15 atm pressure was collimated by an efficient lens system; the radiation emitted consisted of atomic lines greatly broadened and superimposed upon an intense continuum with a maximum near 24,000 cm^{-1}, with relatively little output at frequencies greater than 35,000 cm^{-1}, and in particular only a narrow weak band, at 42,000 cm^{-1}, above the strongly reversed 'resonance' line. Another high-pressure mercury arc, the 125 W. Philips HPK (or MBL/U) lamp operating at 8 atm and run from a Philips L4125 series ballast, had a narrower line emission and a continuum most intense near 31,000 cm^{-1} and extending significantly to 50,000 cm^{-1} (except for the reversed 'resonance' line at 39,413 cm^{-1}). The latter lamp was mounted such that it could directly replace the external Nernst source of the SP 100 spectrometer. A low-pressure mercury lamp, with negligible emission except at the 39,413 and 54,065 cm^{-1} lines, was mounted in the evacuated SP100 sample well adjacent to the radiation shield opposite the sample, as illustrated previously[11].

The chemicals used were prepared by vacuum methods and purified by multiple distillations in a clean high-vacuum system. Diazomethane was prepared by the alkaline hydrolysis of N-methyl, N-nitroso-*p*-toluenesulphonamide (Eastman or Merck, Sharpe and Dohme) in 2-(2-ethoxyethoxy)-ethanol. Hydrogen azide and hydrogen cyanide were prepared from their salts[17]. Methanal azine was prepared by the depolymerisat on of the precipitate obtained by mixing chilled hydrazine with polyoxymethylene[18]. Purity was checked by i.r. and u.v. spectroscopic analysis of the gases. Inert gases were British Oxygen Company spectroscopic grade.

3. ELECTRONIC ABSORPTION OF DIAZOMETHANE

As illustrated in Figs. 1 and 2, there are three distinct regions of absorption of diazomethane in the u.v. The spectrum consists of two diffuse banded regions and, beyond 52,000 cm^{-1}, some narrower bands assigned to Rydberg series of which the discrete structure of some bands has been analysed[19].

The first absorption band, illustrated in Fig. 1, is a very weak continuum with some superimposed diffuse structure. There are two equal maxima at 24,320 and 25,250 cm^{-1}, decadic molar extinction coefficients being $5{\cdot}1 \pm 0{\cdot}4$ $l\text{-mole}^{-1}\,cm^{-1}$. The band is asymmetric with half maximum intensity at 22,300 and 28,100 cm^{-1}. A graphical integration of the area under the absorption curve between 19,000 and 35,000 cm^{-1} yields the value of the oscillator strength $1{\cdot}3 \times 10^{-4}$. There is along the lesser frequency slope of this band a series of inflections which are scarcely distinct but reproducible on

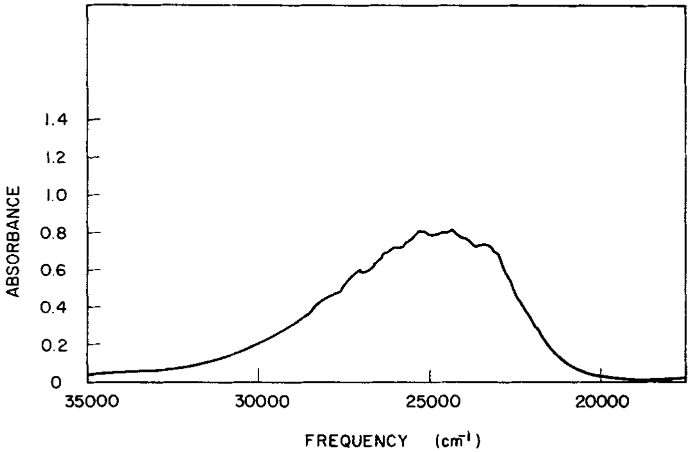


Fig. 1(a). Vibronic absorption of gaseous diazomethane from 17,000 to 35,000 $\mathrm{cm^{-1}}$ (SP800C spectrometer; spectral slitwidth of 30 $\mathrm{cm^{-1}}$). The discontinuity at 27,000 $\mathrm{cm^{-1}}$ is an instrumental artefact. The pressure of gas was 270 Torr. and the path length 100 mm.

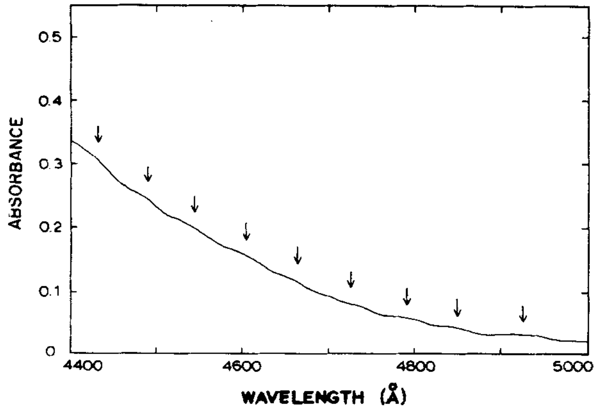


Fig. 1(b). Portion of first band of gaseous diazomethane obtained at a pressure of ~ 100 Torr. and path length 100 mm. (Cary 14 spectrometer; spectral slit width of 6 $\mathrm{cm^{-1}}$.) Arrows indicate apparent maxima of diffuse structure.

all 3 u.v. spectrometers, with minimum slopes at 19,800, 20,100, 20,400, 20,700, 20,950, 21,250, 21,500, 21,800, 22,100, 22,300, 22,650 and 23,000 $\mathrm{cm^{-1}}$ (measured with a spectral slit width of 30 $\mathrm{cm^{-1}}$). Along the top of the band and the other side, there are the more nearly discrete maxima at 23,400, 23,950, 24,320, 24,600, 25,250, 25,670, 26,020, 26,300, 27,200, 28,150 and 29,000 $\mathrm{cm^{-1}}$ (values from SP800C measurements). Both the extinction coefficient at the maxima and the observed structure of the portion of the band in the visible region are in excellent agreement with the early

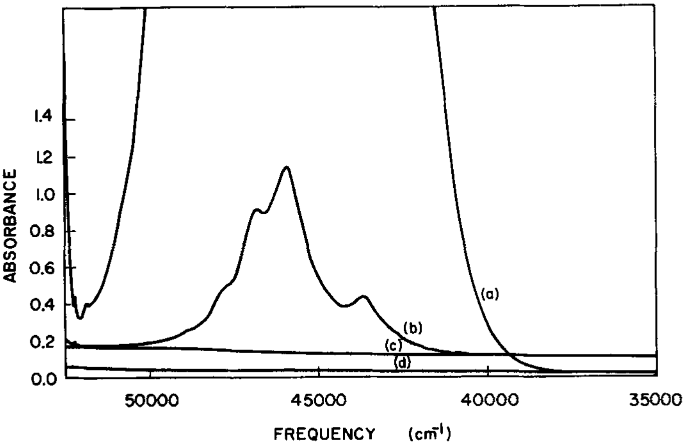


Fig. 2. Vibronic absorption of gaseous diazomethane from 35,000 to 52,500 cm^{-1}. The pressure of gas was 13·5 Torr. for path lengths of (a) 100 and (b) 1·0 mm; the remaining curves are the appropriate base lines for the evacuated cells, (c) 1 m and (d) 100 mm.

data[1], but the fact that the structure is very diffuse (cf. Fig. 1(b)) indicates that the visual examination of photographic plates can be misleading. The structure observed on the other side of the band agrees with that of a published[20] curve, which was also obtained photographically.

The second absorption system, in Fig. 2, is a very intense continuum with some broad but well defined maxima. The maximum extinction coefficient is 13,400, with a probable error of 10 per cent due to inaccuracy of measurement of the small pressure, at 45,880 cm^{-1}; the extinction coefficient at 39,413 cm^{-1} is 100 ± 20. A graphical integration of the intensity between 38,000 and 52,000 cm^{-1} leads to a value of 0·26 for the oscillator strength of the transition. The true maxima of the system are at 43,760, 45,880 and 46,820 cm^{-1}, with additional structure indicated at approximately 44,700, 47,700, 48,900, 49,850 and 50,850 cm^{-1}. This band when also recorded for deuterated diazomethane showed identical frequencies of absorption maxima, but the structure was slightly less diffuse; for instance, the partially resolved shoulder at 47,700 cm^{-1} for H_2CNN became a true maximum in the deuterated case. The values of the frequencies and extinction coefficients for this band are in fair agreement with those mentioned earlier[21] when those values are corrected for the assumed extinction coefficient of 3 at 25,000 cm^{-1}.

Despite the diffuse nature of the band structure, particularly in the first absorption region, its reproducibility on various spectrometers at various times has provided confidence that the structure is real. As the vibrational structure can supply indications of the nature of the electronic transitions, and as the latter is valuable as a basis of discussion of the photochemical processes, assignments of the electronic transitions will now be considered. The presence of two vibrational progressions in the first absorption region is an indication of two over-lapping vibronic transitions. Two transitions of diazoalkanes have already been postulated to occur in this region[22]. The first progression is of vibrational interval approximately 300 cm^{-1}, and can be traced from 19,800 cm^{-1}, where it is barely visible above the base line, to 26,020 cm^{-1}, in the midst of the second progression. Such a long progression, of over twenty quanta of some vibration of the excited state, indicates a marked change in structure. In the ground state ketene is isostructural and isoelectronic with diazomethane[23]. Ketene shows a near u.v. progression of diffuse bands, 26 intervals of 365 cm^{-1}, being reported between 26,000 and 38,000 cm^{-1}[24]. That transition has been assigned as ${}^1A_2 \leftarrow {}^1A_1$, of the type $\pi^* \leftarrow n$, with the molecule remaining planar in the excited state but becoming markedly bent at the central carbon atom[24]. By analogy, a similar assignment can be made for diazomethane; the excited state should really be designated A'' in the point group C_s. The decrease of ν_9 (Mulliken's[25] revised notation) from 421 cm^{-1}[26] in the ground state of H_2CNN to 300 cm^{-1} in the excited state parallels closely the situation for ketene (from 438 [27] to 365 cm^{-1}).

Unlike the first, the second progression, of vibrational interval approximately 950 cm^{-1}, seems to have a fairly well defined origin at 23,400 cm^{-1}; and may therefore belong to an electronically allowed transition for which there seems to be no counterpart for ketene. Whether or not the electronic transition is orbitally allowed, the progression will consist mainly of totally symmetric vibrations. The frequency of 950 cm^{-1} is closest to that of ν_4, 1170 cm^{-1} for H_2CNN, of the appropriate A_1 symmetry of the ground state[26], which is a symmetric skeletal stretching mode. An allowed transition ${}^1A_1' \leftarrow {}^1A_1$, of the type $\pi^* \leftarrow n$, has been postulated[22] to occur in this region, although such an assignment has been questioned[28]. As the nature of the observed absorption is consistent with such an assignment, it will here be repeated. This apparently allowed transition could be expected to account for the majority of the intensity in this region, or the underlying continuum could denote a third electronic transition to energies above the first dissociation limit. The diffuseness of both this and the previously considered vibrational progressions, together with what seems to be an underlying continuous absorption, indicates a strong predissociation, or even a direct dissociation from a different portion of the potential surface. Much chemical evidence[29] attests to a dissociation into methylene radicals and molecular nitrogen by photolysis in this region. This process is consistent with the form of the vibration excited in the ${}^1A_1'$ state as the form is neither truly symmetric nor antisymmetric except for a symmetric molecule of the type YXY.

In the second absorption region there is a vibrational progression of frequency interval 1000 cm^{-1} traceable from 43,760 to at least 50,850 cm^{-1}. The absence of deuterium effect on the frequencies indicates that the transition involves the heavy-atom skeleton. The oscillator strength is appropriate to a strongly allowed electronic transition, as also suggested by the apparent origin of the progression at 43,760 cm^{-1}. A $\pi^* \leftarrow \pi$ transition is suitable to these circumstances, and the previous assignment of this type has been ${}^1A_1'' \leftarrow {}^1A_1$ with the N—N bond in the molecular plane chiefly affected[22]. The lack of deuterium isotope effect on the frequencies supports this assignment. The corresponding transition for ketene has an origin at 46,990 cm^{-1} and a vibrational interval of 1100 cm^{-1}[7(e)]. The antisymmetric skeletal stretching vibrations ν_2 of H_2CCO and H_2CNN are respectively 2152 and 2102 cm^{-1}, and show only a slight deuterium isotope shift[26, 27]. The corresponding vibration frequencies in the excited states might be expected to show the same trend toward decrease, whereas ν_4 of H_2CCO and H_2CNN are respectively 1118 and 1170 cm^{-1}. The latter vibrations also exhibit marked deuterium isotope effects in the ground states. A peculiarity of the diazomethane progression is that the second member of the progression seems to be missing although the third and fourth members are well defined. Too intense to represent a 'hot' band, the first band, at 43,760 cm^{-1}, could of course belong to a separate electronic transition, but then the separation from the next maximum being twice the succeeding separations would represent a suspicious coincidence. Also the postulation of a second transition commencing at 45,880 cm^{-1} would require that the first member of the progression be the most intense and therefore that only a very small bond length increase occur in the excited state. Such a slight increase is incompatible with the nature of the transition with its excitation from a bonding to an anti-bonding orbital, or even to any intra-valence shell transition 46,000 cm^{-1} above the ground state of such a chemically reactive molecule (for instance, the heat of formation is +17,000 cm^{-1}[30]). Therefore to consider the 43,760 cm^{-1} band to belong to the rest of the progression seems advisable. An explanation of both the intensity (Franck–Condon) anomaly and the predissocation effect indicated by the diffuseness of the bands might be that a crossing of the potential surfaces of the terminal state of the optical transition and of the perturbing state causing the predissociation occurs in the vicinity of the first vibrational level ($\nu_2' = 1$). There seems to be a region of continuous absorption in the region of 42,000 cm^{-1}, as the onset of absorption near the origin of the 43,760 cm^{-1} band is very gradual whereas near 41,000 cm^{-1} the absorption curve obtained at a greater path length shows a much steeper rise. Scans obtained under intermediate pressure-path length conditions show no discrete maximum nor even recognisable inflection. However the continuum of absorption, if it does exist apart from the main progression, could be due to a $\sigma^* \leftarrow \pi$ transition which seems generally to be energetically possible at frequencies just less than the $\pi^* \leftarrow \pi$ transition [31].

Although some simple descriptions of the transitions observed for diazomethane have been attempted in the previous paragraphs, final assignments of the transitions cannot be made without at least further experimental data such as accurate absorption curves for isotopic molecules. According to the assignments tendered, the deuterium effect on the $A_2 \leftarrow {}^1A_1$ transition is expected to be negligible, whereas a measurable effect might be produced on the vibrational interval of the adjacent ${}^1A_1' \leftarrow {}^1A_1$ transition. Conversely, diazomethane $H_2C^{14}N^{15}N$ is predicted to show a definite decrease of the intervals in the ${}^1A_1'' \leftarrow {}^1A_1$ transition, but the effect on the ${}^1A_2 \leftarrow {}^1A_1$ transition would not be observable because of the diffuseness of the progression. As the spectra are likely to remain of a diffuse nature, theoretical assistance will be required in the form of extensive computations. The assignments presented here agree with those postulated earlier [22], but are not consistent with the computed order of orbitals in an extended Hückel calculation [28]. However, as the experimental data are more readily treated on the former basis, those assignments are therefore preferred. The scheme of orbital and state energies according to these assignments are presented in Fig. 3.

4. THE DIAZOMETHYL RADICAL SCHEME

Production of HCNN

Even when over half of the diazomethane initially suspended in an argon matrix (ratio greater than 200) at 4°K was decomposed by the use of the unfiltered HPK lamp, no new i.r. absorptions were detected. Particularly notable was the lack of significant increase of the 950 cm^{-1} line of ethene (initially present as impurity). The predicted regions of the methylene vibration frequencies were especially searched without success. However, when the diazomethane sample was exposed to the mercury

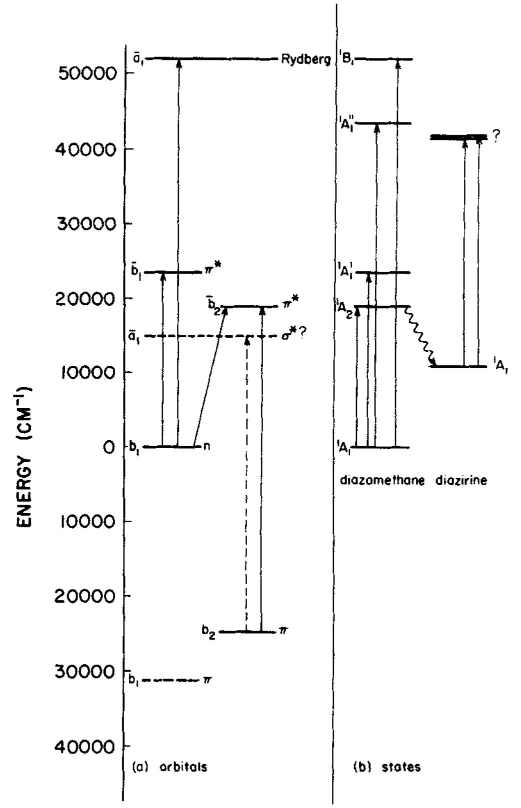


Fig. 3. (a) Orbital energies and excitations deduced from the analysed vibronic spectra of diazomethane. (b) Energies of states and transitions for diazomethane deduced from the spectra, with levels of diazirine for comparison.

resonance lamp, either before or after exposure to the high-pressure lamp, several new absorption lines appeared. The most prominent of these were then reduced in intensity by subsequent use of the HPK lamp, and are labelled *A* (if detected when only H_2CNN is present) or *A'* (if they appear when deuterated diazomethane is used); the data are presented in Tables 1 and 2, and part of the spectrum is illustrated (a) before and (b) after low-pressure lamp irradiation in Fig. 4. When the extent of deuteration was greater than in the experiment yielding the data in Table 2, *A'* but no *A* lines were detected. The ratio of the peak absorbances in Table 2 of the more intense lines *A'* to the closest *A* counterparts is somewhat greater than the ratio of total deuterium to hydrogen in the system. Because not more than one additional line *A'* accompanied each line *A* found in the case that deuterium was not present, it follows directly that the species *A* and its deuterated counterpart *A'*, found together when all three varieties of isotopic-hydrogen diazomethanes were present before photolysis and were all decomposed during photolysis, contain one and only one hydrogen (or deuterium) atom. The slight anomaly of the relative intensities in Table 2 is appropriate to the usual deuterium isotope effect in photo-ejection processes [7(c)]. The *A* and *A'* absorption lines did not appear when diazomethane at a small matrix ratio in argon at 4°K was similarly irradiated.

Table 1(a). Absorption bands recorded before photolysis of H_2CNN in argon

Frequency	After deposition	2 hr HP lamp	1 hr LP lamp	½ hr HP lamp	Assignment
402		0·18	0·16		H_2CNN, ν_7
415		0·13	0·11		H_2CNN, ν_6
426		0·075	0·06		H_2CNN
446		0·02	0·015		H_2CNN
486		0·005	0·005		?
565		0·02	0·015		H_2CNN, ν_5
582		0·01	0·01		
612		0·01	0·01		CH_3?
822	0·011	0·006	0·007	0·009	C_2H_4O
845	0·010	0·005	—	—	?
856	0·26	0·14	0·125	0·11	$H_2CNN, 2\nu_6$
881	0·005	0·01	0·006	0·01	C_2H_4O
950	0·015	0·016	0·013	0·02	C_2H_4
977	0·16	0·08	0·075	0·065	$H_2CNN, \nu_5+\nu_6$
1009	0·010	0·004	0·005	—	?
1035	0·002	0·002	—	—	CH_3OH
1099	0·008	—	0·004	—	?
1107	0·006	—	—	—	H_2CNN, ν_8
1173	0·04	0·018	0·010	0·015	H_2CNN, ν_4
1176	0·007sh	0·002sh	—	—	H_2CNN, ν_4
1263	0·007	0·010	0·008	0·009	C_2H_4O
1399	0·009	—	—	—	H_2CNN, ν_3
1409	0·37	0·21	0·18	0·17	H_2CNN, ν_3
1417	0·008	0·012	0·007	0·01	H_2CNN, ν_3
2001	0·02	0·012	0·007	0·01	$H_2CNN, \nu_3+2\nu_6$
2058	0·016	0·004	—	0·005	$H_2C^{15}NN, \nu_2$
2076	0·013	—	—	0·005	$H_2CN^{15}N, \nu_2$
2090	0·01sh	0·045sh	0·04sh	0·035sh	H_2CNN, ν_2
2099	1·4	0·75	0·70	0·67	H_2CNN, ν_2
2309	0·03	0·015	0·015	0·005	$H_2CNN, 2\nu_4$
2345	0·02	0·02	0·045	0·045	CO_2
2579	0·01	—	0·005	—	$H_2CNN, \nu_3+\nu_4$
3068	0·205	0·115	0·09	0·05	H_2CNN, ν_1
3251	0·03	0·02	0·015	—	$H_2CNN, \nu_2+\nu_4$
3394	0·015	0·02	0·01	—	?
3402	0·01	0·02	0·01	—	?
4170	0·02	—	—	—	$H_2CNN, 2\nu_2$

The tetratomic radicals HNCN and HCNN could result from the loss of a hydrogen atom from H_2CNN. For this process, the energy requirement for diazomethane in the ground state can be estimated[5] to be 38,600 cm^{-1}. HNCN has been observed to result from a secondary reaction in the isothermal flash photolysis of diazomethane, and absorbs at 28,994 cm^{-1}[32]. However, no corresponding absorption band has been recorded by Robinson and McCarty at a similar frequency[9] even though the smaller matrix ratios used in their experiments would tend to favour secondary reactions. The CN bond lengths in HNCN being known fairly accurately to be almost equal[32], this radical can be considered to be derived from carbodiimide rather than cyanamide; the antisymmetric skeletal stretching vibration in alkyl carbodiimides is of frequency ~2140 cm^{-1}[33]. On the other hand, the corresponding vibration of the diazomethyl

Table 1(b).* Absorption bands recorded after photolysis of H_2CNN in argon

Frequency	After deposition	2 hr HP lamp	1 hr LP lamp	½ hr HP lamp	Assignment
661	—	—	0·01	0·01	CO_2
731	—	—	0·01	0·01	C_2H_2
736	—	—	0·01	0·01	C_2H_2
776	—	—	0·005br	—	?
861	—	—	0·28	0·21	*A*
863	—	—	0·13sh	—	*A*
871	—	—	0·015	—	
885	—	—	0·035	0·055	
890	—	—	—	0·01sh	
1005	—	—	—	0·004	
1047	—	—	0·015	0·04	
1049	—	—	0·025	—	
1212	—	—	0·005	0·005	
1589	—	—	0·015	0·01	H_2O
1625	—	0·01	0·005	0·005	H_2CNH ?
1787	—	—	0·145	0·12	*A*
1792	—	—	0·04sh	—	*A*
2055	—	—	0·015	0·025	
2169	—	—	0·02	0·025	*B*
2265	—	—	0·02	0·035	*C*
2650	—	—	0·005	—	?
2750	—	—	0·005	—	CH ?
3233	—	—	0·02	0·015	*A* ?
3712			0·01		H_2O

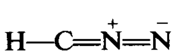
*In Tables 1 and 2, br = broad, sh = incompletely resolved shoulder, and — indicates no measurable absorption. A blank in the intensity columns signifies that that region was not scanned.

anion (as in diazomethyl lithium, supposed from its insolubility[34] in ethoxyethane to have ionic characteristics) has a frequency of 1898 cm^{-1} (sample in paraffin-oil mull). The *A* band at 1787, in shifting only slightly to 1771 cm^{-1} in the deuterated species *A*′, is typical of a (first-row) heavy-atom stretching vibration of a multiple bond; its frequency is certainly closer to that of the diazomethyl anion than to that of simple carbodiimides. What is probably an *A* absorption at 3233 cm^{-1} might be either a CH or an NH valence-stretching vibration, but it is closer to the ν_5 frequency of diazomethane, 3188 cm^{-1}, than to ν_1 of hydrogen azide, 3336 cm^{-1}. The large shift from $A = 861$ to $A' = 725$ cm^{-1} implies that this vibration can be considered to be a hydrogen bending mode, but neither the frequency nor the extent of the shift can be used for the purpose of differentiation between HNCN and HCNN. For HCNN, were it initially formed in the matrix site, to isomerise to HNCN would be unlikely because the energy of activation for such a complicated transformation is not available in a single quantum of the radiation of frequency 39,413 cm^{-1} presumed to be effective in earlier dissociating diazomethane. Thus, compatible with the vibration frequencies and the conditions of production, the probable assignment of the *A* and *A*′ spectrum can be made to the diazomethyl radical. Further evidence to support this assignment is available from the analysis of the bleaching effect and chemiluminescence phenomenon, to be discussed later. The diazomethyl radical frequencies (and intensities) in various matrices are

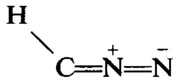
Table 2(a). Absorption bands present before irradiation of deuterated diazomethane in argon (matrix ratio >250) near 4°K

Frequency	After deposition	35 min LP lamp	157 min LP lamp	90 min HP lamp	Assignment
405	0·02		—		H_2CNN, ν_6
471	0·017		0·02		?
477	0·015		—		?
669	0·13	0·125	0·095	0·06	$D_2CNN, 2\nu_6$
723	0·01	0·015	0·01	0·01	C_2D_4
771	0·12	0·10	0·06	0·04	$HDCNN, 2\nu_6$
856	0·018	0·013	0·01	0·01	$H_2CNN, 2\nu_6$
878	0·05	0·05	0·045	0·05	C_2H_4O
908	0·015	0·015	0·005	—	D_2CNN, ν_8
976	0·05	0·047	0·025	0·025	D_2CNN, ν_4
1214	0·26	0·245	0·185	0·13	D_2CNN, ν_3
1305	0·155	0·14	0·10	0·065	$HDCNN, \nu_3$
1407	0·033	0·030	0·022	0·01	H_2CNN, ν_3
1741	0·02br	0·015br	0·01br	0·01br	?
2059	0·045	0·040	0·033	0·025	$D_2C^{15}NN, \nu_2$
2067	0·02	0·015	0·01	0·007	$D_2CN^{15}N, \nu_2$
2079	0·10	0·08	0·055	0·035	$D_2{}^{13}CNN, \nu_2$
2092	1·3	1·05	0·76	0·53	D_2CNN, ν_2
2099	0·58	0·51	0·36	0·24	H_2CNN, ν_2
2172	0·22		0·155	0·11	$D_2CNN, \nu_3+\nu_4$
2218	0·08		0·045	0·05	D_2CNN
2237	0·205		0·14	0·095	D_2CNN, ν_1
2325	0·07		0·035	0·025	$HDCNN, \nu_7$
2343	0·01		0·065	0·07	CO_2
2423	0·14		0·10	0·075	$D_2CNN, 2\nu_3$
2457	0·02		—	—	$HDCNN, \nu_3+\nu_4$
3049	0·015		—	—	$D_2CNN, \nu_2+\nu_4$
3128	0·027		0·02	0·02	$HDCNN, \nu_1$
3291	0·03		0·025	—	$D_2CNN, \nu_2+\nu_3$
4154	0·02		—		$D_2CNN, 2\nu_2$

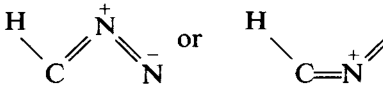
presented in Table 3, and a comparison of the new absorption frequencies attributed to HCNN with frequencies of similar molecules is made in Table 4. On the basis of the available fundamental frequencies, no real distinction between the possible structures I to IV


$H{-}C{=}\overset{+}{N}{=}\overset{-}{N}$

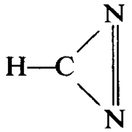
I



II



III



IV

can be made, but II may be the most likely. The pairing of lines in the 860 and 1780 cm^{-1} regions is probably due to the radical's occupancy of crystallographically different trapping sites [35].

It is worth mentioning that methanoic acid (HCOOH) can not be responsible for the *A* lines for the following reasons. The carbonyl-stretching vibration frequency is observed at 1737 cm^{-1} in a nitrogen matrix in which the acid was prepared by the

Table 2(b). Absorption bands recorded after photolysis of deuterated diazomethane in argon (matrix ratio >250) near 4°K

Frequency	After deposition	35 min LP lamp	157 min LP lamp	90 min HP lamp	Assignment
465	—		0·02		CD_3?
664	—	—	0·01sh	0·01	CO_2
725	—	0·025	0·12	0·07	*A'*
752	—	—	0·01	0·015	
852	—	—	—	0·02	
862	—	0·007	0·02	0·015	*A*
1264	—	—	—	0·015	
1279	—	—	0·01	0·015	
1771	—	0·02	0·125	0·09	*A'*
1775	—	—	0·04	0·01	*A'*
1788	—	0·007	0·015	0·005	*A*
2146	—	—	0·01br	0·027	*B'*
2244	—		0·04	0·04	*D*
2260	—		0·02	—	*C*
2543	—		0·01br	0·015	
2587	—		0·01	—	
3641	—		—	0·015	

Table 3. Observed absorptions for HCNN and DCNN in various matrices

HCNN (Ar)	HCNN (Kr)	HCNN (N_2)	DCNN (Ar)
861 (0·28)	860 (0·15)	863 (0·035)*	725 (0·125)
863 (0·13)	866 (0·04)	871 (0·025)*	
1787 (0·145)	1785 (0·07)	1789 (0·035)	1771 (0·125)
1792 (0·04)	1790 (0·03)	1800 (0·085)	1775 (0·04)
3233 (0·02)		3229 (0·035)	

*Interference by other bands makes these intensities uncertain.

Table 4. Comparison of the fundamentals of HCNN with similar molecules

HNNN	H_2CNN	LiHCNN	HCNN	HCN
672	406			
1274	1170	(1152)		
1150	1414		861	713
2140	2102	1898	1787	2089
3336	3184	3215	3233	3312

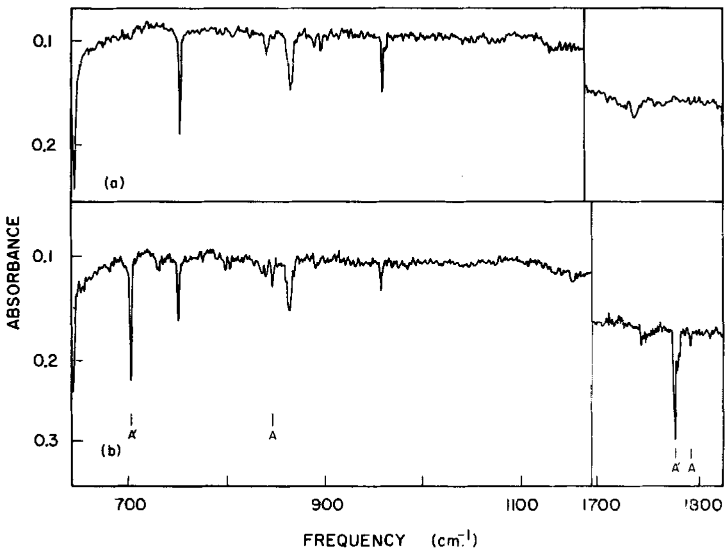


Fig. 4. Vibrational absorption of isotopic diazomethanes in argon (a) before and (b) after irradiation with a low-pressure mercury lamp. Important product absorptions are identified by labels discussed in the main text.

reaction of methylene with deliberately added oxygen[10]. The HCOOH absorption lines were easily detected after use of a medium-pressure mercury lamp unfiltered in Goldfarb's work, but the 1787 cm^{-1} absorption was not detected in this work when the similar radiation from the HPK mercury lamp was first used. Methanoic acid does not absorb near u.v. light strongly enough for the bleaching effect to be operative. In several experiments with varied conditions of deposition rate and of photolysis either simultaneous with deposition or following it, the ratio of the absorbances of the *A* bands at 1787 and 861 cm^{-1} was constant; the 861 cm^{-1} absorption cannot be assigned to methanoic acid, and is distinctly separate from the 878 cm^{-1} absorption of oxirane. Neither bands of other fundamentals of methanoic acid, nor those of methanal and carbon monoxide also reported after the reaction of methylene with oxygen[10], have been detected in these experiments.

Mechanism of production of HCNN

HCNN may be derived from diazomethane simply by ejection of a hydrogen atom. Supporting this dissociation process is the evidence of flash photolysis experiments[3] in which CH appears strongly at no delay under isothermal conditions; in the gas phase the HCNN radical can further dissociate with any excess energy which in the solid matrix is conveniently dissipated through the lattice, or it may be dissociated by a second quantum from the photolysis flash. However, there has been no report of direct detection of HCNN in the gas phase, despite a large number of other radicals produced in such flash photolysis experiments[3]. There is abundant evidence[36] to demonstrate that a small atom can escape from the matrix cage under conditions similar to those of the present experiments. The isotope effect may be partly the result of smaller velocity of photo-ejection of the deuterium atom compared with the hydrogen atom, due to their different masses, but the greater 'tunneling' ability of the hydrogen atom through the potential barrier in the predissociation step is probably more important[37]. However, electron spin resonance (e.s.r.) measurements of diazomethane and (and ketene) experiments in argon and krypton matrices after irradiation by a super-pressure (110 atm) mercury lamp have proved by their characteristic signal methyl radicals[38(a)] to be present at a matrix ratio of 100 but not 300. The mechanism of production was assumed to be primary dissociation of diazomethane to yield methylene (which, owing to the magnitude of its zero-field splitting, could not be directly detected) followed by hydrogen-atom abstraction from a nearby molecule:

$$H_2CNN + h\nu \rightarrow CH_2 + N_2 \tag{1}$$

$$CH_2 + HA \rightarrow CH_3 + A \tag{2}$$

Although impurities were stated[38(a)] to be present, the most probable source of HA was H_2CNN. There was no unambiguous trace of methyl radical absorptions[39, 74] in the present experiments, but at those matrix ratios not even e.s.r. detection was achieved[38(a)]. Further e.s.r. data are pertinent. When diazomethane in argon was irradiated by means of a super-pressure mercury lamp filtered to prevent transmission of frequencies greater than 29,400 cm^{-1}, a spectrum with five lines centred at $g = 2$ was recorded[38(b)], with intensity ratios 1:6:6:1, and a broader line at the centre. The methyl radical and a second species, containing or being CH, were deduced, as well as another radical not characterised[38(b)]. From the present results, the diazomethyl radical is eminently suitable to be the second species. However, both CH_3 and HCNN radicals are unlikely to be trapped in the same cage. Therefore the alternative mechanism can be proposed on the i.r. evidence:

$$H_2CNN + h\nu \rightarrow H + HCNN \tag{1'}$$

The detection of the formyl radical[38(b)] when carbon monoxide was present in the matrix also supports this mechanism, but no hydrogen atoms were directly detected by e.s.r. [38(b)].

The radiation responsible for the dissociation of diazomethane to diazomethyl radical is presumed to be the 'resonance' emission of mercury at 39,413 cm^{-1}. Thus absorption would take place into the tail of the $\pi^* \leftarrow \pi$ absorption band, probably red-shifted slightly in the matrix. Although there is intense absorption[19] by gaseous diazomethane near the resonance frequency, 54,065 cm^{-1}, the transitions in that region have been assigned to Rydberg excitations; transitions of this type have been reported to disappear in noble-gas matrices[31]. There is, as mentioned previously, no isotope effect on the band frequencies in the 43,760 cm^{-1} system. However, although analysis of the vibrational structure of this band suggests that dissociation into methylene and molecular nitrogen is favoured by the form of the vibrations, what matters more is the nature of the dissociation process in the repulsive perturbing state that causes the predissociation. Furthermore, there may be more than one dissociation process in the repulsive state[7(c)]. Even though the methylene dissociation process might be predominant in the gas phase, as methylene reacts with nitrogen[40] to form diazomethane no net reaction would be detected in the matrix unless the methylene radical can escape from the site of production. The long period of search for methylene by optical spectroscopy in cryogenic experiments is in part testimony to the negligible extent of such escape. Thus the minor dissociation process yielding diazomethyl radicals and mobile hydrogen atoms can become dominant in the matrix. Even if the tail of the $\pi^* \leftarrow \pi$ band contained a continuous absorption due to the $\sigma^* \leftarrow \Pi$ transition, the expected products from a direct dissociation from such an excited state might be molecular hydrogen, not atomic hydrogen.

The preferred mechanism of formation, then, for the HCNN radicals detected in this work involves a unimolecular decomposition of diazomethane.

Diazomethyl radical photolysis

As indicated in Tables 1 and 2, the A and A' lines assigned to the diazomethyl radical were produced during low-pressure lamp irradiation. Although several absorption lines initially appearing after the low-pressure lamp irradiation period continued to increase during the bleaching process, it is not possible to correlate any of them with the disappearance of the diazomethyl radical spectrum. That this bleaching effect was produced by the high-pressure mercury lamp but not by the radiation from the Nernst glower i.r. source indicates that frequencies in the region from 16,000 to 36,000 cm^{-1} are responsible. From the e.s.r. results [38], the effective region can be further narrowed to frequencies between 29,000 and probably 36,000 cm^{-1}. Robinson and McCarty have also observed a bleaching effect in their experiments [9], and the result of that was the production of intense spectra of CH, the methylidene radical; the mechanism of their bleaching effect will be considered later. A similar production of CH would seem to be a reasonable decomposition process of the diazomethyl radical in the present experiments. During the bleaching period, no positive new spectrum with absorption at 2733 cm^{-1} (the gas phase zero-line of CH determined from electronic spectra [7(a)] appeared; the reason for this is probably the extremely small intensity of this transition, such that it has never been detected in i.r. emission from flames [41]. The indirect production of CH during initial HPK lamp use, with no measurable concentration of intermediates, would explain the lack of products observed during that operation, even though diazomethane was certainly decomposed. Thus it is postulated that the diazomethyl radical photolysed to methylidene radicals in these cryogenic experiments. Some ethyne (HCCH) was detected in the present experiments even at 4°K, and this molecule would seem to be a reasonable fate for recombining methylidene radicals. Additional support for ethyne production is available in Table 2 of reference [2] in which an intense absorption at 750 cm^{-1} appeared after a diffusion operation, at the frequency near which ethyne crystal exhibits its most intense absorption band [42] (but which is much less than the corresponding band, 838 cm^{-1} [43], for crystalline hydrogen cyanide).

It is difficult to assess the importance of the reactions in the gas phase of the methylidene radical CH. This species would presumably undergo addition and abstraction (or insertion) reactions similarly as methylene and imidogen (NH) radicals. The loss or gain of a hydrogen atom from the products would confuse the distinction between methylene and methylidene reactions. No real study of the reactions of CH has been made except in flames. However, the reaction with the parent molecule diazomethane is likely, serving eventually to produce ethyne possibly via the vinyl radical:

$$\mathrm{CH} + \mathrm{H_2CNN} \rightarrow \mathrm{HCCH_2} + \mathrm{N_2}$$

$$\mathrm{HCCH_2} \rightarrow \mathrm{HCCH} + \mathrm{H}$$

Possible emitters of a red glow

In earlier experiments[2, 44–46], while the temperature of the photolysed sample of diazomethane in argon or nitrogen matrices was increasing, a red emission was observed. The restrictive nature of the SP100 sample compartment precluded such observations with the present apparatus. However, whether the species HCNN or CH could have been involved in the emission mechanism is worthy of brief examination. Dimerisation of these radicals during diffusion could have produced the known molecules 1,2,4,5-tetrazabenzene or ethyne respectively. Tetrazine has a band system observable in both absorption[47] and fluorescence[48], indicating that the transition between zero-point levels of the combining singlet states occurs at 18,130 cm^{-1}; there are only small isotope effects and solvent dependencies on the form and position of the band system. Therefore the facts of the frequency shift of the emission *maximum* to 16,500 cm^{-1} in the warming argon matrix, and the favouring of secondary photolysis of diazomethyl radicals under the best conditions[2, 45] for producing the glow prevent an assignment of tetrazine as the emitter in the matrix. Likewise, consideration of energy transfer mechanisms and Franck–Condon coefficients leads to rejection of ethyne as the emitter. However, the analysis of these factors does provide a basis for future determination of the emitter when further experimental data are accumulated.

5. THE METHANAL AZINE SCHEME

In the previous section concerned with the mechanism of the production of the diazomethyl radical, reference was made to some e.s.r. results which were taken to indicate the occurrence of a methylene abstraction reaction to produce two more trapped radicals[38]. In this case the great sensitivity and selectivity of the e.s.r. method allowed detection of radical intermediates of reactions which were of only minor importance in the overall decomposition scheme. Thus the $10^{12}/\Delta H$ free spins required for an e.s.r. signal is an insignificant fraction of the minimum 10^{17} absorbing molecules of a particular species responsible for i.r. absorption spectra. If the methylene radical were sufficiently mobile in the matrix or if the matrix ratios were so small as to permit reactions such as (2) to occur to a significant extent, the stable products ethene I and methanal azine II would be detected instead, according to the reactions (3) and (4):

$$CH_2 + H_2CNN \rightarrow \underset{\mathrm{I}}{CH_2CH_2} + N_2 \qquad (3)$$

$$CH_2 + NNCH_2 \rightarrow \underset{\mathrm{II}}{H_2CNNCH_2} \qquad (4)$$

Ethene was in fact detected as a product (in negligible yield), cf. Table 1, although some was also present in the sample prior to irradiation; during photolysis some ethene may have been converted to ethyne which is also detected after irradiation. (Separate experiments of irradiation of ethene at 50°K have demonstrated the production of ethyne.) On the other hand, methanal azine is a little known species. As a result of the first matrix experiments on diazomethane photolysis, the suggestion was made[8] that this molecule may participate in the diazomethane decomposition scheme. Because of this relevance, a study of the spectra and photochemistry of methanal azine was undertaken[12]. The electronic spectra and the flash photolysis results have already been presented[49], and the vibration-rotation spectra have also been studied[50]. Some pertinent facts are here repeated. There are three electronic absorption bands in the accessible u.v. above 27,000 cm^{-1}, and photolysis in that region leads to decomposition products to be specified later. The most intense vibrational band of methanal-h_2 azine ($H_2C{=}N{-}N{=}CH_2$) is due to the methylene wagging mode at 1019 cm^{-1}. Further results are interpreted to show that methanal azine is indeed formed and has a distinct existence in the matrix after diazomethane photolysis[2], that it is there subject to secondary photolysis, that the products of this photodecomposition are the same as are produced from a sample of pure methanal azine, and that the methanal azine route is also an important part of the mechanism of photodecomposition of gaseous diazomethane.

First we show that the vibration frequencies of the products of photolysed methanal azine are correlated to some reported matrix frequencies. When a thick film of pure methanal azine at 45°K is subjected to irradiation by means of the low pressure mercury lamp, only the absorption features listed in the third column of Table 5 are produced.

Table 5. Comparison of frequencies observed after methanal azine photolysis with those from published experiments

	Ar(a)	CO_2(a)	CH_2NNCH_2	N_2(b)	Ar, N_2(c)	Label(c)
CH_2NH	1057	1061	1075	1072	1070	*A*
	1060	1061	1083, 1088			
	1120	1123	1141	1115, 1121	1120	*C*
	1342	1372	1379	1363	1355	*C*
	1448	1460	1447, 1451	1456	1455	*A*
	1628	1644	1652	1645	1635	*A*
	2920	2922	2912	2940	2900	*C*
	3032	3048	3027, 3033	3020	3020	*B*
HCN	Gas(d)	Solid(e)				
	713	838	830		735, 785	*D*
	2097	2097	2082, 2085			
	3311	3132	3202			

(a)Reference[51]. (b)Reference[8]. (c)Reference[2]. (d)Reference[7(d)]. (e)Reference[43].

Comparison with known frequencies belonging to matrix-isolated methylenimine[51] and solid hydrogen cyanide[43] leaves no doubt of the identity of the products. The reaction is believed to proceed via the disproportionation of two methyleniminyl (H_2CN) radicals, which have been detected directly after flash photolysis of the gas[49]. Comparison of the same group of frequencies with those reported in previous investigations of diazomethane photolysis in matrices proves these same products have also been detected to proceed ultimately from diazomethane, as Pimentel and co-workers have also reported[46]. However, there is also direct evidence of the intermediacy of methanal in previous experiments, for an absorption band at 1018 cm^{-1} has been reported[2] to reach a maximum intensity early in the photolysis period of the experiment, and then to decrease greatly as methylenimine and hydrogen cyanide bands increase (see Table 2 of reference[2]). Notwithstanding the correlation and labelling of new bands in those experiments[2], the 1018 cm^{-1} feature is probably due to methanal azine, being the frequency of its methylene wagging vibration as previously mentioned. (The 1018 cm^{-1} band was not reported in later experiments[45, 46]; different experimental techniques were presumably employed.) The secondary decomposition of methanal azine evidently occurs by a photolysis mechanism, frequencies above 27,000 cm^{-1} being effective for this purpose; this is shown by the irradiation period dependence of the absorbance of the 1018 cm^{-1} band. Thus there is no necessity to postulate a mechanism of formation of methylenimine as a direct rearrangement of an unstable cyclic intermediate proposed in reference[46]. Formation of methanal azine from two diazomethane molecules initially suspended in the same matrix cage is however acceptable, but on purely statistical grounds it is strange that such a large fraction of the diazomethane should constitute pairs of molecules in this manner at a nominal matrix ratio of 600[2]. In any case, the importance of methanal azine in those matrix experiments has been proved.

Evidence of methanal azine intermediacy in the gas phase photolysis of diazomethane has also been obtained, but direct detection has not been made. The major products from the gas phase photolysis of methanal azine are hydrogen cyanide and ammonia in the ratio of three or four to one respectively, with minor amounts of hydrocarbon products, methane, ethene, ethyne, which are typical of methylene radical reactions [49]. In Fig. 5 is presented a vibration-rotation spectrum of the gases in a cell of which photolysis of diazomethane with a great intensity of u.v. light was for 5 min carried out in the same cell immediately prior to the i.r. scan. The high-pressure mercury arc ME/D was used, and interpolation of a plate glass filter (passing frequencies less than 31,000 cm^{-1}) effected no qualitative difference in the spectrum. The following gases are easily identified: ethene, methane, hydrogen cyanide, ethyne and ammonia, as well as residual (50 per cent) diazomethane. Gas chromatographic analysis (with a flame ionisation detector) of the product gases after total decomposition of diazomethane indicated the presence of many larger hydrocarbon molecules, approximately as listed by Frey[52]. However, Frey failed to detect both hydrogen cyanide and ammonia which are comparatively important products. The presence of both hydrogen cyanide and ammonia (in the ratio of three to one) as major products after both diazomethane and methanal azine are photolysed is taken as an indication of the intermediacy of methanal azine in the gaseous photodecomposition of diazomethane as well as in the solid or matrix phases. Approximately one quater to one third of the diazomethane decomposed is involved in this route, if the production of hydrogen cyanide and ammonia is used as an index. Methylenimine is not stable in the gas phase, particularly in the presence of so many polar reactive substances, and is believed to polymerise on the walls of the cell. The polymerisation to form hexamethylenetetramine in the solid phase has already been noted[51]. The other product obtained from simple stoichiometry according to the equation,

$$6\,H_2CNH \rightarrow (CH_2)_6N_4 + 2\,NH_3$$

is ammonia which should be present to the extent of one third the molar concentration of hydrogen cyanide, as approximately observed, if the HCN and H_2CNH are the major products of the secondary photolysis of methanal azine as found in the solid phase. However, other reactions of methylenimine in the gas phase, such as trimerisation, condensation with diazomethane or other unsaturated molecules, probably

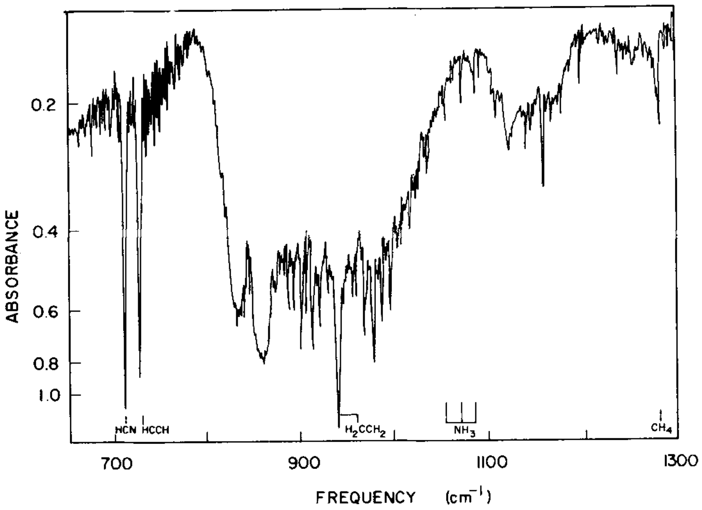


Fig. 5. Vibration-rotation spectra of diazomethane and photolysis products in the gas phase (100 mm path).

occur as well. Thus methanal azine has been shown to play an important role in the photodecomposition of diazomethane in both gas and solid phases.

Hydrogen cyanide was not detected in the product analysis of Kirkbride and Norrish by classical methods[1]. However, in the present experiments in the gas phase, it disappears within an hour, apparently by reaction with diazomethane to form 1,2,3-triazole[53]. Diazomethane and ethene showed no tendency to react during a period of several days in the i.r. gas cell. Therefore the nitrogenous liquid residue recovered by Kirkbride and Norrish was probably the triazole rather than pyrazoline, particularly in view of their relative volatilities. Also the reason for the quantum efficiency exceeding the magnitude 2 can now be qualitatively stated, although even in the case of ketene[54] the quantum efficiency slightly exceeded the value 2 required by the simple reaction scheme:

$$H_2CCO + h\nu \rightarrow CH_2 + CO$$

$$CH_2 + H_2CCO \rightarrow CH_2CH_2 + CO$$

In the case of diazomethane, the value obtained was 4·2[1]. The excess over 2 is due to a combination of chain branching reactions favoured relative to the ketene system by the more energetic methylene radical produced[29] as

$$CH_2 + H_2CNN \rightarrow CH_3 + HCNN$$

which could lead to equivalent amounts of methane and ethyne, as observed in the present work, and condensation reactions, such as those of methylenimine and hydrogen cyanide with diazomethane to form involatile products. The ethene production, probably mainly by reaction (3) similar to the ketene scheme, seems to account for a maximum of 60 per cent of the diazomethene decomposition under the gas phase conditions of these experiments. Thus, although alternative reaction mechanisms might be devised, the principal results of Kirkbride and Norrish[1] have now been qualitatively explained through the use of schemes involving the diazomethyl radical and methanal azine in addition to methylene.

6. DIAZOMETHANE ISOMERS IN THE PHOTOLYSIS SYSTEM

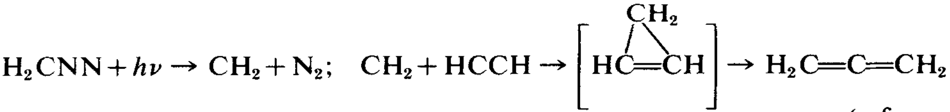
Of the structural isomers depicted by Milligan and Pimentel[2], the most stable ones apart from diazomethane itself are diazirine and cyanamide. Both cyanamide and carbodiimide require a skeletal rearrangement for formation from diazomethane. Although carbodiimide and isocyanamide are both unknown, their alkyl derivatives have been prepared and characterised. On the other hand, formation of both isodiazomethane HCNNH and isocyanamide $CNNH_2$ requires merely the successive transfer of labile hydrogen atoms to the opposite end of the skeleton from their position in H_2CNN. In this selection will be discussed the role of isodiazomethane and the cyclic isomer diazirine in this system.

Isodiazomethane

There has been a suggestion[2] that isodiazomethane may be present or formed photochemically in diazomethane matrix experiments. The species HCNNH has been shown to be an intermediate in the preparation of diazomethane[55] and is believed to have an electronic absorption near 40,500 cm^{-1}[56] and a vibrational absorption near 2150 cm^{-1}[34, 57], both in ethereal solution. By comparison with these frequencies, bands near 40,400 cm^{-1} in matrix experiments[8, 9, 45]and at 2140 cm^{-1} in a nitrogen matrix[26] and in the vicinity of 2150 cm^{-1} in the gas phase[58] (contrast reference [59]) might be attributed to isodiazomethane. Additional i.r. evidence is afforded by the production of the band at 2136 cm^{-1} for an argon matrix sample of hydrazoic acid photolysed in the presence of excess hydrogen cyanide. The mechanism is presumed to be as follows:

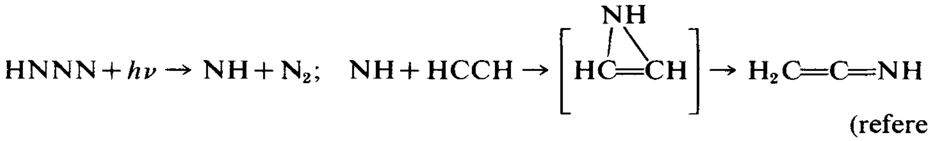
$$HNNN + h\nu \rightarrow NH + N_2; \quad NH + HCN \rightarrow HCNNH$$

by analogy with the known reactions of isoelectronic species, in which a cyclic intermediate has always been postulated:



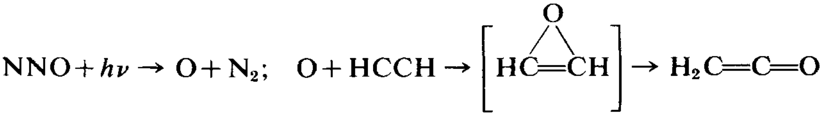
$$H_2CNN + h\nu \rightarrow CH_2 + N_2; \quad CH_2 + HCCH \rightarrow \left[\overset{CH_2}{HC{=}CH}\right] \rightarrow H_2C{=}C{=}CH_2$$

(reference [60])



$$HNNN + h\nu \rightarrow NH + N_2; \quad NH + HCCH \rightarrow \left[\overset{NH}{HC{=}CH}\right] \rightarrow H_2C{=}C{=}NH$$

(reference [60])



$$NNO + h\nu \rightarrow O + N_2; \quad O + HCCH \rightarrow \left[\overset{O}{HC{=}CH}\right] \rightarrow H_2C{=}C{=}O$$

(reference [61])

However carbodiimide might alternatively result from the reaction of imidogen radicals with hydrogen cyanide; its skeletal antisymmetric stretching frequency is also expected to be near 2150 cm^{-1}[33]. In the present work, the bands labelled *B* and *B'* in Tables 1(b) and 2(b) are considered to be due to isodiazomethane HCNNH and DCNNH respectively; recombination of hydrogen atoms with HCNN and DCNN within the matrix cage was a probable mechanism of formation as these absorptions were absent before photolysis with the low-pressure mercury lamp. The above deductions are consistent with the hypothesis that isodiazomethane may have a minor role in this photochemical system[2].

Diazirine

Kirkbride and Norrish believed diazomethane to have a cyclic structure, although their reasoning[1] based on the 25,000 cm^{-1} electronic absorption spectrum might have led to the opposite conclusion. As is now known, the substance which they investigated has a non-cyclic planar structure[23], but a cyclic[62] diazomethane isomer, designated diazirine, has now been systhesised[63]. The transformation from diazirine to diazomethane has been accomplished by photolysis both in a matrix[40] and in the gas[21] phase. There is however disagreement whether the rearrangement is only a dissociation-recombination process[40] or whether it can be in part really a ring-chain isomerisation as well[28]. As yet there has been offered no evidence for the reverse process, and the present *matrix* experiments provide none. However, Robinson and McCarty[9] have photographed many absorption features in the near u.v. region in their experiments in which diazomethane was irradiated during deposition of a krypton matrix at 4°K. (Although these authors emphasise the photolysis in the gas phase as well as in the solid, consideration of the relative periods of illumination under these conditions makes plain that the gas phase decomposition is negligible, at least in the circumstances that the incident radiation is limited by filters to be of frequencies less than 29,400 cm^{-1} in which region diazomethane has very small absorption coefficients. Also, at the matrix ratio of 75 ± 25 employed, even for krypton at 4°K, some secondary reactions undoubtedly occur, as supported by the e.s.r. results[38], although radicals can definitely be trapped at such concentrations [64, 65].) Particularly notable in their experimental results were the sharp lines measured between 30,000 and 33,000 cm^{-1}[9]. The suggestion of these authors that these lines might be due to HCNN can be challenged because, in the experiments with HDCNN and H_2CNN mixtures, lines at 30,046, 30,150, 30,223 and 30,585 cm^{-1} appeared which were reported in neither the H_2CNN nor the D_2CNN experiments. If all the sharp lines were due to only one carrier, then that carrier must contain two hydrogen atoms. Such a carrier is diazirine, which has been found to have a banded spectrum in this region[63, 66]. Although a complete correlation between gas and matrix frequencies is not possible, Table 6 does present some coincidences of vibrational interval, and includes frequencies of an authentic diazirine sample in an argon matrix[67]. It can be seen that three coincidences in vibrational interval have been deduced to occur for H_2CN_2 without unreasonable matrix shifts, and parts of two progressions in a single vibration are seen for D_2CN_2. The very small change in vibrational interval between H_2CN_2 and D_2CN_2 in the matrix spectra, as these lines are now assigned, again parallels the gas phase data. Matrix effects may account for the apparent multiple origins in the progressions noted; even in the spectrum (of much greater absorbance) of the authentic sample[67], there

Table 6. Comparison of gas and matrix frequency intervals for diazirine

H_2CN_2						D_2CN_2			
Gas[a]		Matrix[b]		Matrix[c]		Gas[a]		Matrix[b]	
ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
30970		30652		30874		31061		30702	
								30741	
	791		798		817		788		796, 794
31761		31450		31691		31848		31498	
								31535	
	801		809		798		783		797
32562		32259		32481		32632		32332	
31187		30614		31138					
	844		836		872				
32031		31450		32010					
30970		30531		30874					
	1391		1406		1400				
32361		31937		32274					

[a] Reference[66]. [b] Reference[9]. [c] Authentic diazirine sample in solid argon at 20°K; matrix ratio ~ 600–800; Cary 14 measurements of estimated accuracy ±50 cm^{-1}; reference[67].

are at least four apparent origins of vibrational progressions. Thus, evidence exists for the conversion of diazomethane to diazirine in the fact of the sharp lines of the spectra of Robinson and McCarty[9]. These sharp lines are produced only when irradiation of the sample by frequencies greater than 29,400 cm^{-1} is prevented by filters; the disappearance of these lines and the production of CH, as detected by the 23,120, 25,370 and 31,500 cm^{-1} bands[9], follows illumination with unfiltered light. The decomposition of diazirine with unfiltered light would seem to proceed similarly to the destruction of diazomethane in this work. That is, diazirine is first reconverted to diazomethane, as is known to occur[40], then the decomposition of the acyclic isomer yields, via the diazomethyl radical, methylidene and nitrogen.

Confirmation of the conversion of diazomethane to diazirine was not forthcoming in argon matrix experiments of this study, probably because of severe scattering by the solid film in the attempts that were made, coupled with the reduced intensity of the high-pressure mercury lamp (due to the filtering) and the feeble absorption of diazomethane at frequencies less than 29,400 cm^{-1}. However, when a thick film of diazomethane without a matrix at 48°K was thus irradiated, the i.r. absorption spectrum of the products, although poor in quality, indicated production of diazirine, ethene and methanal azine in comparable yields; all products were volatile. (In contrast, irradiation of a similar diazomethane sample but by the unfiltered low-pressure mercury lamp caused formation of an involatile polymeric material, in part probably polymethylene.) That the production of diazirine from diazomethane seems to occur in the solid film is suggestive of an intramolecular mechanism, a photochemical isomerisation, rather than a dissociation-recombination process to form the cyclic molecule. If photoisomerisation occurs in a solvent-free film, certainly the reaction will also occur in the krypton matrix when competing intermolecular reactions are prevented. The matrix lattice can assist by removing excess energy from the activated molecule after the isomerisation, and may even have a further effect of favoring the cyclic isomer for packing reasons. For such an isomerisation to be observed in the gas phase, a great pressure of inert gas would be required in order to furnish collisional stabilisation before dissociation can occur. There has been no indication of diazirine formation in the flash photolysis experiments on diazomethane[3, 68], but the total pressure there has always been comparatively small. In contrast to evidence from matrix experiments[40], the nature of the assignments of the various electronic transitions provides slight evidence to favour the possibility of the isomerisation process, as the structure of diazomethane in its excited states entered by direct optical excitations seems always to be planar. However, in the low-lying $^1A_2$ state, conveniently situated energetically to allow passage into the ground electronic state of diazirine[30] which then need be only vibrationally excited as a result of the process, the structure which is bent at the central nitrogen atom would require a twisting of the methylene group from the plane before the ring could be formed. Following the discussion of Longuet-Higgins[69] of the allyl-cyclopropyl conversion, the requirement of such a twisting step need prove no great impediment because of the low symmetry of the electronic states involved in the isomerisation process. Therefore, isomerisation would seem to take place most easily from the $^1A_2$ state of diazomethane, the only state of other than C_{2v} symmetry so far identified. Taking the enthalpies of formation of methylene[70], diazomethane and diazirine[30] to be 33,000, 17,200 and 27,800 cm^{-1} respectively, one can understand that the photochemical transformation of diazomethane in the $^1A_2$ state to diazirine can occur via an intramolecular process, whereas, as the first electronic transition of diazirine places that molecule energetically so far above the dissociation limit, the process of methylene recombination with molecular nitrogen is much more likely.

Some of the remaining broad features between 30,000 and 38,000 cm^{-1}[9] may belong to the HCNN and DCNN radicals; the isoelectronic N_3 radical has been found to absorb near 37,000 cm^{-1}[71, 72]. No sign of the H_2CN radical absorptions near 35,000 cm^{-1}[12, 49] are found in the matrix spectra[9], but this fact is consistent with the facile disproportionation process in these conditions. Other features have already been assigned to CNN and NCN radicals[73]. However, no vibration frequencies of the latter radicals have been detected in the present matrix experiments. The remaining vibration frequencies in Tables I and II, and the remaining electronic bands[9] must await further experiments before assignment, as it is likely that the carriers result from complex multimolecular processes possible because of the insufficiently large matrix ratios.

7. CONCLUSIONS

In conclusion, the results of the study presented in this article can be summarised in the energy level diagram of Fig. 3, as far as the vibronic spectrum of diazomethane is concerned, and in the scheme of chemical equations listed in the introductory section. These equations illustrate the decomposition scheme of diazomethane under photolytic conditions both in the cryogenic matrix and in the gas phase, in terms of the diazomethyl radical and methanal azine routes, and of the isomerisation processes. However no vibrational spectrum of the methylene radical has yet been obtained despite the new estimates of the fundamental frequencies.

Finally it should be mentioned that the matrix experiment doubtless overemphasises the importance of the dissociation process whereby the diazomethyl radical is formed.

The formation of methylene must be greatly inhibited by the lattice cage which thereby favours the recombination process, to form either diazomethane or diazirine. There is no theoretical objection to having more than one dissociation process resulting from a particular optical transition[7(c)], and the effect of the cage may be to affect the molecular potential surfaces so as to favour the hydrogen atom expulsion. On the other hand the abundance of methylidene formed by photolysis, by one process or another, provides a reason for caution in gas phase experiments in that the effects previously believed to result from the 'hot' methylene formed from diazomethane might in part be caused by the methylidene radical.

Note added after completion

Very recently Milligan and Jacox have published[74] their observations of many absorptions after far u.v. irradiation of CH_4 in solid nitrogen at 14°K, including 865, 1792, 1802 and 3234 cm^{-1}, almost identical to frequencies assigned to HCNN in this article. Both the lack of other assignment by those authors and the circumstances of formation in their experiments provide strong support for this assignment.

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