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Spectroscopic Study of the Photolysis of Diazomethane in Solid Nitrogen

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RECEIVED SEPTEMBER 4, 1959

Further experiments are described in which diazomethane or partially deuterated diazomethane was suspended in solid nitrogen at 20°K. and photolyzed with filtered light. Spectroscopic study extended from the ultraviolet (2300 Å.) through the infrared (to 420 cm.$^{-1}$). An unstable substance is stored which produces ethylene after diffusion is permitted. This ethylene precursor is absent, as are visible–ultraviolet absorptions at 4182, 3968, and 3050–3300 Å., when the photolyzing radiation includes only wave lengths longer than 3400 Å. In contrast, the infrared absorptions observed earlier by Milligan and Pimentel *are* produced under these conditions, showing that the substance responsible is not the ethylene precursor. The data support the proposal that methylene is the precursor and suggest that some or all of the visible-ultraviolet absorptions are caused by methylene. Absorption at 2620 Å. was detected only in experiments at high concentrations (low M/R), making it extremely unlikely that this absorption is caused by CH_2. Finally, an absorption at 2470 Å. not caused by diazomethane was present before photolysis. This could be the tautomeric compound detected earlier by Müller and Ludsteck and called "*iso*diazomethane."

Infrared spectral studies of the photolysis of diazomethane suspended in solid, inert matrices have been reported by Milligan and Pimentel.[1] Distinct spectral evidence of unstable species was obtained, these unstable species reacting to produce ethylene and other stable molecules upon diffusion. These authors speculate that methylene is produced but conclude that surely some other unstable material is also present, possibly a tautomer of diazomethane. This initial work has now been extended considerably: spectral studies have been conducted through the visible and near ultraviolet regions, deuteriodiazomethane has been prepared and photolyzed in similar, matrix experiments, the influences of some experimental variables (such as concentration in the matrix and frequency of the photolysis light) have been determined and the spectrum of the luminescence which accompanies diffusion has been photographed.

Other, concurrent research directed toward the spectroscopic detection of CH_2 has been reported at the 1959 Ohio State Symposium on Molecular Structure and Spectroscopy.[2,3] Herzberg and Shoosmith have detected the methylene radical in the vacuum ultraviolet region (using flash photolysis methods) but, as yet, no spectral evidence of this species could be found in the visible or near ultraviolet regions.[4] McCarty and Robinson[2] reported experiments of the matrix isolation type with many results which interlock with our work. It has become clear that the spectroscopic study of methylene will be aided by a report of the visible–ultraviolet studies conducted in this Laboratory together with those portions of the infrared work which particularly pertain to the presence and identification of methylene. The examination of the diffusion-induced luminescence and the detailed infrared results are of considerable interest, as well, and these will be reported separately.

Experimental

Diazomethane was prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Eastman, White Label) by a method similar to that described by deBoer and Backer.[5] Deuterated samples were prepared by dissolving the diazomethane in dibutyl ether containing a large excess of alkaline D_2O. The diazomethane gas was recovered by bubbling nitrogen through the ether layer and passing the gas through a trap cooled to 77°K. Three distillations from a trap cooled with a Dry Ice–acetone mixture to one cooled with liquid nitrogen were required to remove completely all of the ether. Two or three such exchanges (each of short duration, five to ten minutes) with large excesses of D_2O were found to be most effective in deuterating the diazomethane without excessive loss of the product through the reaction to form methanol.

The diazomethane samples were exposed to vacuum while in a trap cooled to 140°K. to remove ethylene formed through decomposition. The samples were prepared by distilling the diazomethane into a calibrated bulb and measuring the pressure by means of a mercury manometer. This diazomethane was then transferred to a large sample bulb and diluted with nitrogen gas. The relative amounts of matrix gas (M) and moles of diazomethane (R) are indicated by the mole ratio M/R.

The low-temperature cell has been described previously.[6] The general experimental procedures, sample deposition at 20°K., photolysis, and the "diffusion operation," with intermittent recording of spectra, are described in detail in the earlier publication of Milligan and Pimentel.[1] In the experiments described here the samples were deposited at a rate of about 0.3 l. atm./hr. Photolysis was accomplished with an AH-4 medium pressure mercury arc with the outer glass envelope removed. The light was focused with a quartz lens through a barium fluoride photolysis window onto the sample deposited on the sapphire or cesium bromide cold window.

In the experiments to be described, filters were used to investigate the effect of the wave length of the photolytic radiation. A Corning No. 7740 Pyrex filter was used to eliminate wave lengths below 2800 Å. This filter transmits uniformly through the visible and near-ultraviolet region to a wave length of 3080 Å., where the optical density reaches 0.3 and then the optical density rises sharply, reaching 2.0 at $\lambda = 2800$ Å. A second Corning filter, No. 7380, was used to eliminate wave lengths below 3400 Å. This filter also transmits uniformly through the visible region and reaches optical densities of 0.3 and 1.0 at, respectively, 3620 and 3490 Å.

Visible–ultraviolet spectra were recorded with a Cary Model 14 Recording Spectrophotometer over the wave length range 10,000 to 2200 Å. Infrared spectra were recorded with a Perkin–Elmer Model 21 Spectrophotometer, equipped with sodium chloride and potassium bromide optics.

Results

Experiment 1, CH_2N_2 in N_2, High M/R.—This experiment duplicates conditions used many times

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

[2] M. McCarty, Jr., and G. W. Robinson, Presented at the Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 15–19, 1959.

[3] After the report of McCarty and Robinson,[2] A. E. Douglas reported briefly the detection of CH_2 in the vacuum ultraviolet region by Herzberg and Shoosmith.

[4] G. Herzberg and J. Shoosmith, *Nature*, in press.

[5] T. J. deBoer and H. J. Backer, *Rec. trav. chim.*, **73**, 229 (1954).

[6] E. D. Becker and G. C. Pimentel, *J. Chem. Phys.*, **25**, 224 (1956).

in studies of the infrared spectral features. The primary intent was to determine the near infrared, visible and near ultraviolet spectrum of the species produced during the photolysis of CH_2N_2 in solid N_2 at 20°K. The infrared spectral region was examined to the low frequency transmission limit of sapphire, about 1700 cm.$^{-1}$, but the reproducibility of similar experiments gives us confidence that the spectral behavior between 1700 and 650 cm.$^{-1}$ is essentially identical to that described in Experiment II, ref. 1.

A sample containing 41 μmoles of CH_2N_2 in N_2 at $M/R = 600$ was deposited on the sapphire window (held at 20°K.). Spectra were recorded beginning in the near ultraviolet at 2300 Å. and extending through the infrared. The spectrum showed only two spectral features not attributed to diazomethane. In the infrared region a weak absorption (0.03) at 3725 cm.$^{-1}$ showed the presence of a small amount of water in the monomeric form.[7] (As shown decisively in the earlier studies,[7] this trace impurity gives a distinctive and positive monitor on diffusion of at least one triatomic species during the experiment.) The second spectral feature is a band in the ultraviolet with $\lambda_{\max} = 2470$ Å., half-width $\sim$50 Å. and a peak $\log I_0/I = 0.14$.

The sample was photolyzed for two hours using filter No. 7740. The infrared spectrum showed that approximately 16 μmoles of diazomethane had been decomposed. The ultraviolet absorptions of diazomethane were correspondingly decreased. The feature reported earlier at 3020 cm.$^{-1}$ (due to an unstable product[1]) was observed with optical density 0.21. There were no new absorptions detected in the visible-ultraviolet region and the absorption at 2470 Å. did not change noticeably. Light scattering by the matrix was somewhat higher but the presence of the band at 3725 cm.$^{-1}$ due to monomeric water showed that diffusion had not occurred.

The Pyrex filter then was removed and the sample was irradiated for an additional 45 minutes. The infrared spectrum showed that 12 μmoles of CH_2N_2 were decomposed during this second photolysis period. The band at 3020 cm.$^{-1}$ had decreased somewhat, to $\log I_0/I = 0.19$. In the visible–ultraviolet region a band appeared near 4182 Å. with a width at half height of 60 Å. and a peak optical density of 0.09. A weaker, broad feature centered at 3968 ± 5 Å. also appeared. In addition, there was a third weak, broad absorption region from 3050 to 3300 Å. with a barely detectable maximum of extinction near 3176 Å.

A diffusion operation was carried out and it was accompanied by the usual red chemiluminescence.[1] After this operation, further spectral study was prevented by the increased scattering of light by the sample.

Experiment 2, CH_2N_2 in N_2, Low M/R.—This experiment duplicates Experiment 1 except that the sample consisted of 56 μmoles of CH_2N_2 in N_2 at $M/R = 70$. Prior to photolysis, the spectrum differed somewhat from the corresponding spectrum in the preceding experiment: the band found at 2470 Å. was shifted to 2490 Å.

The initial photolysis with the filter No. 7740 caused the decomposition of about 35 μmoles of diazomethane. In addition to the decrease in absorption by diazomethane, the ultraviolet region showed a well-defined band with $\lambda_{\max} = 2620 \pm 5$ Å., half-width about 70 Å. and maximum optical density, $\sim$ 0.03. A broad, weak absorption without structure appeared between 3000 and 3325 Å.

Photolysis without the filter for 35 minutes decomposed an additional 18 μmoles of diazomethane. The ultraviolet absorptions produced in the first photolysis were not altered significantly but a weak absorption at 4182 Å. ($\sim$ 0.02) and a barely detectable absorption near 3176 Å. appeared. Both of these bands were detected in Experiment 1. Finally, the band at 2490 Å. may have increased in optical density somewhat.

During the diffusion operation only a faint luminescence was observed. There was an increase in scattering by the sample and the ultraviolet–visible absorptions were no longer detectable.

Experiment 3, CH_2N_2 in N_2, High M/R, 7380 Filter.—This experiment differs from Experiment 1 in two ways. Photolysis was conducted using only light transmitted by the filter No. 7380 (transmitting λ above 3400 Å.). Also the sample was deposited on CsBr to permit more complete infrared study. The sample consisted of 62 μmoles of CH_2N_2 in N_2 at $M/R = 500$. Prior to photolysis, the spectrum was the same as the corresponding spectrum in Experiment 1.

After 90 minutes of photolysis using the 7380 filter, 22 μmoles of CH_2N_2 was decomposed. All of the infrared bands observed by Milligan and Pimentel[1] in their Experiment II were reproduced. No absorption was detected in the visible or ultraviolet spectral regions.

No luminescence occurred during the diffusion operation. Subsequent to the diffusion, the infrared spectrum showed the usual disappearance of the infrared features produced by photolysis and possibly an increase in the intensity of the absorptions of diazomethane. *The spectral region near 950 cm.$^{-1}$ showed little or no production of ethylene.*

Experiment 4, $CHDN_2$ in N_2, High M/R.—The sample consisted of 64 μmoles of partially deuterated diazomethane in nitrogen at $M/R = 515$. The percentage deuteration was estimated to be 60 ± 5%, implying approximately 36% CD_2N_2 and 48% $CHDN_2$.

The sample was photolyzed for 75 minutes without a filter, resulting in the decomposition of 47 μmoles of diazomethane. This photolysis produced absorption features like those observed in Experiment 1. The features at 4182 and 3968 Å. were apparently unshifted. The broad absorption between 3050 and 3300 Å. was present but differed noticeably: distinct maxima were evident at 3071 ± 3 Å., 3174 ± 3 Å. and 3285 ± 3 Å. The spectral region between 3800 and 4400 Å. is shown in Fig. 1 (solid line).

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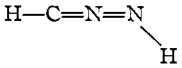
(7) M. Van Thiel, E. D. Becker and G. C. Pimentel, *J. Chem. Phys.*, **27**, 486 (1957).

During a diffusion operation, the red chemiluminescence was observed at apparently the same intensity as in Experiment 1. The infrared spectrum showed that deuterated ethylene was formed during the diffusion. The scattering by the sample increased but without question the absorptions at 4182 and 3968 Å. had disappeared, as shown by the dotted line in Fig. 1. The features between 3050 and 3300 Å. apparently disappeared but this conclusion is less definite because of the scattering in that spectral region.

Experiment 5, $CHDN_2$ in N_2, High *M/R*, 7380 Filter.—This experiment duplicates Experiment 4 except that photolysis was conducted with the 7380 filter. The results are similar to those of Experiment 3: the infrared spectrum showed that diazomethane was decomposed but no absorptions were detected in the visible or ultraviolet regions.

Discussion

Isodiazomethane.—The ultraviolet absorption at 2470 Å. (2490 Å. in Experiment 2) is not caused by diazomethane, as is shown by the fact that this band is not lost during photolysis. It is quite likely that this absorption is caused by the compound prepared by Müller and Ludsteck[8] which they call *iso*diazomethane. This compound was assigned the structure



$$H\text{—}C\text{=}N\text{=}N\text{—}H$$

on the basis of its chemical properties. In ether solution this compound has an intense broad band with $\lambda_{max} = 2470$ Å.[9]

Though this absorption was detected in every experiment in which this spectral region was examined, we have not been able to connect it with any of the infrared, visible or ultraviolet absorptions produced during the photolyses.

The Absorption at 2620 Å. in Experiment 2.—This absorption probably was first observed by DeMore and Davidson[10] in an experiment with conditions which we attempted to duplicate in Experiment 2. DeMore reported[10] that absorptions at 2615, 2545 and 2480 Å. appeared following photolysis (with a Pyrex filter) of diazomethane in solid nitrogen. More recently, McCarty and Robinson[2] reported that three sharp lines near 2600 Å. result from condensing the products of an ethane–krypton discharge and also from photolysis of either diazomethane or ketene in solid krypton.

We feel confident that the absorption at 2620 Å. observed in Experiment 2 corresponds to the band at 2615 Å. of DeMore's experiment. Since DeMore does not present spectra, we are unable to judge whether interference by the broad absorption near 2490 Å. could have prevented our detection of the other two features (or, indeed, whether the band we observed at 2490 Å. could be the *same* feature he reports at 2480 Å.). No doubt there is also connection with the three sharp bands reported by McCarty and Robinson.

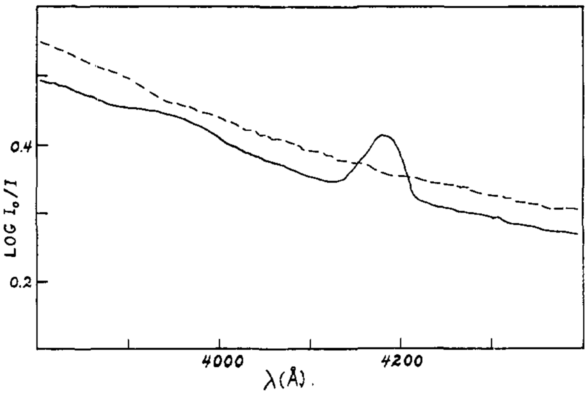


Fig. 1.—Absorption spectrum of $CHDN_2$ in solid N_2 from exp. 4, 75 min. photolysis, $T = 20$°K.; ——— after photolysis; -------- after diffusion.

The band at 2620 Å. was not observed in any experiment except Experiment 2, at low *M/R*. It is quite improbable that this absorption is caused by methylene since storage of methylene is undoubtedly favored by high *M/R*.

The Ethylene Precursor.—Experiment 1 verifies the earlier observation[1] that unfiltered photolysis produces a substance which gives ethylene when diffusion is permitted. Experiment 4 shows that the same result is obtained with deuterated diazomethane. Milligan and Pimentel[1] propose that this ethylene precursor is methylene but they observe that it is possible that the ethylene could be formed from the substance which caused the several Class C infrared absorptions. (This substance could not be CH_2 because of the complexity of its spectrum.) Experiment 3 eliminates this latter alternative. Photolysis with light of $\lambda > 3400$ Å. produces the unidentified Class C infrared features but no ethylene appears after diffusion.

Thus the present work shows that the Class C bands are not associated with the ethylene precursor. This result, though negative, gives substantial support to the proposal that the precursor is methylene, since the only obvious alternative has been eliminated.

Diffusion.—In view of the proposal that methylene is stored in these experiments, it is relevant to review the evidence which indicates that diffusion of a species as small as CH_2 is slow in solid nitrogen at 20°K. The diffusion of water in solid nitrogen is well understood[7] and the presence of monomeric water in Experiment 1 shows that the isolation of this triatomic molecule is maintained throughout the photolysis and spectral study, though not after the diffusion operation. Similar diffusion behavior in solid nitrogen at 20°K. has been observed for NH_3, HN_3, HCN, NO_2 and HBr.[6] It is a reasonable extrapolation, in absence of evidence to the contrary, to assume that if methylene is produced in an isolating matrix cage of solid nitrogen, it can be stored at 20°K.

The Visible–Ultraviolet Absorptions of Experiment 1.—We can correlate the presence of the visible–ultraviolet absorptions observed in Experiment 1 with the presence of the ethylene precursor. Experiment 3 shows that ethylene is not an important product, even after diffusion,

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[8] E. Müller and D. Ludsteck, *Chem. Ber.*, **88**, 921 (1955).

[9] E. Müller and D. Ludsteck, *ibid.*, **87**, 1887 (1954).

[10] See W. B. DeMore, Doctoral Dissertation, California Institute of Technology (1958).

with the photolysis radiation transmitted by the filter No. 7380. This implied absence of the ethylene precursor is accompanied by loss of the absorptions reported at 4182, 3968 and 3050–3300 Å. Similar behavior was found for deuterated diazomethane since the visible–ultraviolet absorptions found in Experiment 4 were absent in Experiment 5 (in which the filter No. 7380 was used). We are led to some important conclusions concerning the observed electronic transitions:

(a) *The substance which causes the infrared absorptions of type C is not the cause of the visible–ultraviolet absorptions of Experiment 1.* The infrared bands are obtained with light transmitted by filter No. 7380; the visible–ultraviolet absorptions are not.

(b) *The ethylene precursor, presumably methylene, could be the species responsible for one or more of the visible–ultraviolet absorptions, 4182, 3968 and 3050–3300* Å.

Conclusions

These results may provide significant aid in the search for absorptions of methylene by more conventional spectroscopic means. Still the identification of methylene as the cause of any or all of these absorptions is quite tentative and a detailed interpretation seems to be unwarranted here. There are, of course, obvious and important implications of the frequencies observed for the normal and deuterated species if methylene is indeed responsible.[11]

Acknowledgments.—Grateful appreciation is expressed for fellowship aid (to T.D.G.) from Texaco Company and for research support by the American Petroleum Institute Research Project 54 and the United States Air Force through the AFOSR of the Air Research and Development Command under Contract No. 49(638)-1. We also wish to thank Drs. G. Herzberg and J. Shoosmith, who kindly sent us a preprint of their note on methylene,[4] and to acknowledge helpful and informative communications from Professor G. W. Robinson.[12]

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[11] These implications are explored in detail in the Doctoral Dissertation of Theodore D. Goldfarb, University of California, Berkeley, 1959.

[12] During the preparation of this manuscript, Professor Robinson kindly forwarded to us a copy of his manuscript with Dr. M. McCarty, Jr. on "The Production and Subsequent Photolysis of Transient Products from the Photodecomposition of Diazomethane at 4.2°K." A comparison to the work presented here emphasizes the interdependence of the two studies. The following specific comments are stimulated by our perusal of the Robinson–McCarty manuscript.

(a) If methylene is isolated, whether in solid krypton or nitrogen, it is surely expected that it will act as an ethylene precursor when diffusion occurs. Hence our failure to observe the growth of ethylene when a filter No. 7380 is used probably indicates the absence of a large amount of methylene under these conditions. This conclusion is not dependent upon the correctness of our conviction that methylene is the ethylene precursor in the present work.

(b) Since Robinson and McCarty indicate a correspondence between their observations in the region near 2600 Å. and those of DeMore and Davidson,[10] we feel the results and discussion of our Experiment 2 pertain to the work of Robinson and McCarty.

(c) The comments of Robinson and McCarty on the different photolytic behavior of deuterated diazomethane are of particular interest to us. We have accumulated a substantial amount of infrared evidence which is in agreement with their conclusion and which is, perhaps, of crucial importance in their interpretations. We have observed that bands analogous to the Class C infrared absorptions are *not* produced from deuterated diazomethane, though the ethylene precursor *is* still produced. This substantiates their conclusion that photolysis of CD_2N_2 differs from that of CH_2N_2 and suggests that the substance responsible for the Class C bands[1] could be important in the studies of Robinson and McCarty.

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[CONTRIBUTION FROM THE CHANDLER LABORATORY OF COLUMBIA UNIVERSITY AND FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

The Effect of Viscosity on the Quantum Yield for Iodine Dissociation

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RECEIVED AUGUST 3, 1959

The quantum yields for dissociation of iodine by the 4358 Å. mercury line have been measured at 25° in a number of hydrocarbon solvents. Data now available for hydrocarbon solvents cover a range of 10^3 in viscosity and two chlorocarbon solvents also have been studied. Quantum yields in the least viscous solvents are not greatly different from those predicted by hydrodynamic theories if dissociating iodine atoms are slowed by viscous drag and then diffuse at random in a structureless viscous continuum. However, quantum yields in hydrocarbons are somewhat greater than the absolute values predicted by the viscous continuum model, while quantum yields in chlorocarbons are less; detailed description of the observations must invoke solvent–solute interactions and must recognize that viscosity is not a sufficient parameter to account for all of the effects of changing solvent. In viscous hydrocarbon solvents, the observed quantum yields are many times those predicted by the viscous continuum model. These quantum yields also approach a limiting value that is not reduced by further increase in viscosity, while the most logical method of applying the viscous continuum model predicts that the quantum yields approach zero with indefinite increase in viscosity. The results suggest ways in which molecular structure of solvent must be introduced in order to describe these systems fully.

Introduction

When a molecule of iodine is dissociated photochemically in solution, the separating atoms are slowed to thermal velocities while the distances traversed are still comparable to molecular dimensions. The atoms then diffuse at random and may either recombine with each other in a very short time or else diffuse apart and subsequently undergo other reactions.

In solvents of low viscosity, the initial separation will be greater and there will be a greater quantum yield for the production of atoms that become permanently separated from their original partners. Although this qualitative picture is clear and in agreement with experiment, a quantitative theory of quantum yields has not been developed at the

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