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The Ultraviolet Absorption Spectra of Gaseous Diazomethane and Diazoethane. Evidence for the Existence of Ethylidine Radicals in Diazoethane Photolysis

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The absorption of gaseous diazoethane begins at about 5400A, increases to a broad maximum of $\epsilon=3.5$ at 4500A and falls to a minimum of $\epsilon=0.15$ at 3200A. At wavelengths shorter than 3000A a second region of rapidly increasing absorption is found. The absorption curve of diazomethane is similar in general shape to this curve but shifted somewhat toward shorter wavelengths. The absorption of diazoethane is continuous over its entire region while in the visible region diazomethane shows a number of broad and very diffuse bands from about 4300A to 3200A which probably overlie a continuum. The presence of 2-butene in the photolysis products of diazoethane is explained by the combination of ethylidine radicals formed by the primary photochemical process

$$CH_3CHN_2+h\nu\rightarrow CH_3CH+N_2.$$

A DETERMINATION of the gaseous ultraviolet and visible absorption spectra of diazomethane and diazoethane has been made as a preliminary to the investigation of the photolysis of diazoethane. The quantitative evaluation of the spectra was carried out similar to the method employed by Blacet, Young, and Roof.[1] A Bausch and Lomb large littrow spectrograph with interchangeable glass and quartz optics was used to take nine photographic plates covering the room temperature (about 27°C) absorption of the two compounds from 2500 to 6000A. The diazoalkanes were introduced into a silica cell with plane parallel windows which was in the almost parallel light beam from a Beckman hydrogen discharge or an incandescent lamp. Cell lengths of 25 cm and 56 cm and diazoalkane pressures from 5 mm to 200 mm of mercury were used. Each plate was calibrated by recording a series of exposures in which the source intensity was reduced to different fraction transmissions with moving calibrated screens interposed in the light path. A reference spectrum from a mercury arc was used for wavelength calibration. Tracings made by a Henson[2] recording microphotometer of both the intensity calibrations and the absorption spectra were used to calculate the molecular extinction coefficients from the equation

$$\epsilon=1/cl\log_{10}I_0/I,$$

where c is expressed in moles/liter and l in cm. These coefficients are plotted as a function of wave number in Fig. 1.

The similar spectra of the two compounds consisting of a visible region of moderate absorption followed by an ultraviolet region of rapidly increasing absorption compare well in general form to the gaseous diazomethane spectrum determined by Kirkbride and Norrish[3] and the absorption of both compounds in cyclohexane solution given by Adamson and Kenner.[4]

The absorption of diazoethane was continuous in both the visible and ultraviolet regions. Atlhough careful observation of the diazomethane spectrographic plates seemed to indicate continuous absorption also, the microphotometer tracings showed a number of very weak, broad, and diffuse bands between 4300 and 3200A which appeared to overlie a continuum. The series of eight diffuse bands found by Kirkbride and Norrish between 4710 and 4250A could not be detected by either careful visual inspection of the plates or from the microphotometer tracings. In addition, the extinction coefficients given by Kirkbride and Norrish are about double those determined in the present study. It is believed that these differences could possibly be explained by the presence of impurities in the diazomethane used by Kirkbride and Norrish. In our study the diazoethane prepared by the action of sodium cyclohexoxide on N-nitroso-β-ethylaminoisobutyl methyl ketone in cyclohexanol solvent[4] had to be carefully purified by repeated distillation in order to remove impurities which caused significant differences in the absorption curve. Diazomethane prepared by reacting aqueous sodium hydroxide and nitrosomethyl urea[5] in di-*n*-butyl ether solvent seemed to contain negligible amounts of impurities.

The presence of radicals in the low temperature pyrolysis[6] and the ultraviolet photolysis[6,7] of diazoethane has been indicated by the removal of metallic mirrors. The similarity of the absorption of diazoethane and diazomethane could well indicate that the primary photochemical reactions of the two compounds are

$$CH_2N_2+h\nu\rightarrow CH_2+N_2 \qquad (1)$$

$$CH_3CHN_2+h\nu\rightarrow CH_3CH+N_2. \qquad (2)$$

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[1] Blacet, Young, and Roof, J. Am. Chem. Soc. **59**, 608 (1937).

[2] Leighton, Smith, and Henson, Rev. Sci. Instr. **5**, 431 (1934).

[3] F. W. Kirkbride and R. G. W. Norrish, J. Chem. Soc. **1933**, 119 (1933).

[4] D. W. Adamson and J. Kenner, J. Chem. Soc. **1937**, 1551 (1937).

[5] Newer Methods of Preparative Organic Chemistry (Interscience Publishers, Inc., New York, 1948), p. 564.

[6] Barrow, Pearson, and Purcell, Trans. Faraday Soc. **35**, 880 (1935).

[7] Volman, Leighton, Blacet, and Brinton, J. Chem. Phys. **18**, 203 (1950).

Study[3,8,9] of the reaction kinetics and the ultimate products from the first of these reactions seems to establish the occurrence of methylene radicals of appreciable stability. If the radicals causing the mirror removal observed in the diazoethane photolysis are ethylidine radicals of some stability, the reaction products should include compounds resulting from combination of this radical

$$2CH_3CH \rightarrow CH_3CHCHCH_3 \qquad (3)$$

or reactions of ethylidine with other molecules in the mixture.

Several gas phase photolyses of diazoethane at about 200 mm pressure were run almost to completion. The unfiltered light of a Hanovia-Type A medium pressure arc was used to irradiate the gas in a cylindrical silica cell. The gaseous reaction products obtained were analyzed by a Consolidated Mass Spectrometer. A typical analysis obtained on basis of nitrogen as 1.00 is $N_2=1.00$, $C_2H_4=0.61$, $CH_3CHCHCH_3=0.06$, $H_2=0.08$, and $C_2H_2=0.06$.

The presence of 2-butene in the products is best explained by the formation and combination of ethylidine radical by reaction (2) and (3). The large amount of ethylene may indicate that a fast rearrangement of this radical occurs

$$CH_3CH \rightarrow C_2H_4 \qquad (4)$$

to give ethylene or that a second primary process

$$CH_3CHN_2 + h\nu \rightarrow C_2H_4 + N_2 \qquad (5)$$

produces the major products by a direct intramolecular decomposition. The formation of hydrogen and acetylene is probably the result of some related process but more study is needed in order to clarify the actual mechanism.

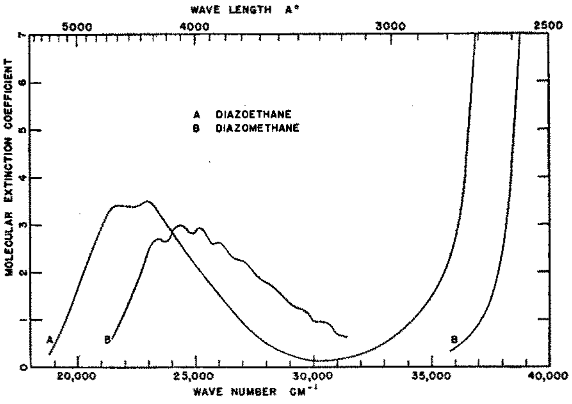

FIG. 1. Absorption spectra of diazoethane and diazomethane.

Further investigation of the photolysis of diazoethane was discontinued because of the hazard from frequent detonations of gas itself and also the liquid even at −180°C. Samples containing impurity were generally stable but the danger of explosion seemed to increase as the purity was enhanced.

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[8] Norrish, Crone, and Saltmarsh, J. Chem. Soc. **1933**, 1533 (1933).

[9] G. B. Kistiakowsky and N. W. Rosenberg, J. Am. Chem. Soc. **72**, 321 (1950).