CANADIAN JOURNAL OF CHEMISTRY. VOL. 46, 1968

and also exhibited identical thin layer chromatographic and infrared spectral values.

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Vibrational absorption of the trapped diazomethyl radical

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Vibrational absorption lines newly discovered after the photolysis, with a low-pressure mercury lamp, of isotopic diazomethanes in inert-gas matrices at $4 \,^{\circ}$ K have been assigned to the diazomethyl radical, HCNN and DCNN.

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Despite much effort (1; 2; 3 and references therein) devoted to the study of the photolysis products of diazomethane in noble gas matrices at cryogenic temperatures, no conclusive absorption spectrum of the methylene radical has yet been obtained. However, a new vibrational spectrum has been recorded following photolysis, using radiation from an unfiltered low-pressure mercury lamp, of diazomethane isolated in several matrices at 4 °K. Conventional apparatus and procedures were employed in these experiments, as previously described (4, 5). The new absorption lines (with absorbance) are listed in Table I. These lines can be distinguished from other, minor absorptions also appearing after photolysis, both because the former appear, and increase in intensity, only during resonancelamp irradiation, and because only they decrease in intensity during subsequent irradiation of the sample in argon with an unfiltered high-pressure mercury lamp. When a mixture of deuteriumsubstituted diazomethanes (H₂CNN, D₂CNN, and HDCNN) is used at a matrix ratio of argon to total diazomethane of 250, at 4 °K, only two sets of absorptions with intensity behavior as above, labeled A and B in Fig. 1, appear after resonance-lamp photolysis. The principal A line,

at 861 cm⁻¹, coincides with the experimental bending vibration of the methylene radical, 861 \pm 7 cm⁻¹, deduced as follows from the vibronic data of Herzberg (6, 7): $v_2' = 71383$ cm⁻¹ (1400.9 Å) – 70696 cm⁻¹ (1414.5 Å) = 686 cm⁻¹; $v_2' - v_2'' = 70522$ cm⁻¹ (1418.0 Å) – 70696 cm⁻¹ = -175 cm⁻¹; therefore $v_2'' =$ 861 cm⁻¹ (only frequency differences have meaning in this calculation). Bending frequencies of HCD and CD_2 are calculated (8) to be 763 and 654 cm^{-1} respectively. Therefore, the A and B lines cannot be assigned to methylene radicals. The A lines are observed in other experiments when pure H_2CNN is used, whereas only the B lines are present when almost pure D₂CNN is in the matrix. Thus the carrier of these absorption lines contains only one hydrogen atom. In diazomethyl lithium, Li⁺HCNN⁻, the CH stretching frequency is 3215 cm⁻¹, and a skeletal stretching frequency is 1898 cm^{-1} (9). The bending frequency of HCN is 712 cm^{-1} , which changes to 569 cm⁻¹ in DCN. On the basis of conditions of formation and resemblance of vibration frequencies with those of similar molecules, these lines may be assigned to the diazomethyl radical, A = HCNN and B = DCNN.

The mechanism of formation is believed to be

2472

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FIG. 1. Vibrational absorption of isotopic diazomethanes and products in argon (a) before and (b) after irradiation with a low-pressure mercury lamp.

Observed ab	sorptions (cm ⁻¹) for H	CNN and DCNN in var	ious matrices
	IAD		

HCNN (Ar)	HCNN (Kr)	HCNN (N ₂)	DCNN (Ar)
861 (0.28)	860 (0.15) 866 (0.04)	863 (0.035)* 871 (0.025)*	725 (0.125)
1787 (0.145) 1792 (0.04) 3233 (0.02)	1784 (0.07) 1790 (0.03)	1789 (0.035) 1800 (0.085) 3229 (0.035)	1771 (0.125) 1775 (0.04)

*Interference by other bands makes these absorbances uncertain; otherwise absorbance accuracy is \pm .01; wavenumber accuracy, ± 2 cm⁻¹.

photodissociation from diazomethane of a hydrogen atom, which, unlike the methylene radical, can escape from the site of production within the matrix lattice:

$$H_2CNN + hv \rightarrow H + HCNN.$$

The photodecomposition of the diazomethyl radical during exposure to the high-pressure mercury lamp can proceed via dissociation to molecular nitrogen and the methylidene radical,

the latter absorbing too weakly in the infrared to be directly detected :

$HCNN + hv \rightarrow CH + N_2.$

In a recent investigation (10) of the extreme ultraviolet photolysis of methane in nitrogen matrices, there have been reported several (unassigned among many others) vibrational absorptions of very similar wavenumbers to those in Table I. The methyl radical was detected (10)

CANADIAN JOURNAL OF CHEMISTRY. VOL. 46, 1968

and resulted from photoejection of a hydrogen atom from methane:

$$CH_4 + h\nu \rightarrow CH_3 + H.$$

Diazomethane was also detected and was formed from reaction of methylene (produced according to the reaction well established from gaseous phase experiments (11):

$$CH_4 + hv \rightarrow CH_2 + H_2$$

with the available nitrogen (12):

$$CH_2 + N_2 \rightarrow H_2CNN$$
.

The diazomethane was then subject to secondary photolysis, as in the present experiments, to produce a hydrogen atom and what is now identified as the diazomethyl radical.

Further results of studies of the diazomethane system will be reported soon. The original experiments were performed in the Department of Physical Chemistry, University of Cambridge.

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2474

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