Heat of Formation and Bond Dissociation Energy of Diazomethane by a Photodissociation Method[1]

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Contribution from the National Bureau of Standards, Washington, D. C. 20234. *Received November 5, 1970*

Abstract: A lower limit for the heat of formation of diazomethane has been obtained from measurement of the minimum energy required to produce the $A^2\Delta$ state of CH in the low-intensity vacuum-ultraviolet photolysis of diazomethane. The value obtained is $\Delta H_f{}^\circ{}_0(CH_2N_2) \geq 51.3$ kcal/mol (2.22 eV). In conjunction with $\Delta H_f{}^\circ{}_0(CH_2) = 93.0$ kcal/mol, the dissociation energy of the C=N bond in diazomethane is ≤ 41.7 kcal/mol (1.81 eV). Reasonable upper limits for $\Delta H_f{}^\circ{}_0(CH_2N_2)$ are discussed.

The thermochemistry of methylene radical reactions is, in part, based upon a knowledge of the heat of formation of its precursors. The latter are most usually ketene or diazomethane. While the heat of formation of CH_2CO has been well established,[2] the value for CH_2N_2 has not been measured thermochemically and is subject to rather large disagreement. Measurement of the appearance potential of CH_2^+ from CH_2N_2 by electron impact led Paulett and Ettinger[3a] to estimate a value of $\Delta H_f^\circ(CH_2N_2)$ equal to 49.3 kcal/mol, based upon $\Delta H_f^\circ(CH_2^+) = 333$ kcal/mol. Using the same technique and value for $\Delta H_f^\circ(CH_2^+)$, a heat of formation of CH_2N_2 equal to 40 kcal/mol may be derived using an appearance potential measurement of other workers.[4] Because of some uncertainties in the state of CH_2^+ produced *via* electron impact,[5] and in the appearance potential of CH_2^+, $\Delta H_f^\circ(CH_2N_2)$ is subject to large uncertainty, with values ranging from 40 to 100 kcal/mol.

RRKM calculations of kinetic studies of methylene–olefin addition reactions, where the methylene is formed from the thermal decomposition of diazomethane, indicate that $\Delta H_f^\circ(CH_2N_2) > 67$ kcal/mol.[6] Subsequent work involving kinetic studies of diazomethane and/or methylene have yielded internally consistent results only by using a heat of formation of diazomethane equal to about 70 kcal/mol.[7] These disparities have prompted us to redetermine the value for $\Delta H_f^\circ(CH_2N_2)$ using the vacuum-ultraviolet photodissociation technique which has been successfully applied by Okabe and coworkers to other simple molecules.[8]

There have been only a few studies of either the spectroscopy or the photodissociation of diazomethane in the vacuum-ultraviolet. Diazomethane has several absorption regions in the ultraviolet. The first, studied by Brinton and Volman,[9a] has a maximum at 3200 Å and the second appears continuous from 2600 to 2000 Å.[9b] Herzberg[10] and, more thoroughly, Merer[11] have observed discrete absorption of diazomethane in the vacuum region between 1900 and 1300 Å, including a Rydberg series leading to an ionization potential of 9 eV.

The flash photolysis of diazomethane has been utilized by Herzberg and coworkers to obtain spectroscopic data on CH_2[10] and CH.[12] In these experiments, intense emission due to excited CH was easily observed. CH emission was also observed by metastable argon sensitization of CH_2N_2 in a flow discharge.[13] The method which will be described depends on measuring the threshold energy, $h\nu$, of the incident photon to produce

$$CH_2N_2 \longrightarrow CH(A^2\Delta) + H + N_2 \tag{1}$$

Then

$$\Delta H_f^\circ(CH_2N_2) \geq \Delta H_f^\circ(CH) + \Delta H_f^\circ(H) + E_e[CH(A^2\Delta)] - h\nu \tag{I}$$

where E_e is the electronic energy of $CH(A^2\Delta)$. Since the thermochemical values in (I) are well established, the threshold energy should give a reliable value for $\Delta H_f^\circ(CH_2N_2)$.

Experimental Section

The present experimental arrangements essentially follow those which have been previously described,[14] with some modifications. Two different sets of measurements were made: (a) onset of fluorescence measurements and (b) an examination of the fluorescence spectrum. Common to all measurements was a 1-m near-normal incidence vacuum-ultraviolet grating instrument which had a bandwidth of 5 Å for the onset measurements and 2 Å for the determination of the fluorescence spectrum. The onset measurements were performed in a monel reaction vessel, 6.95 cm in length, placed behind the exit slit of the monochromator. Monochromatic light was obtained with the monochromator and an ac-operated hydrogen discharge lamp. The fluorescence intensity was measured, at right angles to the incident beam, by a 13-stage photomultiplier in series with glass filters to isolate desired regions of the spectrum.

The fluorescence spectrum was obtained by placing an anodized aluminum cell in front of the entrance slit of the monochromator. The cell was equipped as a flow device with separate inlet and outlet

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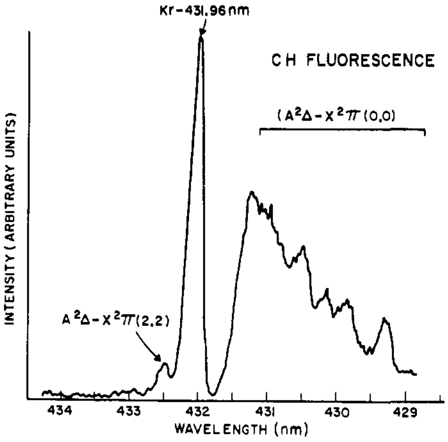

Figure 1. Fluorescence obtained from the photolysis of CH_2N_2 excited by Kr resonance radiation.

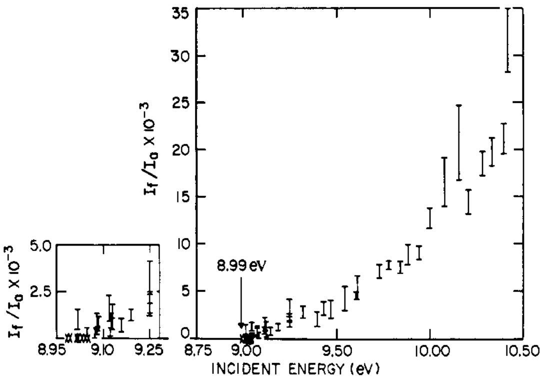

Figure 2. Fluorescence intensity (I_f) as a function of incident photon energy corrected for CH_2N_2 absorption.

ports. In addition, provision was made for a resonance lamp and appropriate light traps which significantly reduced scattered light from the lamp; however, the scattered light was sufficiently intense to permit calibration of the wavelength scale of the monochromator. The fluorescence spectrum was observed, at right angles to the resonance lamp, by a 13-stage photomultiplier behind the exit slit of the monochromator. A scanning speed of 10 Å/min was used to obtain the fluorescence spectrum. An RC circuit with a time constant of 2 sec was incorporated with a recorder to improve the signal-to-noise ratio.

Diazomethane was prepared from the reaction of *N*-nitrosomethylurea and potassium hydroxide and stored as a glass in dibutyl phthalate at −78°.[15] Before each experiment the "glass" was frozen at −196°, degassed, and then rewarmed to −78°. Gas-chromatographic analysis, using cyclopropane as a tracer, on a 7-m, 20% w/w squalane-on-firebrick column indicated that C_2H_4 was present to less than 5% of the diazomethane. The C_2H_4 impurity was not observed to increase with storage time.

Mass spectrometric measurement, at 70 eV and 75°, failed to show the parent peak of CH_2N_2[3a] at *m*/*e* 42, presumably due to the rapid decomposition of the sample in the metal inlet system. However, the absorption spectrum of the sample in the reaction cell showed peaks at 1671, 1530, and 1470 Å corresponding to those obtained by Merer.[11]

Severe problems due to either condensation or polymerization of the substrate, diazomethane, on the walls of the monel reaction vessel were encountered. The usual technique of coating the walls with paraffin wax was not feasible. Instead, onset measurements were obtained by using a fresh sample for each wavelength, recording the fluorescence and absorption (without an external RC circuit), and then immediately removing the sample. With these conditions the diazomethane pressure, as monitored by its absorption at the wavelength of interest, remained constant for the duration of a measurement, about 20 sec.

Pressure measurements were made with a calibrated diaphragm gauge, but these were not very accurate as mentioned above. Pressures of less than 0.2 Torr were sufficient to observe fluorescence, and most measurements were made at pressures of less than about 0.05 Torr. Argon (>99.99% pure) was added in those experiments where pressures of inert gas were needed.

Results

Figure 1 shows the fluorescence spectrum when CH_2N_2 is irradiated with a Kr resonance lamp equipped with a LiF window. The spectrum is the $A^2\Delta$-$X^2\pi$ system of the CH radical and consists of a portion of the Q branch of the (0, 0) transition as well as a feature at 4323 Å. The latter is most probably the (2, 2) transition[16] of the A-X system, as it is not present in the absence of CH_2N_2. It was obtained in a flow system at a pressure of 0.16 Torr of CH_2N_2. Traces of the fluorescence obtained in a static system were unreliable owing to the rapid "disappearance" of the substrate.

Figure 2 shows the fluorescence intensity (I_f), corrected for light absorption by the diazomethane, as a function of incident photon energy. The increase in I_f is clearly not linear, but a straight-line least-squares fit of the data in the threshold region yields an onset equal to 8.99 eV. The error associated with the individual data points is largely due to the low intensity of the fluorescence. No systematic errors were found. The most probable error in the onset value, based upon the instrument bandwidth of 5 Å, is ±0.03 eV.

By changing the filters in front of the fluorescence photomultiplier, it was demonstrated that any emission other than the CH($A^2\Delta$-$X^2\pi$) was absent in the spectral region between 1700 and 6000 Å.

In several experiments, the addition of argon, at pressures as high as 10 Torr, neither affected the emission intensity nor significantly alleviated the problem of apparent diazomethane disappearance on the walls, and it was not used in subsequent experiments. The reported results were obtained from pure diazomethane. The most probable excited species other than CH($A^2\Delta$), resulting from a dissociative process of diazomethane, is expected to be either excited singlet or triplet nitrogen. The first excited N_2 singlet state ($a^1\pi_g$) requires 8.6 eV plus the dissociation energy of the C-N bond in diazomethane. Even at the highest incident energies used, 11.2 eV, the Lyman-Birge-Hopfield emission ($a^1\pi_g$-$X^1\Sigma_u^+$) in the 1600-1700-Å region corresponding to the intense (0, 3) and (0, 4) transitions[17] was absent. Production of the $N_2(A^3\Sigma_u^+)$ state, 6.2 eV above the ground state, is obviously energetically more feasible. The N_2 Vegard-Kaplan ($A^3\Sigma_u^+$-$X^1\Sigma_g^+$) system is spin forbidden, with a small transition probability and long lifetime,[18] and hence we would not expect to be able to observe the emission directly. However, excitation of NO by $N_2(A^3\Sigma_u^+)$ is known to be a very efficient process.[19] The absence of the NO γ emission upon adding NO precludes formation of the excited nitrogen precursor as a significant process in the vacuum-ultraviolet photolysis of diazomethane. The emission expected from CH_2 $\tilde{b}(^1B_1)$-$\tilde{a}(^1A_1)$ in the red also was not found.

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Discussion

The photochemical process which has been observed is

$$CH_2N_2 \xrightarrow{h\nu} CH(A^2\Delta) + H + N_2 \qquad (1)$$

The heat of formation of diazomethane is then simply calculated from

$$\Delta H_f°(CH_2N_2) \geq \Delta H_f°(CH) + E_e[CH(A^2\Delta)] + \Delta H_f°(H) + \Delta H_f°(N_2) - h\nu$$

where $h\nu$ is the observed onset of the CH fluorescence and $E_e[CH(A^2\Delta)]$ is the electronic energy of excitation of the $CH(A^2\Delta)\ v = 0$ state.

The heat of formation of CH is based upon the spectroscopically determined value for $D°_0(CH)$,[20] the dissociation energy of CH. Recently, a revised value for $D°_0(CH) = 3.45 \pm 0.01$ eV[12] resulted in a small change of $\Delta H_f°(CH)$ from the tabulated value.[21] With the revised value of $D°_0(CH)$ and the appropriate values of $\Delta H_f°_0(H)$ and $\Delta H_f°_0(C_g)$ shown in Table I, we arrive at $\Delta H_f°(CH) = 142.1$ kcal/mol.

Table I. Thermochemical Quantities Used to Obtain $\Delta H_f°_0(CH_2N_2)$ and $D(CH_2-N_2)$

Substance	$\Delta H_f°_0$(0°K), kcal/mol	IP, eV	$H°_{298} - H°_0$	Ref
C(gas)	169.98			21
H	51.63			21
N_2	0			21
CH_2N_2			2.887	21
CH_2	93.0	10.4		23

The electronic excitation energy of the $CH(E_e[CH(A^2\Delta)])$ corresponds to the (0, 0) transition of the A–X system and has been accurately determined to be at 23,173 cm^{-1} (66.25 kcal/mol).[22] The diazomethane is photolyzed at room temperatures and possesses internal energy in equilibrium with its surroundings. This suggests that the incident energy required to effect observable fluorescence is less than would be required if the reactant were at absolute zero. $H°_{298} - H°_0$ for CH_2N_2 is 2.887 kcal/mol,[21] of which 1.4 kcal/mol is the internal energy available for dissociation which is then added to the experimentally determined onset of fluorescence of 1380 Å or 8.99 eV (207.31 kcal/mol). Again, using the value for $\Delta H_f°_0(H)$ and that for $\Delta H_f°_0(N_2)$ listed in Table I, we obtain $\Delta H_f°_0(CH_2N_2) \geq 51.3$ kcal/mol. This value is clearly a lower limit, since the threshold photon energy, $h\nu$, is an upper limit as it is possible that (a) the fluorescence process occurs at lower energies but remains undetected and (b) the product photodissociation fragments have excess energy. Although the absorption spectrum of CH_2N_2 below 1780 Å consists primarily of discrete transition of a Rydberg series, in the region below 1400 Å there exist broad diffuse bands of high intensity.[11] The relatively continuous absorption in the region between 1380 and 1400 Å suggests that the limiting wavelength for the appearance of the CH fluorescence is not dictated by absorption characteristics.

The bond dissociation energy is usually defined relative to the molecule and its dissociation products in the ground state at 0°K. Now using the most recent determination of $\Delta H_f°_0(CH_2) = 93.0$ kcal/mol,[23] we obtain our upper limit for the bond energy $D(CH_2-N_2) \leq 41.7$ kcal/mol (<1.81 eV). Another upper limit for $D(CH_2-N_2)$ was provided by Paulett and Ettinger,[3] who obtained 12.3 ± 0.1 eV for the appearance potential of CH_2^+ from CH_2N_2 by electron impact. This value, combined with the ionization potential of CH_2(10.4 eV),[24] gives $D(CH_2-N_2) \leq 1.9 \pm 0.1$ eV. It is not surprising that the electron impact value is somewhat higher than our photodissociation value. In many cases threshold energies obtained by electron impact are as much as 0.5 eV higher than those obtained by the photon impact method.[24,25]

The activation energy for the thermal decomposition of CH_2N_2

$$CH_2N_2 \xrightarrow{\Delta} CH_2 + N_2 \qquad (2)$$

should correspond to an upper limit of $D(CH_2-N_2)$, since the CH_2 produced may be activated. Observed activation energies range from 32 to 35 kcal/mol.[6,26] Then $D(CH_2-N_2) \leq 32$ kcal/mol and $\Delta H_f°_0(CH_2N_2) \geq 61$ kcal/mol are obtained. From the rate of isomerization to propylene of chemically activated c-C_3H_6, ∇^*, produced from the pyrolysis of CH_2N_2 in the presence of C_2H_4, Setser and Rabinovitch[6] computed the internal energy of ∇^* to be about 101 kcal/mol. Since the heat of reaction 3 is exothermic by 95 kcal/mol, on the basis

$$CH_2 + C_2H_4 \longrightarrow c\text{-}C_3H_6 \qquad (3)$$

of 93.0, 14.5, and 12.7 kcal/mol, respectively, for the heats of formation of CH_2, C_2H_4, and c-C_3H_6, the CH_2 formed must have an internal energy of about 6 kcal/mol. This would require reaction 4 to have an activa-

$$CH_2 + N_2 \longrightarrow CH_2N_2 \qquad (4)$$

tion energy of 6 kcal/mol. There are, however, some conflicting observations to this conclusion. For example, Moore and Pimentel[27] and also Milligan and Jacox[28] reported a buildup of an appreciable concentration of CH_2N_2 in a matrix at 20°K by the reaction of CH_2 produced from the photolysis of CH_2N_2 or CH_4 with N_2, indicating that the activation energy for reaction 4 is close to zero. Recent work[29] on the flash photolysis of CH_2CO-N_2 mixtures provides an estimate of the rate constant for reaction 4 to be 1.5×10^{-12} cm^3 $molecule^{-1}$ sec^{-1}. The maximum activation energy for (4), assuming a preexponential factor equal to the collision number, is 3.1 kcal/mol.

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Table II. $\Delta H_f°(CH_2N_2)$ and $D(CH_2\text{-}N_2)$ Obtained by Various Methods

Process	Method	Threshold energy, eV	$\Delta H_f°(CH_2N_2)$ eV	$\Delta H_f°(CH_2N_2)$ kcal/mol	$D(CH_2\text{-}N_2)$ eV	$D(CH_2\text{-}N_2)$ kcal/mol	Remarks
$CH_2N_2 \rightarrow CH(A^2\Delta) + H + N_2$	Photodissociation	8.99 ± 0.05	$\geq 2.22 \pm 0.05$	≥ 51.3	$\leq 1.81 \pm 0.05$	$\leq 41.7 \pm 1$	This work
$CH_2\text{-}N_2 \rightarrow CH_2^+ + N_2$	Electron impact	12.3 ± 0.1	≥ 2.1	≥ 49	≤ 1.9	≤ 44	Ref 3a
		12.7 ± 0.3	≥ 1.7	≥ 40			Ref 4
$CH_2N_2 \rightarrow CH_2 + N_2$	Pyrolysis			>67		≤ 35	Ref 6
$CH_2N_2 + HX \rightarrow CH_3X + N_2$ (X = Br and I)	Decomposition of CH_3X			$>48 + E_I$ $<57 + E_I$			*a*

[a] E_I is the translational and internal energy of CH_3X and N_2. See ref 7a.

Another independent estimate of the upper and lower limits for $\Delta H_f°(CH_2N_2)$ comes from the work of Hassler and Setser.[7a] From the observation that CH_3I formed in reaction 5 decomposes while CH_3Br does not, an internal energy of the activated CH_3X should be above 54 kcal/mol for CH_3I and below 67 kcal/mol for CH_3Br, respectively. $(48 + E_I) \leqq LH_f°(CH_2N_2) \leq (57 + E_I)$ kcal/mol, where E_I is the sum of the energy in various degrees of freedom in CH_3X and in N_2. In order to have an agreement with our lower limit of 51.3 kcal/mol, E_I = 3.3 kcal/mol is obtained, which places an upper limit of 60.3 kcal/mol on $\Delta H_f°(CH_2N_2)$. Our threshold measurement for the production of $CN(B^2\Sigma)$ from various cyanogen compounds[25] indicates that the experimentally determined threshold, in some cases, is as much as 5 kcal/mol above the minimum energy required for the reaction, even when a distinct threshold is observed. In the case of CH_2N_2, three products are formed, each of which can carry excess energy in various degrees of freedom. Therefore, it is not unlikely that the observed threshold is several kcal/mol above the minimum energy required, which is within the range of values set by Hassler and Setser. The activation energy for reaction 4 is given by $\Delta H_f°(CH_2N_2) + E_A - \Delta H_f°(CH_2)$, where E_A is the activation energy for the thermal decomposition of CH_2N_2. Adopting the upper limit $\Delta H_f°(CH_2N_2) \leq 60$ kcal/mol, E_A = 32 kcal/mol, and $\Delta H_f°(CH_2)$ = 93 kcal/mol, almost no activation energy is expected for (4), supporting the observation that the reaction proceeds efficiently even at 20°K.[27,28] A summary of the $\Delta H_f°(CH_2N_2)$ and $D(CH_2\text{-}N_2)$ values obtained by various methods appears in Table II.

$$CH_2N_2 + HX\ (X = Cl, Br, I) \longrightarrow CH_3X + N_2 \qquad (5)$$

Acknowledgment. Thanks are due to Dr. R. F. Hampson, Jr., for many helpful discussions.

Flash Spectroscopy and Photoreduction of Phenazine

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Received September 28, 1970

Abstract: Flash illumination of methylcyclohexane (MCH) and trifluoroethanol (TFE) solutions of phenazine populates both singlet and triplet excited states. The quantum yield of triplet formation is 0.21 in MCH and 0.30 in TFE. Singlet-state reactions are of little consequence in MCH, but are quite complex in TFE, leading to the formation of primary and secondary reduction products, *i.e.*, the phenazine semiquinone and the phenazine cation radical, respectively. The quantum yield of the cation radical is 0.08, and about 15% of this can be stabilized. The quantum yield of phenazine disappearance is ≥0.04 and results completely from excited-singlet-state reactions. Evidence is presented for the inclusion of a dimer-forming reaction in the TFE system.

In recent years the flash photolysis of phenazine has received considerable attention. Studies have been carried out in benzene, water,[2] and acid solutions.[3] All the studies have resolved at least two intermediates. In all cases the lowest triplet state, protonated in the acid systems,[3] was detectable through its triplet–triplet absorption spectrum, and its rate of decay was found to vary from about 2×10^4 to 5×10^3 sec^{-1}, depending on the solvent. In acid solution a long-lived intermediate was also formed, decaying with a rate constant of 120 sec^{-1}. Intermediates of this type were also noted in benzene and water,[3] but the yields were so low that little in the way of quantitative data could be obtained. In weak acid and neutral solutions the major product of the photoreduction was dihydrophenazine.[2-4] In strongly acid solutions, however, the samples became lime green and the isolated product was identified as the phenazine cation radical.[3] In all cases the interme-

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