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Flash Photolysis of Ketene and Diazomethane: The Production and Reaction Kinetics of Triplet and Singlet Methylene

W. BRAUN, ARNOLD M. BASS,* AND M. PILLING†

National Bureau of Standards, Washington, D. C. 20234

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Ketene and diazomethane have been flash photolyzed in their strongest absorption continua in the vacuum ultraviolet and far ultraviolet. Triplet methylene was monitored by kinetic spectroscopy at 141.5 nm. Singlet methylene was not observed directly, but the growth of the triplet absorption as a function of inert-gas pressure indicates that singlet methylene was the major primary product in both the ketene and diazomethane systems. Various inert additives quantitatively quenched the singlet to the triplet state, while reactive additives were able to intercept the singlet before quenching occurred. A number of reactions and deactivations involving singlet methylene ($^1CH_2$) and triplet methylene ($^3CH_2$) have been investigated at 298°K, and their rate constants are listed below ($\mathrm{cm^3\ molecule\cdot^{-1}\ second^{-1}}$):

$$^3CH_2+{}^3CH_2\rightarrow C_2H_2+H_2 \qquad (5.3\pm1.5)\times10^{-11} \tag{1a), (1b}$$

$$^1CH_2+H_2\rightarrow CH_4^*\rightarrow CH_3+H \qquad (7.0\pm1.5)\times10^{-12} \tag{2}$$

$$^1CH_2+H_2\rightarrow {}^3CH_2+H_2 \qquad <1.5\times10^{-12} \tag{3}$$

$$^1CH_2+CH_4\rightarrow C_2H_6^*\rightarrow CH_3+CH_3 \qquad (1.9\pm0.5)\times10^{-12} \tag{4}$$

$$^1CH_2+CH_4\rightarrow {}^3CH_2+CH_4 \qquad (1.6\pm0.5)\times10^{-12} \tag{5}$$

$$^1CH_2+He\rightarrow {}^3CH_2+He \qquad (3.0\pm0.7)\times10^{-13} \tag{11}$$

$$^1CH_2+Ar\rightarrow {}^3CH_2+Ar \qquad (6.7\pm1.3)\times10^{-13} \tag{12}$$

$$^1CH_2+N_2\rightarrow {}^3CH_2+N_2 \qquad (9.0\pm2.0)\times10^{-13} \tag{13}$$

$$^3CH_2+H_2\rightarrow CH_3+H \qquad <5\times10^{-14} \tag{18}$$

$$^3CH_2+CH_4\rightarrow CH_3+CH_3 \qquad <5\times10^{-14}. \tag{19}$$

The absolute reaction rates for the singlet are apparently independent of the source (i.e., ketene or diazomethane), suggesting that the reactions occur via vibrationally cold singlet methylene. No evidence was found for deactivation of the triplet to the singlet, indicating that the energy difference between the two states is greater than kT ($T=298$°K).

I. INTRODUCTION

The chemistry of methylene has received much attention over the past few years, and the subject has been extensively reviewed.[1] The differences in reactivity of the singlet and triplet species, and the mechanism of interconversion of the two spin states are of particular interest. This paper reports a flash-photolytic investigation, whose main aim has been to measure the rates of the singlet–triplet deactivation.

Most experiments have employed low-intensity photolysis of ketene around 300 nm, as the source of methylene. Singlet methylene has been shown to add stereospecifically to olefins and to insert into carbon–hydrogen bonds. Triplet methylene, on the other hand, adds to olefins nonstereospecifically, and is thought to abstract hydrogen atoms. These distinctions have been used as diagnostic tests for the two spin states. In a very successful exploitation of this technique, Bader and Generosa,[2] by examining the pressure dependence of the ratio of the two dimethylcyclopropane isomers produced from the addition of methylene to *cis*-butene-2, demonstrated that the singlet can be collisionally deactivated to the triplet. However, the complexity of their system precluded any detailed measurements of the rates of deactivation. Furthermore, the validity of using the *trans/cis* ratio as a diagnostic test has recently been questioned.[3]

In two recent investigations which utilized photodecomposition of ketene as the source of singlet methylene, either the reaction of singlet methylene with ketene itself,[4] or the reaction with added propane[5] was used as the reference reaction monitoring singlet methylene. Diminution of the reference reaction product by added inert gas (through deactivation of singlet methylene to the triplet) was used to monitor the relative deactivation efficiencies of various inert additives. Oxygen scavenger was used to remove triplet methylene in small enough proportions to minimize any scavenging of singlet methylene. In these investigations it was not possible to distinguish the importance of collision-induced intersystem crossover from excited singlet ketene to the triplet.

In view of these difficulties, there is a need to characterize the photolysis systems more fully, and to delineate conditions under which the chemistry is predominantly governed by one spin state or the other. Mercury-photosensitized decomposition of ketene has been shown to produce the triplet,[6,7] but once again, evidence has been forthcoming for formation of a nonnegligible fraction in the singlet state.[8]

The most satisfactory means of characterizing the photolysis is by direct observation of the methylene species. A major advance in this direction was made by Herzberg,[9] who obtained spectra of both singlet and triplet methylene following flash photolysis of diazomethane. The lowest singlet ($^1A_1$) absorbs weakly, with a many-line spectrum between 550 and 950 nm. The lowest triplet absorbs in the vacuum u.v., with its strongest band at 141.5 nm. Isotopic substitution experiments confirmed that the carrier of both spectra was CH_2. The rotational structure of the 141.5-nm system of CD_2 was analyzed. Although no spin splitting was observed, the transition was assigned to $^3\Sigma_u^- - ^3\Sigma_g^-$, on the basis of the intensity alternation (odd J are strong for CD_2) and of a consideration of the molecular-orbital predictions of the relative energies of the various electronic states of linear CH_2. Further bands occur at shorter wavelengths and form a Rydberg series of which the 141.5-nm system is the first member.

Herzberg also presented evidence for the $^3\Sigma_g^-$ state having less energy than the $^1A_1$ state, and for a collision-induced transition between the two. Both states could only be observed on addition of nitrogen to CH_2N_2, but the singlet state required lower pressures and was shorter lived than the triplet. It was concluded that 210-nm radiation decomposes CH_2N_2 into an excited singlet state of methylene and into N_2 in the $X\ ^1\Sigma_g^+$ state. The methylene is then collisionally deactivated to the $^1A_1$ state, which in turn is deactivated by collisions to $^3\Sigma_g^-$. Herzberg[10] estimated a value of $\lesssim 1$ eV for the singlet–triplet energy separation. Since then, several experimental[11,12] and theoretical estimates[13–15] of this quantity have been made, and the current consensus favors a somewhat lower value (~ 0.1 eV).

Since flash photolysis generates a greater density of transient species than low-intensity photolysis, a direct comparison of product ratios and dominant reactions in the two systems is invalid. However, in view of the direct nature of the former technique, it can be used to solve certain problems more simply, and its results can be applied, with reservations, to assist in the detailed interpretation of steady-state experiments.

II. EXPERIMENTAL

The vacuum ultraviolet flash-photolysis apparatus and optical train have previously been described in detail.[16,17] The essential elements are a 4000-J vacuum ultraviolet photolysis flash lamp with a pulse half-width of 5 μsec; a 500-J Garton–Wheaton analysis lamp[18] with a time resolution of better than 1 μsec; and a 2-m focal-length Eagle vacuum spectrograph. The grating was ruled with 1800 lines/mm, and provided first-order dispersion of 0.28 nm/mm. With a 0.05-mm slit this gave a spectral resolution of 0.015 nm. Quartz and suprasil reaction vessels were employed for the diazomethane and ketene experiments, respectively.

Spectra were recorded on Kodak SWR plates, and the density/light intensity dependence was repeatedly checked, and all concentration measurements made by reference to this calibration. For stable species, calibrations of absorption vs concentration were made over a wide range of pressures. For diffuse absorption bands, the Beer–Lambert law was found to hold rigorously. Methylene and methyl radicals were monitored by means of their absorptions at 141.5 and 150.4 nm, respectively. For CH_2 and CH_3, these bands are diffuse, as shown by their high-resolution spectra,[9] and the applicability of the Beer–Lambert law was assumed. Absolute concentration measurements for these transient species were made by measuring stable products resulting from their reactions. End-product analyses were performed using vapor-phase chromatography, with a squalane column and flame ionization detection. Calibrated samples were always introduced to the reaction vessel and analyzed in the same manner as products from actual experiments. The accuracy of this technique was verified by the good agreement between photometric and chromatographic determinations of the concentrations of stable species.

Diazomethane was freshly prepared for each experiment by the action of 70% aqueous KOH on N-nitrosomethylurea. The product was passed through several dry ice/acetone traps to eliminate water, and then trapped at liquid-nitrogen temperatures and thoroughly pumped to eliminate noncondensible gases. The purity of the samples was determined by chromatographic and spectral analyses. Ethylene was found to be the major impurity (~10%). It was not possible to remove small amounts of ethylene from the diazomethane, and the diazomethane samples were used as prepared. If samples were allowed to stand in the reaction vessel (up to 10 min), further deterioration was observed by monitoring the diazomethane and ethylene vacuum uv absorption spectrum. CD_2N_2 was prepared from N-nitrosomethylurea-d_3 and KOD.

Ketene was prepared by the pyrolysis of acetic anhydride and purified in the same manner as diazomethane. It was stored at liquid-nitrogen temperatures. The ketene samples were of high purity (~99%), checked by mass spectrometer and chromatograph, and were found to be free from the deterioration difficulties encountered with diazomethane. Consequently, most of the quantitative stoichiometric measurements were made with ketene as the source of methylene. CD_2CO was made from acetic anhydride-d_6 after thoroughly deuterating the walls of the generator.

Low-pressure measurements ($<500\ \mathrm{N\,m^{-2}}$) were made by using a calibrated capacitance micromanom-

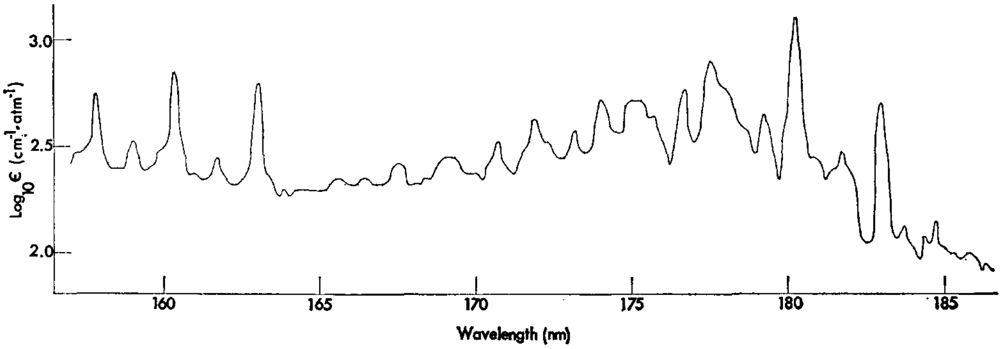

FIG. 1. Absorption coeficients for ketene (cm^{-1}·atmosphere^{-1} as a function of wavelength.)

eter, and high-pressure measurements (5×10^2–10^5 N m^{-2}) with precision dial gauges. Gas mixtures were prepared in large flasks, with a precision of about 1%, and samples were allowed to mix thoroughly before use. The flasks were coated on the inside with paraffin wax and painted black, to avoid surface as well as photochemical decomposition of the substrate. Employing these precautions samples of diazomethane could then be stored for several hours and ketene for several days without any noticeable decomposition.

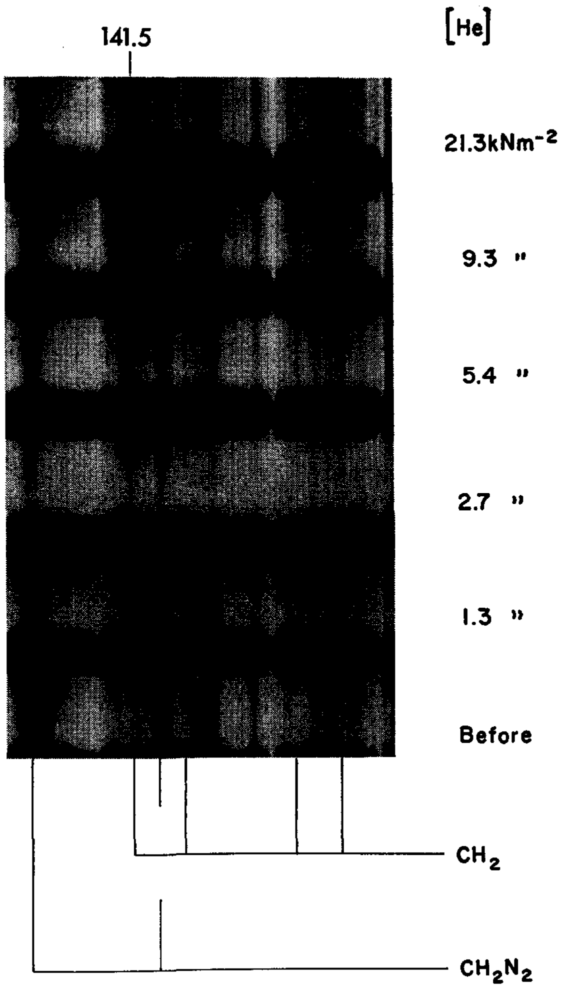

FIG. 2. Triplet methylene absorption as a function of helium pressure (10 N m^{-2} CH_2N_2 before flash and 10 μsec after flash over helium pressure range 1.3–21.3 k N m^{-2}).

The absorption spectra of ketene and diazomethane were monitored by using a 0.75-m Ebert monochromator, having a grating with 3600 lines/mm blazed at 130 nm (first-order dispersion of 0.3 nm/mm). Hydrogen, zenon, and krypton continua were employed as background sources.

III. RESULTS

A. Extinction Coefficients for Ketene

The absorption spectrum of ketene has previously been reported, both in the near-[19] and vacuum ultraviolet.[20] However, the investigation by Price, Teegan, and Walsh was apparently invalidated by the presence of water vapor in the sample.[20] Consequently, we have re-examined the absorption spectrum over the region of interest in our photolysis system, and Fig. 1 shows extinction coefficients over the wavelength range 157–187 nm.

B. Preliminary Observations

Diazomethane absorbs strongly above 200 nm.[21,22] By reproducing Herbzerg's[9] experimental conditions and using a quartz cell we were able to observe the triplet methylene absorption at 141.5 nm with short time delays (~10 μsec). Several higher Rydberg transitions were detected at shorter wavelengths. In addition, we found that triplet methylene could be produced in diazomethane/helium mixtures (Fig. 2). Similar total pressures ($\lesssim 3\times10^3$ N m^{-2}) were required to maximize the absorption for all three diluent gases, He, Ar, N_2. In the case of nitrogen, pressures much higher than 10^4 N m^{-2} resulted in a reduction in the triplet methylene absorption, while for argon and helium the triplet concentration remained constant. For nitrogen the loss in triplet methylene was attributed to reaction of CH_2 with N_2.

Ketene absorbs strongly below 200 nm (Fig. 1), and,

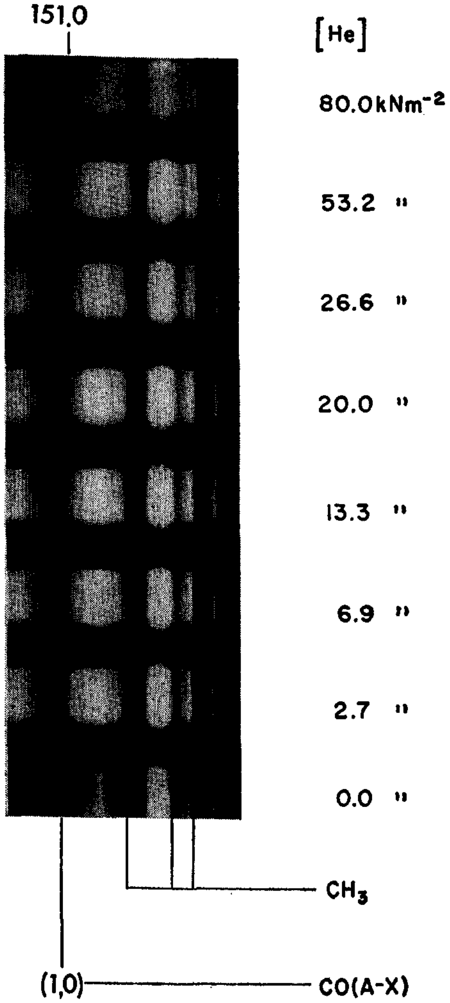

FIG. 3. The dependence of methyl radical absorption on helium pressure, 10 N m^{-2} CH_2CO, 2.6 k N m^{-2} H_2.

by employing a suprasil reaction vessel, thus extending the flash radiation to these wavelengths, we were able to generate $^3CH_2$ from the flash photolysis of ketene. Once again, nitrogen, argon, and helium were effective in enhancing the triplet absorption.

At high inert-gas pressures, the triplet methylene absorption obtained from ketene was comparable to that from diazomethane, for similar percentage decompositions of the parent compounds. Under our conditions, the methylene product, in both ketene and diazomethane, was acetylene. As will be shown later, the acetylene results from a reaction which is of the second order in methylene, presumably

$$CH_2+CH_2\rightarrow C_2H_4^*, \tag{1a}$$

$$C_2H_4^*\rightarrow C_2H_2+H_2. \tag{1b}$$

The acetylene yield was independent of total pressure, up to inert gas pressures as high as one atmosphere. Calculations based on the large exothermicity of Reaction (1a) predict that pressures considerably in excess of this would be required to stabilize the excited ethylene.

Addition of hydrogen to diazomethane or ketene, at low inert-gas pressures, resulted in the formation of methyl radicals, and the suppression of triplet methylene. The major final product was ethane. High pressures of methane added to the flash mixture led to the formation of both triplet methylene and methyl radicals, and to acetylene and ethane, in roughly equal amounts, as the final products. If successively higher inert-gas pressures were added to a mixture of ketene or diazomethane and hydrogen or methane, the methyl radical concentration decreased (Fig. 3), while the triplet methylene absorption was enhanced. For high inert-gas/hydrogen (or methane) ratios, at hydrogen (or methane) pressures as high as 3 k N m^{-2} the methyl absorption could be almost completely eliminated, and the methylene absorption developed to about the same intensity as was found in substrate/inert-gas mixtures. This result indicates that triplet methylene is relatively unreactive towards hydrogen and methane.

These preliminary experiments can be interpreted in terms of a precursor to $^3CH_2$, which can be reacted with H_2 or CH_4, or, alternatively, be deactivated to the triplet state of methylene by inert gas. If we assume that the precursor is the singlet state of methylene, then a careful analysis of the competition between reaction of the singlet with hydrogen, and deactivation by helium, coupled with an absolute determination of the rate of deactivation, should permit an evaluation of the rate constant for Reaction (2),

$$^1CH_2+H_2\rightarrow CH_4^*, \tag{2a}$$

$$CH_4^*\rightarrow CH_3+H. \tag{2b}$$

Since the excess energies in the ketene and diazomethane systems differ, a comparison of the rates of Reaction (2) for $^1CH_2$ generated from these two compounds is of interest in determining the importance, if any, of the reaction of vibrationally excited $^1CH_2$ in our system.

These results are discussed below.

C. Photochemistry

1. *Ketene*

The absorption spectrum shows a relatively strong underlying continuum between 170 and 190 nm, with an average extinction coefficient of about 300 cm^{-1}·atm^{-1}. The major fraction of the photolysis took place over this range since absorption at longer wavelengths is much weaker. A suprasil reaction vessel was employed, and consequently, wavelengths below about 150 nm could in no way influence the photochemistry.

C^3P absorption was observed at 165.7 nm but its low concentration (<0.1 N m^{-2}) estimated from earlier calibrations[23] did not represent an appreciable fraction of the ketene decomposed. A weak CH absorption was observed at 137 nm. Since there is no available absorption coefficient for this transition it is not possible to assess the importance of CH in the primary decomposition; however, the chemical results, and isotope experiments discussed in detail below, indicate that this species does not play an important role in the photochemistry of ketene.

Experiments with 10 N m^{-2} of ketene led to 30%±5% decomposition of the parent compound. Under conditions where all the methylene was ultimately produced in the triplet state, the following stoichiometry was found:

$$(3\pm0.5)\ \mathrm{N\ m^{-2}\ CH_2}\rightarrow(1.1\pm0.1)\ \mathrm{N\ m^{-2}\ C_2H_2}.$$

Thus the major fraction of the dissociated ketene gave acetylene. Both ethane and ethylene constituted less than 10% of the total products, which included, as well, trace amounts of allene and methyl acetylene.

The photodissociation of ketene in hydrogen gave

$$(3\pm0.5)\ \mathrm{N\ m^{-2}\ CH_2}\rightarrow(0.48\pm0.05)\ \mathrm{N\ m^{-2}\ C_2H_2}+(1.1\pm0.1)\ \mathrm{N\ m^{-2}\ C_2H_6}.$$

If the acetylene was produced via Reaction (1), and the ethane via association of methyl radicals formed in Reaction (2), then this result corresponds to complete conversion of the methylene into ethane and acetylene. The presence of a finite amount of acetylene can be interpreted in terms of either direct production of the triplet in the photodecomposition, or deactivation of the singlet to the triplet by hydrogen via

$$^1\mathrm{CH_2}+\mathrm{H_2}\rightarrow{}^3\mathrm{CH_2}+\mathrm{H_2}. \qquad (3)$$

Additional independent evidence favors the former possibility, and we conclude that roughly 30% of the photodecomposition of ketene at 180 nm takes place via a spin-forbidden route, and that the ratio k_2/k_3 is $\gtrsim 5$.

Photolysis of ketene/methane mixtures produce nearly equal concentrations of acetylene and ethane,

$$(3\pm0.5)\ \mathrm{N\ m^{-2}\ CH_2}\rightarrow(0.72\pm0.05)\ \mathrm{N\ m^{-2}\ C_2H_2}+(0.86\pm0.05)\ \mathrm{N\ m^{-2}\ C_2H_6}.$$

The enhancement of the acetylene was presumably due to deactivation of the singlet methylene to the triplet by methane. From the acetylene/ethane ratio, it can be deduced that the ratio of the rates of the reactions

$$^1\mathrm{CH_2}+\mathrm{CH_4}\rightarrow\mathrm{C_2H_6}^*\rightarrow\mathrm{CH_3}+\mathrm{CH_3}, \qquad (4)$$

$$^1\mathrm{CH_2}+\mathrm{CH_4}\rightarrow{}^3\mathrm{CH_2}+\mathrm{CH_4}, \qquad (5)$$

is ~1.5. This interpretation is substantiated by photometric experiments described below.

Ethylene, the dominant low-intensity product in ketene/inert-gas mixtures, was of only minor importance throughout these experiments, indicating that the reaction of $^3\mathrm{CH_2}$ with ketene is considerably slower than the association of triplet methylene.

2. *Diazomethane*

In diazomethane/helium mixtures, at low total pressures, ethane was produced in about the same concentration as acetylene. Increasing the helium pressure significantly reduced the ethane yield and, at 10^4 N m^{-2}, the acetylene/ethane ratio was about 5. Two possible mechanisms could account for the ethane:

$$^1\mathrm{CH_2}+\mathrm{CH_2N_2}\rightarrow\mathrm{CH_3}+\mathrm{CHN_2}, \qquad (6)$$

$$^1\mathrm{CH_2}+{}^1\mathrm{CH_2}\rightarrow\mathrm{CH}+\mathrm{CH_3}. \qquad (7)$$

To differentiate between these two possibilities, experiments were conducted at reduced light intensity. If Reaction (7) were responsible, then the increased He/$^1\mathrm{CH_2}$ ratio should have increased the probability of deactivation relative to singlet disproportionation and the acetylene/ethane ratio should have risen. However, the acetylene/ethane ratio decreased slightly, thus favoring Reaction (6). Reaction with diazomethane also readily explains the difference between the two photolysis systems, if one postulates a more difficult hydrogen-atom abstraction reaction from ketene. If Reaction (7) were responsible, then it would be necessary to invoke some difference, presumably in energy content, between methylene generated in ketene and diazomethane, which is contrary to the conclusions made below. It must be pointed out that these observations were only preliminary, and very few experiments were conducted on the diazomethane system. A large ethylene impurity (~10%) proved particularly troublesome since it made it impossible to detect the production of small amounts of ethylene. In addition, ~30% of the ethylene was photolyzed, to give mainly acetylene. The total acetylene yield was corrected to allow for this, but the accuracy of the results was necessarily impaired. The proposal of hydrogen-atom abstraction by the singlet is, therefore, put forward only tentatively.

Just as in the ketene system, addition of hydrogen greatly simplified the chemistry. For 9 N m^{-2} of substrate, and (35%±5%) photolysis, addition of hydrogen gave the following stoichiometry:

$$(3.1\pm0.5)\ \mathrm{N\ m^{-2}\ CH_2}\rightarrow(1.2\pm0.1)\ \mathrm{N\ m^{-2}\ C_2H_6}.$$

Acetylene was less than 10% of the ethane, and we conclude that the major fraction of the dissociation of diazomethane results in singlet methylene.

In view of the simpler chemistry of the ketene system and the accessibility of the pure substrate, most of the experiments discussed below utilized ketene as the source of methylene. In the presence of either hydrogen or methane, however, diazomethane photolysis presented no apparent complications, and a comparison of the two systems was, therefore valid.

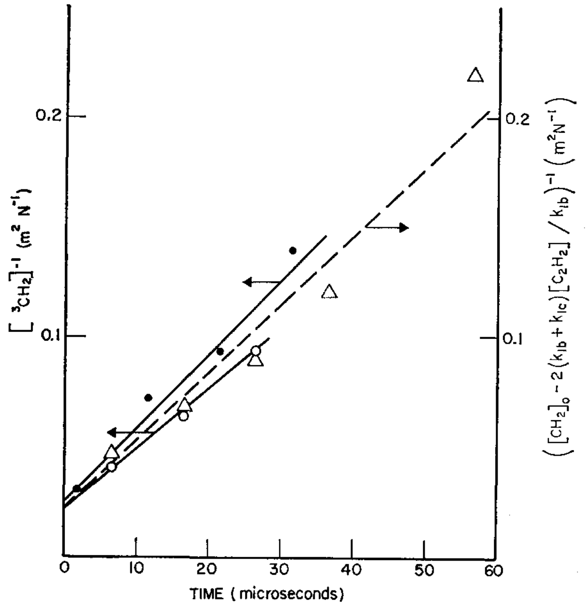

FIG. 4. The decay of triplet methylene with time, and the determination of the rate constant for association. ○, Δ 10 N m^{-2} CH_2CO, 2.7×10^3 N m^{-2} He; ●, 10 N m^{-2} CH_2CO, 9.3×10^4 N m^{-2} He.

D. Association Reactions of CH_2 and CH_3

1. *CH_2*

Triplet methylene decayed very rapidly with time, and could not be monitored for delays longer than about 40 μsec. The ketene concentration, on the other hand, remained fairly constant after about 10 μsec. Since a large fraction of the substrate (~30%) was converted into methylene, this observation favors a methylene loss mechanism not involving ketene consumption, and the most obvious reaction is associative formation of acetylene [Reactions (1a), (1b)]. For a reaction which is second order in CH_2, the methylene decay should follow Equation (A):

$$[CH_2]^{-1} - [CH_2]_0^{-1} = 2k_1t. \qquad (A)$$

Figure 4 shows a plot of $[CH_2]^{-1}$ against time for helium pressures of 2.7×10^3 and 9.3×10^4 N m^{-2}. These give rate constants of $(6.4\pm0.8)\times10^{-11}$ and $(7.7\pm1.0)\times10^{-11}$ cm^3 $molecule^{-1}\cdot sec^{-1}$, respectively. The absolute concentration of methylene was determined by equating $[CH_2]_0$ with the amount of ketene decomposed. It is unlikely that this should produce much error since, as was discussed above, there was little evidence for any competing primary processes. Furthermore, as will be shown below, under the pressure conditions employed at least 90% of the singlet had been deactivated to the triplet.

Since acetylene was the major product, it should be possible to evaluate k_1 by measuring the rate of formation of acetylene. Thus, if acetylene were the only product,

$$[CH_2]_0 - 2[C_2H_2] = [CH_2],$$

and

$$([CH_2]_0 - 2[C_2H_2])^{-1} - [CH_2]_0^{-1} = 2k_1t. \qquad (B)$$

One possible mechanism involves two dissociation channels for the excited ethylene formed in Reaction (1a):

$$CH_2 + CH_2 \rightarrow C_2H_4^*, \qquad (1a)$$

$$C_2H_4^* \rightarrow C_2H_2 + H_2, \qquad (1b)$$

$$C_2H_4^* \rightarrow CH + CH_3. \qquad (1c)$$

Under these circumstances, CH_2 would decay by a compound bimolecular process, and Equation (B) would become

$$([CH_2]_0 - 2(k_{1b}+k_{1c})[C_2H_2]/k_{1b})^{-1} = 2k_1t + [CH_2]_0^{-1}. \qquad (C)$$

In Fig. 4, the lhs of Eq. (C) is plotted against time. k_{1b}/k_{1c} was determined from the stoichiometry, i.e.,

$$k_{1b}/(k_{1b}+k_{1c}) = [C_2H_2]\infty / ([CH_2CO] \text{ decomposed}).$$

This gives $k_{1a} = (7.0\pm1.5)\times10^{-11}$ cm^3 $molecule^{-1}\cdot sec^{-1}$, in good agreement with the value determined from direct observation of methylene. This mechanism is supported by the detection of CH absorption at 136.9 nm, in low-pressure mixtures of ketene and helium. The CH was absent at the shortest time delays, but built up to a maximum at ~35 μsec, and subsequently, decayed. However, the difference in the exothermicities of the disproportionation and acetylene-producing reactions (8 and 129 kcal, respectively), necessitates a very large *A* factor for 1c if it is to compete with 1b.

The incomplete conversion of CH_2 into C_2H_2 could also be caused by reaction with ketene:

$$CH_2CO + CH_2 \rightarrow C_2H_4 + CO \qquad (8)$$

or

$$CH_2CO + CH_2 \rightarrow CH_3 + CHCO. \qquad (9)$$

The decay of triplet methylene, and the increase in acetylene were calculated[24] for various values of $k_{1a,1b}$ and (k_8+k_9), using the OMNITAB general purpose computer program.[26] By setting maximum limits on the amounts of ethane and ethylene produced, the following rate constants were determined:

$$k_{1a,1b} = (4\pm2)\times10^{-11}\ cm^3\ molecule^{-1}\cdot sec^{-1},$$

$$10^{-12}\ cm^3\ molecule^{-1}\cdot sec^{-1} < k_8 + k_9 < 5\times10^{-12}\ cm^3\ molecule^{-1}\cdot sec^{-1}.$$

The calculated rate constant for acetylene production, assuming concurrent first-order–second-order kinetics $k_{1a,1b} = (4\pm2)\times10^{-11}$ cm^3 $molecule^{-1}\cdot sec^{-1}$, agrees well with the previously calculated rate constant for acetylene production assuming compound bimolecular processes (1a, 1b, 1c),

$$k_{1a}\{k_{1b}/k_{1b}+k_{1c}\}=(5.3\pm1.5)\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\cdot\text{sec}^{-1}.$$

Because the acetylene accounts for the major fraction of the photolysis products, the value deduced for $k_{1a,1b}$ is largely unaffected by the nature of the minor methylene decay processes.

2. *CH_3*

Addition of hydrogen quantitatively converted the singlet methylene into methyl radicals at low inert-gas pressures. Figure 5 shows plots of $[CH_3]^{-1}$ against time for ketene/hydrogen and ketene/methane systems. Assuming complete conversion of methyl radicals into ethane the absolute methyl concentrations were determined by measuring the total amount of ethane produced, and equating twice this value to the methyl absorption extrapolated to zero time. The two plots give $k_{10}=(6.5\pm0.2)\times10^{-11}$ and $(8.0\pm0.2)\times10^{-11}$ cm³ molecule⁻¹·sec⁻¹, respectively, for the methyl association reaction

$$CH_3+CH_3+M\rightarrow C_2H_6+M. \qquad (10)$$

At these temperatures and pressures, stabilization of the excited ethane adduct is complete,[27,28] and the rate constants quoted are the limiting high-pressure values. A possible complicating factor is the reaction of CH_2 with CH_3. The ratio of the methyl/methylene concentrations in the methane system was ~1.0, while in the hydrogen system it was ~2.0. This could possibly account for the small difference in the two measured rates. An additional complication in the methylene/hydrogen system which we have not adequately explored at this time is the competing reaction of methyl radicals with hydrogen atoms. The decay of the methyl radicals was determined since it was required in the development of certain following sections of this work. Since the methyl combination reaction has not been extensively investigated over a wide enough range of experimental conditions, the reported rate constant ($k_{10}=7\times10^{-11}$ cm³ sec⁻¹·molecule⁻¹) is only rough with an uncertainty of probably less than a factor of 2. The value for the bimolecular combination reaction reported here can be compared with the value determined by Kistiakowsky and Roberts,[28] $k_{10}=6.2\times10^{-11}$ cm³ molecule⁻¹·sec⁻¹ (at 463°K). The agreement is only moderately good.

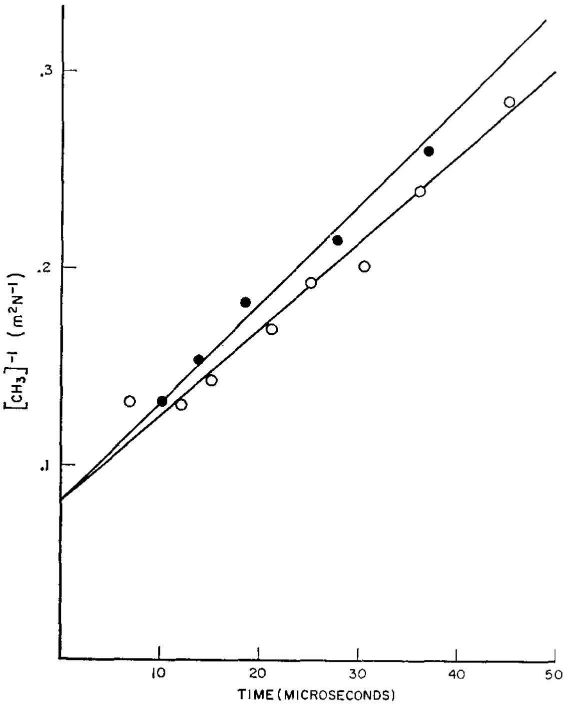

FIG. 5. The decay of methyl radicals with time, and the determination of the rate constant for association. ○, 6.7 N m⁻² CH_2CO, 1.3×10^3 N m⁻² H_2; ●, 6.7 N m⁻² CH_2CO, 1.3×10^3 N m⁻² CH_4. The two plots have been normalized, in both concentration and time, to give the same methyl concentration at zero time.

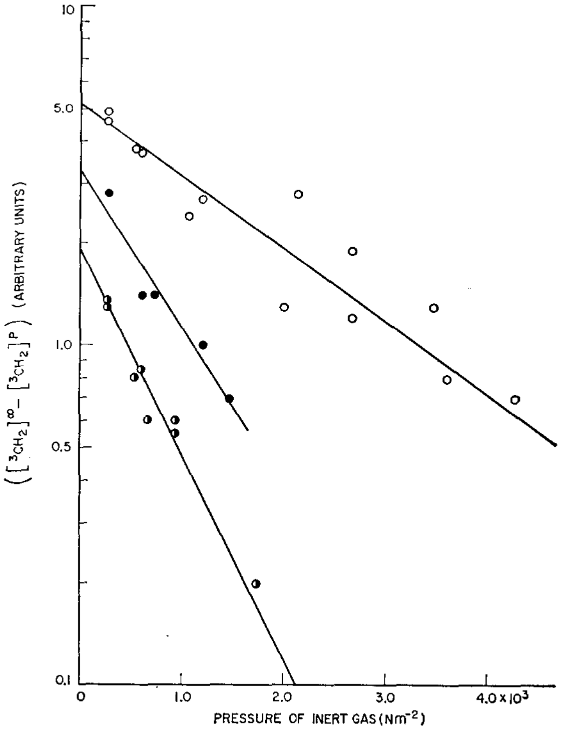

FIG. 6. The decrease in singlet methylene concentration $([^3CH_2]^\infty-[^3CH_2]p)$ as a function of inert gas pressure, 10 N m⁻² CH_2CO. ○ He; ● Ar; ◑ N_2.

E. Deactivation of $^1CH_2$

The rate of the singlet–triplet deactivation

$$^1CH_2+M\xrightarrow{k_m}{}^3CH_2+M \qquad (11), (12), (13)$$

was measured by monitoring $^3\mathrm{CH}_2$ as a function of inert-gas pressure.

If $[^3\mathrm{CH}_2]^\infty$ is the limiting high-pressure concentration of triplet methylene, $[^1\mathrm{CH}_2]^0$ and $[^3\mathrm{CH}_2]^0$ are the concentrations of the singlet and triplet at zero pressure, and $[^1\mathrm{CH}_2]p$ and $[^3\mathrm{CH}_2]p$ are their concentrations at a given pressure p, then

$$[^1\mathrm{CH}_2]p=[^3\mathrm{CH}_2]^\infty-[^3\mathrm{CH}_2]p,$$

since, as will be discussed below, the singlet can be quantitatively deactivated to the triplet. Thus,

$$\log_{10}([^3\mathrm{CH}_2]^\infty-[^3\mathrm{CH}_2]^0)-\log_{10}([^3\mathrm{CH}_2]^\infty-[^3\mathrm{CH}_2]p)=k_m\Delta t[\mathrm{M}]/2.303. \qquad \text{(D)}$$

Figure 6 shows a plot of $\log_{10}([^3\mathrm{CH}_2]^\infty-[^3\mathrm{CH}_2]p)$ against pressure for helium, argon, and nitrogen, at a delay time of 6.5 μsec. The values thus obtained for the three rate constants are

He: $k_{11}=(3.0\pm0.7)\times10^{-13}$ cm^3 molecule$^{-1}\cdot$sec^{-1};

Ar: $k_{12}=(6.7\pm1.3)\times10^{-13}$ cm^3 molecule$^{-1}\cdot$sec^{-1};

N$_2$: $k_{13}=(9.0\pm2.0)\times10^{-13}$ cm^3 molecule$^{-1}\cdot$sec^{-1}.

Since the observations were made at very short delay times, slight variations in the photolysis pulse shape could invalidate the results. In order to eliminate this possibility, the dependence of the methylene concentration on helium pressure was computed for the actual pulse shapes encountered during the experiments, and a variable rate of deactivation. Good agreement was found with the rate constants derived by assuming an invariant pulse shape. The effective time delay Δt between the photolysis flash and the analysis flash was also determined using this technique. The computed methylene dependences were correlated with the rate constants used in the program, enabling Δt to be evaluated from Eq. (D).

Since some decay of methylene occurs via methylene association at the shortest possible delay between the photolysis and analysis flash, the major source of error in the above treatment is the assumption of constant total methylene concentration (during this interval), independent of the inert-gas pressure. This will only be valid if the singlet/singlet, singlet/triplet, and triplet/triplet associations take place at the same rate. An alternative set of rate constants were derived by assuming no reaction between the singlet and triplet, and these are listed below:

$k_{11}=(3.2\pm0.7)\times10^{-13}$ cm^3 molecule$^{-1}\cdot$sec^{-1},

$k_{12}=(6.8\pm1.3)\times10^{-13}$ cm^3 molecule$^{-1}\cdot$sec^{-1},

$k_{13}=(9.0\pm2.0)\times10^{-13}$ cm^3 molecule$^{-1}\cdot$sec^{-1}.

The rate constants are apparently insensitive to the model chosen for CH$_2$ association, and this technique for determining them may, therefore, be assumed valid.

It is possible to estimate $[^3\mathrm{CH}_2]^0$ by extrapolating $\log_{10}([^3\mathrm{CH}_2]^\infty-[^3\mathrm{CH}_2]p)$ to zero pressure. This gives a value of 30%±10% for the fraction of triplet methylene produced in the primary photolysis, in good agreement with the value obtained in Sec. III.C.

F. Reaction of $^1\mathrm{CH}_2$ with H$_2$ and CH$_4$

The rate of reaction of singlet methylene with hydrogen was measured by investigating the competition between singlet methylene reaction with hydrogen and deactivation to the triplet by added inert gases (He, Ar, and N$_2$).

Assuming no association of the methyl radicals,

$$[\mathrm{CH}_3]_t=[k_2[\mathrm{H}_2][\mathrm{CH}_2]_0/(k_2[\mathrm{H}_2]+k_m[\mathrm{M}])]\times(1-\exp\{-(k_2[\mathrm{H}_2]+k_m[\mathrm{M}])_t\}). \qquad \text{(E)}$$

The competition can be studied most easily by choosing a pressure of hydrogen sufficiently large so that, in comparison with the delay time, the reaction is instantaneous (i.e., the exponential becomes zero). Thus, Eq. (E) simplifies to

$$[\mathrm{CH}_3]_t^0/[\mathrm{CH}_3]_t=1+k_m[\mathrm{M}]/k_2[\mathrm{H}_2], \qquad \text{(F)}$$

where the superscript zero refers to zero inert-gas pressure.

However, since the observations were made at delay times of 6.5 μsec or longer, some methyl association must have taken place, cf. Sec. III.D. and Fig. 5. Since the reaction of singlet methylene with hydrogen can be considered instantaneous, Eq. (F) refers to the methyl concentration at zero time, and

$$[\mathrm{CH}_3]_0^{-1}=[\mathrm{CH}_3]_t^{-1}-2k_{10}t,$$

where the value of k_{10} has been evaluated in Sec. III.D. Thus, Eq. (F) must be modified to the following form:

$$\frac{(1/[\mathrm{CH}_3]_t-2k_{10}t)}{(1/[\mathrm{CH}_3]_t^0-2k_{10}t)}=1+\frac{k_m[\mathrm{M}]}{k_2[\mathrm{H}_2]}. \qquad \text{(G)}$$

In Fig. 7, the lhs of Eq. (G) is plotted against inert-gas pressure for the competition between 1.3×10^3 N m^{-2} of hydrogen, and argon, nitrogen, and helium. Similar results were obtained with both diazomethane and ketene as the substrate gas. The ratios of the rate constants, k_2/k_m, were evaluated from the pressures ($[\mathrm{M}]_{1/2}$) required to reduce $[\mathrm{CH}_3]_0$ to half its initial value since

$$k_2/k_m=[\mathrm{M}]_{1/2}/[\mathrm{H}_2].$$

The competition between methane and helium was also investigated, and Fig. 8 shows a graph of $[\mathrm{CH}_3]_0^0/[\mathrm{CH}_3]_0$ against [He] for three methane pressures. The plots for [N$_2$] vs [H$_2$] and [He] vs [CH$_4$] exhibit curvature, and the mechanism for this will be discussed later. In both cases, the initial slope was taken as a measure of $k_2[\mathrm{H}_2]/k_{13}$ or $k_3[\mathrm{CH}_4]/k_{11}$.

In Fig. 9, the half-pressures are plotted against hydrogen pressure. The data shows the anticipated linear dependence, and the ratios of the rate constants were derived from the slopes. These are summarized in Table I. Figure 9 also shows the results of some experiments with D_2.

Taking the mean of Column 3 gives $k_2 = (7.0 \pm 1.5) \times 10^{-12}$ cm^3 molecule$^{-1}\cdot$sec^{-1}. The relative rates of deactivation by helium, argon, and nitrogen determined from Fig. 9 are in good agreement with the ratios of the absolute rate constants, as is shown in Columns 4 and 5.

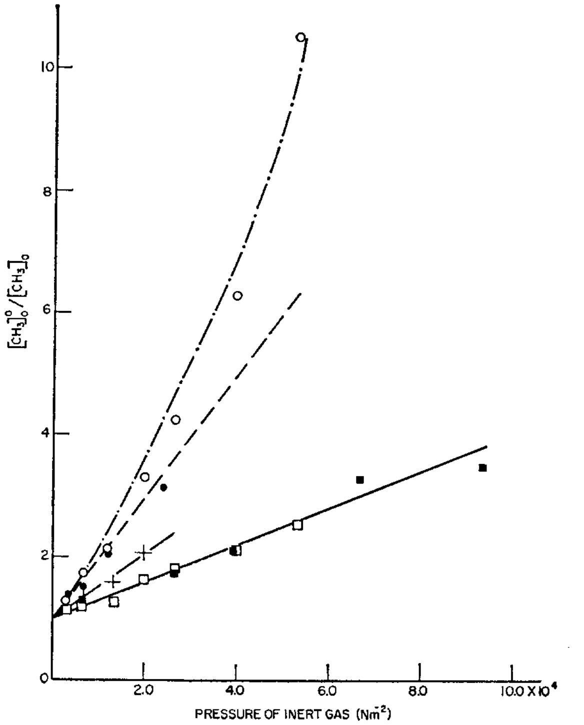

FIG. 7. Plot of the methyl radical concentration at zero inert-gas pressure ($[CH_3]_0^0$) divided by the methyl radical concentration on addition of inert gas ($[CH_3]_0$) as a function of inert-gas pressure. The methyl radical concentrations refer to zero time. ○, 6.7 N m^{-2} CH_2CO+N_2; ●, 6.7 N m^{-2} $CH_2N_2+N_2$; +, 6.7 N m^{-2} CH_2CO+Ar; □, 6.7 N m^{-2} CH_2CO+He; ■, 6.7 N m^{-2} CH_2N_2+He, 1.3×10^3 N m^{-2} H_2. —·—, calculated dependence assuming reaction of $^1CH_2$ with N_2 (see text).

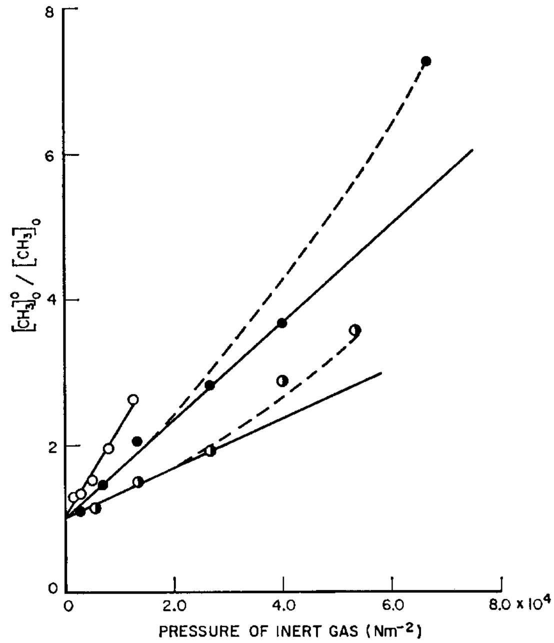

FIG. 8. Plot of methyl radical concentration at zero helium pressure ($[CH_3]_0^0$) divided by the methyl radical concentration on addition of helium ($[CH_3]_0$) as a function of helium pressure. The methyl radical concentrations refer to zero time. ○, 6.7×10^2 N m^{-2} CH_4; ●, 1.3×10^3 N m^{-2} CH_4; ◑, 2.7×10^3 N m^{-2} CH_4. – – –, calculated assuming $k_{15}/k_{16} = 5.5 \times 10^4$ N m^{-2} (see text).

The methane data gave a rate constant of $(3.5 \pm 0.7) \times 10^{-12}$ cm^3 molecule$^{-1}\cdot$sec^{-1} for the reaction of singlet methylene and methane. This is a composite rate constant $(k_4 + k_5)$, and k_4/k_5 has already been shown to be ~1.5. The photometric experiments can also be used to derive a value for this ratio. The methyl concentration at zero time from the hydrogen experiments, divided by half the methyl concentration at zero time for the methane experiment, is equal to $(k_4 + k_5)/k_4$, provided hydrogen is relatively inefficient at deactivating the singlet. Various indirect pieces of evidence (*q.v.*) favor this conclusion, and the photometric experiments, after paying due attention to slight variations in the percent decomposition, give a value of 1.0 for k_4/k_5. The mean of the two estimates and the methane/helium half-pressures give $k_4 = (1.9 \pm 0.5) \times 10^{-12}$ and $k_5 = (1.6 \pm 0.5) \times 10^{-12}$ cm^3 molecule$^{-1}\cdot$sec^{-1}.

G. Isotopic Investigation of the Methylene/Hydrogen Reaction

Callear and Connor[29] have reported the production of a large percentage of CD_3 in the flash photolysis of diazomethane and deuterium. This is contrary to the findings of Bell and Kistiakowsky,[30] and it was considered of interest to reinvestigate this aspect of the reaction.

In Fig. 10, a plate showing methyl radical absorption as a function of helium pressure is reproduced. This clearly demonstrates that, at low helium pressures, the methyl absorption consisted entirely of CD_2H and CDH_2. As the helium pressure was raised, the total

TABLE I. The competition between deactivation of $^1CH_2$ and reaction with H_2.

Inert gas	k_2/k_m	k_2 (10^{-12}) cm^3 molecule$^{-1}\cdot$ sec^{-1})	k_{11}/k_m (from Fig. 9)	k_{11}/k_m (from Fig. 6)
He	20±3	6.0±1.7	1	1
Ar	13±2	8.7±2.2	0.65±0.14	0.45±0.13
N_2	7.0±1.5	6.3±1.8	0.35±0.09	0.33±0.10

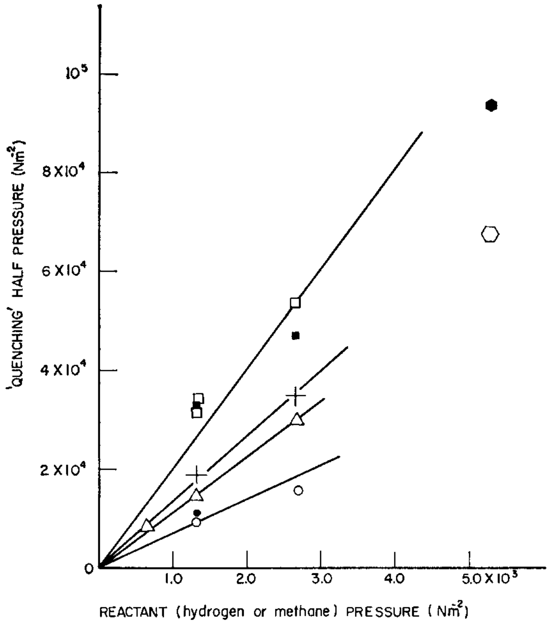

FIG. 9. Dependence of the methyl "quenching" half-pressure ($=k_2[H_2]/k_m$ or $(k_4+k_5)[CH_4]/k_m$) on reactant (hydrogen or methane) pressure. □, 6.7 N m^{-2} $CH_2CO+He+H_2$; ■, 6.7 N m^{-2} $CH_2N_2+He+H_2$; filled-in hexagon, 13.3 N m^{-2} $CH_2CO+He+D_2$; +, 6.7 N m^{-2} $CH_2CO+Ar+H_2$; open hexagon, 13.3 N m^{-2} $CH_2CO+He+D_2$; ○, 6.7 N m^{-2} $CH_2CO+N_2+H_2$; ●, 6.7 N m^{-2} $CH_2N_2+N_2+H_2$; △, 6.7 N m^{-2} $CH_2CO+He+CH_4$.

methyl absorption decreased but CD_3 grew in, apparently at the expense of CDH_2. At the highest pressures investigated, the CD_3 and CD_2H absorptions were of about equal intensity, i.e., about 1/10 of the total methyl absorption at low pressures. Similar results were obtained with $CH_2N_2+D_2$. For CD_2CO or $CD_2N_2+H_2$, the change in the isotopic composition of the methyl radical was much less marked. There was a barely detectable absorption corresponding to CH_3, which appeared at the highest helium pressures. Otherwise the only species present were CD_2H and CDH_2.

H. The Deactivation of Excited Ethane by Methane and Helium

The excited ethane formed in Reaction (4) has a much longer lifetime[27] than the excited methane formed in Reaction (2a).[27] Consequently, an additional pressure-dependent mechanism for the loss of methyl radicals must be considered, i.e., stabilization of the excited ethane adduct before it can dissociate into methyl radicals.

In a mixture of ketene and methane,

$$[CH_3]_0^0 = \frac{k_{4a}[CH_4][^1CH_2]_0}{k_{4a}[CH_4]+k_5[CH_4]} \frac{k_{4b}}{k_{4b}+k_{4c}[CH_4]},$$

where k_{4a}, k_{4b}, and k_{4c} refer to the processes

$$CH_2+CH_4 \rightarrow C_2H_6^*, \qquad (4a)$$

$$C_2H_6^* \rightarrow CH_3+CH_3, \qquad (4b)$$

$$C_2H_6^*+CH_4 \rightarrow C_2H_6+CH_4, \qquad (4c)$$

the subscript zero refers to zero time, and the superscript zero refers to zero pressure of inert gas. Thus,

$$\frac{1}{[CH_3]_t^0} - 2k_{10}t = \frac{(k_{4a}+k_5)}{k_{4a}[^1CH_2]_0} \frac{(1+k_{4c}[CH_4])}{k_{4b}}.$$

Figure 11 shows a plot of $(1/[CH_3]_t^0 - 2k_{10}t)$ against methane pressure. This gives $k_{4b}/k_{4c} = (6.0 \pm 2.0) \times 10^4$ N m^{-2}.

The plots in Fig. 8 of $[CH_3]_0^{-1}$ against helium pressure are curved, and this can be attributed to stabilization of the excited ethane adduct by helium. By applying an analysis similar to that given above for stabilization by methane, a value for k_{4b}/k_{4d} of $(2.0 \pm 0.7) \times 10^5$ N m^{-2} can be obtained, where k_{4d} refers to the process

$$C_2H_6^*+He \rightarrow C_2H_6+He. \qquad (4d)$$

I. The Pressure-Dependent Reaction between Methylene and Nitrogen

Because of the short lifetime[27] of the excited methane formed in (2a), it is extremely unlikely that the curva-

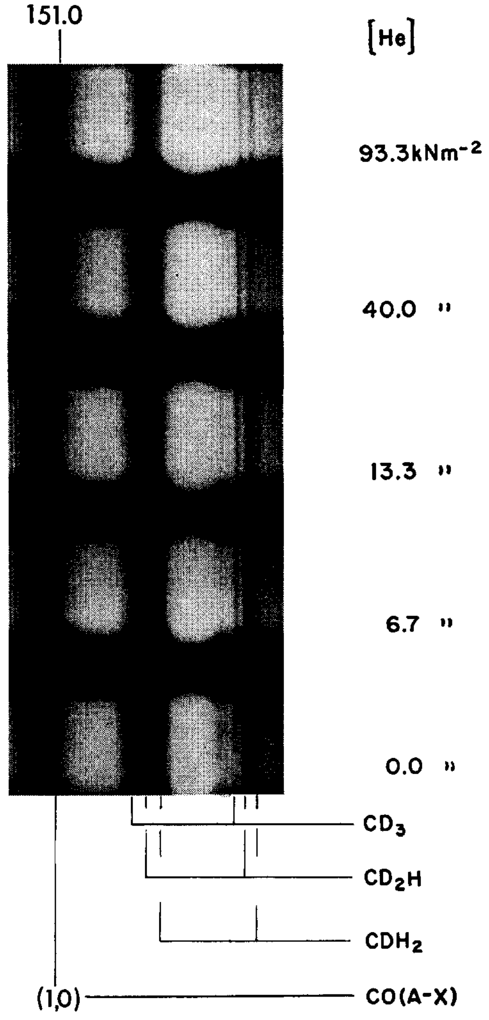

FIG. 10. The dependence of the deuterated methyl radicals on helium pressure, 13.3 N m^{-2} CH_2CO, 1.3 k N m^{-2} D_2.

ture shown in the dependence of $[\mathrm{CH_3}]_0^{-1}$ on $[\mathrm{N_2}]$ is due to stabilization of the excited adduct by nitrogen. The most reasonable mechanism, therefore, is a pressure-dependent reaction between methylene and nitrogen to form diazomethane. This is supported by the observation that the triplet methylene absorption reached a maximum and then decreased as the nitrogen pressure was raised in ketene/nitrogen mixtures.

Considering the reaction scheme

$$^1\mathrm{CH_2}+\mathrm{H_2}\rightarrow\mathrm{CH_3}+\mathrm{H}, \qquad (2)$$

$$^1\mathrm{CH_2}+\mathrm{N_2}\rightarrow{}^3\mathrm{CH_2}+\mathrm{N_2}, \qquad (13)$$

$$^1\mathrm{CH_2}+\mathrm{N_2}\rightarrow\mathrm{CH_2N_2}^*, \qquad (14)$$

$$\mathrm{CH_2N_2}^*\rightarrow\mathrm{CH_2}+\mathrm{N_2}, \qquad (15)$$

$$\mathrm{CH_2N_2}^*+\mathrm{N_2}\rightarrow\mathrm{CH_2N_2}+\mathrm{N_2}, \qquad (16)$$

and applying the steady-state assumption to $\mathrm{CH_2N_2}^*$,

$$\frac{[\mathrm{CH_3}]_0^0}{[\mathrm{CH_3}]_0}=1+\frac{k_{13}[\mathrm{N_2}]}{k_2[\mathrm{H_2}]}+\frac{k_{14}[\mathrm{N_2}]}{k_2[\mathrm{H_2}]}\,\frac{k_{16}[\mathrm{N_2}]}{k_{15}+k_{16}[\mathrm{N_2}]}. \qquad (\mathrm{F})$$

Although the high-pressure data are somewhat sparse, an analysis of Fig. 7, using Eq. (F), gives $k_{14}\sim1.5\times10^{-12}$ cm^3 molecule$^{-1}\cdot$sec^{-1} and $k_{15}/k_{16}\sim5.5\times10^4$ N m^{-2}.

IV. DISCUSSION

A. Deactivation of Singlet Methylene

Contrary to previous observations,[2] helium is capable of deactivating the singlet to the triplet. The mechanism for this transfer cannot involve enhancement of spin–orbit coupling due to the proximity of the inert gas. The most reasonable explanation is a difference in interaction between the inert gas and the singlet and triplet states so that in a collision, the two sets of vibrational and rotational energy levels corresponding to the singlet and triplet manifolds would then move slightly with respect to one another. The spin–orbit coupling in methylene is small ($\sim$10 cm^{-1}), but it is conceivable that many rotational levels could be brought within an energy separation of this magnitude, leading to fairly efficient transfer from the singlet to the triplet. The crossover presumably occurs from the ground vibrational levels of the singlet to an excited set of vibrational levels in the triplet. A fairly high density of levels might, therefore, be anticipated in the triplet state. In addition, angular momentum need only be conserved in the total collision complex, and not just in the methylene. The measured rate constants are presumably composites, and include both the rate of transfer and the rate of relaxation to the ground vibrational state of the triplet. In view of the efficiency of the whole process, the energy separation between the two states is probably small, (somewhat larger than kT).

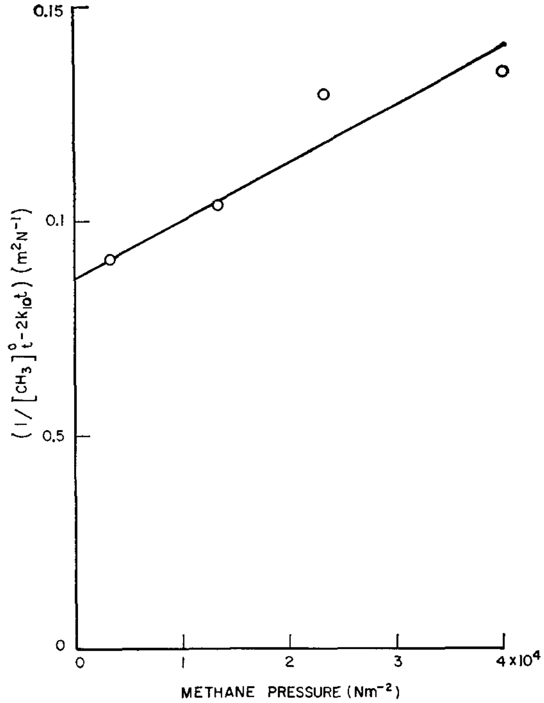

FIG. 11. Quenching of excited ethane by methane. Plot of $(1/[\mathrm{CH_3}]_t^0-2k_{13t})$ against methane pressure.

Our results apparently disagree with those of Bader and Generosa[2] since they could find no evidence for deactivation of the singlet by helium. However, their system was complex, and detailed interpretation rather difficult. On the other hand, Cox and Preston[4] and Eder *et al.*[5] found helium to be effective in quenching singlet methylene to the triplet. Our relative deactivation efficiencies for He, Ar, and $\mathrm{N_2}$ (1.0, 2.2, 3.0), respectively, can be compared with those of Cox and Preston[4] (1.0, 0.80, 2.9) and those of Eder *et al.*[5] (1.0, 2.7, 4.1). We agree fairly well with the first-mentioned reference with respect to the $\mathrm{N_2}$/He deactivation ratio and also with the second concerning the Ar/He deactivation ratio. Deactivation by $\mathrm{N_2}$, as our results indicate, poses a special problem in that this deactivation is not inert toward singlet $\mathrm{CH_2}$. This could account for the somewhat larger deactivation efficiency measured by Eder *et al.* The discrepancy in the relative Argon deactivation efficiency, however, cannot be simply rationalized.

The possibility that the singlet–triplet transfer takes place in excited ketene or diazomethane can be eliminated. If this were the case, then the production of the triplet would not compete directly with reaction of the singlet with hydrogen. Consequently, the same half-pressure for methyl radical removal would be found at all hydrogen pressures. This is clearly not the case, and if a collision induced cross over in the parent molecule were postulated, then it would be necessary to invoke a mechanism whereby the methyl radicals were produced in a reaction between excited ketene (or diazomethane) and hydrogen. This is unlikely in view of the similarity of the results in these two systems (Fig. 9).

B. The Reaction of Singlet Methylene and Hydrogen

The sole production of CD_2H and CH_2D following the low-pressure photolysis of ketene/hydrogen mixtures confirms the conclusion of Bell and Kistiakowsky[30] that the reaction between singlet methylene and hydrogen takes place via an excited methane adduct, and not by hydrogen abstraction.

$CH_2\,{}^3\Sigma_g^-$ and $H_2\,{}^1\Sigma_g^+$, which lie 102 kcal above the ground (${}^1A_1$) state of methane, correlate with the lowest triplet state (${}^3F_2$), which lies ~200 kcal above ${}^1A_1$. Thus any reaction between triplet methylene and hydrogen which proceeds via an excited methylene adduct, must either have an extremely high activation energy or involve a curve crossing to the ${}^1A_1$ state. This crossing would have to take place at very large internuclear distances. In view of the efficiency of the production of methyl radicals, one can, therefore, effectively rule out any possibility that they might originate from a reaction between vibrationally excited triplet methylene and hydrogen.

Because of the high efficiency of the singlet–triplet transfer, it was necessary to carry out experiments at low total pressures, and it might be argued that the singlet methylene was still hot, perhaps vibrationally, when reaction with hydrogen took place. Because of the difference in the bond energies of ketene and diazomethane,

$$CH_2CO \rightarrow CH_2+CO; \quad \Delta H=80.1 \text{ kcal}$$

$$CH_2N_2 \rightarrow CH_2+N_2; \quad \Delta H=\sim 25 \text{ kcal},$$

the excess energies for the two photolysis systems, at their absorption maxima, are ~80 and ~110 kcal, respectively. One might, therefore, expect the methylene to be produced with a higher degree of excitation in the diazomethane system. The equivalence of the rate constants measured in the two systems is evidence in favor of reaction of thermalized methylene.

The presence of CD_3 in CH_2CO/D_2 mixtures, at higher helium pressures, is difficult to explain in terms of CH_2. Callear and Connor[29] first observed the production of CD_3 following the flash photolysis of diazomethane/deuterium mixtures, and they attributed its formation to molecular elimination of H_2 from the excited methane adduct (17e), and subsequent reaction of the ${}^1CD_2$ with D_2:

$$CH_2+D_2 \rightarrow CH_2D_2^*, \tag{17a}$$

$$CH_2D_2^* \rightarrow CH_2D+D, \tag{17b}$$

$$CH_2D_2^* \rightarrow CD_2H+H, \tag{17c}$$

$$CH_2D_2^* \rightarrow CH_2+D_2, \tag{17d}$$

$$CH_2D_2^* \rightarrow CD_2+H_2. \tag{17e}$$

Reaction (17e) has a smaller exothermicity than (17b), and Callear and Connor deduced that if molecular elimination is to be important, $A_{17e}/A_{17b} \sim 10^3$.

However, the absolute increase in the CD_3 concentration on increasing the pressure does not conform very well to this mechanism since the fraction of the total methylene concentration which reacts with deuterium decreases as the helium concentration is raised.

Atomic carbon was not present in sufficient concentration to account for the CD_3, and it is unlikely that C_2O is responsible in the ketene system since one would have to postulate similar behavior for CN_2 in the diazomethane system.

The most likely mechanism is reaction of CH with D_2,

$$CH+D_2 \rightarrow CD_2+H; \quad \Delta H \sim (3\pm1) \text{ kcal}.$$

The heat of reaction quoted is for the triplet, while the singlet would have to be produced if CD_3 were to be formed subsequently. However, the increase in ΔH would be small. The CH radical has been shown to react with H_2 at a rate of 10^{-12} cm^3 molecule$^{-1}\cdot$sec^{-1},[14] but the products of the reaction are not known. Direct production of methyl,

$$CH+H_2 \rightarrow CH_3; \quad \Delta H=-109.2 \text{ kcal},$$

could conceivably be a more important path, in which case CH could not be invoked to explain the above results. It is perhaps relevant to report that the yield of CH, at short time delays, increased as the pressure was raised in ketene/helium mixtures, and this would explain the enhancement of the CD_3 absorption at the higher pressures.

The mechanism of CD_3 production remains obscure, but since it formed only a small percentage (<10%) of the total photolysis products it is unlikely that the quantitative methyl radical experiments were invalidated.

In ketene-helium mixtures, as much as a fivefold reduction was observed in the methyl concentration as the helium pressure was increased, with no evidence for any departure from linearity in the plots of $1/[CH_3]_0$ against [He]. Clearly the reaction of the triplet with hydrogen is very slow, and an upper limit for the rate constant of $\sim 5\times10^{-14}$ cm^3 molecule$^{-1}\cdot$sec^{-1} may be deduced.

From the linearity of these plots, one may also infer that a large fraction of the triplet is not being reactivated to the singlet at the higher pressures. Thus the energy separation between the two states must be equal to or greater than kT. Furthermore, since ~80% of the singlet was deactivated without any evident approach to an asymptote, it may be concluded that the singlet can be virtually completely converted into the triplet by addition of an inert gas.

C. Stabilization of Excited Methylene Adducts

A half-pressure ($S/D=1$) of 6×10^4 N m^{-2} for the stabilization of the excited ethane formed in Reaction (4) is considerably greater than the value of 3.5×10^3 N m^{-2} obtained by Bell and Kistiakowsky.[30] Their experiments were performed with CD_4, and allowance for the secondary isotope effect increases this value to $\sim2\times10^4$ N m^{-2}. The origin of the discrepancy is not apparent, but both sets of data show considerable scatter. Ausloos, Gordon, and Lias[31] also investigated the effect of pressure on Reaction (4). Their source of methylene was methane photolysis at 1236 nm, and analysis of their data gives a half-pressure of $\sim1.1\times10^5$ N m^{-2}. The difference could conceivably be due to a higher energy content in the methylene produced in the methane system.

In the production of diazomethane from the reaction of singlet methylene and nitrogen, $k_{16}[N_2]$ becomes equal to k_{15} at a nitrogen pressure of 5.5×10^4 N m^{-2}. If the collisional stabilization efficiency of nitrogen lies between 1 and 0.1, then 5×10^9 sec$^{-1}<k_{15}<5\times10^8$ sec^{-1}. On the basis of simple RRK theory, these values are consistent with five effective oscillators in the diazomethane molecule

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[†] Visiting Scientist, Physical Chemistry Division, 1968–1969; permanent address: Physical Chemistry Department, Cambridge University, Cambridge, England.

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[24] The kinetic analysis is analogous to the case described in Sec. III.D of Ref. 25. A typographical error occurred in Eq. (D) of this reference, which should have read

$$[C_2H_4]=(a/b)(\{\ln[ac\exp(at)-b]/(ac-b)\}-at).$$

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