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COLLISIONAL REMOVAL OF CH$_2$ ($^{1}A_1$): ABSOLUTE RATE CONSTANTS

FOR ATOMIC AND MOLECULAR COLLISION PARTNERS AT 295 K

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ABSTRACT

The technique of cw laser resonance absorption has been used to monitor the time evolution of individual CH$_2$ ($^{1}A_1$) rotational levels following the excimer laser photolysis of CH$_2$CO. Absolute rate constants for the removal of CH$_2$ ($^{1}A_1$) by He, Ar, Kr, N$_2$, CO, O$_2$, CH$_4$, C$_2$H$_6$, C$_3$H$_8$, C$_2$H$_4$, i-C$_4$H$_8$, and CH$_2$CO have been determined at 295K. Removal efficiencies range from nearly gas-kinetic for the higher hydrocarbons and CH$_2$CO to $10^{-2}$ for He. For He, Ar, and CH$_2$CO removal rates were measured for the v$_2$ = 1 excited bending vibrational level and found to be identical to the ground state rates. Pseudo-first-order rate constants for equilibration of the nascent rotational distribution in collisions with He and CH$_2$CO were found to be factors of 17 and 2.7 faster than the respective removal rates.
I. INTRODUCTION

Despite the fundamental importance of methylene to synthesis, molecular structure, and chemical kinetics, its chemistry is not well established.\textsuperscript{1} Many of the problems and much of the interest stem from the existence of two low-lying electronic states which differ significantly in reactivity and structure. The energy difference between the triplet ground state ($^3B_1$) and the singlet first excited state ($^1A_1$) remains a subject of controversy.\textsuperscript{2–6}

Although CH\textsubscript{2} ($^1A_1$) absorbs in the visible,\textsuperscript{7} kinetic measurements based on spectroscopic detection have been hampered by the short lifetime of this state under collisional conditions. By contrast, electronic transitions from the relatively long-lived ($^3B_1$) state lie in the less accessible vacuum ultraviolet.\textsuperscript{7,8} Experimental studies of gas phase methylene reactions have therefore been confined primarily to indirect methods such as end product analysis. Distinguishing the chemistry of singlet and triplet methylene by such methods is complicated by the efficient collision-induced intersystem crossing which converts singlet methylene to the triplet ground state. Indirect studies of singlet chemistry therefore rely on the use of radical scavengers to preferentially remove triplet methylene from the reaction system. Interpretation of such studies is not always straightforward.

The use of pulsed laser-induced fluorescence (LIF) for detecting CH\textsubscript{2} ($^1A_1$) has been successfully demonstrated in several laboratories.\textsuperscript{2,3,9–12} The first direct measurements of CH\textsubscript{2} ($^1A_1$) removal rates have recently been reported by Ashfold et al.\textsuperscript{11,12} who used LIF to monitor CH\textsubscript{2} ($^1A_1$) and CD\textsubscript{2} ($^1A_1$) produced in the ir multiphoton dissociation (MPD) of acetic anhydride. These workers reported rate
constants for CH₂ (¹A₁) removal approximately one order of magnitude larger than previously accepted values inferred primarily from studies of CH₂ (³B₁) kinetics. These new results provide information essential for the further development of theoretical descriptions of collision-induced intersystem crossing in methylene. In conjunction with earlier product analysis studies, these results also imply that CH₂ (¹A₁) is removed by many hydrocarbons with near gas-kinetic collision efficiency.

In the present study, cw laser resonance absorption (LRA) has been used to monitor individual rotational levels of singlet methylene produced in the near uv photolysis of ketene. This technique offers the advantages of continuous temporal detection with the narrow linewidth of a cw laser and thus permits studies of photodissociation and reaction processes with greater detail than is practical with pulsed probing techniques. Absolute rate constants for CH₂ (¹A₁) removal by the following processes have been determined at 295 K:

\[ \text{CH}_2 (¹A₁) + \text{CH}_2\text{CO} \rightarrow \text{C}_2\text{H}_4 + \text{CO} \]  \hspace{1cm} (1)

\[ \text{CH}_2 (¹A₁) + \text{He} \rightarrow \text{CH}_2 (³B₁) + \text{He} \]  \hspace{1cm} (2)

\[ \text{CH}_2 (¹A₁) + \text{Ar} \rightarrow \text{CH}_2 (³B₁) + \text{Ar} \]  \hspace{1cm} (3)

\[ \text{CH}_2 (¹A₁) + \text{Kr} \rightarrow \text{CH}_2 (³B₁) + \text{Kr} \]  \hspace{1cm} (4)

\[ \text{CH}_2 (¹A₁) + \text{N}_2 \rightarrow \text{products} \]  \hspace{1cm} (5)

\[ \text{CH}_2 (¹A₁) + \text{CO} \rightarrow \text{products} \]  \hspace{1cm} (6)

\[ \text{CH}_2 (¹A₁) + \text{O}_2 \rightarrow \text{products} \]  \hspace{1cm} (7)

\[ \text{CH}_2 (¹A₁) + \text{NO} \rightarrow \text{products} \]  \hspace{1cm} (8)

\[ \text{CH}_2 (¹A₁) + \text{H}_2 \rightarrow \text{products} \]  \hspace{1cm} (9)

\[ \text{CH}_2 (¹A₁) + \text{CH}_4 \rightarrow \text{products} \]  \hspace{1cm} (10)

\[ \text{CH}_2 (¹A₁) + \text{C}_2\text{H}_6 \rightarrow \text{products} \]  \hspace{1cm} (11)
\[ \text{CH}_2 \left( ^1\text{A}_1 \right) + \text{C}_3\text{H}_8 \rightarrow \text{products} \quad (12) \]
\[ \text{CH}_2 \left( ^1\text{A}_1 \right) + \text{C}_2\text{H}_4 \rightarrow \text{products} \quad (13) \]
\[ \text{CH}_2 \left( ^1\text{A}_1 \right) + \text{i-C}_4\text{H}_8 \rightarrow \text{products} \quad (14) \]

The rotational and vibrational level dependence of inert gas removal rates have also been studied. The results are compared with previous experimental and theoretical work.

II. EXPERIMENTAL

A. Apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. Singlet methylene \( ^1\text{A}_1 \) was produced by photolysis of ketene at 308 nm with a XeCl excimer laser (Lumonics TE-262) operated with output energies of less than 20 mJ and repetition rates of 1-5 Hz. The 12 ns FWHM pulse and beam cross section of 7 x 25 mm (in the photolysis cell) resulted in a maximum single pass energy fluence of 10 mJ/cm\(^2\) and a maximum power density of 0.5 MW/cm\(^2\). The photolysis cell was constructed entirely of quartz, 5 cm i.d. x 80 cm long with quartz windows, flat to \( \lambda/4 \), sealed on at Brewster's angle using glass transfer tape (Vitta Corp. G-105).

An Ar\(^+\)-pumped ring dye laser (Spectra-Physics 171-06/380 A) with a linewidth of 20 MHz was used to detect \( \text{CH}_2 \left( ^1\text{A}_1 \right) \) through absorption at rotational lines between 590 and 610 nm.\(^7\) The laser wavelength was determined to within 0.02 cm\(^{-1}\) with a commercial wavemeter (Burleigh WA-20). The dye laser beam was collimated to a diameter of 2 mm and reflected into the photolysis cell. The photolysis beam was coupled into the cell through a flat dichroic mirror which transmitted 70% of the uv while reflecting > 98% of the visible light. The visible beam
was reflected 8 times between this mirror and a 2 m f.1. visible high reflector (> 99%) 1 meter away to give a total absorption pathlength of 720 cm. Approximately 25% of the transmitted uv was reflected back into the cell by the high reflector. Since the cross-sectional area of the photolysis beam was much larger than the probe beam, the loss of \( \text{CH}_2 \) through diffusion from the reaction volume was negligible on the timescale of collisional removal.

Absorption of the dye laser beam by \( \text{CH}_2 (^1A_1) \) resulted in a transient attenuation of the light incident on a fast photodiode (EG&G SGD 100A biased at -90 V) and a corresponding decrease in the dc output. Approximately 40% of the probe beam was split off prior to the photolysis cell and directed onto an identical photodiode. This beam was attenuated by a polarizer (pol.) which served as a variable neutral density filter in order to match the intensity on the signal photodiode (typically 20 mW). The output of each photodiode was amplified 10 times (Keithley 104 wideband amplifier) and the resulting signals subtracted and digitized by a Tektronix 7912AD with a 7A24 differential plug-in. Baseline noise due to fluctuations in the dye laser intensity was reduced by approximately a factor of ten through the subtraction. The absorbance necessary to give a single shot signal-to-noise ratio of one was approximately 0.5% with this configuration. Kinetic data was obtained by averaging the transient absorbances (typically 64 times) with the aid of an LSI-11 minicomputer. High resolution kinetic absorption spectra were obtained by integrating the absorption with a boxcar (PAR 162/164), and scanning the dye laser.
B. Sample Handling

Ketene was prepared by pyrolysis of acetic anhydride$^{15}$ and multiply distilled from 156 K to 77 K before use. The purity of samples stored at 77 K to prevent polymerization was periodically checked by FTIR spectroscopy. Nitric oxide (Matheson 99.0%) was purified by distillation through a silica gel trap kept at 195 K to remove NO$_x$ impurities. Other gases, He (LBL extra pure 99.999%), Ar (Matheson UHP 99.999%), Kr (Baker research grade 99.995%), N$_2$ (LBL 99.999%), CO (Baker research grade 99.97%), H$_2$ (Baker research grade 99.9995%), O$_2$ (Baker research grade 99.995%), CH$_4$ (Matheson UHP 99.97%), C$_2$H$_6$ (Scientific Gas Products C.P. 99.2%, with less than 0.2% each H$_2$, CH$_4$, and C$_2$H$_4$ and 0.1% N$_2$ and O$_2$), C$_3$H$_8$ (Matheson research grade 99.99%), C$_2$H$_4$ (Matheson C.P. 99.5%), and i-C$_4$H$_8$ (Matheson C.P. 99.3%, with less than 0.4% 1-butene, 0.2% n-C$_4$H$_{10}$, and 0.1% i-C$_4$H$_{10}$) were used without further purification. Gases were transferred to the cell from a standard glass and grease vacuum line with a base pressure of 10$^{-6}$ Torr. Pressures were measured using a 0 - 10 Torr capacitance manometer (Baratron 145AH-10) accurate to within ± 0.1%.

In typical experiments with He, Ar, Kr, and N$_2$, ketene was first loaded into the cell and the desired partial pressure of the added gas expanded in from a high pressure reservoir. When other gases were used, ketene was frozen into a sidearm of the cell while the reactant gas was added. The ketene was then allowed to thaw and the desired partial pressure of helium added as before. Mixing times of several minutes were generally adequate for the low pressures (< 10 Torr) used in these experiments. All experiments were performed at an ambient temperature of 295 ± 2 K.
III. RESULTS AND ANALYSIS

A. Production of CH₂ (1A₁).

At 308 nm, all of the methylene produced through single-photon excitation of ketene is in the 1A₁ state.¹⁶ Rate constants for the collisional removal of CH₂ (1A₁) were obtained primarily from the analysis of absorption data for the 4₁₄ rotational level, monitored via the 4₀₄(0,1₄,0) + 4₁₄(0,0,0) transition near 16928.79 cm⁻¹.⁷ A high resolution spectrum of the P₀₁, J (J) sub-branch containing this transition is shown in Fig. 2. Although perturbations in the upper state of this transition prohibit the determination of rotational populations,⁷,⁹ the 4₁₄ level was found to have the strongest absorbance near 590 nm under rotationally thermalized conditions. The temporal evolution of this level under typical conditions is shown in Fig. 3.

Even though the 4₁₄ level always decayed exponentially due to bimolecular collisions under pseudo-first-order conditions, the decay was preceded by an exponential rise reaching a maximum several hundred nanoseconds after the 12 ns photolysis pulse. Bi-exponential analysis of the absorbance leads to production and removal rates proportional to collision gas pressure (Figs. 4 and 5). This indicates that the 4₁₄ level is populated primarily through bimolecular relaxation of the initial population rather than direct dissociation. The production rate constants obtained from the data in Figs. 4 and 5 are consistent with rotational relaxation. The production of CH₂ 1A₁ by electronic quenching of CH₂ 5B₁ formed via two-photon excitation of ketene can be ruled out through the linear fluence dependence of the CH₂ (1A₁) absorbance (Fig. 6). Vibrational relaxation from the (0,1,0) level also seems to be unimportant (see below). Deconvolution of the exponential
decay from this rise should therefore give removal rates for thermalized \( \text{CH}_2 \left( ^1\text{A}_1 \right) \).

B. Removal of \( \text{CH}_2 \left( ^1\text{A}_1 \right) \).

1. Absolute Rate Constants

Absolute rate constants for \( \text{CH}_2 \left( ^1\text{A}_1 \right) \) removal by helium and ketene were derived from a linear least-squares fit of Eq. (15) using decay rates obtained over ketene and helium pressure ranges of 0.05 to 0.50 Torr and 1 to 10 Torr, respectively.

\[
K_{\text{exp}} = k_1[\text{CH}_2\text{CO}] + k_2[\text{He}].
\]  \( (15) \)

Some of these data are shown in Figs. 4, 5, and 7. Figures 4 and 5 indicate that for ketene pressures below 0.20 Torr and helium pressures above 3 Torr, the rotational relaxation rate is more than an order of magnitude faster than the decay rate. Under these conditions, the rise can be neglected and the data analyzed as a single exponential decay. Whenever possible, the experimental conditions were chosen to permit this simplification.

Rate constants for \( \text{CH}_2 \left( ^1\text{A}_1 \right) \) removal by Ar, Kr, and \( \text{N}_2 \) were determined by a least-squares fit of decay rates covering an inert gas pressure range of 3 to 10 Torr with a constant partial pressure of 0.100 or 0.200 Torr \( \text{CH}_2\text{CO} \). The value of \( k_1 \) was constrained to \( 2.7 \times 10^{-10} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \) (determined from \( \text{CH}_2\text{CO}/\text{He} \) experiments) in these fits. The pressure dependence of \( \text{CH}_2 \left( ^1\text{A}_1 \right) \) decay rates in He, Ar, Kr, and \( \text{N}_2 \) are shown in Fig. 7.

The rotational-level independence of these removal rates, illustrated for \( \text{N}_2 \) in Fig. 8, probably results from rotational equilibration which is fast on the timescale of collisional removal. The levels shown in Fig. 8, spanning a rotational energy range of nearly
500 cm\(^{-1}\), were probed via absorptions in the \(P_{Q1,J}\) (J) and \(P_{P1,J-1}\) (J) branches near 16930 cm\(^{-1}\). Rate constants for the removal of vibrationally excited \(CH_2\) (\(^1A_1\)) (0,1,0) by He, Ar, and \(CH_2CO\) were determined using the \(2_{11}(0,15,0) + 1_{01}(0,1,0)\) transition at 16405.25 cm\(^{-1}\). The absorbance due to this level was approximately 10\% of the \(4_{14}(0,0,0)\) absorbance. The (0,1,0) removal rate constants were found to be equal within experimental error to the ground state values (Fig. 9). For He and Ar, these results imply that vibrational-translational transfer from the (0,1,0) level is probably slow compared to intersystem crossing. This conclusion is consistent with measured rates for deactivation of the bending modes of \(H_2O\), \(D_2O\), \(D_2S\), \(H_2Se\),\(^{17,18}\) and \(NH_2\)\(^{19}\) by inert gases which are 10-100 times slower than the methylene intersystem crossing rates.

Rate constants for \(CH_2\) removal by reactive species were obtained from a least-squares fit of Eq. (16) using decay rates from mixtures with partial pressures of 0.100 or 0.200 Torr ketene and 4.0 or 6.0 Torr helium. Reactant pressures were varied from 0.05 to 0.50 or 1.00 Torr depending on the reaction rate.

\[
K_{\text{exp}} = k_1[CH_2CO] + k_2[He] + k_R[R].
\] (16)

In these fits, \(k_1\) and \(k_2\) were constrained to the values in Table I. Some of these results are shown in Figs. 10 and 11.

2. Error Estimates

The error limits given in the first column of Table I are estimates of the total uncertainty associated with each rate constant measurement. These limits are in all cases greater than one standard deviation in the result of the least-squares fit. The most important sources of error in these measurements are: 1) uncertainty in the data
analysis and ii) uncertainty in the reactant pressures.

Uncertainties in the data obtained by single exponential analysis can result from insufficient separation of the rise and decay. In typical mixtures with 0.200 Torr $\text{CH}_2\text{O}$ and 6.0 Torr He, rotational relaxation was 95% complete within 200 ns. The single exponential fits were typically initiated at times much longer than 200 ns and the quality of each fit could be checked by increasing or decreasing the delay between $t = 0$ and the origin of the fit. Uncertainties due to the analysis are therefore less than 10%.

Although the Baratron used for pressure measurements should be accurate to within 0.08%, uncertainties in the partial pressures of various gases could result from depletion of the reactant molecules and the buildup of reaction products over the course of a photolysis run. The ketene absorption cross section of $2.5 \times 10^{-20}$ cm$^2$/molecule at 308 nm$^{20}$ with a quantum yield of unity for the production of $\text{CH}_2$ ($^1\text{A}_1$), implies that irradiation of 0.100 Torr of ketene with the maximum energy fluence of 10 mJ/cm$^2$ produced approximately $10^{13}$ molecules/cm$^3$ $\text{CH}_2$ ($^1\text{A}_1$). Since the reaction volume (defined as the volume swept out by the photolysis beam) of 140 cm$^3$ was less than 10% of the total cell volume, less than 0.03% of the ketene was photolyzed per shot. If only 3 Torr of helium was present in the cell, an additional 0.02% was removed through reaction (1). The net loss of ketene over the course of 64 shots, the typical number required to obtain signal-to-noise ratios comparable to Fig. 3, was therefore always less than 4%. Depletion of other reactants was even less. No systematic changes in reaction rates due to reactant depletion or product buildup were observed, even over the course of several hundred laser shots.
III. DISCUSSION

Absolute rate constants for the removal of CH₂ (1A₁) by various gases are shown in Table I. The present results, listed in the first column, and the results of Ashfold et al.¹² in the second column, are the only absolute rate constants based on direct measurements of singlet concentrations. These rate constants are approximately one order of magnitude larger than those of Braun, Bass, and Pilling⁸ (third column) which are based on the appearance rates of CH₂ (3B₁) produced by intersystem crossing or CH₃ formed through reaction of the singlet with H₂ or CH₄. The source of this discrepancy, noted in ref. 12, stems from the incorrect assumption that reaction (1) is too slow to compete with intersystem crossing for CH₂ (1A₁) removal. Although this assumption renders the absolute rate constants from ref. 8 incorrect, a self-consistent set of relative rate constants is obtained. These rate constants, normalized to a value of 1.0 for singlet removal by He, are compared to relative values from the two direct studies in Table II.

Relative rate constants from three product analysis studies are included in Table II for comparison. These studies are but a small fraction of an extensive literature recently reviewed by Laufer.¹ Cox and Preston²¹ photolyzed ketene at 249 nm and 280 nm in mixtures with O₂ or CO to scavenge triplet CH₂ (3B₁). Relative rates for intersystem crossing induced by the addition of inert gases were determined from the reduced yield of C₂H₄ produced by reaction (1). These rates are therefore normalized to a value of 77 for k₁. With the exception of k₄, the rates shown in Table II are from 280 nm photolyses with CO as a scavenger.

Eder and Carr²² photolyzed ketene in the presence of propane,
oxygen, and various inert gases at 260 nm, 313 nm, 334 nm, and 350 nm. Rate constants were measured relative to the reaction of CH₂ (1A₁) with C₃H₈. The rates listed in Table II are those obtained at 313 nm and are normalized to a value of 69 for singlet reaction with propane.

The experimental method of Bell²³ was similar to that of ref. 22 except that CH₂ (1A₁) was produced by the 405 nm photolysis of diazomethane. These rates are also normalized to a value of 69 for CH₂ (1A₁) reaction with C₃H₈.

A. CH₂ (1A₁) Removal by Rare Gases

The absolute values of rate constants for CH₂ (1A₁) removal by He, Ar, and Kr reported in ref. 12 agree with the present results to within 15%. Relative values of k₂ and k₃ from ref. 8, and k₂ and k₄ from ref. 21 are in reasonable agreement with the absolute values. The rare gas rates determined by Bell²³ are significantly faster than the values from other studies.

Although it is clear that inert gases can remove singlet methylene by inducing intersystem crossing to the triplet ground state, the mechanism is not completely understood. The modest heavy atom effect, Table I, shows that intersystem crossing induced by collisions with rare gases depends on the spin-orbit coupling within the methylene molecule itself. Translation of the rare gas interacts with the vibrational and rotational coordinates of the two states of methylene. Transitions may occur during a collision as vibration-rotation energies of singlet levels cross those of triplet levels. Dahler and co-workers²₄,²₅ have treated such resonances involving only the bending levels. Since these are spread by several kT in energy, calculated S-T quenching rates depend strongly on the level spacing in the free molecule and hence on
the singlet-triplet energy gap. The inclusion of rotational energies and C-H stretching should decrease this strong dependence on vibrational level position. The small changes in S-T quenching rates with singlet vibrational excitation (Fig. 7) and with deuteration\textsuperscript{12} suggest that accidental vibrational resonances do not change rates by orders of magnitude. Freed, Gelbart, and co-workers\textsuperscript{26–28} consider the modest singlet-triplet perturbations which must exist in the free molecule for some rotational levels of the singlet vibrational ground state. The mixing of vibration, rotation, and translation during the collision then gives S-T rates proportional to the product of a vibration-rotation relaxation rate within the triplet manifold and the square of a coefficient for triplet character in singlet levels. The observed rates of a few percent gas kinetic then imply that triplet perturbations with at least a few percent intensity should exist in singlet spectra.

It is probable that collision-induced intersystem crossing rates are strong functions of the singlet vibration-rotation quantum numbers. Experimentally, this cannot be observed since rotational relaxation within the singlet manifold is more than an order of magnitude faster than intersystem crossing (Figs. 4 and 5).

B. \textit{CH}_2 (^{1}A_1) Removal by Inorganic Molecules

When the collision partner is a molecule, reactive processes may also contribute to the removal of \textit{CH}_2 (^{1}A_1). Since the present experiments did not distinguish products, the relative contributions of reactive channels and intersystem crossing to the measured removal rates were not directly determined. The expected products for many of these reactions are discussed in ref. 1.

Reactions between \textit{CH}_2 (^{1}A_1) and diatomic molecules probably form highly excited addition products. Since the lifetimes of such small
molecules with 50 - 100 kcal mol\(^{-1}\) excess energy are typically less than one nanosecond, stabilization of these adducts or buildup of a steady state concentration is negligible over the pressure range used in the present experiments.

1. \(\text{CH}_2 (^1\text{A}_1) + \text{N}_2\)

The present rate constant for \(\text{CH}_2 (^1\text{A}_1)\) removal by \(\text{N}_2\) is approximately 25\% greater than the value of Ref. 12. Braun, Bass, and Pilling\(^8\) found that stabilization of half the diazomethane formed in the addition reaction requires nitrogen pressures in excess of 400 Torr. This conclusion is based on a decrease in the \(\text{CH}_2 (^3\text{B}_1)\) yield with increasing \(\text{N}_2\) pressure. Quantitatively, the rate of adduct formation was found to be approximately 60\% greater than the rate of direct inter system crossing. The excellent agreement (< 5\%) between the present rate for \(\text{CH}_2 (^1\text{A}_1)\) removal by \(\text{N}_2\) and the relative rate for direct inter-system crossing from ref. 8 implies that the adduct dissociates primarily to \(\text{CH}_2 (^1\text{A}_1)\) rather than \(\text{CH}_2 (^3\text{B}_1)\).

2. \(\text{CH}_2 (^1\text{A}_1) + \infty\)

The absolute values of \(k_6\) reported in ref. 12 and the present study differ by less than 15\%. In product analysis studies, DeGraaff and Kistiakowsky\(^29\) and Cox and Preston\(^21\) found relative efficiencies for the removal of \(\text{CH}_2 (^1\text{A}_1)\) by \(\infty\) and \(\text{CH}_2\infty\) to be 0.14 and 0.12, respectively. The approximations required in analysis of these indirect measurements are larger than the difference from the present result of \(k_6/k_1 = 0.18 \pm 0.02\). The production of \(^{14}\infty\) in the reaction of \(^{14}\text{CH}_2 (^1\text{A}_1)\) with \(\infty\) led Montague and Rowland\(^30\) to conclude that an oxirene adduct forms in collisions of \(^1\text{CH}_2\) with \(\infty\). They reported that a \(\infty\) pressure of 840 Torr was necessary to stabilize 50\% of the excited oxirene complexes. A complex dissociation rate of \(3 \times 10^9 \text{s}^{-1}\) was
inferred. Their indirectly measured complex formation rate was 0.1 $k_1$. However, to the extent that oxirene decomposes to $\text{CH}_2 (^1\text{A}_1) + \text{CO}$, the oxirene formation rate is not included in the value of $k_9$ reported here.

3. $\text{CH}_2 (^1\text{A}_1) + \text{O}_2$

The only significant disagreement between this study and ref. 12 is the factor of 2.5 difference between values of $k_7$. Indirect values of this rate constant also vary considerably. Eder and Carr$^{22}$ found that a value of $k_7/k_{12}$ which decreased at longer photolysis wavelengths (0.44 at 260 nm, 0.46 at 313 nm, 0.20 at 334 nm, and 0.095 at 350 nm) provided the best fit to their data. This decrease was attributed to a small activation barrier to reaction, surmountable by internal excitation of $\text{CH}_2$. This interpretation was favored by Ashfold et al. since the MPD value of $k_7/k_2$ was consistent with Eder and Carr's values of $k_7/k_{12}$ and $k_2/k_{12}$ when the former was determined at 350 nm. This comparison may not be valid, however, since more recent experiments indicate that $\text{CH}_2 (^1\text{A}_1)$ is not produced in the 350 nm photolysis of ketene.$^6$ In addition, $k_2/k_{12}$ was determined only at 313 nm in ref. 22 and relative rate constants for singlet removal by other species (including Ar and Xe) were found to be wavelength dependent in that study.

Since both direct measurements of $k_7$ are representative of thermalized $\text{CH}_2 (^1\text{A}_1)$, the discrepancy may be related to the method of $\text{CH}_2$ production. In a preliminary account,$^{11}$ Ashfold et al. described the production of substantial visible luminescence following the multiphoton dissociation of $(\text{CH}_3\text{CO})_2 \text{O}$ in the presence of $\text{O}_2$. This luminescence (and the discrepancy in rate constants) may perhaps be due to reaction between vibrationally excited acetic anhydride or ketene
with oxygen.

4. \( \text{CH}_2 (^1\text{A}_1) + \text{NO} \)

The only reported rate constant for singlet \( \text{CH}_2 \) removal by \( \text{NO} \) is \( k_8/k_1 = 1.25 \) determined through product analysis by Laufer and Bass.\(^{31}\) This ratio is more than double the present value \( k_8/k_1 = 0.55 \) and possibly includes contributions from \( \text{CH}_2 (^1\text{B}_1) \) produced in the vacuum ultraviolet photolysis of ketene. The relative efficiencies of reaction and intersystem crossing are unknown.

5. \( \text{CH}_2 (^1\text{A}_1) + \text{H}_2 \)

The absolute values for \( k_9 \) differ by approximately 20%. A relative value of \( k_9/k_2 \) determined by Braun, Bass, and Pilling\(^8\) is 10% lower than the present ratio. These workers spectroscopically observed the production of \( \text{CH}_3 \) in the reaction of \( \text{CH}_2 (^1\text{A}_1) \) with \( \text{H}_2 \) and by isotopic substitution determined that the reaction proceeds through an excited methane adduct. Product analysis in that study indicated that the intersystem crossing rate was approximately 20% of the reaction rate.

C. \( \text{CH}_2 (^1\text{A}_1) \) Removal by Organic Molecules

1. Alkanes

In reactions with alkanes, \( \text{CH}_2 (^1\text{A}_1) \) inserts into the C-H bonds to form excited alkane adducts.\(^{32}\) Relative rates for insertion into the various C-H bonds of several alkanes have been reported by Halberstadt and Crump\(^{13}\) who produced singlet methylene by 313 nm photolysis of ketene. These rates are in good agreement with the relative insertion rates determined by Hase and Simons,\(^{14}\) and the relative \( \text{CH}_2 (^1\text{A}_1) \) removal rates determined in this study (Table III). The absolute rate constant for \( \text{CH}_2 (^1\text{A}_1) \) removal by \( \text{CH}_4 \) reported in ref. 12 differs from
the present result by less than 5%.

The good agreement between relative rates derived from insertion product yields and the relative CH₆ (¹A₁) removal rate implies that intersystem crossing is probably unimportant in these collisions. The generally good agreement between the relative rates from this study and the rates of Eder and Carr²² measured relative to CH₂ (¹A₁) reaction with propane lends support to this conclusion. Carr and co-workers²²,³³ have also indicated that the correlation of intersystem crossing rates with collision partner polarizability (derived from inert gas removal rates) implies intersystem crossing rates which are only 4 - 6% of the insertion rate for collisions with CH₄, C₂H₆, and C₃H₈.

These conclusions are seemingly at odds with other studies including that of Braun, Bass, and Pilling⁸ which found comparable efficiencies for intersystem crossing and insertion in collisions between CH₂ (¹A₁) and CH₄. This result is based both on product analysis and spectroscopic observation of the CH₃ (from C₂H₆* dissociation) and CH₂ (³B₁) products. In addition, Bell²³ found CH₂ (¹A₁) removal rates (relative to reaction with propane) significantly greater than the present rates indicating that intersystem crossing is very important in collisions with C₃H₈.

These differences may be linked to the method of CH₂ (¹A₁) production. In studies based on competition with insertion reactions, it must be assumed that the fate of the insertion products is known. If the degree of stabilization of these products is overestimated, the resulting removal rates will be too large relative to the insertion reaction since the apparent yield of insertion products is too small. Since the probability of stabilizing these products depends on the
degree of internal excitation, the amount of energy available for internal excitation (determined by the excess energy available for CH₂ (1A₁) excitation in the photodissociation process) can affect the results. This may explain why the relative rates determined by Bell,²³ with ~ 45 kcal mol⁻¹ available for CH₂ (1A₁) excitation in the 405 nm photolysis of CH₂N₂,⁸ are significantly greater than both the present rates and the rates of Eder and Carr²² and Halberstadt and Crump¹³ (~ 8 kcal mol⁻¹ available for CH₂ (1A₁) excitation.⁶) This hypothesis is consistent with the results of Braun, Bass, and Pilling from CH₂ (1A₁) produced in the vacuum ultraviolet photolysis of ketene and diazomethane (≥ 70 kcal mol⁻¹ available for CH₂ (1A₁) excitation) which indicate that intersystem crossing is important under those conditions.

2. Alkenes

Singlet methylene reacts with olefins primarily through addition to the double bonds.³²,³⁴ Although absolute rate constants for CH₂ (1A₁) removal by olefins have not been reported previously, Krzyzankowski and Cvetanovic have measured rate constants for the addition of CH₂ (1A₁) to ethylene, propylene, 1-butene, cis-2-butene, trans-2-butene, trimethylethylene, tetramethylethylene, and 1,3-butadiene relative to isobutene addition.³⁴ These rates range from 0.54 (ethylene) to 1.73 (1,3-butadiene) times as fast as the isobutene rate. The present ratio of k₁₃/k₁₄ = 0.67 is in reasonable agreement with these results. The relative rates for trans-2-butene and isobutene from ref. 34, together with the present values of k₁ and k₁₄, imply relative rates for trans-2-butene and ketene in good agreement with the ratio reported by Carr and Kistiakowsky.³⁵

Taylor and Simons have reported the relative efficiencies for
meopentane/isobutene and n-butane/cis-2-butene pairs to be 0.87 and 1.09 respectively.\textsuperscript{36} The relative efficiencies for isobutene and cis-2-butene implied from these results and the work of Hase and Simons (Table III) are also in good agreement with the results of Krzyanowski et al. The absolute rate constant for isobutene implied from the work of Taylor and Simons and the data in Tables I and III is approximately 50\% greater than the present value of $k_{14}$.\textsuperscript{26}

3. Ketene

Ketene removes singlet methylene with virtually every collision, the most efficient of fourteen collision partners used in the present study. This occurs primarily through reaction (1), with possible contributions ($< 10\%$) from intersystem crossing.\textsuperscript{23} There is no evidence that singlet methylene reacts with ketene by other channels.\textsuperscript{1}

An estimate of $k_{1} = 4 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ reported by Lengel and Zare\textsuperscript{2} compares favorably to the present value of $2.7 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. This result is based on LIF detection of the ketene photoprocess. Earlier rate constants obtained by indirect methods are one to two orders of magnitude lower than these values.\textsuperscript{31,37}

V. CONCLUSIONS

Absolute rate constants for the removal of CH$_2$ ($^1A_1$) by NO, C$_2$H$_6$, C$_3$H$_8$, C$_2$H$_4$, i-C$_4$H$_8$, and CH$_2$CO have been directly measured for the first time, using the technique of laser resonance absorption. Absolute rate constants for He, Ar, Kr, N$_2$, CO, and H$_2$ obtained by this method are in excellent agreement with those obtained by laser-induced fluorescence. Comparisons between these results and those of product analysis studies indicate that carefully interpreted indirect studies can provide
accurate relative rate constants. These may prove particularly valuable for measurements of CH₂ (1A₁) removal rates at pressures significantly greater than 10 Torr where direct measurements will be hampered by the rapid rate of collision-induced intersystem crossing.

The intersystem crossing rate appears to be independent of CH₂ (1A₁) bending vibrational excitation. Thus a strong dependence of rate on the 1A₁ - 3B₁ vibronic level gaps appears unlikely. Since the rotational state dependence of intersystem crossing rates is obscured by rapid rotational equilibration, the ability of kinetic measurements to test theories of collision-induced intersystem crossing is reduced. A better understanding of collision-induced intersystem crossing in methylene may be provided by spectroscopic studies. In particular, it has been suggested that interactions between (1A₁) and (3B₁) levels may lead to perturbations in the (1B₁) + (1A₁) absorption spectrum.38,39 A search for such perturbations through Doppler-limited kinetic absorption spectroscopy is currently underway.

ACKNOWLEDGEMENTS

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REFERENCES

TABLE I: Absolute rate constants $\times 10^{12}$ (cm$^3$ molec$^{-1}$ s$^{-1}$) and average cross sections ($\AA^2$) for CH$_2$ ($^1A_1$) removal

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$^a \sigma = k(8 KT/\mu)^{-1/2}$

$^b$From ref. 12.

$^c$From ref. 8
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TABLE III: Relative rate constants for CH\textsubscript{2} (\textsuperscript{1}A\textsubscript{1}) collisions with alkanes

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<td>—</td>
<td>3.9</td>
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\textsuperscript{a}Relative rates based on singlet methylene removal.

\textsuperscript{b}Relative rates based on insertion product yields.
FIGURE CAPTIONS

Figure 1. Schematic diagram of laser photolysis/laser resonance absorption apparatus (top view, see text for details). The dye laser beam passes beside the dichroic mirror (D.M.), then is multiply passed between H.R. and D.M. before passing beside the high reflector (H.R.) onto the detector.

Figure 2. Absorption spectrum of several rotational lines in the \( \tilde{P} Q_{1, J} \) sub-branch near 16,929 cm\(^{-1}\) obtained from the photolysis of 0.50 Torr CH\(_2\) with 4.0 Torr He. The 500 ns boxcar gate was opened at the same time as the photolysis pulse. The assignments are from ref. 7.

Figure 3. Temporal evolution of the \( 4_{14} \) rotational level of CH\(_2\) (\( ^1A_1 \)) in 0.200 Torr CH\(_2\)CO with 3.00 Torr He after 64 laser shots. The solid line corresponds to the rates given in Fig. 4.

Figure 4. Production (○) and decay (●) rates for CH\(_2\) (\( ^1A_1 \)) in 3.00 Torr He and 0.050 to 0.500 Torr CH\(_2\)CO. The solid lines correspond to production rate constants of \( 7.3 \times 10^{-10} \) and \( 5.9 \times 10^{-11} \) cm\(^3\) molec\(^{-1}\) s\(^{-1}\) and removal rate constants of \( 2.7 \times 10^{-10} \) and \( 3.5 \times 10^{-12} \) cm\(^3\) molec\(^{-1}\) s\(^{-1}\) for CH\(_2\)CO and He respectively. Uncertainties for the production rate constants are ~ 10%.

Figure 5. Production (△) and decay (▲) rates for CH\(_2\) (\( ^1A_1 \)) in 0.200 Torr CH\(_2\)CO and 1.25 to 9.00 Torr He. The solid lines correspond to the rate constants from Fig. 4.
Figure 6. Fluence dependence of CH$_2$ (1$^1A_1$) production in 0.500 Torr CH$_2$CO and 6.00 Torr He. The triangles correspond to the difference between the peak absorbance and the baseline.

Figure 7. Pseudo-first-order decay rates for CH$_2$ (1$^1A_1$) in 0.200 Torr CH$_2$CO and He, Ar, Kr, and N$_2$. The solid lines correspond to rate constants given in Table I.

Figure 8. Pseudo-first-order decay rates for the 1$_{10}$, 3$_{13}$, 4$_{14}$, and 7$_{16}$ rotational levels of CH$_2$ (1$^1A_1$) in 0.200 Torr CH$_2$ and added N$_2$. The rotational energies are 31, 108, 170, and 533 cm$^{-1}$ respectively. The solid line corresponds to the rate constant from Table I.

Figure 9. Pseudo-first-order decay rates for the (0,1,0) and (0,0,0) vibrational levels of CH$_2$ (1$^1A_1$) as a function of added He (△, △) and Ar (○, ○). The CH$_2$CO pressures are 0.300 Torr for the (0,1,0) decays and 0.200 for the (0,0,0) decays. The solid lines correspond to the (0,0,0) rate constants from Table I.

Figure 10. Pseudo-first-order decay rates for CH$_2$ (1$^1A_1$) in 0.100 Torr CH$_2$CO, 6.00 Torr He, and added CO, O$_2$, H$_2$, and NO. The solid lines correspond to the rate constants given in Table I.

Figure 11. Pseudo-first-order decay rates for CH$_2$ (1$^1A_1$) in 0.100 Torr CH$_2$CO, 6.00 Torr He, and added CH$_4$, C$_2$H$_6$, and C$_3$H$_8$. The solid lines correspond to the rate constants given in Table I.
Fig. 4
Fig. 7

The graph shows the decay rate (μs⁻¹) plotted against quenching gas pressure (Torr) for different gases: N₂, Kr, Ar, and He. Each gas is represented by a different symbol and line style.
Fig. 10

Decay Rate (μs⁻¹) vs Reactant Gas Pressure (Torr)

- NO
- H₂
- O₂
- CO
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