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CONSTANTS FOR ATOMIC AND MOLECULAR COLLISION
PARTNERS AT 295 K

Andrew O. Langford, Hrvoje Petek, and
C. Bradley Moore

December 1982

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COLLISIONAL REMOVAL OF CH₂ (¹A₁): ABSOLUTE RATE CONSTANTS

FOR ATOMIC AND MOLECULAR COLLISION PARTNERS AT 295 K

Andrew O. Langford, Hrvoje Petek, and C. Bradley Moore

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ABSTRACT

The technique of cw laser resonance absorption has been used to monitor the time evolution of individual CH₂ (¹A₁) rotational levels following the excimer laser photolysis of CH₂CO. Absolute rate constants for the removal of CH₂ (¹A₁) by He, Ar, Kr, N₂, CO, O₂, CH₄, C₂H₆, C₃H₈, C₂H₄, i-C₄H₈, and CH₂CO have been determined at 295K. Removal efficiencies range from nearly gas-kinetic for the higher hydrocarbons and CH₂CO to 10⁻² for He. For He, Ar, and CH₂CO removal rates were measured for the v₂ = 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 CH₂CO were found to be factors of 17 and 2.7 faster than the respective removal rates.

I. INTRODUCTION

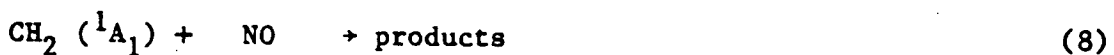
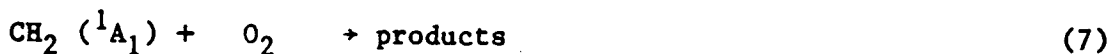
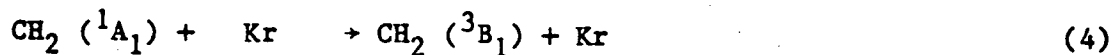
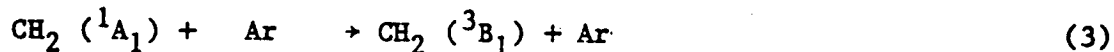
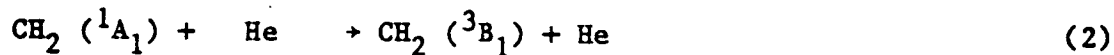
Despite the fundamental importance of methylene to synthesis, molecular structure, and chemical kinetics, its chemistry is not well established.¹ Many of the problems and much of the interest stem from the existence of two low-lying electronic states which differ significantly in reactivity and structure.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

Although CH_2 (1A_1) absorbs in the visible,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.^{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_2 (1A_1) has been successfully demonstrated in several laboratories.^{2,3,9-12} The first direct measurements of CH_2 (1A_1) removal rates have recently been reported by Ashfold et al.^{11,12} who used LIF to monitor CH_2 (1A_1) and CD_2 (1A_1) produced in the ir multiphoton dissociation (MPD) of acetic anhydride. These workers reported rate

constants for CH_2 ($^1\text{A}_1$) removal approximately one order of magnitude larger than previously accepted values inferred primarily from studies of CH_2 ($^3\text{B}_1$) kinetics.⁸ 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 CH_2 ($^1\text{A}_1$) is removed by many hydrocarbons with near gas-kinetic collision efficiency.^{13,14}

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 CH_2 ($^1\text{A}_1$) removal by the following processes have been determined at 295 K:





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/cm² and a maximum power density of 0.5 MW/cm². 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 CH₂ ($^1\text{A}_1$) 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.l. 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 CH_2 through diffusion from the reaction volume was negligible on the timescale of collisional removal.

Absorption of the dye laser beam by CH_2 ($^1\text{A}_1$) 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 anhydride¹⁵ 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%), N₂ (LBL 99.999%), CO (Baker research grade 99.97%), H₂ (Baker research grade 99.9995%), O₂ (Baker research grade 99.995%), CH₄ (Matheson UHP 99.97%), C₂H₆ (Scientific Gas Products C.P. 99.2%, with less than 0.2% each H₂, CH₄, and C₂H₄ and 0.1% N₂ and O₂), C₃H₈ (Matheson research grade 99.99%), C₂H₄ (Matheson C.P. 99.5%), and i-C₄H₈ (Matheson C.P. 99.3%, with less than 0.4% 1-butene, 0.2% n-C₄H₁₀, and 0.1% i-C₄H₁₀) 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 N₂, 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 CH_2 (${}^1\text{A}_1$).

At 308 nm, all of the methylene produced through single-photon excitation of ketene is in the $\tilde{\text{a}}({}^1\text{A}_1)$ state.^{6,16} Rate constants for the collisional removal of CH_2 (${}^1\text{A}_1$) were obtained primarily from the analysis of absorption data for the 4_{14} rotational level, monitored via the $4_{04}(0,14,0) + 4_{14}(0,0,0)$ transition near 16928.79 cm^{-1} .⁷ A high resolution spectrum of the $\text{P}_{\text{Q}_{1,J}}$ (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 4_{14} 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 4_{14} 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 4_{14} 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 CH_2 $\tilde{\text{a}}$ (${}^1\text{A}_1$) by electronic quenching of CH_2 $\tilde{\text{b}}$ (${}^1\text{B}_1$) formed via two-photon excitation of ketene can be ruled out through the linear fluence dependence of the CH_2 (${}^1\text{A}_1$) 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 CH_2 ($^1\text{A}_1$).

B. Removal of CH_2 ($^1\text{A}_1$).

1. Absolute Rate Constants

Absolute rate constants for CH_2 ($^1\text{A}_1$) 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.

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

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 CH_2 ($^1\text{A}_1$) removal by Ar, Kr, and 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 CH_2CO . 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 CH_2 ($^1\text{A}_1$) decay rates in He, Ar, Kr, and N_2 are shown in Fig. 7.

The rotational-level independence of these removal rates, illustrated for 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 $P_{Q_1,J}$ (J) and $P_{P_1,J-1}$ (J) branches near 16930 cm^{-1} .⁷ 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} .⁷ 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.

$$K_{\text{exp}} = k_1[\text{CH}_2\text{CO}] + k_2[\text{He}] + k_R[\text{R}]. \quad (16)$$

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 CH_2O 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 $2.5 \times 10^{-20} \text{ cm}^2/\text{molecule}$ at 308 nm^{20} with a quantum yield of unity for the production of CH_2 ($^1\text{A}_1$), implies that irradiation of 0.100 Torr of ketene with the maximum energy fluence of $10 \text{ mJ}/\text{cm}^2$ produced approximately $10^{13} \text{ molecules}/\text{cm}^3$ 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 CH_2 ($^1\text{A}_1$) 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 CH_2 ($^3\text{B}_1$) produced by intersystem crossing or CH_3 formed through reaction of the singlet with H_2 or CH_4 . 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 CH_2 ($^1\text{A}_1$) 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 O_2 or CO to scavenge triplet CH_2 ($^3\text{B}_1$). Relative rates for intersystem crossing induced by the addition of inert gases were determined from the reduced yield of C_2H_4 produced by reaction (1). These rates are therefore normalized to a value of 77 for k_1 . With the exception of k_4 , 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 CH_2 ($^1\text{A}_1$) with C_3H_8 . 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 CH_2 ($^1\text{A}_1$) was produced by the 405 nm photolysis of diazomethane. These rates are also normalized to a value of 69 for CH_2 ($^1\text{A}_1$) reaction with C_3H_8 .

A. CH_2 ($^1\text{A}_1$) Removal by Rare Gases

The absolute values of rate constants for CH_2 ($^1\text{A}_1$) removal by He, Ar, and Kr reported in ref. 12 agree with the present results to within 15%. Relative values of k_2 and k_3 from ref. 8, and k_2 and k_4 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-workers^{24,25} 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 deuteration¹² suggest that accidental vibrational resonances do not change rates by orders of magnitude. Freed, Gelbart, and co-workers²⁶⁻²⁸ 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. CH_2 ($^1\text{A}_1$) Removal by Inorganic Molecules

When the collision partner is a molecule, reactive processes may also contribute to the removal of CH_2 ($^1\text{A}_1$). 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 CH_2 ($^1\text{A}_1$) 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. CH₂ (¹A₁) + N₂

The present rate constant for CH₂ (¹A₁) removal by N₂ is approximately 25% greater than the value of Ref. 12. Braun, Bass, and Pilling⁸ 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 CH₂ (³B₁) yield with increasing N₂ pressure. Quantitatively, the rate of adduct formation was found to be approximately 60% greater than the rate of direct intersystem crossing. The excellent agreement (< 5%) between the present rate for CH₂ (¹A₁) removal by N₂ and the relative rate for direct intersystem crossing from ref. 8 implies that the adduct dissociates primarily to CH₂ (¹A₁) rather than CH₂ (³B₁).

2. CH₂ (¹A₁) + CO

The absolute values of k₆ reported in ref. 12 and the present study differ by less than 15%. In product analysis studies, DeGraff and Kistiakowsky²⁹ and Cox and Preston²¹ found relative efficiencies for the removal of CH₂ (¹A₁) by CO and CH₂CO 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 k₆/k₁ = 0.18 ± 0.02. The production of ¹⁴CO in the reaction of ¹⁴CH₂ (¹A₁) with CO led Montague and Rowland³⁰ to conclude that an oxirene adduct forms in collisions of ¹CH₂ with CO. They reported that a CO pressure of 840 Torr was necessary to stabilize 50% of the excited oxirene complexes. A complex dissociation rate of 3 x 10⁹ 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_6 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 Carr²² 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 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 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 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. CH₂ (¹A₁) + NO

The only reported rate constant for singlet CH₂ removal by 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 CH₂ (¹B₁) produced in the vacuum ultraviolet photolysis of ketene. The relative efficiencies of reaction and intersystem crossing are unknown.

5. CH₂ (¹A₁) + H₂

The absolute values for k_9 differ by approximately 20%. A relative value of k_9/k_2 determined by Braun, Bass, and Pilling⁸ is 10% lower than the present ratio. These workers spectroscopically observed the production of CH₃ in the reaction of CH₂ (¹A₁) with H₂ 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. CH₂ (¹A₁) Removal by Organic Molecules

1. Alkanes

In reactions with alkanes, CH₂ (¹A₁) 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 Crump¹³ 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 CH₂ (¹A₁) removal rates determined in this study (Table III). The absolute rate constant for CH₂ (¹A₁) removal by CH₄ 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 CH_2 ($^1\text{A}_1$) 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 CH_2 ($^1\text{A}_1$) reaction with propane lends support to this conclusion. Carr and co-workers^{22,33} 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 CH_4 , C_2H_6 , and C_3H_8 .

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 CH_2 ($^1\text{A}_1$) and CH_4 . This result is based both on product analysis and spectroscopic observation of the CH_3 (from C_2H_6^* dissociation) and CH_2 ($^3\text{B}_1$) products. In addition, Bell²³ found CH_2 ($^1\text{A}_1$) removal rates (relative to reaction with propane) significantly greater than the present rates indicating that intersystem crossing is very important in collisions with C_3H_8 .

These differences may be linked to the method of CH_2 ($^1\text{A}_1$) 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 CH_2 ($^1\text{A}_1$) excitation in the photodissociation process) can affect the results. This may explain why the relative rates determined by Bell,²³ with $\sim 45 \text{ kcal mol}^{-1}$ available for CH_2 ($^1\text{A}_1$) excitation in the 405 nm photolysis of CH_2N_2 ,⁸ are significantly greater than both the present rates and the rates of Eder and Carr²² and Halberstadt and Crump¹³ ($\sim 8 \text{ kcal mol}^{-1}$ available for CH_2 ($^1\text{A}_1$) excitation.⁶) This hypothesis is consistent with the results of Braun, Bass, and Pilling from CH_2 ($^1\text{A}_1$) produced in the vacuum ultraviolet photolysis of ketene and diazomethane ($\geq 70 \text{ kcal mol}^{-1}$ available for CH_2 ($^1\text{A}_1$) 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 CH_2 ($^1\text{A}_1$) removal by olefins have not been reported previously, Krzyzanowski and Cvetanovic have measured rate constants for the addition of CH_2 ($^1\text{A}_1$) 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 $k_{13}/k_{14} = 0.67$ 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 k_1 and k_{14} , 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

neopentane/isobutene and n-butane/cis-2-butene pairs to be 0.87 and 1.09 respectively.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} .

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.²³ There is no evidence that singlet methylene reacts with ketene by other channels.¹

An estimate of $k_1 = 4 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ reported by Lengel and Zare² 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 photoproduct. Earlier rate constants obtained by indirect methods are one to two orders of magnitude lower than these values.^{31,37}

V. CONCLUSIONS

Absolute rate constants for the removal of CH_2 ($^1\text{A}_1$) by NO, C_2H_6 , C_3H_8 , C_2H_4 , 1- C_4H_8 , and CH_2CO 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 CH_2 ($^1\text{A}_1$) 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 CH_2 ($^1\text{A}_1$) bending vibrational excitation. Thus a strong dependence of rate on the $^1\text{A}_1 - ^3\text{B}_1$ 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 ($^1\text{A}_1$) and ($^3\text{B}_1$) levels may lead to perturbations in the ($^1\text{B}_1$) + ($^1\text{A}_1$) absorption spectrum.^{38,39} A search for such perturbations through Doppler-limited kinetic absorption spectroscopy is currently underway.

ACKNOWLEDGEMENTS

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TABLE I: Absolute rate constants $\times 10^{12}$ ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)
and average cross sections (\AA^2) for CH_2 ($^1\text{A}_1$) removal

	σ^a	k	k^b	k^c
He	0.25	3.5 ± 0.3	3.1 ± 0.3	0.30 ± 0.07
Ne	0.50^b	-----	4.2 ± 0.6	-----
Ar	0.75	5.8 ± 0.5	6.0 ± 0.5	0.67 ± 0.13
Kr	1.1	7.9 ± 0.6	7.0 ± 0.6	-----
Xe	2.3^b	-----	16 ± 2	-----
N_2	1.3	11 ± 1	8.8 ± 0.3	0.90 ± 0.2
∞	6.0	49 ± 4	56 ± 6	-----
O_2	9.2	74 ± 5	30 ± 4	-----
NO	20.	160 ± 15	-----	-----
H_2	5.6	105 ± 5	130 ± 10	7.0 ± 1.5
CH_4	7.6	70 ± 4	73 ± 6	3.5 ± 1.0
C_2H_6	23	190 ± 20	-----	-----
C_3H_8	31	240 ± 20	-----	-----
C_2H_4	18	150 ± 60	-----	-----
$i\text{-C}_4\text{H}_8$	30	225 ± 20	-----	-----
$\text{CH}_2\infty$	35	270 ± 20	-----	-----

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

^bFrom ref. 12.

^cFrom ref. 8

TABLE II: Relative rate constants for CH_2 ($^1\text{A}_1$) removal

	this work	ref. 12	ref. 8	ref. 21	ref. 22	ref. 23
He	1.0	1.0	1.0	1.3	0.7	—
Ne	—	1.4	—	—	—	—
Ar	1.7	1.9	2.2	1.1	2.1	8.3
Kr	2.3	2.3	—	2.5	—	—
Xe	—	5.2	—	6.0	3.2	20
N_2	3.1	2.8	3.0	4.1	3.4	5.5
CO	14	18	—	9	—	—
O_2	21	9.7	—	—	32	43
NO	46	—	—	—	—	—
H_2	30	42	28	—	—	—
CH_4	20	24	12	—	—	33
C_2H_6	54	—	—	—	—	—
C_3H_8	69	—	—	—	69	69
C_2H_4	43	—	—	—	—	—
$i\text{-C}_4\text{H}_{10}$	64	—	—	—	—	—
CH_2CO	77	—	—	77	—	—

TABLE III: Relative rate constants for CH_2 ($^1\text{A}_1$) collisions with alkanes

	This work ^a	ref. 13 ^b	ref. 14 ^b
CH_4	1.0	1.0	—
C_2H_6	2.7	2.52	—
C_3H_8	3.4	3.32	3.3
n- C_4H_{10}	—	4.28	4.1
i- C_4H_{10}	—	3.89	3.5
n- C_5H_{12}	—	—	3.9

^aRelative rates based on singlet methylene removal.

^bRelative 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 $PQ_{1,J}(J)$ sub-branch near $16,929 \text{ cm}^{-1}$ 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_2CO 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_2CO . The solid lines correspond to production rate constants of 7.3×10^{-10} and $5.9 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and removal rate constants of 2.7×10^{-10} and $3.5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for CH_2CO and He respectively. Uncertainties for the production rate constants are ~ 10%.

Figure 5. Production (Δ) and decay (\blacktriangle) rates for CH_2 (1A_1) in 0.200 Torr CH_2CO 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 ($^1\text{A}_1$) production in 0.500 Torr CH_2CO 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 ($^1\text{A}_1$) in 0.200 Torr CH_2CO 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 ($^1\text{A}_1$) 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 ($^1\text{A}_1$) as a function of added He (Δ, \blacktriangle) and Ar (\circ, \bullet). The CH_2CO 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 ($^1\text{A}_1$) in 0.100 Torr CH_2CO , 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 ($^1\text{A}_1$) in 0.100 Torr CH_2CO , 6.00 Torr He, and added CH_4 , C_2H_6 , and C_3H_8 . The solid lines correspond to the rate constants given in Table I.

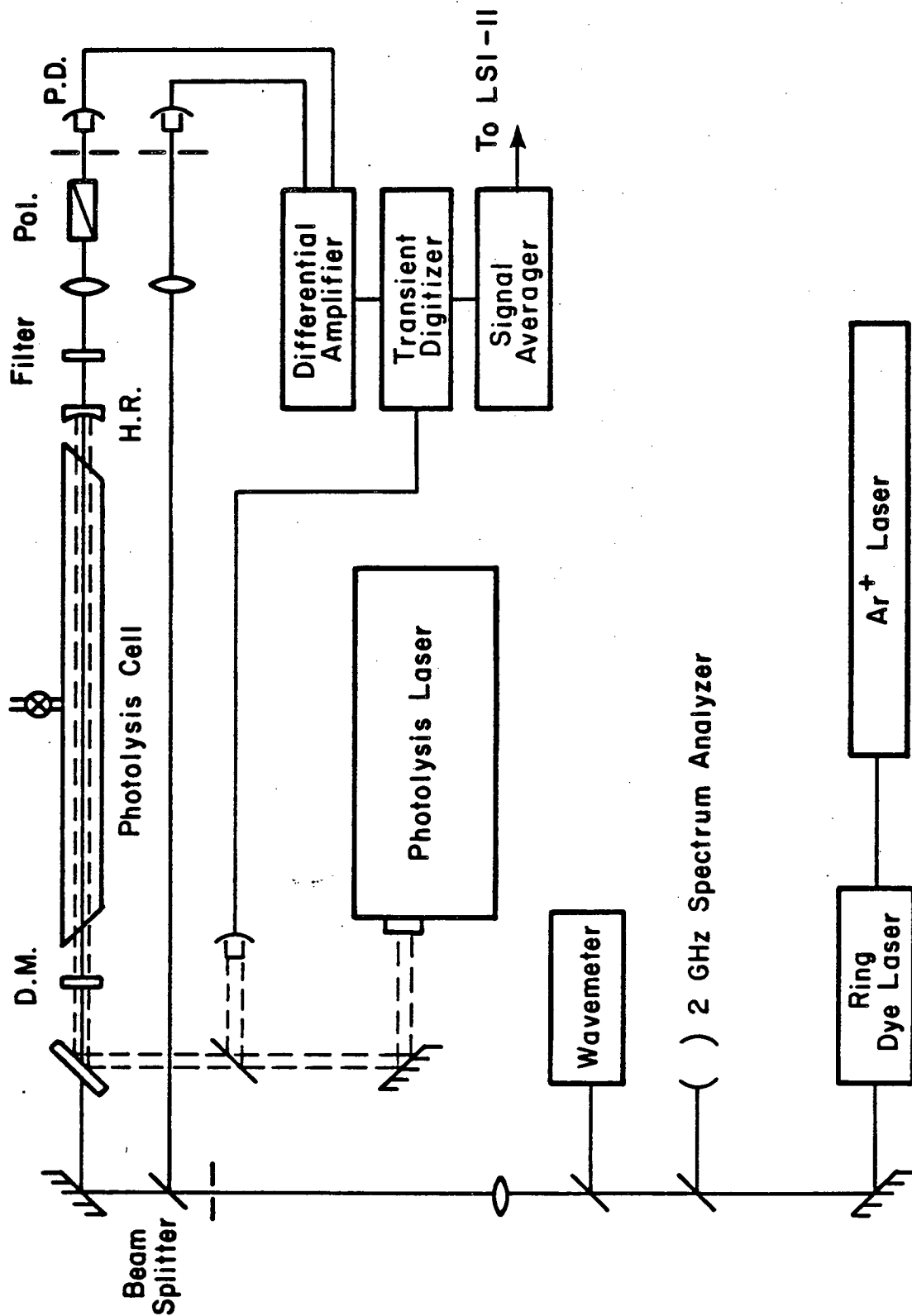


Fig. 1

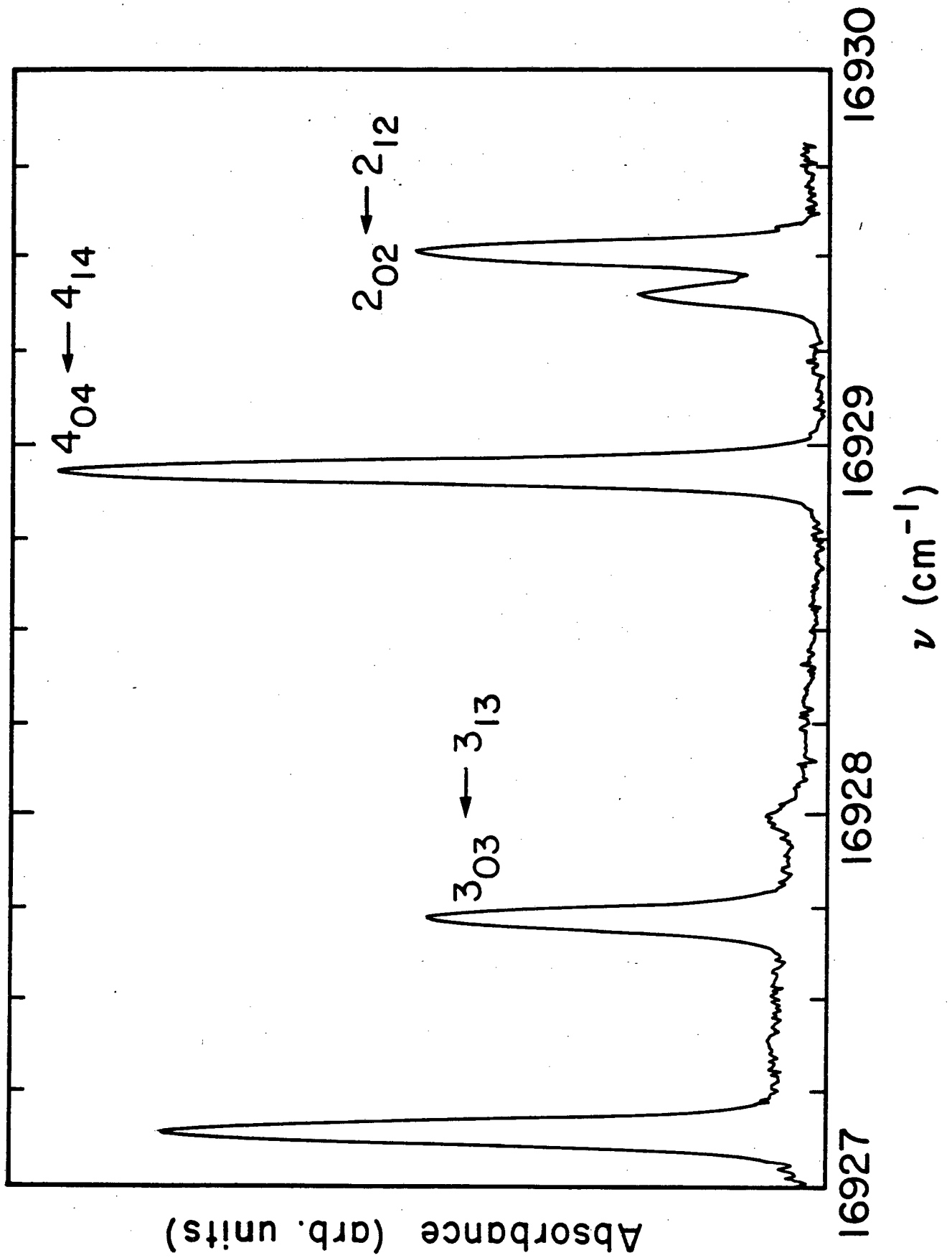


Fig. 2

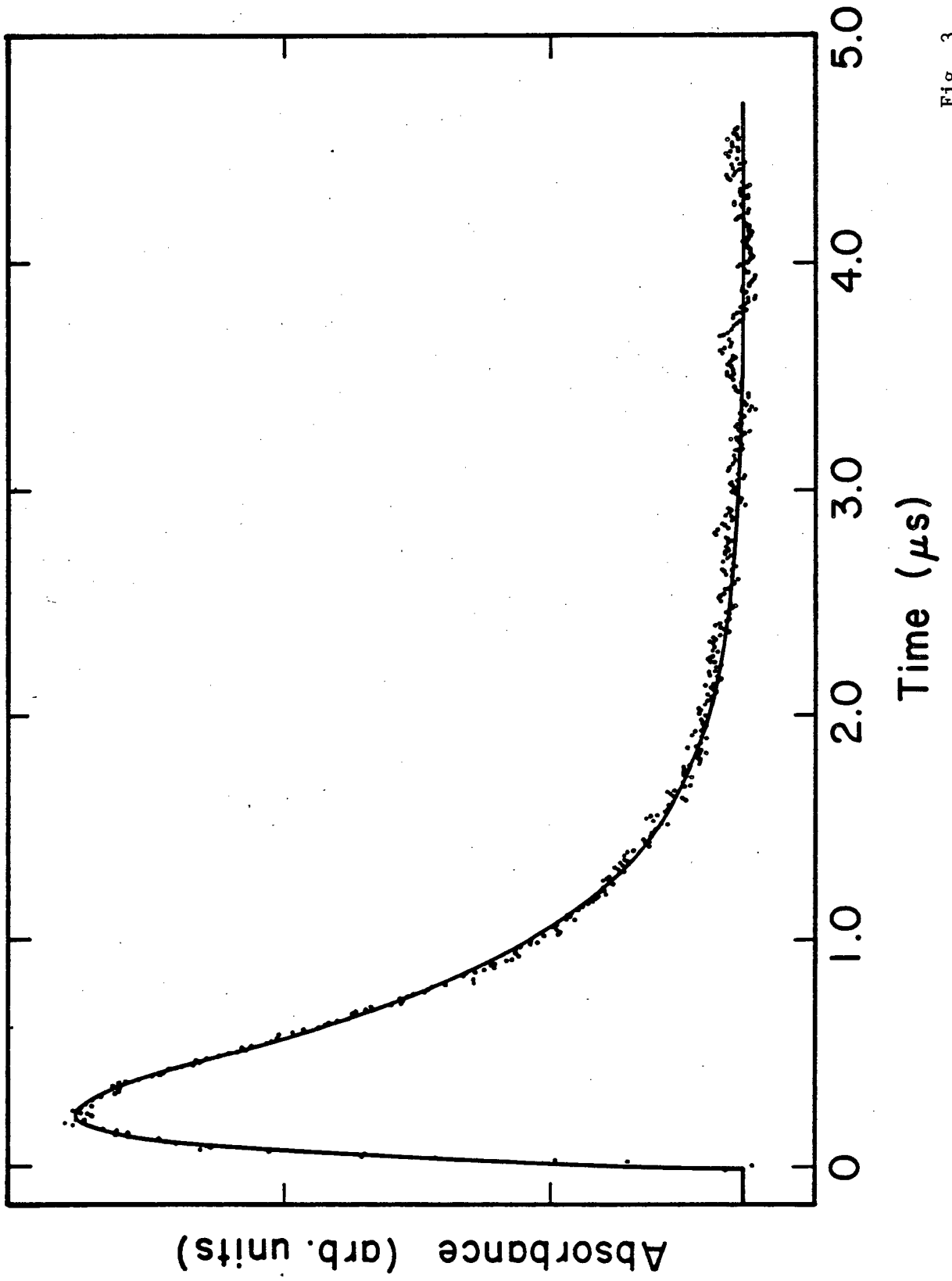


Fig. 3

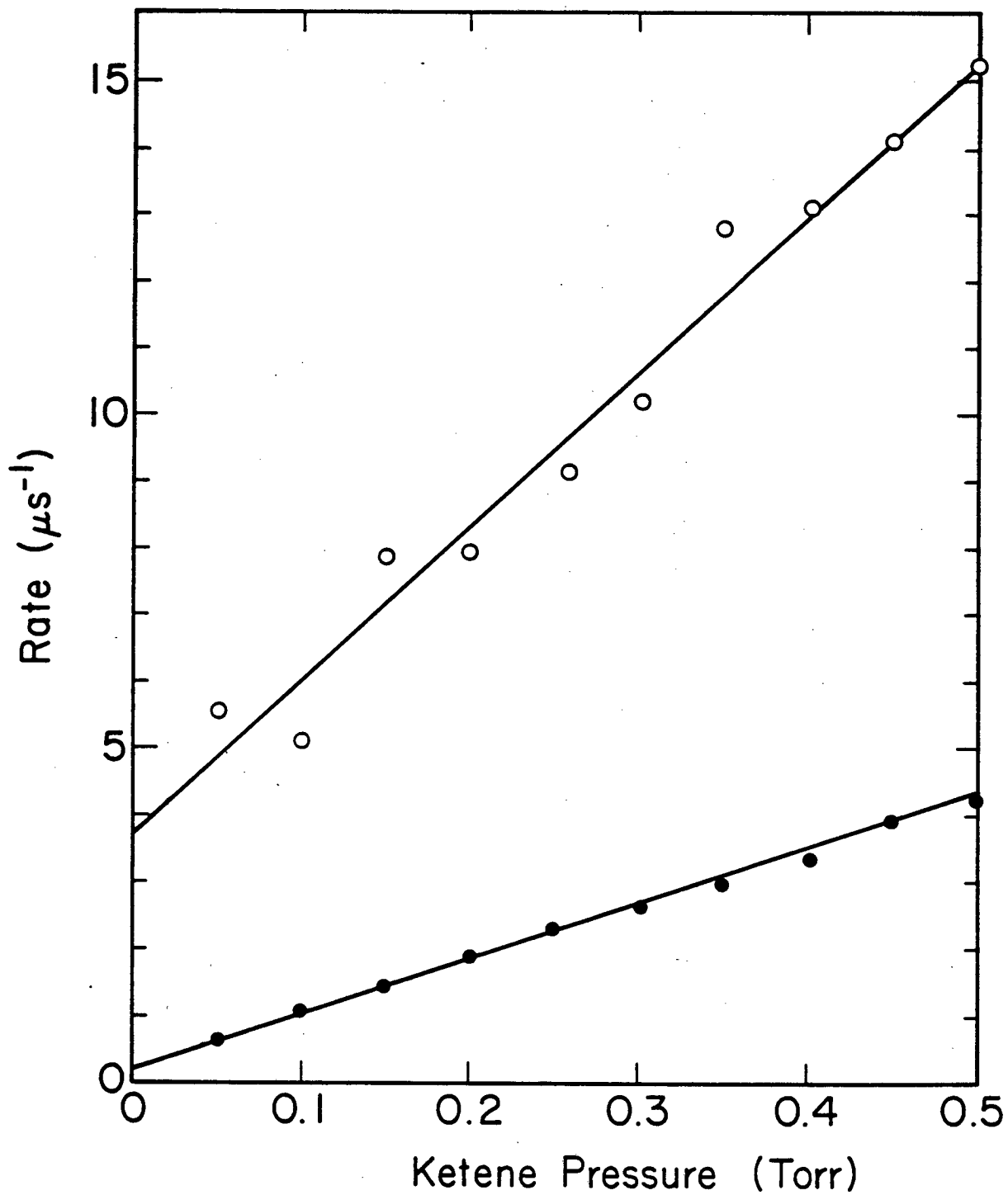


Fig. 4

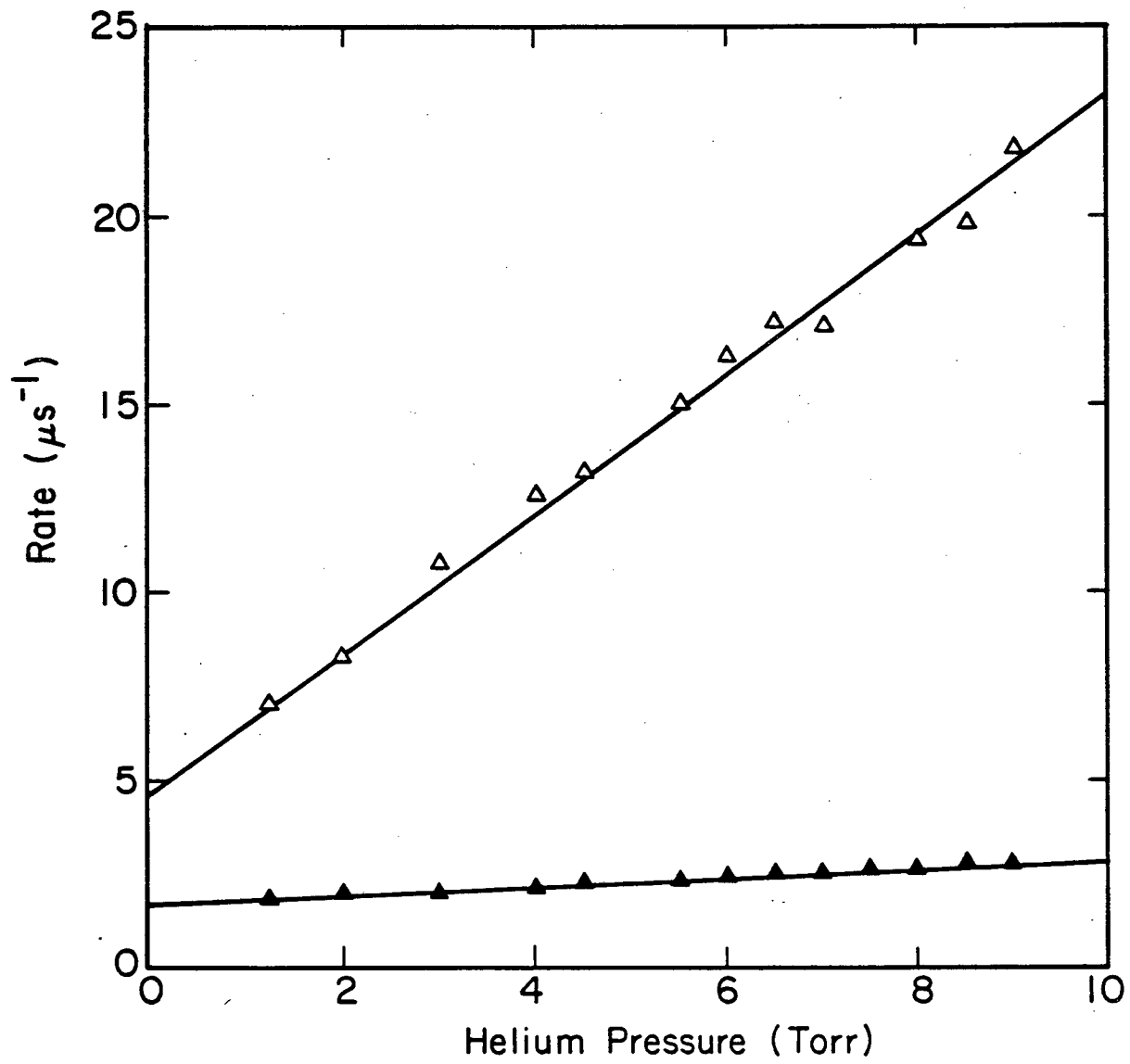


Fig. 5

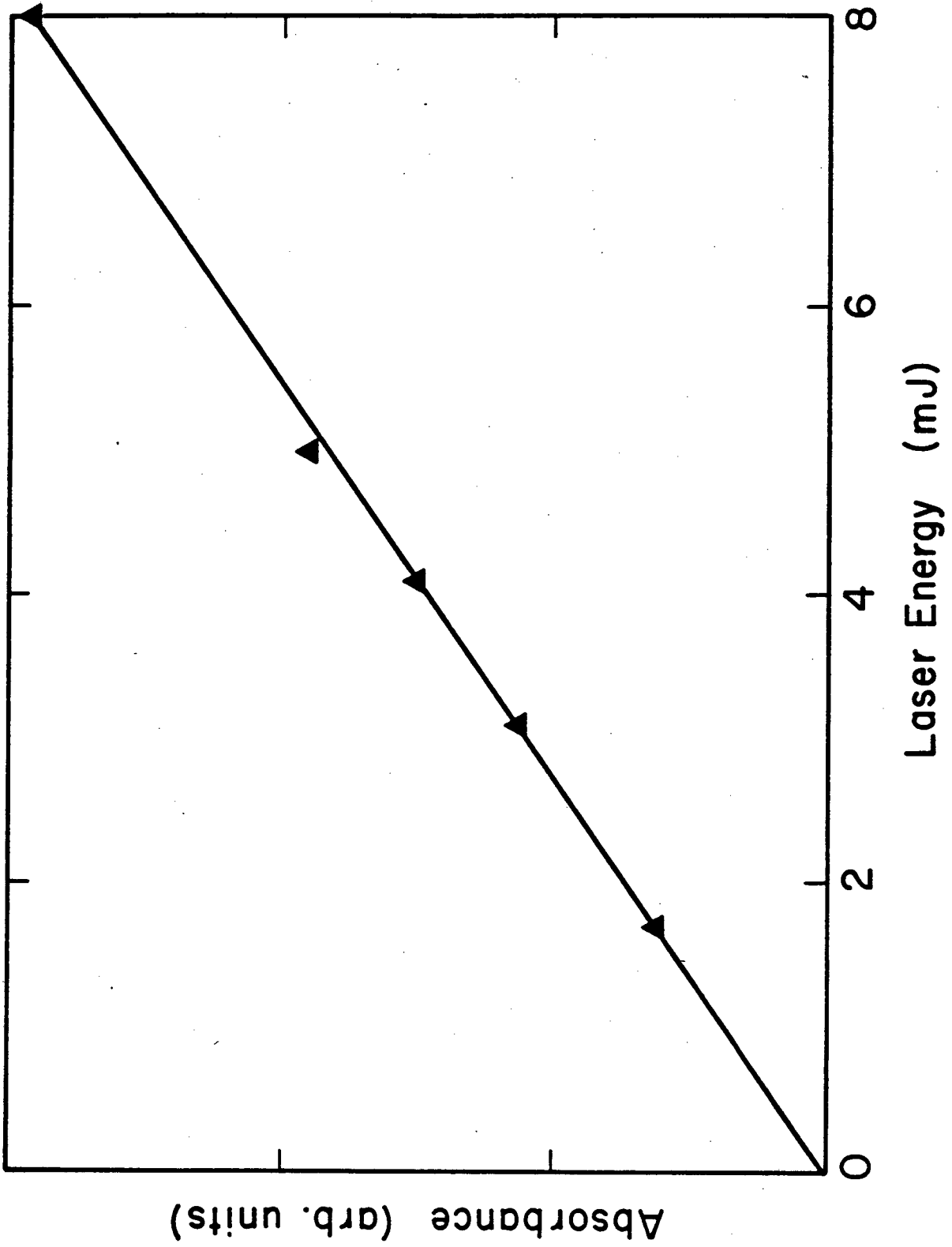


Fig. 6

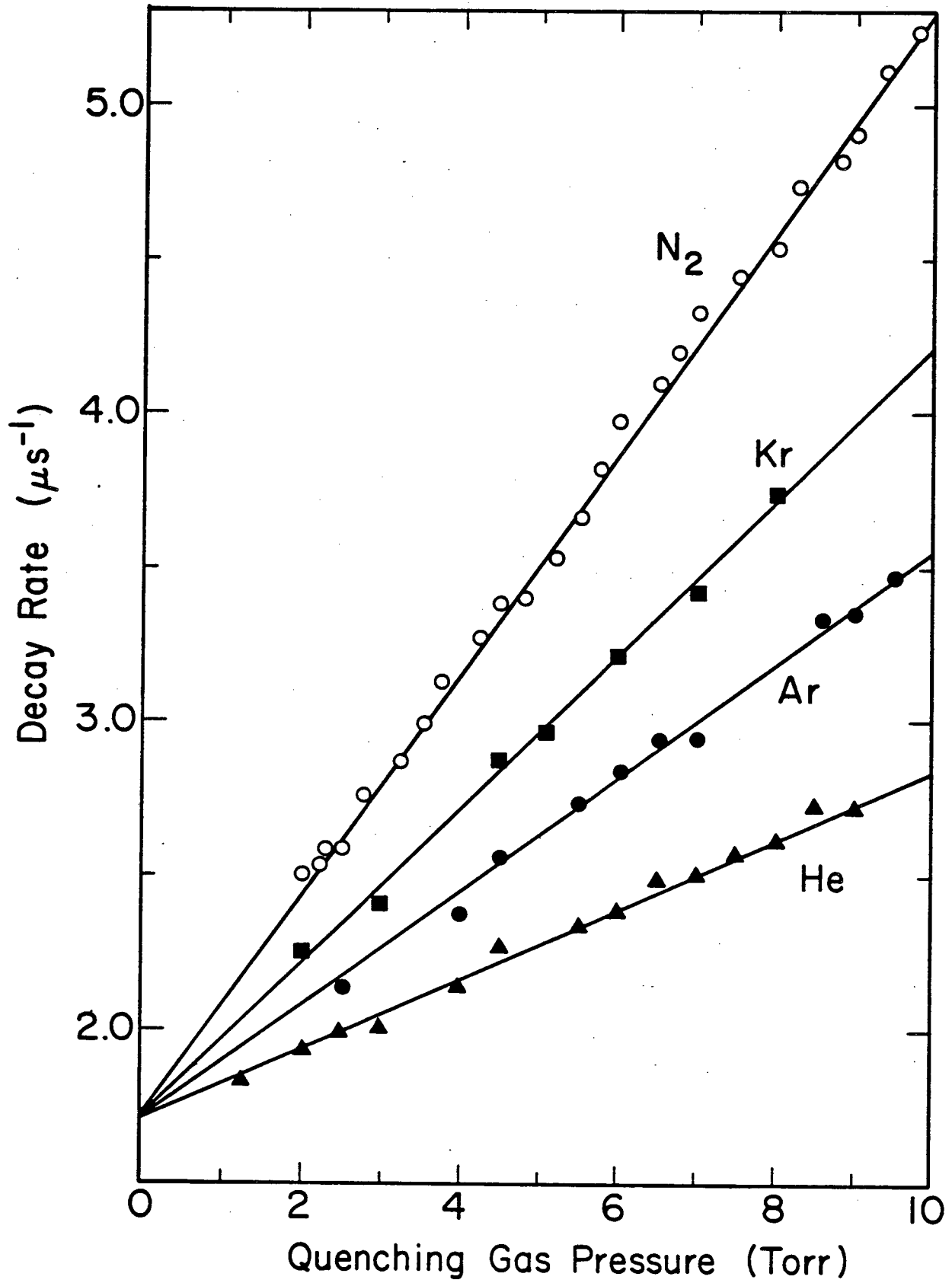


Fig. 7

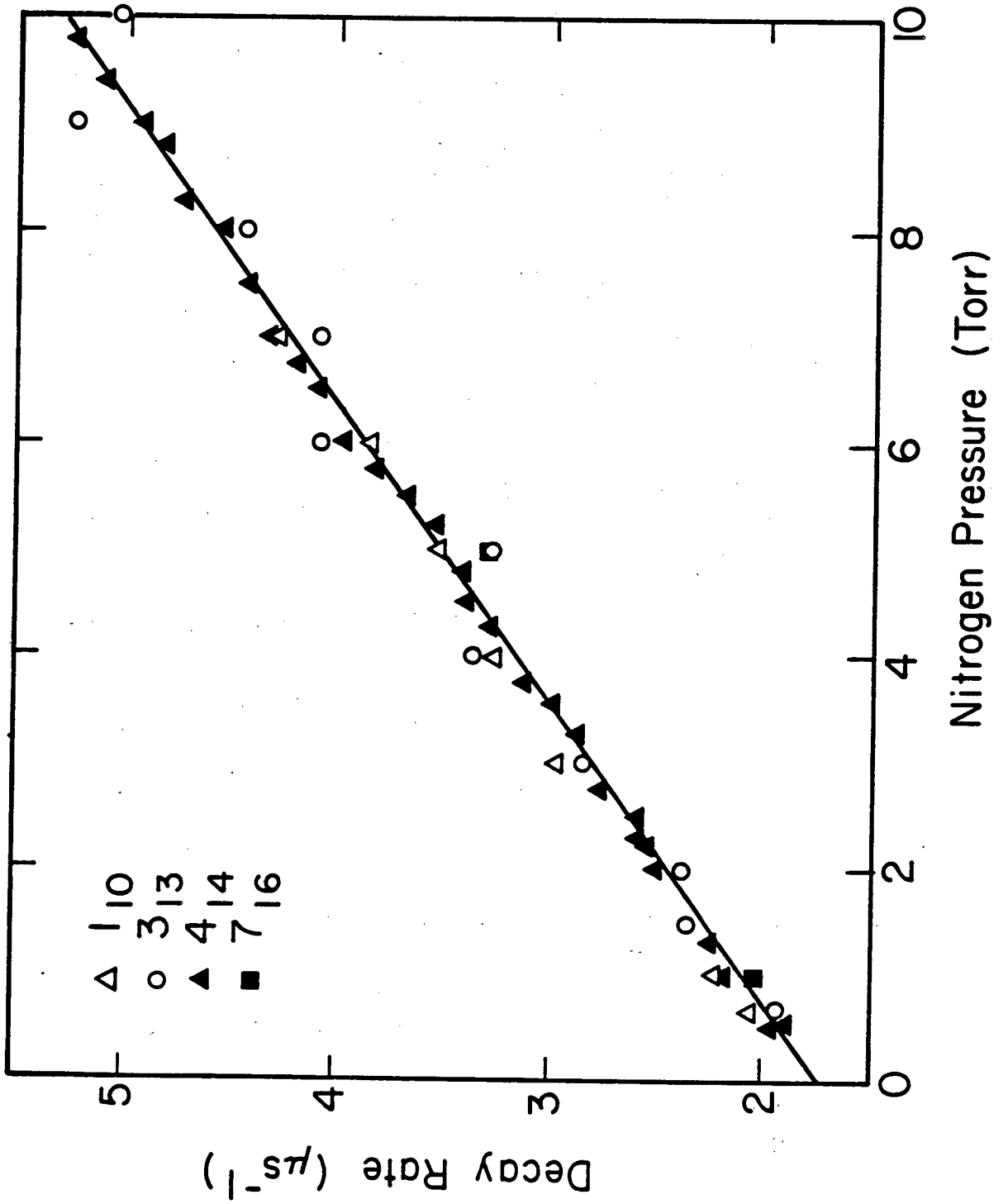


Fig. 8

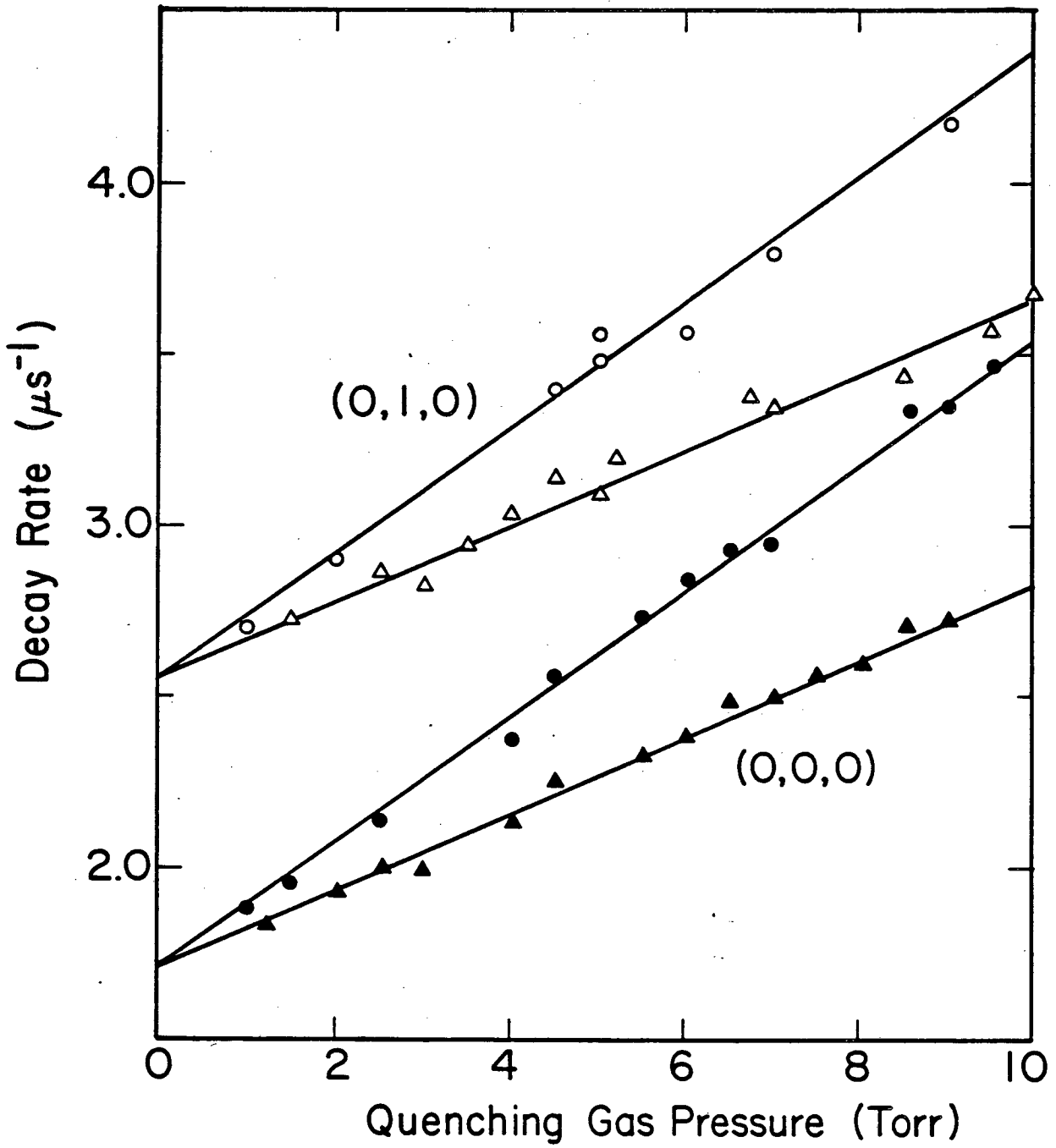


Fig. 9

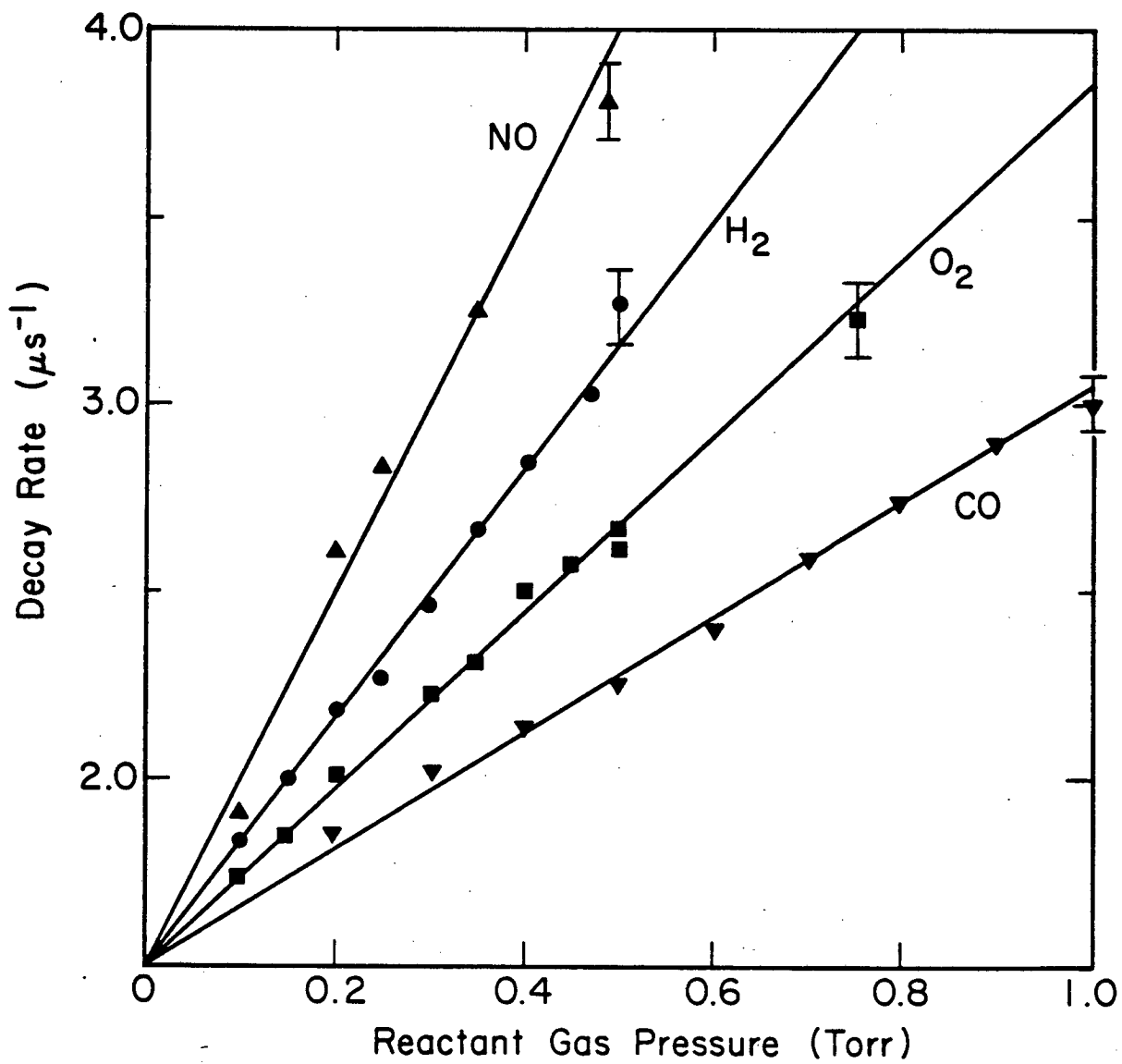


Fig. 10

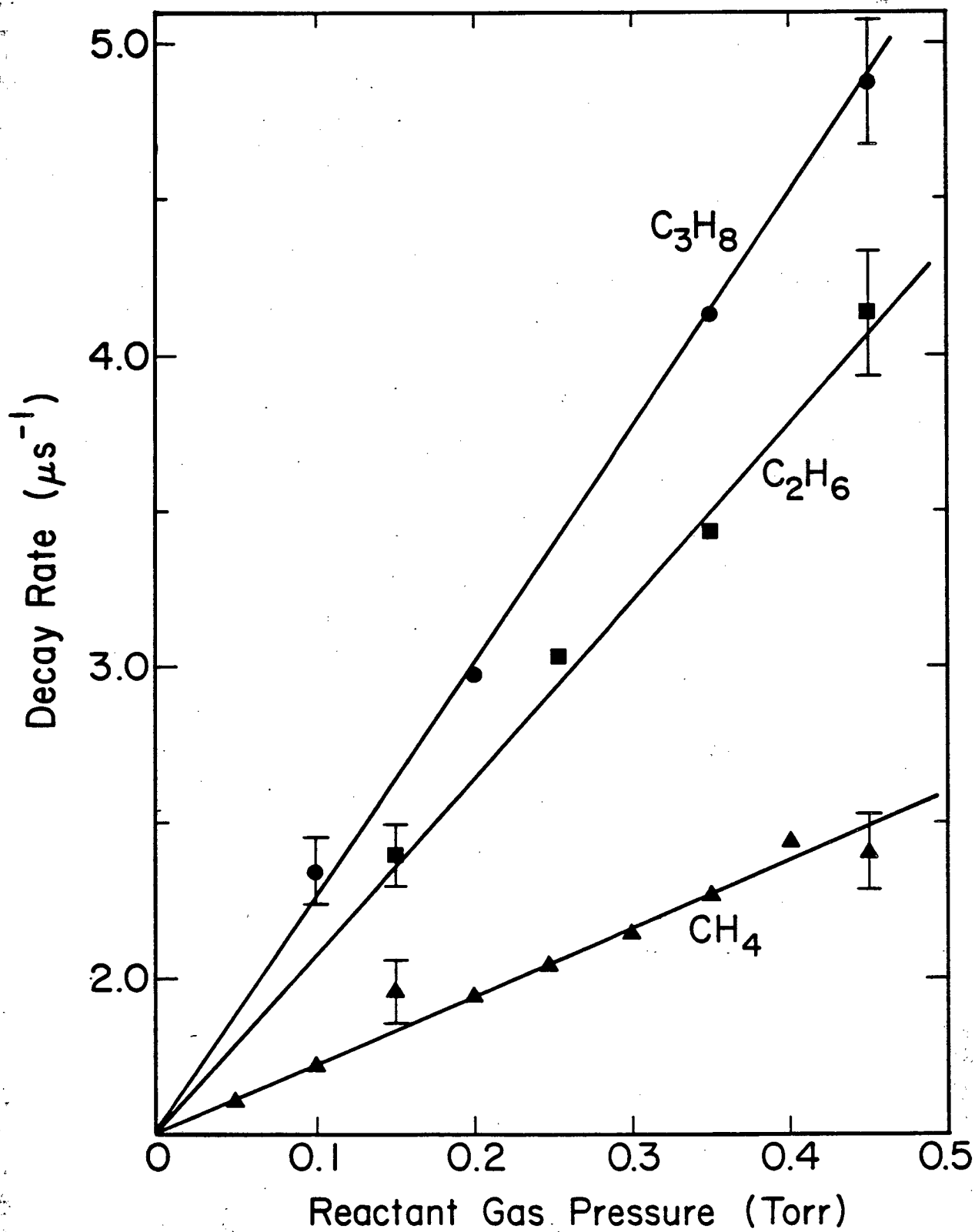


Fig. 11

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