DIRECT MEASUREMENTS OF ã $^1A_1$ CH$_2$ REMOVAL RATES

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Summary

The rates of collisional removal of ã $^1A_1$ CH$_2$ radicals were directly measured. IR multiple photon dissociation was used to produce the species and laser-induced fluorescence was used to monitor their decay. The rate constants for $^1A_1$ CH$_2$ removal by helium, argon, xenon, N$_2$ and O$_2$ were measured to be 2.8×10^{-12}, 5.6×10^{-12}, 16×10^{-12}, 7.9×10^{-12} and 27×10^{-12} cm^3 molecule^{-1} s^{-1} respectively. Possible processes contributing to these decay rates are discussed.

1. Introduction

Despite the large number of experimental investigations of the gas phase chemistry of the methylene radical in its ground $^3B_1$ and low lying $^1A_1$ states, there have been few direct determinations of the rates of removal of these species. For $^1A_1$ methylene (^{1}CH$_2$), the measurements of Braun *et al.* [1] have provided absolute values of the removal rates both for physical quenching and for chemical reaction with a variety of added gases, and these values have been used in subsequent measurements of the comparative rate constants for ^{1}CH$_2$ removal by other molecules [2 - 4].

^{1}CH$_2$ has recently been detected by laser-induced fluorescence (LIF) following its production by UV photodissociation of ketene [5, 6] and by IR multiple photon dissociation (MPD) of acetic anhydride [7]. MPD has been shown to be a convenient pulsed source for kinetic studies of reactive fragments in their ground or low lying metastable states, *e.g.* C$_2$(a$^3\pi_u$) [8] and CH [9], with LIF being used to measure their rates of removal. This report describes the application of this technique to the first time-resolved measurements of the removal rates of ^{1}CH$_2$ with argon, helium, xenon, N$_2$ and O$_2$.

2. Experimental

Figure 1 shows a block diagram of the essential experimental features. $^1CH_2$ was formed by the IR MPD of low pressures of a precursor molecule in an excess of quenching gas. As in the work of Feldmann et al. [7], acetic anhydride was used as the precursor except in a single experiment where it was replaced by dimethyl malonate. The photolysis source was a pulsed TEA CO_2 laser (Lumonics K103) operating on the R(20) 10.25 μm line. For the majority of experiments an output pulse of energy 4.5 J was used which consisted of a spike of length 150 ns containing 25% of the total energy and a low intensity tail lasting some 3 μs. A NaCl lens was used to bring the laser output to a weak focus (diameter 2.5 mm) at the centre of the fluorescence cell, where the total fluence at the termination of the laser pulse was about 70 J cm^{-2}. For measurements at different fluences calibrated polyethylene sheets were used to attenuate the beam.

The CO_2 laser was crossed at right angles by the output of a pulsed N_2-pumped dye laser (Molectron DL200, band width 0.02 nm, pulse energy approximately 200 μJ in 7 ns), which was tuned to an absorption feature of the $\tilde{b}\ ^1B_1-\tilde{a}\ ^1A_1$ transition in CH_2 [10]. Two excitation wavelengths were used: 590.53 nm, corresponding to absorption in the Q branch head of the $\Sigma(0,14,0) \leftarrow (0,0,0)$ transition, and probing the 1_{11}, 2_{12} and 4_{14} rotational levels of $^1A_1$ CH_2; and 537.55 nm, the Q branch head of the $\Sigma(0,16,0) \leftarrow (0,0,0)$ transition, in which case the 1_{11}, 2_{12}, 3_{13} and 4_{14} rotational levels of the $^1A_1$ state were probed. The laser beam was arranged to be of slightly larger diameter (4.5 mm) than the CO_2 beam at the crossing point. Fluorescence was detected perpendicular to the plane of the two beams by a photo-
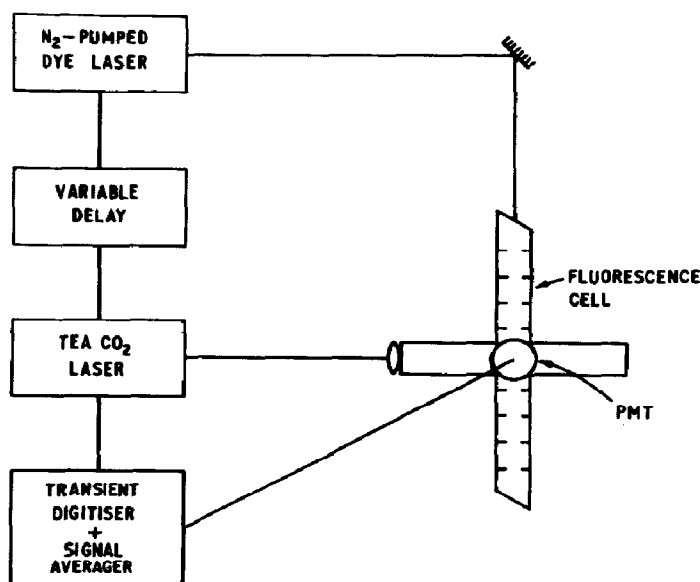

Fig. 1. A block diagram of the experimental arrangement.

multiplier (EMI 9558 or Mullard 56 AVP) and the resultant fluorescence decay signal was digitized with 10 ns resolution and was averaged for a preset number of CO_2 pulses. Scattered light from the dye laser was largely removed by baffles in the fluorescence cell arms, enabling the photomultiplier to view the interaction zone without cut-off or interference filters.

A time delay between the CO_2 laser output and the probing dye laser pulse was used to sample the relative fluorescence signals, proportional to the number of excited $^1B_1$ CH_2 radicals produced by the dye laser and hence proportional to the concentration of $^1A_1$ methylene radicals formed, as a function of time following the CO_2 pulse. For a given total pressure measured by a capacitance manometer and corresponding to a known premixed and equilibrated ratio of precursor-to-quenching gas, the decay rate of $^1CH_2$ radicals could thus be measured. The measurements were always commenced well after the end of the CO_2 laser pulse.

The acetic anhydride and dimethyl malonate were freeze–thaw cycled to remove dissolved air. Helium (B.O.C., 99.998%), argon (B.O.C., 99.996%), xenon (B.O.C. Research Grade, 99.997%), O_2 (B.O.C., 99.5%) and N_2 (B.O.C., 99.9%) were used without further purification.

3. Results

Mixtures of acetic anhydride and quenching gas in ratios varying from 1:100 to 1:2000 were found to give decay rates which were single exponential under all the conditions studied. For favourable fluorescence intensities, the decays were measured to times at which the signal had decreased by more than a factor of 100, and in all cases by at least a factor of 10. Care was taken to subtract background signals due to luminescence (the formation of electronically excited species with no dye laser present), caused predominantly by collisional dissociation following IR multiple photon absorption.

Figure 2 presents the measured decay rates of $^1CH_2$ in the presence of argon at pressures between 0.05 and 1.2 Torr. The open circles represent measurements with the dye laser set at 590.53 nm and at partial pressures of the acetic anhydride precursor between 0.5 and 2 mTorr. The lowest precursor pressure compatible with an adequate fluorescence signal-to-noise ratio was in general used, with the lowest precursor pressure employed at the lowest total pressure. The triangles represent excitation at 537.55 nm and with a constant partial pressure of 1mTorr acetic anhydride. In order to evaluate a quenching rate constant from data of this kind, it is important to allow for, or preferably to eliminate, effects of self quenching by the precursor molecule or its MPD products. If the partial pressure of precursor is kept constant, it is valid to identify the slope of a plot such as the triangles of Fig. 2 with the quenching rate constant of $^1CH_2$ by argon (and the intercept as containing a contribution from the quenching of $^1CH_2$ by the precursor) only if the self-quenching rate remains constant with argon pressure. This may not be so for an MPD process if the dissociation yield is
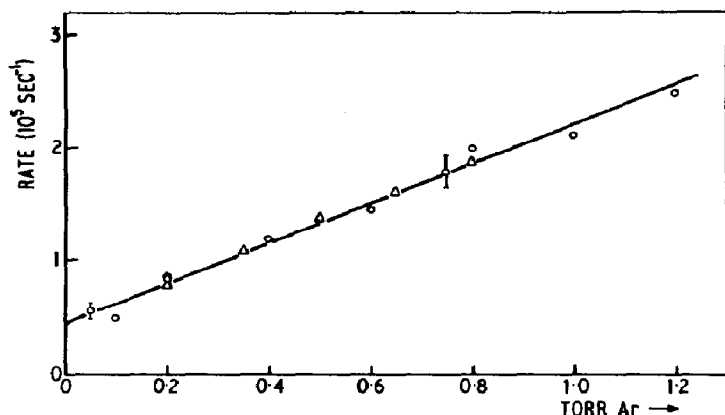
Fig. 2. Removal rates of $\tilde{a}\ ^1A_1$ CH_2 as a function of argon pressure. The circles and triangles represent excitation at two wavelengths as explained in the text. Representative error bars are shown for two of the points.

dependent on the total pressure (due to collisions during the absorption process), because the MPD products may quench $^1CH_2$ at rates which are different from the parent molecule if their yield is high. This possibility was eliminated in the present experiments by measuring the decay rates at different CO_2 laser fluences; although the absolute value of the fluorescence signal was reduced by an order of magnitude (indicating less dissociation) at lower fluence values than those normally used, the decay rates were identical to those at 70 J cm^{-2}. Furthermore, both the circles and the triangles of Fig. 2 lie on a single straight line, indicating no significant contribution to the overall decay rate by the precursor molecules in the range 0.5 to 2 mTorr (*e.g.* the almost indistinguishable circles at an argon pressure of 200 mTorr are for acetic anhydride pressures at precisely the limits of this range).

In previous kinetic measurements using MPD as a radical source, relatively high pressures (about 5 Torr) of argon were added to the reaction mixture to prevent diffusive loss of radical fragments out of the probing dye laser beam [8, 9]. Argon is effective in removing $^1CH_2$ in the present experiments, precluding its use at high pressure, and thus diffusive effects need to be carefully considered. Experimentally the observation of a linear decrease in decay rate with decreasing pressure, from the highest pressure used (1.2 Torr) to below 200 mTorr, would indicate that diffusive loss is small. The rate of this process was calculated from the measured sizes of the two laser beams, taken to be cylinders overlapping at right angles. The diffusive rates were in general not well represented by first order kinetics but their magnitudes showed that, within the time scales over which the measurements were made, their contribution to the overall decay rate would be less than 15% at 200 mTorr and negligible at higher pressures.

A single experiment was carried out to test the effect of changing the identity of the precursor molecule. Dimethyl malonate was found to produce $^1CH_2$ and the decay rate was measured for the MPD of 1 mTorr of this

precursor in 500 mTorr argon. Although the absolute fluorescence signal was smaller than that for the MPD of a mixture of 1 mTorr acetic anhydride in 500 mTorr argon, the decay rate was found to be identical.

All the measurements were carried out at room temperature (298 K). No apparent heating of the reaction mixture by degradation of absorbed IR radiation was observed; any effect of this kind would have been apparent in experiments at different fluences and at different precursor mixing ratios, where the amounts of absorbed energy were varied.

Figure 3 shows measured decay rates of $^1CH_2$ in the presence of helium. Excitation was at 590.53 nm and with partial pressures of acetic anhydride between 0.4 and 1.7 mTorr; no evident dependence on precursor pressure was seen. Significant contributions (greater than 10%) from diffusion to the measured rate were calculated to take place at pressures below 500 mTorr, although, as for argon, a linear decrease in decay rate was observed at lower pressures.

Table 1 lists the measured rate constants for argon and helium together with those for removal of $^1CH_2$ by xenon, N_2 and O_2, the latter three being measured at 1 mTorr precursor pressure and excitation at 590.53 nm. Diffusion problems for these gases were of less significance than for helium or argon because of larger removal rates by quenching at lower pressures. For O_2 the larger errors reflect more scatter in the data, caused by considerable luminescence present at short delays following the CO_2 pulse.

4. Discussion

Table 1 compares data from the present study with the previous direct measurements of $^1CH_2$ kinetics [1], and also lists relative rate constants for comparison with previous studies [2 - 4, 11]. Although the relative values are seen to be in reasonable agreement with those previously measured, the absolute rate constants for $^1CH_2$ removal by helium, argon and N_2 are almost
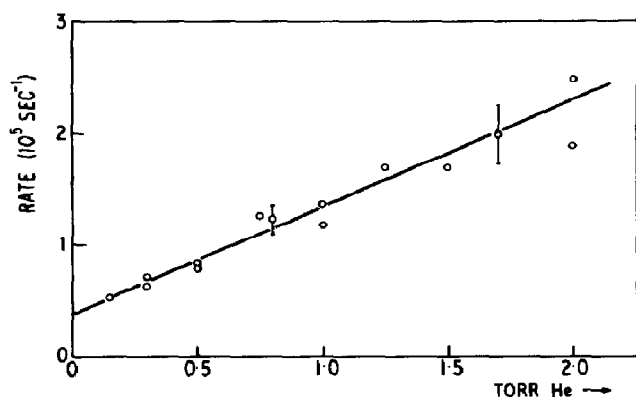

Fig. 3. Removal rates of ã $^1A_1$ CH$_2$ in the presence of helium. Representative error bars are shown for two of the points.

TABLE 1

Rate constants for removal of $\tilde{a}\ ^1A_1\ CH_2$

Added gas	$k \times 10^{12}$ (cm³ molecule⁻¹ s⁻¹)		Relative rate constants[a]					
	This work	Ref. 1	This work	Ref. 1	Ref. 4	Ref. 2	Ref. 11	Ref. 3
Helium	2.8 ± 0.3	0.3	1.0	1.0	1.0	1.0	1.0	–
Argon	5.6 ± 0.5	0.67	2.0	2.2	–	3.0	0.8	2.0
Xenon	16 ± 2	–	5.7	–	–	4.7	4.1	4.5
N_2	7.9 ± 0.3	0.9	2.8	3.0	–	–	2.9	1.25
O_2	27 ± 4	–	9.6	–	<100	–	–	10

[a]The relative rates are scaled to unity for quenching by helium except for the data from ref. 3 which are scaled to 2.0 for quenching by argon.

an order of magnitude faster than those reported from the flash photolysis study. Before considering a comparison of these sets of data, the various relaxation mechanisms which can influence the observed removal rates will be discussed.

In the cases where chemically reactive removal processes are absent (such as for quenching by the rare gases and very probably by N_2), clearly the eventual collisional fate of the $^1CH_2$ radicals is conversion to the ground $^3B_1$ state. If the individual quantized levels of the $^1A_1$ and $^3B_1$ states are considered to be isolated in the absence of collision (*i.e.* if intramolecular perturbations between singlet and triplet states are neglected), then three separate collisional steps need to be considered in the kinetic scheme, namely, relaxation within the initially produced $^1CH_2$ manifold, collisional intersystem crossing from $^1A_1 \rightarrow ^3B_1$ and collisional relaxation within $^3B_1$.

Vibrational relaxation within $^1A_1$ CH_2 should have little effect on the observed kinetics because of the nature of the IR MPD process forming the radicals. By analogy with previous measurements of internal energies of various fragments of MPD processes, the vibrational distribution of $^1CH_2$ is expected to be Boltzmann at temperatures in the range 500 - 1000 K [12], implying that less than 15% of the molecules will be formed in levels other than the ground vibrational state. This is an important feature of the MPD process compared with dissociation by single photon absorption, in that the former will in general produce fragments with much lower average internal energies characterized by a vibrational temperature in contrast with the non-thermal distribution often found for the latter process. Rotational relaxation of the initially formed $^1CH_2$ is expected to be rapid, but its influence on the present measurements is difficult to assess. The lack of dependence of the argon relaxation rate on the slightly different compositions of the probed levels excited at 537.55 and 590.53 nm indicates that no overwhelming rotational effect is of importance. On simple momentum transfer grounds the relative efficiencies for the rotational relaxation of hydrogen-containing molecules by rare gases is expected to be more efficient with helium than with argon or xenon, the opposite effect to that observed here [13]. Although this would suggest that the present measurements are not influenced by rotational relaxation, direct evidence for this would require observation of the relaxation of the individual $^1CH_2$ rotational levels.

If relaxation within the $^1A_1$ state can be neglected, then the simple 'isolated state' scheme would interpret the observed single exponential decay rates, and their linear dependence on pressure, as arising from the rate determining step in the sequence of collision-induced $^1A_1 \rightarrow ^3B_1$ crossing and collisional relaxation of the $^3B_1$ states formed. Previous studies have favoured the former step as rate determining [2, 11], arguing that the relative removal efficiencies of $^1CH_2$ by the rare gases, similar to those observed here, are in the opposite order to that expected for vibrational de-excitation on the distorted wave approximation. However, some experimental evidence has been reported which suggests that vibrational de-excitation of CH_3 occurs faster with argon

than with helium [14], observations which make the identification of the rate determining step for the present results less distinct.

The possibilities outlined assume that the singlet and triplet states contain essentially pure rovibronic levels. If mixing of the states is considered, then the observed relaxation rates take on a different mechanistic interpretation. Freed and his coworkers have discussed examples of this kind and, specifically for $^1CH_2$, have shown that the observed de-excitation rates can contain contributions from both intramolecular mixing coefficients and vibrational relaxation rates [15]. If the mixing depends on the rotational state then this could affect the relaxation rate of the individual levels and should be experimentally observable.

Finally, chemical reaction needs to be considered in the case of quenching by O_2. The rapid rate observed compared with that for N_2 suggests that one or more of the several possible exothermic chemical reactions may be taking place, for example the (spin forbidden) formation of $CO + H_2O$ or $H_2 + CO_2$, or the less exothermic routes to form free radical products.

The present data are clearly insufficient to determine which of these features contribute most to the observed removal rates. Further work is in progress to extend the range of quenching gases, to examine the behaviour of the individual rotational levels of $^1CH_2$ and to search for the $^1CD_2$ radical and measure its removal rates in an attempt to clarify the interpretation. However, the discrepancy between the present results and those of Braun et al. [1] can be considered. The latter study relied on the spectral observation of ground state $^3B_1$ CH_2 for the kinetic measurements, and relaxation within the triplet manifold to the observed levels (presumably the ground vibrational $^3B_1$ state) could have been the rate determining step, and thus slower than the rates measured in the present work. The almost identical relative rates observed for quenching by the gases common to the two studies, helium, argon and N_2, would at first suggest that the rate determining step in both cases is relaxation within the triplet manifold, with the difference in absolute values simply reflecting relaxation within high (present study) and low (Braun et al.) vibrational levels of $^3B_1$ CH_2. However, the trend in the rates with the mass of the rare gases is not explained by this possibility. Reasonable agreement between most of the previously reported relative removal rates and the present results (Table 1) are to be expected as the relative values were based on competitive removal processes for $^1CH_2$.

In their study of the $^1A_1$–$^3B_1$ CH_2 splitting, Lengel and Zare estimated a rate constant of 4×10^{-10} cm^3 molecule^{-1} s^{-1} for the removal of $^1CH_2$ by CH_2CO, measured by laser-induced fluorescence at a single pressure of ketene [6]. If the previous value for the rate of $^1CH_2$ removal by the reaction

$$^1CH_2 + CH_2CO \rightarrow C_2H_4 + CO \tag{1}$$

relative to $^1CH_2$ removal by helium [4] is combined with the present absolute rate constant for helium, k_1 is found to be 3×10^{-10} cm^3 molecule^{-1} s^{-1}, a value which suggests that reaction (1) is the predominant mechanism for $^1CH_2$ removal by ketene.

Two further points from the present study need to be made. (1) $^1CH_2$ is undoubtedly not the only MPD product; in particular $^3B_1$ CH_2 will be present in an unknown concentration and could affect the interpretation of the results. (2) No explanation is given of the clear intercept at zero pressure of the quenching gas in Figs. 2 and 3 which is observed in all the quenching experiments. Possible effects due to diffusion, to interference by quenching by the parent molecule and to any truly first order singlet–triplet crossing rate are under investigation.

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