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Rate Constant for Reaction of CH (X $^2\Pi$) with Ketene

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A bimolecular rate constant for the reactive removal of CH (X $^2\Pi$) by ketene (CH_2CO) has been measured under pseudo-first-order conditions using multiphoton dissociation of CH_2CO at 308 nm to generate the radicals and laser induced fluorescence to detect them. A value of $(2.4 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} was obtained at room temperature (295 $\pm$ 2 K).

The CH radical is of considerable importance as a reactive intermediate in a wide variety of complex reaction schemes including, in particular, hydrocarbon combustion processes.[1] Despite the typically low concentrations of CH the radical plays a key role in the chemi-ionisation of hydrocarbon flames,[2] the generation of chemiluminescence[3] or as the precursor of soot particles.[4] The published data for the kinetics of CH with a range of hydrocarbon and inorganic species have recently been reviewed by Sanders and Lin.[5] Knowledge of the reactions of CH is also important for the modelling of reaction schemes initiated by photolysis of a suitable precursor molecule. One of these schemes involves the photolysis of ketene at 308 nm,[6] and production of CH was included as a result of secondary reactions involving the species CH_2 ($\tilde{a}\,^1A_1$) and CO, the products of the single-photon dissociation of ketene at this wavelength. We have recently shown that CH is itself a direct photolysis product in the multiphoton dissociation of CH_2CO in the near UV, as has been widely demonstrated to be the case for other precursor molecules in previous measurements of CH kinetics, where multiphoton dissociation of $CHBr_3$ at 193 nm[7] and 266 nm,[8] CH_2Br_2 and $CHClBr_2$ at 248 nm[9] or CH_3I at 193 nm[10] have all been used as sources of the CH radical. Here the rate constant for the total removal of CH by CH_2CO [reaction (1)] is reported for the first time,

$$CH + CH_2CO \xrightarrow{\;k_{CH}\;} \text{products} \qquad (1)$$
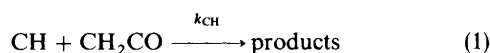
as part of a wider study into the multiphoton dissociation of ketene.

Experimental

A conventional pulsed UV laser photolysis–laser-induced fluorescence (LIF) technique was used for the kinetic measurements, with time resolution provided by sequentially altering the delay between photolysis and probe lasers using a home-built pulse delay generator. The CH radicals were generated in the X $^2\Pi$ electronic ground state by two-photon dissociation of CH_2CO in the pressure range 20–60 mTorr,† using the output of an XeCl excimer laser at 308 nm (Questek 2240, 20 ns pulse width, energy 20 mJ pulse^{-1}). The excimer beam was focused, with a 30 cm focal length quartz lens, to a beam diameter of 4 mm at the centre of a blackened, cubic stainless-steel reaction cell. Excitation radiation to monitor the CH radical concentration by LIF in the A $^2\Delta$–X $^2\Pi$ band system was provided by the output of a nitrogen laser-pumped dye laser system (Molectron UV14/DL200,

maximum energy 20 μJ pulse^{-1}) operating with a solution of stilbene 3 dye. A check on the linearity of LIF signal with probe laser intensity was performed to confirm that there was no saturation of transitions. To eliminate problems of scattered light the probe laser beam was collimated and passed into the cell through long arms containing a series of baffle rings of varying aperture[11] and with Brewster-angled entrance and exit windows.

The undispersed fluorescence was collected on-resonance to the excitation transition through a Schott interference filter centred at 430 nm by a photomultiplier tube (EMI 9813QKB) positioned perpendicular to the intersection of the photolysis and probe laser beams. Further lenses and baffle rings between the fluorescence-scattering region and the detector ensured that the photomultiplier tube (PMT) observed the LIF signal in preference to other scattered light. The output of the PMT was averaged over typically 20 laser shots using a 20 MHz Thurlby DSA 524 digital storage adaptor. The signal could be displayed directly on an oscilloscope or taken to a personal computer. The lasers were operated at a repetition rate of 10 Hz.

Most experiments were carried out on a static sample of a fixed pressure of CH_2CO only, at an ambient temperature of 295 $\pm$ 2 K although, as mentioned below, in some cases Ar was added to the precursor. Pressures were measured using a Datametrics 0–10 Torr capacitance manometer. Ketene was prepared by the pyrolysis of acetone[12] and purified, first by multiple trap-to-trap distillations between liquid nitrogen and dry ice–trichloroethylene slush baths, and then by pumping on the sample in a liquid nitrogen–isopentane cooled trap at 113 K. Product purity was confirmed quantitatively by taking both a mass spectrum and a UV absorption spectrum between 200 and 400 nm.[13] The ketene was stored in a darkened bulb at low pressure during experiments to prevent polymerisation.

Results and Discussion

The relative CH (X $^2\Pi$) concentrations were obtained by tuning the probe laser wavelength to give the maximum LIF signal at the Q branch head of the A $^2\Delta$–X $^2\Pi$ (0, 0) band at 431.3 nm.[14] Probe delays of <5 μs were not used in these experiments owing to the production of large amounts of spontaneous fluorescence on photolysis, in excess of the magnitude of the LIF signal being detected following excitation at the Q branch head. A spectrum of the dispersed spontaneous fluorescence showed it to be emission from the B $^2\Sigma^-$ and A $^2\Delta$ excited electronic states of CH formed additionally in the multiphoton dissociation of CH_2CO at 308 nm. Consideration of thermodynamic data indicates that while production of the X $^2\Pi$ ground state of CH is an energetically

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† 1 Torr = (101 325/760) Pa.

allowed two-photon process (consistent with the observation of a quadratic dependence of the LIF signal on photolysis laser intensity), absorption of more than two photons at 308 nm is required to yield electronically excited CH.

All kinetic data were rcorded under pseudo-first-order conditions since the concentration of CH produced in the two-photon process is small, and certainly lower than for single-photon absorption where calculation shows that <2% of CH_2CO is dissociated per shot in the focal volume under these conditions. An exponential decay in the LIF signal (over a range of at least two to three decay lifetimes) was always observed for all times >5 μs from photolysis. The experimental first-order decay rates, k_{1st}, were obtained from the least-squares linear fit to a semi-logarithmic plot of the data at each fixed ketene pressure in the range 20–60 mTorr. The bimolecular rate constant, k_{CH}, for reaction (1) was extracted in the standard way from the definition of the experimental pseudo-first-order decay rate, $k_{1st} = k_{CH}[CH_2CO]$, and a plot of k_{1st} against pressure of CH_2CO is shown in Fig. 1. The slope of this plot gives a value of $(2.4 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the rate constant of removal of CH by CH_2CO. The quoted range represents an estimate for the total errors associated with the measurement and is slightly greater than ± 1 σ statistical uncertainty obtained from the fit to the first-order plot.

At the low total gas pressures used in these experiments, the competing removal process of diffusion of the CH radical out of the detection zone must be considered. The chemical removal of CH by CH_2CO is extremely fast and application of diffusion equations for the experimental geometry shows that corrections need only be applied to small signals at the tail of the exponential decays. The good fits of the observed decays to first-order kinetics, the increase in the values of k_{1st} with ketene pressure, and the observation that an extrapolation of the line through the data in Fig. 1 essentially intercepts the origin all indicate that diffusion of CH or other removal processes do not contribute to loss of CH under the experimental conditions employed. This was confirmed by carrying out a single experiment at 20 mTorr CH_2CO to which 5 Torr Ar was added, and as can be seen from the value of the first-order decay rate extracted and shown on Fig. 1, the value was in good agreement with that measured for removal in the presence of ketene alone. This result also shows that the effect of collisional cascading of the nascent CH (X$^2\Pi$) quantum-state distribution into levels probed at the Q branch head does not affect the measured rate con-
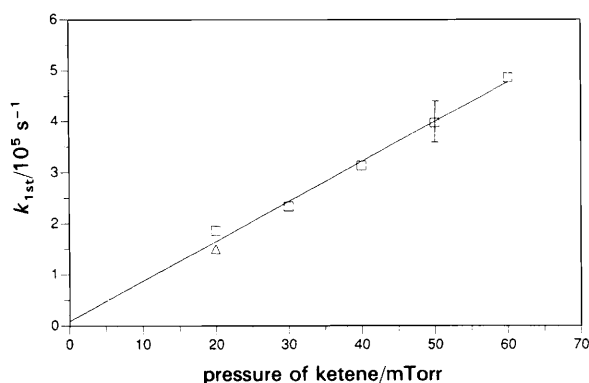
stant. The initial distribution in $v = 0$ can be represented by a temperature of ca. 1200 K (no $v = 1$ is observed) and estimates of the rotational relaxation rate with Ar showed that even for the highest levels observed ($N = 12$) quenching in the presence of 5 Torr Ar would be complete in the 5 μs before observations were started. This rapid rotational relaxation is, however, accompanied by marked changes in Λ doublet population ratios for a given value of N, and will be reported elsewhere.

The use of an excess of inert gas in this experiment also resulted in a non-exponential behaviour in the temporal profile of CH at long times (after ca. 3–4 decay lifetimes). In addition to the chemical removal after photolysis, a slower subsidiary formation of CH was observed with a plateau at ca. 50 μs and a maximum concentration ca. 15 times lower than that produced directly on photolysis. The CH signal in the 'tail' was detectable up to several hundred μs after the photolysis pulse and is attributed to the production of CH from a secondary chemical source that does not operate in the absence of Ar. The methylene radical is the product of the single-photon dissociation of CH_2CO and at 308 nm is produced almost entirely in its first excited singlet electronic state, $^1CH_2$ (ã $^1A_1$).[15,16] The presence of 5 Torr Ar rapidly quenches $^1CH_2$ to the nearby triplet electronic ground state $^3CH_2$ (X̃ $^3B_1$) by collision-induced intersystem crossing.[17] This radical is relatively long lived under these conditions and its primary removal pathway is the recombination reaction,[18]

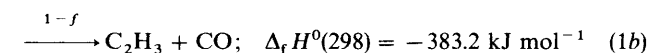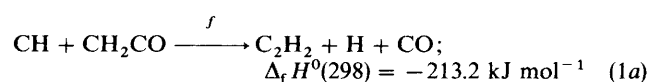$$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + 2H;$$
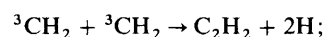
$$k = 5.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (2)$$

giving hydrogen atoms as opposed to molecular hydrogen as the major product.[19] Subsequent reaction of H atoms produced in reaction (2), or possibly directly by multiphoton dissociation of ketene, with further $^3CH_2$ may be responsible for the formation of CH by the process,[20]

$$^3CH_2 + H \rightarrow CH + H_2;$$
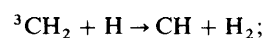
$$k = 2.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (3)$$

No measured value for k_{CH} has previously been reported in the literature, but rate constants for the reaction of CH (X$^2\Pi$) with a wide variety of other hydrocarbon and inorganic species have been determined.[5] The rate constants are generally very fast, approaching gas-kinetic efficiencies for saturated and unsaturated hydrocarbons and formaldehyde. The value of 2.4×10^{-10} cm^3 molecule^{-1} s^{-1} obtained in the present work for the reaction of CH with CH_2CO corresponds to a collision efficiency of ca. 0.6 and the rate constant may be compared to values of $(3.7 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the reaction with H_2CO,[21] or values of $(1.15 \pm 0.15) \times 10^{-10}$,[22] $(2.1 \pm 0.8) \times 10^{-10}$,[23] or $(4.2 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1},[24] for total reaction with C_2H_4. Reaction of CH can take place by insertion into a C—H bond or by addition to the unsaturated C—C π bond.[5] An addition reaction to ketene would result in a very strained three-carbon ketonic ring, so insertion to give $H_2\dot{C}$—CH=C=O is the preferred intermediate. This will dissociate to yield the following overall pathways,[25,26]

Fig. 1 First-order decay rates k_{1st}, at 295 K for the removal of CH by CH_2CO, as a function of CH_2CO pressure; (□), in the presence of CH_2CO only; (△), with the addition of 5 Torr Ar. A representative error bar is shown on the 50 mTorr data. All decay rates were measured at the Q branch head of the A $^2\Delta$–X $^2\Pi$ band near 431.3 nm. The solid line corresponds to a bimolecular rate constant, k_{CH}, of 2.4×10^{-10} cm^3 molecule^{-1} s^{-1}

$$CH + CH_2CO \xrightarrow{f} C_2H_2 + H + CO;$$
$$\Delta_f H^0(298) = -213.2 \text{ kJ mol}^{-1} \quad (1a)$$

$$\xrightarrow{1-f} C_2H_3 + CO; \quad \Delta_f H^0(298) = -383.2 \text{ kJ mol}^{-1} \quad (1b)$$

The enthalpy of reaction in both cases is highly exothermic and it may be expected that both pathways will be competi-

tive channels in the reaction. Since the total removal rate is of the order of gas collision efficiency it is likely that there is little or no activation energy for these pathways. Canosa-Mas et al.[6a] have included the above reactions in an extensive kinetic scheme, modelling the observed end products from the pulsed photolysis of ketene at 308 nm. An overall rate constant of 2.1×10^{-10} cm^3 molecule^{-1} s^{-1} for reaction of CH with CH$_2$CO has been determined indirectly by these workers, a value which is in extremely close agreement with that reported here. Further modelling studies[19] yield a refined branching ratio of $f = 0.85$ for the pathway leading to acetylene as a product.

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