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Short Communication

The formation of CH radicals during the photolysis of CH_2N_2 in the presence of hydrogen and oxygen atoms

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1. *Introduction*

The methylidyne radical CH has been found to be an important intermediate in hydrocarbon combustion. It leads to chemi-ionization [1, 2] and OH^* chemiluminescence [3, 4]. Two radicals, CH_2 and C_2O, have so far been proposed as possible precursors for CH radicals occurring in hydrocarbon flames. Reactions of CH_2 with oxygen atoms [5], OH [6], and hydrogen atoms [6] have been suggested as sources of CH radicals:

$$CH_2 + O \longrightarrow CH + OH \qquad (1)$$

$$\Delta H = -8 \text{ kJ mol}^{-1}$$

$$CH_2 + OH \longrightarrow CH + H_2O \qquad (2)$$

$$\Delta H = -79 \text{ kJ mol}^{-1}$$

$$CH_2 + H \longrightarrow CH + H_2 \qquad (3)$$

$$\Delta H = -15 \text{ kJ mol}^{-1}$$

Of these, reaction (3) has been supported by Homann and coworkers [7, 8] in their low pressure C_2H_2 + O flame studies.

In contrast, C_2O radicals were first suggested as the precursor for the vacuum UV chemiluminescence of CO^* in the C_3O_2 + O and C_2H_2 + O systems [9], and later they were also proposed as the precursor for CH radicals in the CH_2CO + O + H, C_2H_2 + O + H and C_3O_2 + O + H systems [10, 11]:

$$C_2O + H \longrightarrow CH + CO \qquad (4)$$

$$\Delta H = -107 \text{ kJ mol}^{-1}$$

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The predominant formation of CD radicals in the C_2H_2 + O + D system [12] suggests that the CH radical precursor may not contain hydrogen atoms, which is consistent with reaction (4). Recently, C_2O radicals have been identified by means of laser-induced fluorescence in the C_3O_2 + O system [13] and in the C_2H_2 + O system [14]. The overall rate constant for the reaction of C_2O with hydrogen atoms has been determined as $(3.7 \pm 1.0) \times 10^{-11}$ cm^3 s^{-1} [15]. CH and CO are the most probable products of this reaction.

On the basis of the assumption that the photolysis of CH_2N_2 generates CH_2, it was examined whether CH_2N_2 photolysis would give CH in the presence of hydrogen atoms.

2. *Experimental details*

The measurements were carried out at room temperature under a total pressure of 1.5 Torr in argon using a discharge flow apparatus similar to that used in a previous study [16]. A photolysis unit and a cell were coupled to it for observing $CH(X\,^2\Pi)$ radicals by laser-induced fluorescence. CH_2N_2, diluted with argon to a ratio of 1:20 and stored in a wax-coated 20 l flask, was passed through a capillary and introduced into the observation cell, after a further dilution with the argon carrier gas to a ratio of 1:40. A quartz tube section 15 cm in length was provided about 20 cm upstream of the cell for the photolysis of CH_2N_2. Hydrogen and oxygen atoms were generated by microwave discharges in H_2–Ar and CO_2–Ar mixtures respectively in separate flow tubes and mixed with the CH_2N_2–Ar mixture in the cell. The atom concentrations were calibrated by titration with NO_2.

The laser-induced fluorescence of CH radicals was excited in the wavelength range 425 - 435 nm by a pulsed dye laser pumped by an N_2 laser [16]. The fluorescence signal was monitored at right angles to the dye laser beam through a bandpass filter centred at 430 nm by a photomultiplier (1P28) and processed by a boxcar integrator. The relative CH concentration was determined from the integrated intensity of the Q branch of the $A\,^2\Delta \rightarrow X\,^2\Pi$ (0, 0) transition at 431.5 nm.

A high pressure mercury lamp (Osram HBO 350 W) was used for the photolysis of CH_2N_2. The spectral distribution of the lamp output showed a continuum extending from the UV to the IR region with a uniform intensity in addition to broadened mercury lines. This covered most of the absorption of CH_2N_2 [17]. The lamp continuously irradiated the quartz section; both the lamp and the quartz section were surrounded by a cylindrical aluminium reflector.

CH_2N_2 was prepared by the alkaline decomposition of nitrosomethylurea, using bicyclo[4.4.0]decane (decalin) as the CH_2N_2 absorber [18]. After the decalin–CH_2N_2 solution cooled to -196 °C had been thoroughly degassed, CH_2N_2 was carefully transferred to a cold trap maintained at -196 °C and was purified by several trap-to-trap distillations. The purity of the final CH_2N_2 sample was about 95%. The residue consisted mainly of C_2H_4. Argon (purity, 99.97%), hydrogen (purity, 99.99%) and CO_2 (purity, 99.995%) were used as received.

3. *Results and discussion*

When CH_2N_2 at a pressure of 9 mTorr and hydrogen atoms at a pressure of 10 mTorr were reacted the characteristic CH fluorescence was observed even without photolysis. The relative CH concentration was about 5% of that observed in the reference system C_2H_2(1 mTorr) + O(5 mTorr) + H(10 mTorr). The effect of the photolysis of CH_2N_2 on the CH concentration was examined in the CH_2N_2 + H system, and the results are shown in Fig. 1. Under the irradiation, the CH radical concentration decreased steadily with the nominal output of the photolysis lamp.

It is generally accepted that the photolysis of CH_2N_2 yields CH_2 radicals in the first excited singlet state ($\tilde{a}\ ^1A_1$) over a wide wavelength range [19, 20]. The singlet CH_2 is either collisionally quenched by argon to $CH_2(\tilde{X}\ ^3B_1)$ with a rate constant of about 6×10^{-12} cm^3 s^{-1} [21, 22] or depleted in the reaction with CH_2N_2 to form C_2H_4 and N_2 for which a rate constant of 3.1×10^{-11} cm^3 s^{-1} has been reported [19]. Under typical conditions, the average flow time of the CH_2N_2–Ar mixture between the photolysis section and the cell was about 5 ms. Thus, about 90% of the $CH_2(^1A_1)$ radicals are expected to be converted to ground state CH_2 before reaching the reaction zone in the cell. The rate constant for the reaction $CH_2(^3B_1)$ + CH_2N_2 has been reported to be about 60 - 70 times larger [19] than that for the reaction with CH_2CO, for which $k \approx 10^{-17}$ cm^3 s^{-1} [23, 24] has been given. Most of the $CH_2(^3B_1)$ radicals very probably reach the observation zone without depletion by reaction with CH_2N_2. Therefore if CH radicals are formed in the reaction of $CH_2(^3B_1)$ with hydrogen atoms (reaction (3)) the CH concentration should increase with increases in the lamp output. The decrease in the CH concentration with the photolysis power (Fig. 1) should be interpreted as a result of the decrease in the CH_2N_2 concentration from which CH radicals are directly produced without irradiation.

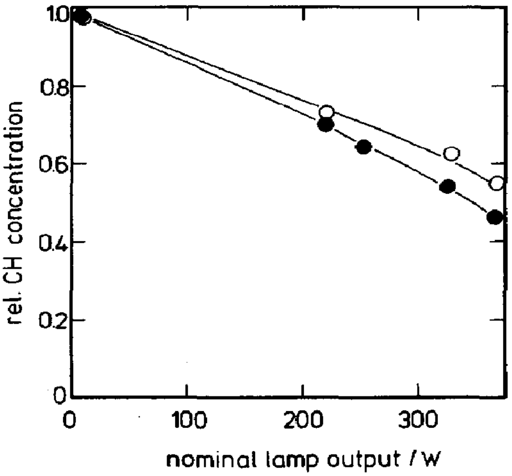

Fig. 1. The dependence of the relative CH concentration on the intensity of the CH_2N_2 photolysis (total pressure, 1.5 Torr; CH_2N_2 pressure, 9 mTorr): ○, CH_2N_2 + H system (hydrogen atom pressure, 10 mTorr); ●, CH_2N_2 + O system (oxygen atom pressure, 5 mTorr).

Additional experiments with oxygen atoms instead of hydrogen atoms and in the presence of both hydrogen and oxygen atoms were carried out under similar conditions. With oxygen atoms at a pressure of 5 mTorr the relative concentration of CH radicals was about five times that observed in the CH_2N_2 + H system. The effect of the photolysis in this case was found to be similar to the results observed in the CH_2N_2 + H system as shown in Fig. 1. It was found that the CH concentration produced from CH_2N_2 in the presence of both hydrogen and oxygen atoms was equal to the sum of the CH concentrations produced separately in the CH_2N_2 + H and CH_2N_2 + O systems.

In the absence of irradiation, CH radicals may be formed by the following primary steps:

$$CH_2N_2 + H \longrightarrow CH + N_2 + H_2 \tag{5}$$

$$CH_2N_2 + O \longrightarrow CH + N_2 + OH \tag{6}$$

The occurrence of these reactions depends strongly on the heat of formation of CH_2N_2 for which a large uncertainty seems to exist, ranging from 167 to 420 kJ mol^{-1} [25]. With values $\Delta H_f°(CH_2N_2) \geqslant 375$ kJ mol^{-1} and $\Delta H_f°(CH_2N_2) \geqslant 383$ kJ mol^{-1} respectively, reactions (5) and (6) become exothermic. A further possibility could be the formation of CH radicals via energy transfer reactions involving metastable Ar($^3P_{0,2}$) atoms [26]. However, it is quite unlikely that metastable argon atoms reach the reaction zone in the presence of H–H_2 or O–O_2 mixtures.

In conclusion, the formation of CH radicals in the CH_2N_2 + H system during irradiation with a mercury lamp is explained by hydrogen atom reactions with CH_2N_2. The decrease in the CH concentration during the photolysis is attributed to be a depletion of CH_2N_2. No indication was found that CH_2 as a photolysis product of CH_2N_2 forms CH radicals by reaction with hydrogen atoms. Because a depletion of CH_2N_2 was clearly observed, the photolysis yield should have been sufficiently large to show any possible CH production from CH_2 + H in addition to the CH formation from CH_2N_2 + H without irradiation. The conclusion, however, is based on the argument that CH_2 radicals have not been depleted in the reaction zone by uncontrolled fast removal processes.

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