Kinetic Investigation of the $CH_2(\tilde{X}^3B_1) + H \rightarrow CH(X^2\Pi) + H_2$ Reaction in the Temperature Range 400 K < T < 1000 K

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650, and 950 K, p = 2 Torr) as well as in C₂H₂/O systems (T = 590 and 890 K, p = 4 Torr) using dischargeflow/molecular beam sampling mass spectrometry techniques (D-F/MBMS). The first rate coefficient data at temperatures intermediate between room and flame temperature are presented. The $CH_2(\bar{X}^3B_1) + H$ rate constant was measured relative to the well-known $k(CH_2(\tilde{X}^3B_1) + O) = (1.3 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} from the change of the quasi-steady state CH₂ concentration upon varying the [H]/[O] ratio at given CH₂ formation rate. In the temperature range of interest, the k_1 coefficient was found to exhibit a clear-cut negative temperature dependence. The following k_1 values were obtained: (i) using the CH₂CO + O reaction as CH₂ source, $(2.93 \pm 0.80) \times 10^{-10}$ at 400 K, $(2.05 \pm 0.57) \times 10^{-10}$ at 500 K, $(1.22 \pm 0.31) \times 10^{-10}$ at 650 K, and $(1.18 \pm 0.32) \times 10^{-10}$ at 950 K; (ii) using the C₂H₂ + O system as CH₂ source, $(1.90 \pm 0.58) \times 10^{-10}$ at 590 K and $(1.12 \pm 0.36) \times 10^{-10}$ at 890 K (k in cm³ molecule⁻¹ s⁻¹; 95% confidence intervals, including possible systematic errors). The data obtained with the two CH_2 sources are in good mutual agreement. The decrease of k_1 with temperature is in accord with literature k_1 data at room temperature on one side and in the 1500-2500 K range on the other. However, the observed temperature dependence in the 300-1000 K range is much less steep than predicted by the recommended $k_1(T)$ expression in a recent evaluation.⁴⁴ An equation that fits all available data reasonably well is $k_1 = 3.8 \times 10^{-10} \exp \left[-1.3 \times 10^{-3} T (\text{K})\right] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, for T = 300 - 2500 K.

Introduction

The reaction of triplet methylene with H atoms

$$CH_2(\tilde{X}^3B_1) + H \rightarrow CH(X^2\Pi) + H_2$$
(1)

has been proposed as major source of CH(${}^{2}\Pi$) radicals¹⁻³ in fossil-fuel combustion processes. Owing to their ability of insertion into σ -bonds and cyclo-addition into π -bonds, CH-(${}^{2}\Pi$) radicals are of key importance for the formation of higher unsaturated hydrocarbons and PAH's. Other unusual properties of these extremely reactive CH(${}^{2}\Pi$) radicals are their capability to form chemi-ions by their reaction with oxygen atoms^{1,4} and their ability to convert molecular nitrogen into NO.^{5,6}

Reaction 1 is also of particular interest from a more fundamental point of view due to its nature as a radical-radical association/elimination reaction. The reaction most probably proceeds via a vibrationally excited CH_3^+ combination adduct which rapidly dissociates exoergically into $CH(^2\Pi)$ and H_2 .⁷ Collisional stabilization of the CH_3^+ adduct can become important only in conditions of high pressure and low temperature.

$$CH_{2}(^{3}B_{1}) + H \longrightarrow CH_{3}^{\dagger} \longrightarrow CH(^{2}\Pi) + H_{2} \qquad \Delta H_{r,0} = -3.0 \pm 0.5 \text{ kcal/mo}$$

$$\downarrow^{M}_{r,0}$$

$$CH_{3}(^{2}A_{2}'')$$

Several measurements of the rate constant k_1 have been made at room temperature, all agreeing that reaction 1 is very fast. Böhland et al.³ studied the CH₂(³B₁) + H reaction, applying laser magnetic resonance detection of both CH₂(³B₁) and CH-(²Π). They first measured a k_1 value of $(2.7 \pm 1.0) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at 290 K,^{3a} using the CH₂CO + O reaction with HCCO, which is another primary photoproduct of the 193 nm photolysis of ketene.^{8,9} Langhans⁸ obtained a k_1 value of $(3.1 \pm 1.4) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at 290 K from relative CH₂ concentration vs time profiles in C₂H₂/O/H systems measured by molecular beam sampling mass spectrometry. In a more recent MBMS study of C₂H₂/O systems, Boullart and Peeters¹⁰ measured the rate constant of the CH₂(³B₁) + H reaction relative to the known $k(CH_2(^3B_1) + O)$ and obtained a k_1 value of $(2.7 \pm 1.0) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at 290 K. On the other hand, investigations in the high-temperature range (T > 1500 K) all resulted in a k_1 value about 10–20 times smaller than that at room temperature. By fitting [H] profiles in shock-heated acetylene/oxygen mixtures at 1500– 2570 K, Löhr and Roth¹¹ derived a k_1 value of 5×10^{-11} cm³

as CH₂ source. A later redetermination,^{3b} where CH₂ was

generated by 193 nm ketene photolysis, led to a value of (1.8

 \pm 0.5) \times 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ which is probably somewhat too low because of regeneration of CH₂ via reaction of H atoms

molecule⁻¹ s⁻¹. Frank et al.¹² derived a rate constant of 1.3×10^{-11} cm³ molecule⁻¹ s⁻¹ for the CH₂(³B₁) + H reaction at $T \sim 2400$ K from the evolution of [H] in the thermal decomposition of ketene. From MBMS studies of methane and ethylene flames Peeters and Vinckier¹ estimated a k_1 value of $\sim 1.7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at $T \sim 2000$ K.

The unusual difference between the reported k_1 values at room and flame temperatures implies a surprisingly strong negative temperature dependence for this reaction. A theoretical RRKM study carried out by Hauchecorne¹³ predicts that k_1 diminishes only by a factor of 3–5 when the temperature increases from 300 to 2000 K. A rather weak negative T dependence of k_1 was also computed by Wagner.¹⁴

The principal objective of the present investigation is to determine the rate constant of the $CH_2({}^{3}B_1) + H$ reaction in the intermediate temperature range 400 K < T < 1000 K where

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data are lacking so far. Two distinct sources of triplet methylene radicals will be used: (i) the $CH_2CO + O$ reaction and (ii) the $C_2H_2 + O$ reaction.

Experimental Section

The discharge-flow/molecular beam sampling mass spectrometry technique (D-F/MBMS) applied in this work has been described previously;^{15,16} only a brief summary will be presented here.

The flow reactor consists of a cylindrical quartz tube (i.d. =16.5 mm) equipped with a discharge side arm, an axially movable central injector tube, and an additional side inlet to admit carrier gas. The reactor is treated with a 10% HF solution to suppress radical loss on the reactor walls. Oxygen atoms were generated by passing a flow of O₂ (400,500 K) or N₂O (590,650,890,950 K) diluted in He through a microwave discharge. C₂H₂ or CH₂CO, also diluted in He, was added through the central injector. The advantage of using N2O rather than O₂ as oxygen atom source is that at a dissipated power of 75 W the N₂O \rightarrow N₂ + O dissociation is nearly complete (~98%) in our conditions, while the O_2 dissociation yield is only about 15%. The N₂O source does not give NO or other potentially interfering species except for some O_2 . The much lower O2 concentration than obtained when generating O atoms from O_2 will reduce the fraction of $CH_2(^{3}B_1)$ radicals reacting with O_2 , so that the $CH_2(^3B_1)$ destruction kinetics is chiefly governed by the reactions with O and H atoms.

All experiments were carried out at T = 400-1000 K and at a total pressure of 2 Torr (\geq 98% helium), except for those at T = 590 K and T = 890 K where the total pressure was 4 Torr. Depending on temperature, the flow velocities ranged from 35 to 68 m/s and the corresponding maximum reaction times from $t_{\text{max}} = 6.8$ to 3.5 ms.

Qualitative and quantitative analysis of the reaction mixtures was carried out by molecular beam sampling and mass spectrometric detection. Sampling occurs downstream of the reactor through a 0.3 mm pinhole in a quartz cone giving access to the first of two differentially pumped low-pressure chambers. In the first stage the gas jet is mechanically chopped to allow phase sensitive detection. The resulting modulated molecular beam then enters the second low-pressure chamber, which houses an electron-impact ionizer and an Extranuclear quadrupole mass spectrometer. A lock-in amplifier was used to distinguish between the beam and background ions.

The nominal electron energies were only 0.2-3 eV above the ionization potentials (IP) of the species being monitored, in order to suppress signal contamination by fragment ions. When monitoring CH₂, special care was taken to minimise CH₂⁺ formation from CH₂CO, on the one hand used as initial reagent or on the other hand formed as a minor product in the C₂H₂/O system. The electron energy adopted for recording the CH₂ signals was 10.6 eV, i.e., only 0.2 eV above the IP of the CH₂ triplet state. The CH₂ signals were duly corrected for the small, remaining contribution of CH₂⁺ fragment ions from ketene.

Absolute concentrations of the molecules C_2H_2 , O_2 , and H_2 were derived from the measured flows of certified high-purity gases and from the total pressure. The absolute concentrations of O and H atoms were determined by partial dissociation of O_2 and H_2 , respectively, in the microwave discharge and application of the discharge on/off method.^{15,16} Gases and mixtures, used without further purification, were He (99.9996%, L'Air Liquide) as discharge-inlet carrier gas, He (99.995%, L'Air Liquide) as additional carrier gas, and certified 1–10% mixtures of C_2H_2 (99.6%), N₂O (99.5%), O₂ (99.998%), and H₂ (99.999%) in UHP He (99.9996%) (all UCAR). Ketene was obtained by pyrolysis of $(CH_3)_2CO$ at T = 900 K and purified up to ~99% by distillation.

Methodology

The quantification of the rate constant of the $CH_2({}^{3}B_1) + H$ reaction was undertaken in CH_2CO/O systems (T = 400, 500, 650, and 950 K) as well as in C_2H_2/O systems (T = 590 and 890 K); in both systems the CH_2 radical is formed in fairly large amounts. An absolute determination of $k(CH_2({}^{3}B_1) + H)$ in such systems is hampered by the competing $CH_2({}^{3}B_1)$ destruction reactions with O atoms, being one of the reagents, and to a lesser extent with O₂. Therefore, experiments were designed to measure the $CH_2({}^{3}B_1) + H$ rate constant relative to the well-known kinetic coefficient of the $CH_2({}^{3}B_1) + O$ reaction.^{11,16–18} Basically, the method involves recording the relative change of the quasi-steady state CH_2 concentration upon varying the [H]/[O] ratio at given CH_2 formation rate.

A. The CH₂CO/O System. The reaction of O atoms with ketene has already proved to be a suitable source of triplet methylene radicals:^{3a,17}

$$CH_2CO + O \rightarrow CH_2(^3B_1) + CO_2$$
 (4a)

$$\rightarrow$$
 H₂CO + CO (4b)

$$\rightarrow$$
 HCO + HCO (4c)

$$\rightarrow$$
 HCO + H + CO (4d)

Mack and Thrush¹⁹ determined a total rate constant for reaction 4 of $(5.6 \pm 0.5) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 293 K from the O atom decay followed by EPR spectroscopy. They indicated the formyl radical as an important primary product. This was confirmed by Washida et al.;²⁰ they obtained the following Arrhenius expression over the temperature range 230-449 K: $k_4 = 2.9 \times 10^{-12} \exp[-680/T(\text{K})] \text{ cm}^3$ molecule⁻¹ s⁻¹. Bley et al.²¹ found that the CH₂(³B₁) radical is the dominant primary product; they derived a CO₂/CO yield ratio of 70/30. As will be shown later, neither the value of k_4 nor the CH₂(³B₁) yield of reaction 4 need be known for our study.

Destruction of the $CH_2(^{3}B_1)$ radical in CH_2CO/O systems occurs mainly through reaction with O and H atoms and, for a smaller fraction, with O_2 molecules.

$$CH_2(^{3}B_1) + H \rightarrow CH(^{2}\Pi) + H_2$$
(1)

$$CH_2(^{3}B_1) + O \rightarrow CO + 2H$$
 (2a)

$$\rightarrow CO + H_2$$
 (2b)

$$CH_2(^{3}B_1) + O_2 \rightarrow products$$
 (3)

Regarding the rate constant of the CH₂(³B₁) + O reaction, studies by Vinckier and Debruyn¹⁶ and by Böhland et al.¹⁷ led to nearly identical results: $k_2 = (1.3 \pm 0.3) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at T = 295-535 K and $(1.4 \pm 0.5) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at 290 K, respectively. Frank et al.¹⁸ reported a shock tube k_2 determination of about 1.4×10^{-10} cm³ molecule⁻¹ s⁻¹ at 1900–2300 K, which is in good agreement with the k_2 value of 1.5×10^{-10} cm³ molecule⁻¹ s⁻¹ derived by Löhr and Roth¹¹ at an average temperature of 2000 K. One can conclude that k_2 is nearly independent of temperature; below, the value $k_2 = (1.3 \pm 0.3) \times 10^{-10}$ was adopted for the entire range of 400–1000 K.

Only few measurements of $k(CH_2({}^{3}B_1) + O_2)$ have been carried out over our T range from 400 to 1000 K. Vinckier

and Debruyn¹⁶ obtained $k_3(T) = 2.2 \times 10^{-11} \exp[-750/T (K)]$ cm³ molecule⁻¹ s⁻¹ for T = 295-573 K, while Bley et al.²² measured somewhat higher values: $k_3(T) = 1.5 \times 10^{-11} \exp[-505/T (K)]$ cm³ molecule⁻¹ s⁻¹ for T = 233-433 K. Dombrowsky and Wagner²³ found that the kinetics of this reaction exhibits a negative temperature dependence in the range T = 1000-1800 K. They fitted their k_3 determinations and the results of the above studies by the following three-parameter expression: $k_3(T) = 7.8 \times 10^{-11}(500/T)^{3.3} \exp[-1445/T (K)]$ cm³ molecule⁻¹ s⁻¹, which was used throughout our study.

In the present experiments, wall termination of methylene radicals¹⁶ and their destruction by CH₂CO,²⁴ the only other major species in CH₂CO/O systems, account for only $\sim 1\%$ each of the total CH₂(³B₁) loss rate by reactions 1, 2, and 3 combined and can therefore be neglected.

In quasi-steady state conditions the $CH_2(^{3}B_1)$ concentration is given by

$$[CH_{2}(^{3}B_{1})]_{st} = \frac{k_{4a}[CH_{2}CO][O]}{k_{1}[H] + k_{2}[O] + k_{3}[O_{2}]}$$
(I)

The quantities that control the $CH_2({}^{3}B_1)$ concentration at a given formation rate are the three destruction frequencies, i.e., $k_1[H]$, $k_2[O]$, and $k_3[O_2]$. From the way the relative $CH_2({}^{3}B_1)$ concentration depends on the concentration-ratios [H]/[O] and [H]/[O₂] one can determine the k_1 value, since k_2 and k_3 are known. Since in our systems removal of $CH_2({}^{3}B_1)$ by O atoms is between 4 and 10 times more important than by O₂, this procedure amounts to determining k_1 relative to the well-quantified k_2 . Expressing $[CH_2({}^{3}B_1)]_{st}$ and $[CH_2CO]$ in terms of their respective mass spectrometric signals i_{CH_2} and i_{CH_2CO} , and rearranging, the steady-state equation can be linearized:

$$\frac{i_{\rm CH_2CO}}{i_{\rm CH_2}} \frac{[O]}{[H]} = \frac{S_{\rm CH_2CO}}{k_{4a}S_{\rm CH_2}} (k_2 \{[O] + (k_3/k_2)[O_2]\}/[H] + k_1) \quad (II)$$

where S_{CH_2} and S_{CH_2CO} are the mass spectrometric sensitivities for CH₂ and CH₂CO.

A plot of the left-hand side of eq II vs the quantity $\{[O] + (k_3/k_2)[O_2]\}/[H]$ should yield a straight line, with a intercept/ slope ratio equal to k_1/k_2 . It is clear that the constant $S_{CH_2CO}/(k_{4a}S_{CH_2})$ need not be known since it is common to both the slope and the intercept.

The above is only valid provided that quasi-steady state conditions are reached for $CH_2({}^{3}B_1)$. In our experimental conditions the time for achieving the quasi-steady state (i.e., approximately thrice the CH_2 lifetime) is about 0.1 ms, while the time scale for the change of the $CH_2({}^{3}B_1)$ concentration is several milliseconds. Therefore, the CH_2 quasi-steady state will be rapidly established and closely maintained; deviations amount to at most a few percent, as ascertained by kinetic modeling.

B. The C₂H₂/O System. The CH₂(³B₁) chemistry in C₂H₂/O systems is well established.^{10,25-30} It comprises formation via three different pathways, and destruction—as in CH₂CO/O systems—through reaction with O and H atoms and with O₂ molecules. Besides direct, primary CH₂(³B₁) production via reaction channel 5b, there is also a delayed secondary CH₂ formation via a reaction between the products of the other, major primary route 5a:^{10,26}



The total rate coefficient of reaction 5 is well-known over a wide T range. In their recent survey of all available data in the range T = 195-2500 K, Michael and Wagner²⁵ recommend the three-parameter expression: $k_5 = 1.2 \times 10^{-17}T^{2.09}$ exp[-786/T (K)] cm³ molecule⁻¹ s⁻¹, which is adopted in the present study. The product distribution of reaction 5 which had been controversial up to about 10 years ago is now well established; all recent studies^{10,25,26} agree on a k_{5a}/k_{5b} ratio of 80/20, nearly independent of temperature for T = 290-1200 K. Of course, only part of the HCCO formed in C₂H₂/O systems reacts with H; a major fraction is removed by the HCCO + O reaction.

$$HCCO + O \rightarrow 2CO + H \tag{7a}$$

$$\rightarrow$$
 CO₂ + CH(X²\Pi and/or a⁴ Σ^{-}) (7b)

Other possible HCCO processes, such as reaction with O₂ and wall termination, are negligible in the type of C₂H₂/O systems investigated here.³¹⁻³⁴ Therefore, the fraction of the HCCO that reacts with H atoms in reaction 6 is equal to [H]/{[H] + (k_7/k_6) [O]}. The ratio k_7/k_6 figuring in this fraction is well established; it has been measured (as such), over a large temperature range:^{29,35b,36} $k_7/k_6 = 0.70 \pm 0.15$ from 300 to 2000 K.

The secondary CH_2 formation, mainly in the metastable singlet state, by reaction 6

$$HCCO + H \rightarrow CH_2(^1A_1) + CO$$
 (6a)

$$\rightarrow CH_2(^{3}B_1) + CO \tag{6b}$$

has been suggested earlier by Faubel and Wagner²⁷ and was more recently identified by Peeters et al.²⁸ The CH₂(¹A₁)/CH₂-(³B₁) product ratio of the HCCO + H reaction was determined by Boullart and Peeters;¹⁰ they measured a CH₂(¹A₁) yield of 0.92 ± 0.15 .

In the conditions of our experiments, at $p_{tot} = 4$ Torr with He as bath gas, and reactant concentrations of a few milliTorr only, the dominant fate, by far, of singlet $CH_2({}^1A_1)$ is fast deactivation to the triplet $({}^{3}B_{1})$ state by collisions with He. The quenching coefficient is already $3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} at room temperature^{37,38} and increases almost linearly with temperature;³⁹ in our conditions the $CH_2({}^1A_1 \rightarrow {}^3B_1)$ quenching rate is about 4×10^5 s⁻¹. Two other CH₂(¹A₁) reactions of some relevance in our systems are $CH_2({}^{1}A_1) + C_2H_2$ and CH_2 - $({}^{1}A_{1}) + O_{2}$; their total rate constants and quenching fractions are well characterized.³⁹⁻⁴¹ The $CH_2(^1A_1)$ reactions with H and O, with estimated rate coefficients and quenching fractions of respectively 2.0×10^{-10} cm³ molecule⁻¹ s⁻¹ (66% quenching) and 1.3×10^{-10} cm³ molecule⁻¹ s⁻¹ (no quenching), account together for only about 3% of the $CH_2({}^1A_1)$ removal in conditions typical for our experiments.

Summarizing, the HCCO + H reaction will result in secondary $CH_2({}^{3}B_1)$ for a total fraction f_T that can be quantified precisely and that in any case is very close to unity; the values in our experimental conditions range from 0.95 to 0.98. The total rate of secondary $CH_2({}^{3}B_1)$ production can therefore be written as the product of the rate of reaction 5a, the fraction of the HCCO that reacts with H, and the fraction f_T defined above. Adding the rate of production of primary $CH_2({}^{3}B_1)$, i.e., the rate of reaction 5b, and dividing by the total removal frequency of $CH_2({}^{3}B_1)$, gives the quasi-steady state concentration of triplet CH_2 :

$$[CH_{2}({}^{3}B_{1})]_{st} = \frac{k_{5}[C_{2}H_{2}][O]}{k_{1}[H] + k_{2}[O] + k_{3}[O_{2}]} \left\{ \frac{k_{5b}}{k_{5}} + \frac{k_{5a}}{k_{5}} \frac{[H]}{[H] + (k_{7}/k_{6})[O]} f_{T} \right\}$$
(III)

Apart from k_7/k_6 , the only other critical quantity in this expression is the "primary" branching ratio k_{5a}/k_{5b} . As already stated, this ratio is well established over our full T range.^{10,25,26}

It is important to note that the total $CH_2({}^{1}A_1)$ removal frequency, which for typical conditions is about $4 \times 10^5 \text{ s}^{-1}$, is much higher than the destruction frequency of $CH_2({}^{3}B_1)$, which amounts to about 10^4 s^{-1} . Detailed kinetic modeling shows that for the given experimental conditions the singlet CH_2 concentration is less than 2% of the triplet CH_2 concentration. The high removal frequencies of the two CH_2 states imply that quasi-steady states will be attained for both within less than 0.1 ms, i.e., in a time scale more than an order of magnitude below that of the CH_2 concentration changes in our experiments. Hence, the quasi-steady states will be attained rapidly and maintained quasi-rigorously.

After the $[CH_2({}^{3}B_1)]_{st}$ is replaced by the mass spectrometric signal i_{CH_2} , the quasi-steady state expression eq III can be rearranged and linearized:

$$\frac{[C_2H_2][O]}{i_{CH_2}k_2[H]} \left\{ k_{5b} + k_{5a} \frac{[H]}{[H] + (k_7/k_6)[O]} f_T \right\} = \frac{1}{S_{CH_2}} \left\{ \frac{k_1}{k_2} + \frac{[O] + (k_3/k_2)[O_2]}{[H]} \right\}$$
(IV)

where S_{CH_2} is the mass spectrometric sensitivity for CH₂.

A plot of the left-hand side of eq IV vs the quantity $\{[O] + (k_3/k_2)[O_2]\}/[H]$ should yield a straight line with an intercept to slope ratio of k_1/k_2 . The constant $1/S_{CH_2}$ need not be known since it is common to both the slope and the intercept.

Results

A. The CH₂CO/O System. Measurements were carried out at temperatures of 400, 500, 650, and 950 K, each time on three or four CH₂CO/O mixtures, at total pressures of 2 Torr, with helium as bath gas. The initial reactant concentrations are listed in Table 1. The listed ketene concentrations are based on pressure increases and therefore only approximate. However, as was shown above, the absolute concentration of ketene need not be known; its mass spectrometric signals are sufficient for our investigation. Along with the i_{CH_2CO} and i_{CH_2} signals, also the absolute concentrations of O, H and O₂ were monitored at six equidistant reaction times between 0 and t_{max} , with the latter in the range 3.5-6.8 ms, depending on temperature.

The data of all mixtures were first analyzed seperately because the unknown mass spectrometric sensitivity S_{CH_2} , figuring in eq II, is expected to show slight day to day (i.e., mixture to mixture) fluctuations of about $\pm 20\%$. It should be stressed again that S_{CH_2} need not be known for the determination of the intercept/slope ratio k_1/k_2 since it cancels out in that ratio.

For each of the mixtures, a plot of the left-hand side of eq II vs the quantity $\{[O] + (k_3/k_2)[O_2]\}/[H]$ gives straight lines with correlation coefficients ≥ 0.95 . The k_1/k_2 values, equal to the intercept/slope ratios for the individual mixtures by temperature, are given in Table 2.

A simultaneous treatment of the mixtures grouped by temperature was implemented by using the "maximum overlap" criterion, i.e., by scaling the eq II left-hand side values of mixture i by a factor that minimizes the sum of the squared deviations from the data for a chosen reference mixture. The

TABLE 1: Initial Composition of the Investigated CH₂CO/ O Mixtures (Concentration in 10^{13} molecules cm⁻³) at a Total Pressure of 2 Torr (He Bath Gas)

mixture	[CH ₂ CO] ₀	[O] ₀	[O ₂] ₀
	T = 400	K	
1	25.0	17.4	62.3
2	27.0	25.0	119
3	36.0	37.6	128
	T = 500	К	
1	29.0	19.3	77.2
2	20.0	18.2	81.7
3	22.0	21.6	75.7
	T = 650	К	
1	15.0	14.7	33.6
2	16.0	15.0	39.5
3	13.0	15.0	14.5
	T = 950	К	
1	9.0	9.5	9.14
2	7.6	8.0	22.0
3	7.6	8.1	24.5
4	7.6	7.7	25.7

TABLE 2: Experimental k_1/k_2 Ratios Determined in Individual CH₂CO/O Mixtures at the Four Experimental Temperatures (95% Confidence Limits)

<i>T</i> (K)	mixture	k_1/k_2
400	1	2.16 ± 0.47
	2	1.77 ± 1.07
	3	2.65 ± 0.63
500	1	2.06 ± 0.44
	2	1.66 ± 0.66
	3	1.15 ± 0.26
650	1	0.94 ± 0.13
	2	0.92 ± 0.23
	3	1.05 ± 0.47
950	1	0.76 ± 0.31
	2	0.91 ± 0.32
	3	0.76 ± 0.35
	4	0.97 ± 0.31

optimum scaling factors generally range from 0.7 to 1.3, in agreement with the expected day to day sensitivity changes. In this simultaneous treatment, the full set of points of a mixture was given a relative weight in accordance with the standard deviation in the individual plot. In this way, one obtains combined eq II plots, examples of which are shown in Figure 1 for T = 650 K and T = 950 K. The resulting k_1/k_2 values, together with the k_1 results derived by using the literature k_2 value of 1.3×10^{-10} cm³ molecule⁻¹ s⁻¹, are summarized in Table 3. The indicated errors correspond to the 95% confidence intervals; they include the uncertainties on the respective intercepts and slopes and on the k_2 value.

B. The C₂H₂/O System. In C₂H₂/O systems, the determination of the rate constant of the CH₂(³B₁) + H reaction was undertaken in three mixtures at 590 K and in four mixtures at 890 K. The initial mixture compositions are shown in Table 4. In all the mixtures the absolute C₂H₂, O, H, and O₂ concentration vs time profiles were recorded, together with the relative i_{CH_2} vs time profile. As explained above, the reactor pressure was raised to 4 Torr to minimize the CH₂(¹A₁) contribution to the total CH₂ signal and to ensure that quenching of singlet CH₂ to triplet CH₂ is close to quantitative.

The same procedure to determine k_1/k_2 as for the CH₂CO/O system was used here. Separate plots of the left-hand side of eq IV vs the quantity {[O] + (k_3/k_2) [O₂]}/[H] yield straight lines with correlation coefficients ≥ 0.97 . The derived k_1/k_2 values, equal to the intercept/slope ratios for the individual mixtures, are listed by temperature in Table 5.

Again the "maximum overlap" criterion was employed to allow a simultaneous treatment of all mixtures. The optimum



Figure 1. CH₂CO/O system. Plot of left-hand side of eq II, in arbitrary units, vs the quantity $\{[O] + (k_3/k_2)[O_2]\}/[H]$ (denoted as X) at T = 650 and T = 950 K; the intercept/slope ratio is equal to k_1/k_2 ; -, weighted linear regression line (see text).

TABLE 3: k_1/k_2 and k_1 Determination at T = 400-950 K in the CH₂CO/O System and Associated Overall 2σ Error Margins

T (K)	k_1/k_2	k_1 (cm ³ molecule ⁻¹ s ⁻¹)
400	2.25 ± 0.33	$(2.93 \pm 0.80) \times 10^{-10}$
500	1.58 ± 0.25	$(2.05 \pm 0.57) \times 10^{-10}$
650	0.94 ± 0.10	$(1.22 \pm 0.31) \times 10^{-10}$
950	0.91 ± 0.13	$(1.18 \pm 0.32) \times 10^{-10}$

TABLE 4: Initial Reactant Concentrations in the Investigated C_2H_2/O Mixtures (in 10^{13} molecules cm⁻³) (Bath Gas: Helium; Total Pressure: 4 Torr)

mixture	$[C_2H_2]_0$	[O] ₀	[O ₂] ₀
	T = 590	K	
1	7.96	6.95	20.1
2	9.85	7.40	27.8
3	7.26	8.10	20.5
	T = 890	K	
1	5.42	6.52	20.8
2	6.57	6.10	16.7
3	7.78	8.77	22.4
4	7.55	5.98	17.0

TABLE 5: Experimental k_1/k_2 Ratios for Each Mixture at T = 590 and 890 K (95% Confidence Limits)

T (K)	mixture	k_1/k_2
590	1	1.39 ± 0.17
	2	1.53 ± 0.20
	3	1.54 ± 0.12
890	1	0.86 ± 0.08
	2	0.85 ± 0.14
	3	1.05 ± 0.18
	4	0.70 ± 0.35

scaling factors thus found varied from 0.80 to 1.20. Figure 2 shows the combined eq IV plots for T = 590 K and T = 890K. The resulting k_1/k_2 values, together with the k_1 results, are summarized in Table 6; the indicated 95% confidence intervals include the uncertainties on the respective intercepts and slopes, and possible systematic errors induced by the uncertainties on k_2 , the k_{5a}/k_{5b} branching fraction, and k_7/k_6 . The following



Figure 2. C_2H_2/O system. Plot of left-hand side of eq IV, in arbitrary units, vs the quantity $\{[O] + (k_3/k_2)[O_2]\}/[H]$ (denoted as X) at T = 590 and T = 890 K; the intercept/slope ratio is equal to k_1/k_2 ; -, weighted linear regression line (see text).



Figure 3. Semilog k_1 vs T plot of literature data and data of this work; ---, fit by the equation $k_1 = 3.8 \times 10^{-10} \exp[-1.3 \times 10^{-3}T \text{ (K)}].$

TABLE 6: k_1/k_2 and k_1 Determination at T = 590 and 890 K in the C₂H₂/O System and Associated Overall 2σ Error Margins

0			
T (K)	k_1/k_2	k_1 (cm ³ molecule ⁻¹ s ⁻¹)	
590 890	$\begin{array}{c} 1.46 \pm 0.10 \\ 0.86 \pm 0.08 \end{array}$	$(1.90 \pm 0.58) \times 10^{-10}$ $(1.12 \pm 0.36) \times 10^{-10}$	

standard errors were adopted: $\sigma(k_2) = 0.15 \times 10^{-10}$, ¹⁶ $\sigma(k_{5a}/k_{5b}) = 1.6$, ¹⁰ and $\sigma(k_7/k_6) = 0.08$. ^{35b} The overall error was obtained by the conventional error propagation rule.

Discussion

The rate constant of the $CH_2({}^{3}B_1) + H$ reaction has been measured for the first time over a temperature range T = 400-1000 K, intermediate between room and flame temperature. The results show that the kinetic coefficient exhibits a clear-cut negative temperature dependence, in accord with the literature data at room temperature^{3,8,10} on one side and in the 1500-2500 K range^{1,11,12} on the other.

All the determinations from the literature, along with our results, are shown in the semilog plot of k_1 vs T in Figure 3. All these data can be represented reasonably well by the two-parameter relation:



Figure 4. Schematic potential energy diagram of the $CH_2(\tilde{X}^3B_1) + H$ reaction; (a) and (b), see text.

$$k_1 = ae^{-bT} \tag{V}$$

It is stressed here that this fit expresses merely the empirical dependence of the rate constant k_1 on the temperature. The following parameters were derived: $a = 3.8 \times 10^{-10}$ and $b = 1.3 \times 10^{-3} \text{ K}^{-1}$. Fitting to an Arrhenius expression of the form $k_1 = AT^n \exp[-E_a/RT]$ is not quite useful here since the parameters A, n, and E_a do not necessarily have a concrete physical meaning.

From Figure 3, it can be appraised that the present measurements in the T = 400-1000 K range fall in well with the existing k_1 data at 290 K and at T = 1500-2500 K.

The non-Arrhenius behavior of the rate coefficient of the CH₂- $({}^{3}B_{1}) + H$ reaction can be qualitatively explained as follows,⁴² with reference to the schematic potential energy diagram⁴³ of Figure 4. A vibrationally excited CH₃[†] adduct is formed via barrierless combination of the reagents. Its vibrational energy content is the sum of the well depth, of 109 kcal/mol, plus thermal energy from the vibration and relative translation and rotation of the reagents.

(a) At room temperature, this thermal energy is only about 0.9 kcal/mol. The CH_3^{\dagger} species can then decompose in two ways:

$$CH_3^{\dagger} \rightarrow CH_2(^{3}B_1) + H \qquad \Delta E_{exc} = -0.9 \text{ kcal/mol} \quad (i)$$

$$CH_3^{\dagger} \rightarrow CH(^2\Pi) + H_2 \qquad \Delta E_{exc} = -3.9 \text{ kcal/mol} \quad (ii)$$

with the respective (average) excess energies above the zeropoint levels, ΔE_{exc} , given at 300 K. Since process (ii) is 4 times more exoergic than redissociation into the reagents, the former, energetically favored reaction path will be dominant.

(b) At higher temperatures, the CH_3^{\dagger} intermediate possesses much more thermal energy (an additional ~11 kcal/mol at 2000 K), so that the small difference between the two excess energies becomes relatively unimportant and no longer controls the direction in which the CH_3^{\dagger} adduct dissociates. Here the entropic or quantum-statistical aspects will decide the fate of CH_3^{\dagger} : the variational transition state to the reagents is expected to be very loose, and thus to exhibit low vibration frequencies, which implies a high density of states. On the contrary, the cyclic variational transition state to the reaction products should be much tighter, with higher vibration frequencies and accordingly a lower density of states. Energetically, both are equally accessible, but since the transition structure to the reagents offers a higher sum of states, this path will get the statistical upper hand, entailing a decrease of the rate constant for product formation, k_1 .

Conclusions

In this work, we have measured the rate coefficient k_1 of the $CH_2(^3B_1) + H$ reaction, relative to the well-known rate

coefficient of the $CH_2({}^{3}B_1) + O$ reaction, over a temperature range of 400-1000 K. The $CH_2({}^{3}B_1)$ radical was formed via two distinct sources: (i) the $CH_2CO + O$ reaction and (ii) the $C_2H_2 + O$ system. The data obtained with the two sources are in good mutual agreement.

The results in the 400–1000 K range point to a moderately strong negative temperature dependence for k_1 . The result at 400 K is still about equal to the average k_1 literature value at 300 K, but at 950 K the coefficient has decreased already by a factor of 2.5. The observed trend is in accord with the reported low k_1 data at flame temperatures.^{1,11,12} The full set of data, from 300 to 2500 K, can be fitted fairly well by the purely empirical relation

$$k_1 = 3.8 \times 10^{-10} \exp[-1.3 \times 10^{-3} T (\text{K})]$$

However, it is worth noting that the observed decrease in the 300-1000 K range is much less steep than predicted by Baulch et al.,⁴⁴ who recommend $k_1 = 1.0 \times 10^{-11} \exp[900/T$ (K)]. Such an Arrhenius expression, with a negative "activation energy", implies a steep change at low temperatures and asymptotic behavior toward higher temperatures. The observed behavior is nearly opposite; furthermore, it is qualitatively in line with the interpretation of the negative temperature dependence in the preceding section.

At 1750 K the rate coefficient of the $CH_2({}^{3}B_1) + H \rightarrow CH_1({}^{2}\Pi) + H_2$ reaction is already 7 times smaller than at room temperature, i.e., only about 3.9×10^{-11} cm³ molecule⁻¹ s⁻¹. On the other hand, extrapolation of the rate coefficient $k_{7b} = 4.9 \times 10^{-11} \exp[-560/T \text{ (K)}] \text{ cm}^3$ molecule⁻¹ s⁻¹ of the recently identified^{35a,35b} reaction channel

HCCO + O
$$\rightarrow$$
 CO₂ + CH(X²\Pi and/or a⁴ Σ^{-}) (r7b)

gives a k_{7b} value of 3.6×10^{-11} cm³ molecule⁻¹ s⁻¹ at 1750 K, i.e., almost equal to k_1 . This confirms the view^{35b} that the HCCO + O reaction channel 7b is a competitive formation route of CH radicals in flames and should be incorporated in flame chemistry models.

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