Temperature dependence of the reaction C_2H (C_2D) + O_2 between 295 and 700 K

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Abstract

The rate coefficients for the reactions of C_2H and C_2D with O_2 have been measured in the temperature range 295 K $\leqslant T \leqslant$ 700 K. Both reactions show a slightly negative temperature dependence in this temperature range, with $k_{C_2H+O_2}$ = $(3.15 \pm 0.04) \times 10^{-11}$ $(T/295 \text{ K})^{-(0.16 \pm 0.02)}$ cm^3 molecule^{-1} s^{-1}. The kinetic isotope effect is k_{C_2H}/k_{C_2D} = 1.04 ± 0.03 and is constant with temperature to within experimental error. The temperature dependence and the $C_2H + O_2$ kinetic isotope effect are consistent with a capture-limited metathesis reaction, and suggest that formation of the initial HCCOO adduct is rate-limiting.

1. Introduction

Because of its important role in many chemical systems, reactions of the ethynyl radical (C_2H) have been investigated from many different points of view. The ethynyl radical is important in combustion processes [1,2], where it is formed by H atom abstraction from acetylene and several other reactions, e.g. $O + C_3H$. Once formed under combustion conditions, ethynyl radicals, as hydrogen deficient radicals, are thought to aid in the initiation of soot formation [3–5]. The C_2H radical has also been detected in planetary atmospheres [6] and in the interstellar medium [7,8], which has motivated recent experimental studies of the low-temperature kinetics of C_2H.
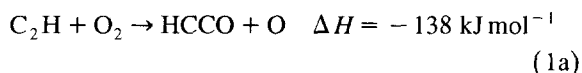
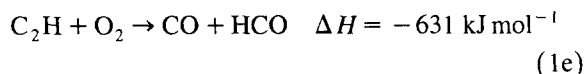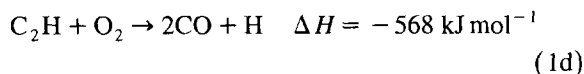The kinetics of elementary reactions of C_2H with other species important in hydrocarbon combustion have been the subject of numerous investigations. Besides the present reaction:
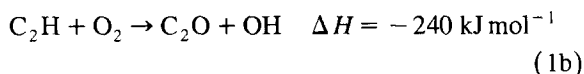
$$C_2H + O_2 \rightarrow \text{products} \tag{1}$$

there have been measurements of rate coefficients for the reactions of ethynyl radicals with saturated and unsaturated hydrocarbons [9–15], H_2 [10,11,13, 16], NO [12], CO [14], and H_2O [17]. Reaction (1) has been studied using several different experimental approaches [10–12,15,17–21]. The reported overall rate coefficient at room temperature varies in a range of $k_1 = 0.5–4.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Reaction (1) can lead to the following thermodynamically allowed product channels:

$$C_2H + O_2 \rightarrow HCCO + O \quad \Delta H = -138 \text{ kJ mol}^{-1} \tag{1a}$$

$$C_2H + O_2 \rightarrow C_2O + OH \quad \Delta H = -240 \text{ kJ mol}^{-1}$$
$$(1b)$$

$$C_2H + O_2 \rightarrow CH + CO_2 \quad \Delta H = -363 \text{ kJ mol}^{-1}$$
$$(1c)$$

$$C_2H + O_2 \rightarrow 2CO + H \quad \Delta H = -568 \text{ kJ mol}^{-1}$$
$$(1d)$$

$$C_2H + O_2 \rightarrow CO + HCO \quad \Delta H = -631 \text{ kJ mol}^{-1}$$
$$(1e)$$
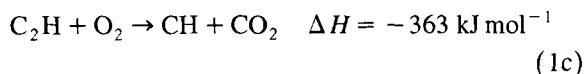
Of these possible products CH [11,18], CO [11,18–20], CO_2 [11,18,20], and HCCO [10] have been detected directly. The OH radical could not be detected, thus suggesting that reaction (1b) plays only a minor role. The time dependence of the CO concentration indicated the formation by at least two different pathways. Besides direct formation via reactions (1d) and (1e), CO can also be formed by secondary reactions of HCCO and HCO with excess O_2. Additional formation of CO in a reaction of the HCCOO collision complex with O_2 or the ethynyl precursor, as discussed by Lander et al. [20], requires a relatively long lifetime for the complex. This may be unlikely given the observed lack of a pressure dependence for the reaction.

Reaction (1) is assumed to proceed via a peroxy radical HCCOO in analogy to the reaction $C_2H_3 + O_2$ [22,23]. Rearrangement of the peroxy radical via the following three- or four-membered rings:
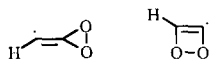
has been claimed to be energetically accessible from $C_2H + O_2$ [21]. These structures can explain all of the observed products. More detailed information about the rate limiting product channels, may be available from the kinetic isotope effect of reaction (1). Secondary deuterium kinetic isotope effects have been useful for elucidation of reaction pathways where isomerization of an intermediate is important, for example in the reactions of CH (CD) + [13]CO [24]. The total rate coefficients of many capture-limited reactions can be described by simple loose transition state models [25], i.e., models where the frequencies of the reactant molecule vibrations are unchanged in the transition state. However, recent investigations of other capture-limited radical/molecule and radical/radical reactions, e.g. CH + CH_4 and C_2H_2 [26], and CH + O_2 [27] have shown a kinetic isotope effect inconsistent with simple loose transition state models. Interpretation of the kinetic isotope effect in such systems requires more rigorous consideration of the transitional modes and more detailed calculation of the transition state characteristics.

In this Letter, the temperature dependence and the kinetic isotope effect for the reaction C_2H (C_2D) + O_2 are presented. The data are taken using time resolved chemiluminescence from the $CH(A^2\Delta)$ product. The rate coefficients were measured at temperatures between 295 and 700 K and at pressures from 20 to 300 Torr. The reaction exhibits a slight negative temperature dependence which is consistent with a capture-limited reaction, and a kinetic isotope effect of $k_{C_2H}/k_{C_2D} = 1.04 \pm 0.03$ at 295 K. The small isotope effect indicates that the transition state for the reaction is relatively insensitive to deuterium substitution and suggests that isomerization of a presumed HCCOO peroxy radical intermediate may not be rate-limiting.
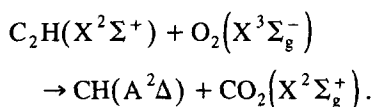
2. Experimental

The kinetic data are taken in a laser photolysis/chemiluminescence apparatus under quasistatic conditions. The experimental setup has been described earlier using LIF [24] as well as chemiluminescence detection [27]. Only a brief overview is given in the following section.

The reactor consists of a stainless steel cell which can be resistively heated. The temperature is measured directly above the reaction volume with a thermocouple. The pressure in the reactor is monitored with two capacitance manometers. All gas flows in the reactor are controlled by calibrated mass flow controllers. Acetylene (99.7%) is used as precursor for the ethynyl radical and is passed through

an activated charcoal filter prior to use to trap acetone. A GC/MS analysis of the cleaned acetylene confirmed the success of this procedure. To achieve sufficiently small gas flows of the precursor, the acetylene is premixed with He (99.9999%) and stored in 12 1 glass bulbs. The acetylene concentration is typically about 1%. Oxygen is used as a commercially prepared mixture (10.1%) in He.

The ethynyl radicals are prepared by laser photolysis of acetylene at 193 nm. The output of the excimer laser ($\approx$ 10 mJ pulse energy) is coupled into the reactor without focusing, in order to avoid generation of other multiphoton products like C_2 or CH [28]. The decay of the C_2H concentration with time is followed by observation of the $CH(A \rightarrow X)$ chemiluminescence at 430 nm. $CH(A)$ is formed in reaction (1c) via:

$$C_2H(X^2\Sigma^+) + O_2(X^3\Sigma_g^-)$$

$$\rightarrow CH(A^2\Delta) + CO_2(X^2\Sigma_g^+).$$

The yield of $CH(A)$ in this reaction has recently been determined to be 1.1×10^{-3} [29]. The collision free lifetime of $CH(A)$, 500 ns [30], is much shorter than the reactive lifetime of C_2H (typically 10–30 μs under the given experimental conditions). In this case, the intensity of the CH ($A^2\Delta$) chemiluminescence is proportional to the C_2H concentration.

The chemiluminescence is detected with a photomultiplier tube (PMT) operated in single photon counting mode. Before entering the PMT, the chemiluminescence passes a narrow band filter to minimize scattered light from the photolysis laser. The PMT signal is then transferred to a multichannel scaler. A reasonable signal to noise ratio was obtained by summing over 3000–6000 laser firings. A typical concentration time profile for C_2H is shown in Fig. 1. At very low reaction times (3 μs) another fast decaying signal is superimposed on the CH chemiluminescence. This signal is also observed in absence of acetylene in the reactor. The source for this signal is most probably fluorescence induced by the photolysis laser in the quartz windows of the reactor and the band pass filter. Since this signal decays very fast, the concentration time profiles are fitted by simply neglecting the first microseconds.

The experiments are carried out with the oxygen concentration in a large excess over the ethynyl
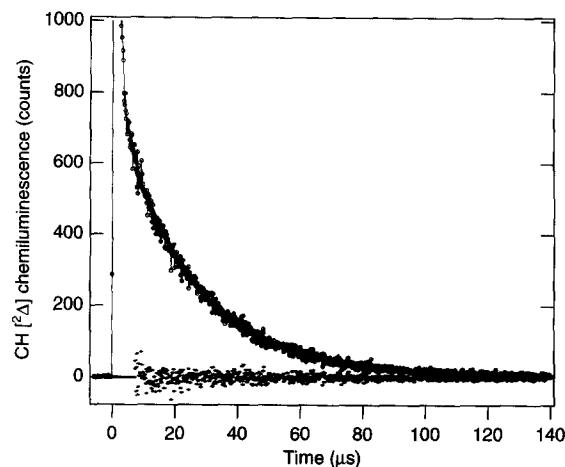

Fig. 1. Typical decay profile for $CH(A^2\Delta)$ chemiluminescence arising from the reaction of C_2H with O_2. Experimental conditions: $T = 691$ K, total pressure 100 Torr, $[C_2H_2] = 9.51 \times 10^{13}$ cm^{-3}, $[O_2] = 1.45 \times 10^{15}$ cm^{-3}. At short reaction times, a sharp spike due to fluorescence of the reactor windows and the narrow band filter is seen. The solid line in the figure represents an exponential fit to the time trace after the spike has become negligible. The residuals to the fit are also shown.

radicals. For a particular temperature and pressure, typically eight experiments with different oxygen concentrations are performed. Data for the temperature dependence are taken at a pressure of 100 Torr. The particle density for the acetylene during the
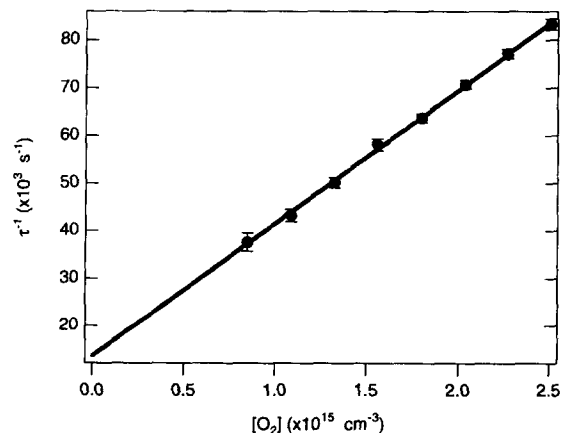

Fig. 2. Plot of the experimental decay constant versus $[O_2]$ for 100 Torr and 616 K. The line represents the linear fit through the data points. The intercept is governed mainly by the fast reaction of C_2H with the photolytic precursor acetylene.

measurements is about 1.6×10^{14} cm^{-3}, and the oxygen density is varied in the range 0.6–8.2×10^{15} cm^{-3}. The concentration versus time profiles are fitted to an exponential function, and the inverse decay times are then plotted against the oxygen concentration and fitted to a straight line as shown in Fig. 2. All the experimental errors reported in this work are twice the standard deviation of the error of the fit, taking the precision of the individual experimental decay rates into account.

3. Results

The rate constant for reaction (1) at room temperature is determined to be $(3.17 \pm 0.07) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The reaction rate at room temperature is independent of the pressure between 20 and 300 Torr as shown in Table 1 and in Fig. 3. The reaction of ethynyl radicals with oxygen has been recently investigated using two different methods of probing C_2H. Lander et al. [14] and Opansky et al. [21] used a laser photolysis/IR absorption setup, reporting rate constants of $(2.9 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $(3.3 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [14,21]. Van Look et al. [17] used a laser photolysis/chemiluminescence setup comparable to the one used in this work, and report a rate coefficient of $(3.3 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The value obtained in this work is in excellent agreement with these results.

The reaction of ethynyl radicals with oxygen shows a slightly negative temperature dependence. The rate coefficients determined in the present work are given in Table 2. A fit of the experimental data

Table 1
Pressure dependence of the rate coefficient for $C_2H + O_2$ at 297 K

Pressure (Torr)	k_1 (10^{-11} cm^3 molecule^{-1} s^{-1})
20	3.29 ± 0.08
35	3.34 ± 0.08
50	3.2 ± 0.1
75	3.25 ± 0.05
100	3.17 ± 0.07
150	3.07 ± 0.08
200	3.07 ± 0.08
300	3.16 ± 0.08

Error bars represent $\pm 2\sigma$ (precision only).
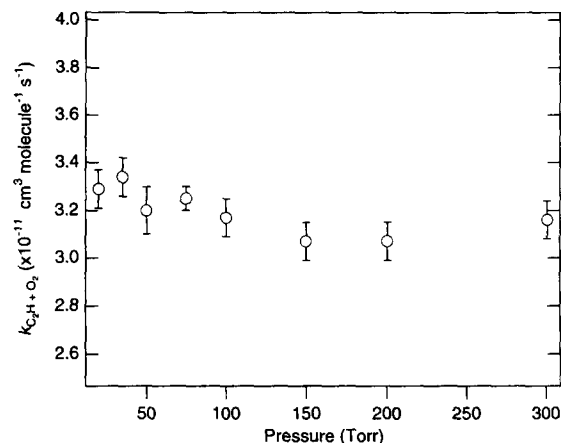

Fig. 3. Pressure dependence of the reaction of C_2H with O_2 at 297 K.

to a T^{-n} expression yields $k_{C_2H} = (3.15 \pm 0.04) \times (T/295 \text{ K})^{-(0.16 \pm 0.02)} \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The temperature dependence has previously been investigated by Opansky et al. [21] and Van Look et al. [17]. Fig. 4 shows that the data from this work are in good agreement with the previous results in the overlapping temperature range, however the present work extends the temperature range by 250 K. Opansky et al. fit their data to an effective activation energy $E_a/R = -230 \pm 36$ K between 193 and 350 K, and Van Look and Peeters report $E_a/R = -160 \pm 15$ K between 295 and 450 K. The observed temperature dependence in the present study is

Table 2
Rate coefficients for $C_2H(C_2D) + O_2$ vs. temperature

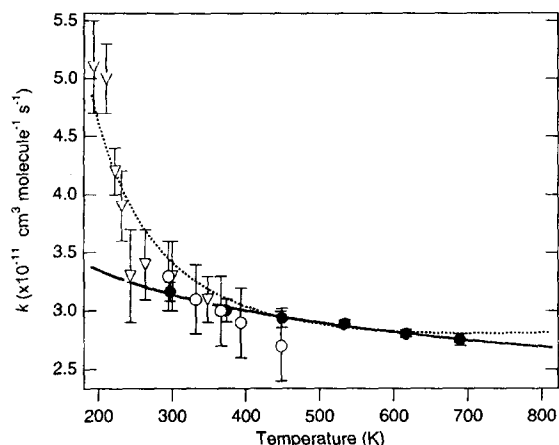| T (K)	k_{C_2H} (10^{-11} cm^3 molecule^{-1} s^{-1})	k_{C_2D} (10^{-11} cm^3 molecule^{-1} s^{-1})
297	3.17 ± 0.07	3.04 ± 0.08
371		3.0 ± 0.1
373	3.0 ± 0.1	
449	2.94 ± 0.08	
461		2.81 ± 0.07
533	2.89 ± 0.03	
543		2.74 ± 0.03
617	2.81 ± 0.03	
630		2.76 ± 0.07
689	2.76 ± 0.05	
700		2.69 ± 0.03

Error bars represent $\pm 2\sigma$ (precision only).

Fig. 4. Comparison of the temperature dependence of the rate coefficient for $C_2H + O_2$. ($\triangledown$) Opansky et al. [21], ($\bigcirc$) Van Look et al. [17], ($\bullet$) this work. The solid line is a fit to the present data which yields $k = (3.15 \pm 0.04) \times 10^{-11} (T/295 \text{ K})^{-(0.16 \pm 0.02)}$ cm^3 molecule^{-1} s^{-1}. The dashed line is a weighted fit to an Arrhenius form of all the available temperature dependent data, yielding $k = 1.4 \times 10^{-11} (T/295 \text{ K})^{-0.37} \exp[270/T] cm^3$ molecule^{-1} s^{-1}.

somewhat shallower than that reported at lower temperature; an Arrhenius fit to the present data gives $E_a/R = -70 \pm 8$ K.

The temperature dependence of the reaction of C_2D with oxygen shows the same negative dependence as in the case of C_2H. In the temperature

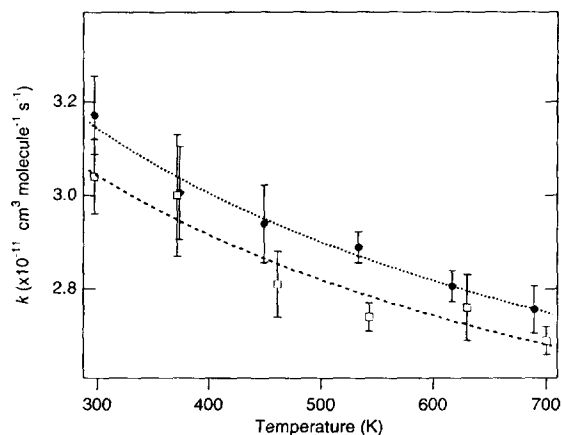Fig. 5. Rate coefficients for the reactions of C_2H ($\bullet$) and C_2D ($\square$) with O_2 over the temperature range 295–700 K. Error bars represent $\pm 2\sigma$ (precision only). The dashed lines are fits to a T'' dependence, which yield $k_{C_2H} = (3.15 \pm 0.04) \times 10^{-11} cm^3$ molecule^{-1} s$^{-1} (T/298)^{-(0.16 \pm 0.02)}$ and $k_{C_2H} = (3.04 \pm 0.08) \times 10^{-11} cm^3$ molecule^{-1} s$^{-1} (T/298)^{-(0.15 \pm 0.04)}$.

range 295–700 K, the data can be represented by $(3.04 \pm 0.08) (T/295 \text{ K})^{-(0.15 \pm 0.04)} \times 10^{-11} cm^3$ molecule^{-1} s^{-1}. The kinetic isotope effect is $k_{C_2H}/k_{C_2D} = (1.04 \pm 0.03)$ and is constant, to within experimental error, over the temperature range 295–700 K. There are to our knowledge no other data for the kinetic isotope effect of this reaction available.

4. Discussion

The rate constant for the reaction is quite large, within an order of magnitude of the gas kinetic collision number, suggesting little repulsion in the entrance channel. The lack of a noticeable barrier is also supported by the negative temperature dependence of this reaction. This behavior is in accordance with an addition mechanism. The absence of a pressure dependence further suggests that the initially formed collision complex decomposes very fast to the different reaction products. The large exothermicity to these reaction pathways makes a unimolecular dissociation back to the reactants unlikely. The temperature dependence measured in the present study is noticeably shallower than that determined at lower temperatures [17,21]. A flattening of the temperature dependence at higher temperatures has been previously noted in a number of capture-limited reactions [31], and appears to be characteristic of such systems. The negative temperature dependence in barrierless association reactions is thought to arise principally from a shift of the microcanonical transition state region to smaller intermolecular separations as higher energy and higher angular momentum collisions contribute. At higher temperatures this effect seems to become less pronounced.

The kinetic isotope effect (KIE) observed in this reaction is very small. The experimental value at 297 K of (1.04 ± 0.03) can be almost completely explained by the difference in the collision frequency due to the slightly smaller velocity of C_2D compared to C_2H. The square root of the ratio of the reduced masses yields in a KIE of 1.01. A similar result is obtained based on the transition state theory in the limit of loose transition states, that is to say, a model where the frequencies of the reactant vibrations are unchanged in the transition state. Since any influence arising from the potential energy surface or from the conserved vibrational modes is ratioed out, the iso-

tope effect in these models is governed by changes in the partition functions as the fragment rotations are transformed into internal vibrations of the transition state.

The reaction of ethynyl radicals with oxygen can be compared with other reactions which take place via a capture limited mechanism. In the reaction of NH_2 (ND_2) + NO a comparably small KIE is found (1.05 ± 0.03) [32], matching the difference in collision frequency. However several other capture-limited reactions show an isotope effect significantly larger than the collision theory result (e.g. $CH/CD + CH_4/CD_4$ and $CH/CD + C_2D_2/C_2D_2$ [26], $CH/CD + O_2$ [24], $CH/CD + HCN/DCN$ [33]). Approximate loose-transition state treatments using hindered rotor partition functions for the transitional modes also appear to fail in several of these cases. Explanation of the isotope effects in these systems evidently requires more detailed consideration of the transition state, including explicit consideration of the nature of the transitional motions as well as possible changes in the preserved modes. The $C_2H + O_2$ transition state, conversely, seems relatively insensitive to deuterium substitution.

The small value of the KIE obtained here suggests that no reaction pathway resulting in a primary isotope effect is rate limiting. This is consistent with the observed small branching fraction to OH product in this reaction, since production of OH would require hydrogen transfer. If isomerization of an initially formed HCCOO adduct were rate limiting, the isotope effect would reflect differences in the isomerization rate. The secondary deuterium kinetic isotope effect for the isomerization could still be substantial. A significant isotope effect has been suggested for HCCO isomerization based on the CH + CO exchange reaction [27], and β-deuterium isotope effects on solvolysis reactions are typically 5–15% per D atom [34]. It seems likely that formation of either cyclic species in (2) would significantly change the C–H bonding from the reactant C_2H and thus exhibit a larger deuterium kinetic isotope effect. The present results cannot definitively exclude a rate-limiting isomerization, but the temperature dependence and the isotope effect measurements suggest that any rearrangement of the intermediate complex is rapid and facile, and that the total reaction rate is governed by the initial complex formation.

Acknowledgements

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