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Acetylene combustion reactions. Rate constant measurements of HCCO with O₂ and C₂H₂

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Received 31 January 1992; in final form 2 March 1992

The second-order rate constant for the reaction of the ketenyl radical (HCCO) with O₂ was measured at room temperature by using infrared kinetic spectroscopy as $6.5(6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. An upper bound for the rate constant for the reaction between HCCO and C₂H₂ was determined as $1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. HCCO was produced by 193 nm excimer laser photolysis of ketene and probed with a tunable infrared diode laser operating at 2014 cm⁻¹.

1. Introduction

Acetylene oxidation takes place not only in oxygen-acetylene flames [1] but also during the combustion of larger hydrocarbon fuels [2], which are oxidized primarily via a sequence of reactions in which alkyl radicals, formed by abstraction, decompose by thermal elimination of alkenes to yield C₁ and C₂ fragments that are subsequently oxidized [3]. Acetylene also plays a major role in the growth of soot particles in fuel rich flames.

In flames acetylene [4] is primarily removed by reaction with atomic oxygen to form ketenyl (HCCO) by one channel, and triplet methylene by another:



Although reactions (1) have been studied extensively for a number of years, the contribution of reaction (1a) to the overall process has been the subject of some dispute [5,6]. Only recently has it been found that this reaction (1a) constitutes the dominant channel (60%–80%) not only at room temperature but also at flame temperatures [7]. Flame reactions leading to the destruction of HCCO are less well understood. What is known about them has been obtained from mass spectrometric studies on the re-

action between acetylene and oxygen atoms [5,8–11].

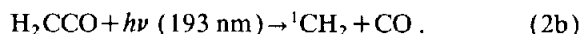
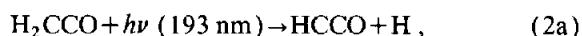
A major impediment to the study of acetylene combustion has been the lack of a sensitive spectroscopic probe of the ketenyl radical. Although the microwave spectrum of ketenyl has been observed by Endo and Hirota [12], and a tentative identification has been made of the ν_2 heavy atom asymmetric stretch mode in matrix isolation [13], a report of the LIF spectrum of HCCO has been shown to be in error [14–16]. However, the recent observation in this laboratory [17] of the high resolution infrared spectrum of the ν_2 mode of HCCO provides an opportunity to study reactions of the ketenyl radical directly, and in this Letter we report direct measurements at room temperature ($\approx 22^\circ\text{C}$) on reactions with molecular oxygen and acetylene.

2. Experimental

The diode laser infrared kinetic spectrometer has been described in detail elsewhere [18,19], and will be only briefly discussed here. Infrared light from a microcomputer-controlled tunable diode laser operating in the 5 μm region is directed into a multipass White cell [20] having a total IR pathlength of approximately 50 m. The UV excimer beam is directed along the cell at a slight angle to the axis so

that overlap between the UV and IR beams occurs over roughly the central third of the cell. Transmitted IR light is focused into a liquid nitrogen cooled InSb detector whose output is amplified and read by a microcomputer controlled transient digitizer.

Ketene was produced in situ by 900 K pyrolysis of diketene (Aldrich, 98%) entrained in a stream of helium carrier gas, and was photolyzed in a 1 m cell using 25 to 150 mJ pulses from a 193 nm ArF excimer laser,



The ketenyl radical produced in (2a) was detected by transient infrared absorption. A second channel, the well-known photolytic route (2b) to methylene at longer wavelengths [21], is quite possibly open at 193 nm as well. However in these studies, any singlet methylene formed would react with the precursor, ketene, at a rate sufficiently fast ($k = 2.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [22] to ensure its total removal from the photolysis cell within 1 μs .

The concentration of ground state ketenyl was monitored by setting the diode laser to the ${}^9\text{P}_0(22)$ transition of HCCO at 2014.426 cm^{-1} . Temporal decay curves were obtained from averages of between 10^3 and 10^4 excimer shots. All reagent gasses were commercially obtained and had the following purities: helium 99.995%, O_2 99.6%, acetylene 99%. Acetylene was additionally purified by passing it through an activated charcoal filter. The total gas pressure was typically set at 30 Torr, and the flow rates were adjusted so that the cell volume was replenished in approximately 25 s.

Precautions had to be taken to ensure that the rate of reaction of ketenyl with other radicals produced by photolysis was much lower than the rate of the reaction chosen for study. Since the ketenyl radical is known to react on nearly every collision ($k = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [11] with the hydrogen atoms co-produced with HCCO in the initial photolysis reaction, (2a), the extent of photolysis had to be reduced to the minimum required to produce an acceptable infrared signal of ketenyl. This was achieved by decreasing the excimer power to 25 mJ/pulse, and by reducing the ketene concentration. Under these conditions the time taken to deplete the

concentration of ketenyl to one half of its original value by radical-radical reactions could be calculated to be more than 80 μs . In the experiments reported here, sufficient O_2 was added to remove ketenyl in 5 to 20 μs .

3. Results

Typical concentration-time traces for the reaction of HCCO with O_2 are shown in fig. 1. Although signal-to-noise was sacrificed in order to eliminate the effects of HCCO-radical reactions, the signal-to-noise was sufficient to allow first-order exponential decay constants to be fitted to the experimental data. In the fitting procedure, all data points were weighted by their value above the zero signal level, which was determined by fitting pre-flash and post decay signals. Decay constants were obtained for various O_2 pressures ranging from 2 to 8 Torr; fig. 2 shows the resulting Stern-Volmer plot. The rate constant for the reaction of HCCO with O_2 was determined from this plot as $6.5(6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Here the uncertainty is based on our previous experience in measuring rate constants with this technique and on the scatter evident in fig. 2.

The addition of acetylene to the reaction cell did not alter the ketenyl decay to any significant extent. This is demonstrated in fig. 3 which shows the decay of ketenyl recorded in the presence and absence of

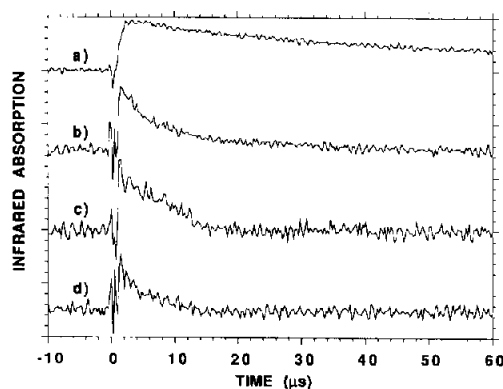


Fig. 1. HCCO infrared absorption time behavior at various O_2 pressures: (a) no added O_2 , (b) 3.0 Torr O_2 , (c) 5.6 Torr O_2 , (d) 6.9 Torr O_2 . Signal-to-noise has been sacrificed in order to limit the contribution of radical-radical reactions to the decay.

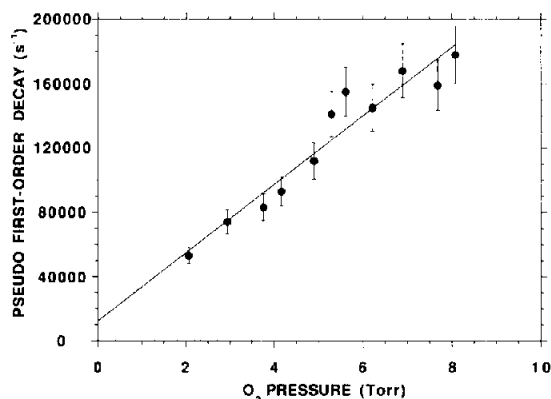


Fig. 2. Stern-Volmer plot for the reaction of HCCO and O_2 . Errors are estimated as $\pm 10\%$ of the measured pseudo first-order decay rate and are so indicated by the error bars on the plot. The second-order rate constant of $6.5(6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was determined from the slope of the least squares fit line.

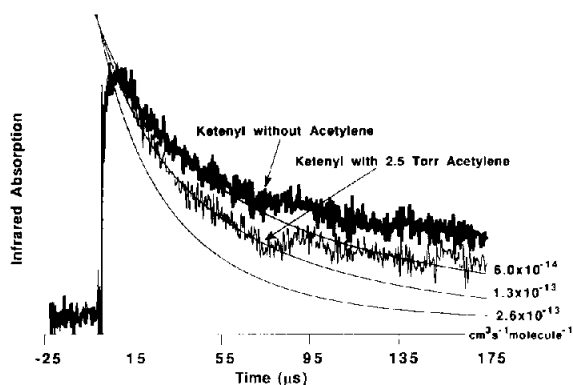


Fig. 3. HCCO infrared absorption time behavior in the presence and absence of 2.5 Torr HCCH. Also shown are three decay curves computed assuming that ketenyl, in the presence of acetylene, decays by simultaneous first- and second-order decay processes with the second-order contribution equal to that observed for ketenyl in the absence of acetylene. From a comparison of the actual decay to those predicted in the three simulations, an upper bound for the rate constant of the reaction of HCCO with acetylene was estimated as $1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

2.5 Torr of acetylene, the maximum partial pressure of acetylene that could be added without causing significant extra absorption of the 193 nm excimer radiation. Fig. 3 also shows three decay curves computed by using rate constants for the reaction between ketenyl and acetylene of 0.65×10^{-13} , 1.3×10^{-13} , and $2.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. In all of these simulations, contributions to the overall

decay from second-order rate processes were included. These contributions were chosen to reproduce the experimentally observed second-order decay of ketenyl in the absence of acetylene (we imagine this to be due to reaction with atomic hydrogen, whose initial concentration is equal to that of HCCO). From a comparison of the actual decay to those predicted in the three simulations, an upper bound to the rate constant for reaction of HCCO with acetylene could be estimated as $1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Since the reaction of HCCO with molecular oxygen can occur, in principle, via several different exothermic channels, an attempt was made to identify the major reaction channel by determining the yield of CO from this reaction. In a series of experiments performed using excimer pulse energies greater than those used to measure rate parameters, carbon monoxide was observed in its ground state and in various vibrationally excited states (up to $v=5$) in both the presence and absence of O_2 . The vibrationally excited states were observed to relax with decay constants ranging from approximately 10 to 15 μs , whilst the ground state was observed to grow asymptotically to a constant level that was reached in about 30 μs . The most striking feature of all of these experiments was that the final yield of CO did not change as O_2 was added to the reaction mixture.

4. Discussion

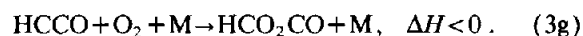
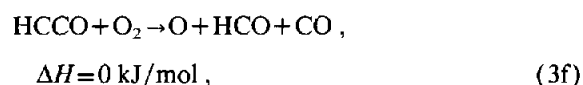
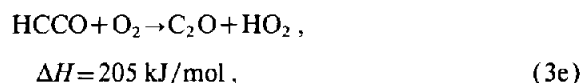
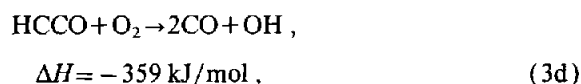
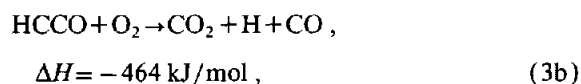
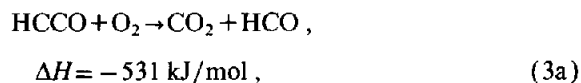
The rate constant for the reaction of ketenyl with O_2 measured in this study compares well with the value of $6.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Peeters et al. [5] but is more than an order of magnitude greater than the value of $3.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Jones and Bayes [9]. Both previous determinations were made by using mass spectroscopic detection to monitor, in a discharge-flow system, various species produced and consumed during the reaction of atomic oxygen with acetylene. Peeters et al. devised a scheme to obtain an absolute calibration of their ketenyl spectra, and we suspect that this calibration procedure together with the use of a more accurate and complete mechanism for the C_2H_2/O reaction allowed them to determine a more reliable rate constant.

The upper bound of $1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ determined for the rate of reaction between ketenyl and acetylene is probably overly conservative. Atomic hydrogen, which is known to be produced in the 193 nm photolysis of acetylene, reacts rapidly with ketenyl and this species probably accounts for the somewhat faster decay of HCCO that is evident, in the presence of acetylene, in fig. 3 at very short reaction times. At longer reaction times, no acceleration of the reaction rate was observed although the concentration of acetylene, which was added in great excess, could not have been sensibly diminished by either photolysis or reaction. Our determination of the rate constant is consistent with the upper bounds of 8×10^{-16} and $2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Jones and Bayes [8] and Homann and Wellmann [10], respectively. In order to be consistent with the value of $5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ measured by Vinckier et al. at 535 K [11], the activation energy for this reaction would have to be greater than 9.2 kJ/mol.

In flames and other combustion systems, ketenyl is presumably destroyed by reactions with O_2 , the fuel, and the most prevalent free radical species present (usually O, H, and OH). Rate constants for reactions of HCCO with several active species are given in table 1. As can be seen, the reaction between HCCO and O_2 is approximately 200 times slower than those between HCCO and either O or H, both of which occur on almost every collision. Since numerous experimental measurements [23,24] and computer modelling studies [1] indicate that $[\text{O}_2]$ is at least 100 times greater than the concentration of free radicals in lean (oxygen-rich) flames, and since the rate of reaction of HCCO with O_2 is likely to increase with temperature, the reaction with O_2 must be the major one removing ketenyl in lean

flames. In fuel rich flames, the concentration of H increases to levels that make reaction with it the primary loss mechanism for ketenyl [25]. The slowness of the reaction of ketenyl with acetylene suggests that this reaction is unlikely to be of importance in combustion systems.

Several possible channels exist for the reaction of ketenyl with molecular oxygen:



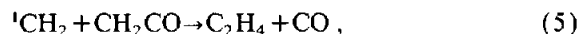
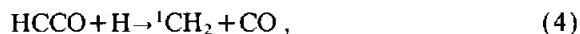
Here, heats of reaction were determined from the JANAF tables [26], using the heat of formation of HCCO determined by Oakes and Ellison [27] (177 kJ/mol), and that for C_2O (372 kJ/mol) calculated by Walch [28].

In the absence of molecular oxygen, HCCO reacts with atomic hydrogen to produce CO and singlet methylene [29], which then reacts with ketene primarily to produce ethylene and a second molecule of CO [22],

Table 1
Rates of HCCO destruction reactions at 298 K ^{a)}

Reagent	This work	Ref. [11]	Ref. [8]	Ref. [5]	Ref. [9]	Ref. [10]	Ref. [7]
H		1600 ^{a)}					
O		1200(300)	20(5)	1300(300)			
O_2	6.5(6)			6.3	0.37(19)		
HCCH	<1	<5	<0.008			<0.2	
NO							390(5)

^{a)} Rate ($10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).



although in this latter reaction some deactivation (<30%) to produce methylene in its less reactive triplet state has been reported [30]. The observation that the final concentration of CO produced was not changed when O₂ was added to the system suggests that reaction (3d) may be the major reaction channel, since this channel produces two molecules of CO for every molecule of HCCO consumed (although we cannot rule out (3f) as the HCO would react with O₂ in our system to produce HO₂ and a second CO). Unfortunately this conclusion concerning reaction (3d) can only be regarded as tentative until a definitive measurement is made of the relative quantum yields of ketenyl and singlet methylene in the 193 nm photolysis of ketene.

Acknowledgement

This work was supported by the Robert A. Welch Foundation and the Department of Energy. KGU and KKM wish to thank the Robert A. Welch Foundation for pre and post doctoral fellowships, respectively.

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