The Ketyl Radical in the Oxidation of Ethyne by Atomic Oxygen at 300–600 K

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The reaction of ethyne with atomic oxygen was investigated in the temperature range 300-600 K, at a pressure of 2 torr. With molecular beam mass spectrometry, both methylene and the ketyl radical were shown to be important primary products. An absolute measurement was made of the rate constant of reaction 7 of HCCO with O at T = 535 K: $k_7 = (1.10 \pm 0.10)$ $\times 10^{14}$ cm³ mol⁻¹ s⁻¹. The activation energy E_7 was found to be $E_7 = 0.6 \pm 0.3$ kcal mol⁻¹. Reaction 2 of HCCO with H atoms is even faster; in Stern-Volmer experiments the ratio k_2/k_1 was determined to be 1.4 ± 0.4 at T = 535 K and 1.3 \pm 0.2 at T = 285 K.

Introduction

In spite of various investigations, the nature of the primary products of the reaction of ethyne with atomic oxygen is still a matter of controversy:

 $C_2H_2 + O \rightarrow CH_2 + CO \quad \Delta H = -47 \text{ kcal mol}^{-1}$ (1a)

 \rightarrow HCCO + H $\Delta H = -19$ kcal mol⁻¹ (1b)

\rightarrow other products

Fenimore¹ suggested reaction 1a as the dominant reaction path at flame temperatures. The view that CH_2 is the major product, while HCCO formation-at least at low to moderate temperatures-is negligible, was supported by the crossed molecular beam experiments of Hoyermann et al.,² by the modeling of stable product formation of Homann et al.,³ and by the Hproduction analysis of Lohr et al.⁴ in shock tubes.

On the other hand, ab initio calculations by Harding⁵ show that the H-displacement path 1b is energetically favored; also the HCCO radical was detected in crossed molecular beam experiments by Clemo.⁶ The occurrence of both reaction paths simultaneously is also proposed by several groups: Bayes⁷ found at least 12 and probably 25% methylene formation; Williamson⁸ concluded that route 1b accounts for about 40% of the total product formation. Both CH₂ and HCCO were detected as major products in a crossed molecular beam experiment by Gutman.⁹ From an approximate calibration of the CH₂ concentration Vinckier¹⁰ deduced that reaction channel 1a accounts for about 50% of the primary C₂H₂ destruction rate. According to Aleksandrov¹¹ the production of hydrogen atoms shows that at room temperature 5% and at 600 K 16% of the primary reaction proceeds via HCCO.

In addition to the conflicting views regarding the importance of the ketyl radical as a primary product, little is known concerning the kinetics of its destruction reactions. An early investigation of the reactions of HCCO with O and O_2 led Bayes to conclude that both were rather slow processes.^{12,13} Since in the ethyne–O

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TABLE I: Selected Electron Energies

					C ₃ H ₄ ,		
species	CH_2	0	C_3H_2	C ₃ H ₃	C ₂ O	HCCO	
$E_{\rm el}/{\rm eV}$	13.1	15.4	14.4	12.7	14.4	12.9	

system nearly every reacting oxygen atom releases one hydrogen atom, high concentrations of hydrogen atoms can be established rapidly so that reactions with intermediates might become important. The reaction of HCCO with H is of special interest because it could be an additional source of CH₂ in the C₂H₂-O oxidation and/or an important formation route for C₂O, as proposed by Becker²⁹ and Faubel:²¹

HCCO + H \rightarrow CH₂ + CO $\Delta H = -29$ kcal mol⁻¹ (2a)

$$\rightarrow C_2 O + H_2 \quad \Delta H = -5.5 \text{ kcal mol}^{-1}$$
 (2b)

 \rightarrow HCCOH* $\Delta H = -55$ kcal mol⁻¹ (2c)

Recently determined values of $\Delta H_{\rm f}(\rm HCCO) = 42.4 \ \rm kcal \ mol^{-1.14}$ and $\Delta H_{f}(C_2O) = 89$ kcal mol⁻¹¹⁵ are used for the calculation of reaction enthalpies. Methylene^{16,17} as well as C₂O^{18,19} are proposed to be the main precursor of the CH radical, of key importance in soot formation processes in flames²⁰ as well as in chemi-ionization.¹⁶ The adduct formed in reaction 2c could lead to C₂H and polyacetylene formation.²¹

In this work, the primary character of both HCCO and CH₂ in the C_2H_2 + O reaction will be examined as well as the kinetics of reactions of the ketyl radical with O and H in the temperature range of 285-540 K. Also a maximum rate constant of its reaction with ethyne will be derived.

Experimental Section

The experimental setup has been described previously^{10,22} and only the major characteristics will be repeated here. It consists of a quartz fast-flow reactor (i.d. = 1.6 cm), passivated with HF, with continuous flows of reagents at a total pressure of 2 torr. Oxygen atoms were generated by passing a mixture of oxygen in helium through a microwave discharge operating at 2450 MHz. The oxygen atom concentration was determined from O₂ con-

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Figure 1. Ion signal profiles of O (\bullet), HCCO (\Box), and CH₂ (O): T = 535 K, $[C_2H_2]_0 = 4.3 \times 10^{-10}$ mol cm⁻³, $[O]_0 = 4.5 \times 10^{-13}$ mol cm⁻³. The solid lines are calculated by assuming formation via reaction 1 and first-order destruction with C_2H_2 : (A) $k_5 = 3 \times 10^{11}$ cm³ mol⁻¹ s⁻¹; (B) $k_4 = 1.5 \times 10^{11}$ cm³ mol⁻¹ s⁻¹.

centrations with the discharge on and off, respectively. Hydrogen atoms were produced and their concentration was measured in a similar way. Atom concentrations were verified by the usual titration techniques. Ethyne, diluted in helium, was added through a coaxial movable injector tube, allowing variation of the reaction time from 0 to 10 ms at room temperature, at a linear flow velocity of 23 m s⁻¹. With a heating tape strapped around the reactor, temperatures up to 550 K could be obtained.

At the downstream end of the reactor tube, gas is sampled through a 0.3-mm pinhole in a hollow quartz cone giving access to the first of two differentially pumped low-pressure chambers. After chopping in the first stage and skimming, the resulting molecular beam is analyzed by means of an Extranuclear quadrupole mass spectrometer mounted in the second chamber. Ionization occurs by electron impact at an electron energy only a few electronvolts above the ionization potential of the species that is being monitored (Table I). Corrections of the HCCO signals due to contribution of the mass 41 isotope of C_3H_4 are made when necessary. A lock-in amplifier distinguishes between the beam signal and background ions. The detection limit for most species is in the range of 20 to 100 ppb.

The reagents used are 99.9996% He (L'Air Liquide) and mixtures containing 1% H₂ in 99.9999% He (Matheson), 1% O₂ in UHP He, and 1% C₂H₂ in HP He (both Gardner Cryogenics).

A statistical analysis of the results was made by using the method of least squares and 95% confidence limits were determined with the Student's t method.

Results and Discussion

Identification of CH_2 and HCCO as Primary Products. At a sufficiently large excess of ethyne and at a low oxygen atom concentration, the latter will be converted nearly quantitatively into primary products. Also, in those circumstances, secondary reactions involving atomic oxygen will be negligible. In order to obtain a sufficiently high primary reaction rate at a moderate C_2H_2 concentration, the experiment was carried out at a temperature of 535 K; k_1 is then about ten times higher than at room temperature. Experimental conditions were as follows: $[C_2H_2]_0 =$ 4.3×10^{-10} mol cm⁻³, $[O]_0 = 4.5 \times 10^{-13}$ mol cm⁻³, $[O_2]_0 = 9 \times 10^{-13}$ mol cm⁻³.

Relative concentration profiles of O, CH₂, HCCO, C₃H₂, C₃H₃, and C₂O/C₃H₄ are shown in Figures 1 and 2. The observed rate of decay of O agrees reasonably well with the known rate constant of the primary reaction.²³ At reaction times of 1 and 3 ms, respectively 42 and 79% of the oxygen atoms are converted.



Figure 2. Ion signal profiles of $C_3H_2(\Box)$, $C_3H_3(O)$, and $C_3H_4/C_2O(\bullet)$. The conditions are the same as in Figure 1.

Large product signals were observed for both HCCO and CH₂; their profile shapes are similar and characteristic for primary products. Secondary formation of HCCO out of CH₂ obviously would require two additional steps, one of them involving either O or O₂. Due to the fast decay of the oxygen atom concentration only a minor fraction of the primary products disappears in secondary reactions with O. Using a destruction rate constant, k_{sec} , of 1×10^{14} cm³ mol⁻¹ s⁻¹, one calculates that less than 3% of the primary products react with O. Since the concentration of C₂H₂ exceeds by a factor of 500 the molecular oxygen concentration, reaction of the latter with methylene will be negligible; the rate constant of the reaction of CH₂ with O₂ is only 2²⁴ to 4²² times higher than that of the reaction with ethyne. Also, the reaction

$$C_3H_3 + O_2 \rightarrow HCCO + CH_2O \quad \Delta H = -67 \text{ kcal mol}^{-1} \quad (3)$$

cannot account for HCCO formation as one can readily see by comparing the HCCO and C_3H_3 profile shapes. The rate of HCCO formation by reaction 3 would still rise at the end of the reaction zone, since the O_2 concentration remains constant, while the rate of loss of HCCO, mainly by reaction with C_2H_2 , is constant, implying that the HCCO concentration should keep increasing.

Likewise, secondary formation of methylene out of the ketyl radical by the reaction

$$HCCO + H \rightarrow CH_2 + CO$$
 (2a)

can be rejected on the grounds that the CH_2 profile shape would then be markedly sigmoidal, in conflict with the observations.

Both the observed magnitude and the rapid growth of the CH_2 and HCCO signals strongly indicate that these species are major primary products. These observations are also in agreement with a first-order dependence of both HCCO and CH_2 signals on the initial ethyne concentration varying between 5×10^{-11} and 60×10^{-11} mol cm⁻³ at constant [O].^{12,22}

The C_2O radical, also suggested to be a primary product

$$C_2H_2 + O \rightarrow C_2O + H_2 \quad \Delta H = -24 \text{ kcal mol}^{-1} \quad (1c)$$

cannot be distinguished from C_3H_4 with our experimental technique. However, it can be judged to account for no more than a few percent of the total products, on the basis of the signal strength (see Figure 2). This is in agreement with earlier observations.⁷

The presence of C_3H_2 and C_3H_3 is indicative of subsequent reactions of CH_2 and HCCO with ethyne:

$$CH_2 + C_2H_2 \rightarrow C_3H_2 + H_2 \quad \Delta H = -26 \text{ kcalmol}^{-1}$$
 (4a)

$$\rightarrow$$
 C₃H₃ + H $\Delta H = -13 \text{ kcal mol}^{-1}$ (4b)

HCCO + C₂H₂ \rightarrow C₃H₃ + CO $\Delta H = -42 \text{ kcal mol}^{-1}$ (5)

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TABLE II: CH₂ and HCCO Signals as a Function of Reaction Time^a

-	•		
t/ms	$i_{\rm CH_2}/\mu { m V}$	i _{HCCO} /µV	
0.2	28.5	97	
0.6	29.0	89	
1.1	29.5	93	
1.9	31.0	98	

 a [C₂H₂]₀ = 3.4 × 10⁻¹⁰ mol cm⁻³, [O]₀ = 2.5 × 10⁻¹⁰ mol cm⁻³.

The weak m/e 40 signal excludes the C₃H₄ species from being an important product of reaction 4, in agreement with earlier findings.¹⁰

The decay of HCCO and CH₂ at larger reaction times can be ascribed to the reactions 4 and 5 with C₂H₂. A good fit is obtained with $k_1 = 1.25 \times 10^{12}$, $k_4 = 1.5 \times 10^{11}$, and $k_5 = 3 \times 10^{11}$ cm³ mol⁻¹ s⁻¹, at T = 535 K (see calculated curves A and B in Figure 1). The k_4 value thus obtained should be regarded as a lower limit because of possible secondary formation of CH₂ by reaction 2a. Evidence for the occurrence of this reaction path is provided by the detection of methylene in the C₃O₂/H system,²⁵ where HCCO is formed as a primary product.²¹

$$C_3O_2 + H \rightarrow HCCO + CO \quad \Delta H = -14 \text{ kcal mol}^{-1} (6)$$

The k_5 value on the other hand could be overestimated since reaction with H can also contribute to HCCO removal. Bayes¹² reported an upper limit $k_5 \le 5 \times 10^8$ cm³ mol⁻¹ s⁻¹ at 300 K for this reaction.

Though the former experiment verifies the primary character of both CH₂ and HCCO, it cannot be excluded that one of them is a product of a heterogeneous reaction between ethyne and atomic oxygen on the reactor wall. In order to investigate this possibility an experiment was carried out in which both products were measured, starting from a short reaction time of about 0.2 ms. Experimental conditions were T = 285 K to reduce diffusion velocities, $[C_2H_2]_0 = 3.4 \times 10^{-10}$ mol cm⁻³, $[O]_0 = 2.5 \times 10^{-10}$ mol cm⁻³, and p = 2 torr. Using Einstein's diffusion law, one can estimate the mean time needed for a product formed on the wall to reach the center of the reactor where the sampling probe is situated. If a diffusion coefficient $D = 300 \text{ cm}^2 \text{ s}^{-1}$ at 285 K and at 2 torr is assumed, this mean time is about 1.1 ms. Table II shows the constancy of both CH2 and HCCO, already at very short reaction times. These reaction times, derived from the distance between mixing and sampling point, could be somewhat underestimated due to back diffusion. Nevertheless, it is obvious that neither CH₂ nor HCCO can be formed solely on the reactor wall. These observations lead us to conclude that both CH₂ and HCCO are important primary products of the gas-phase reaction between ethyne and atomic oxygen.

It is clear from the above that in the modeling of the ethyne oxidation both CH_2 and HCCO will have to be taken into account. Unfortunately this work did not allow us to quantify the relative importance of channels 1a and 1b.

Kinetics of HCCO Reactions. In order to evaluate the behavior of the ketyl radical and its role in ethyne oxidation, kinetic information regarding the destruction reactions of HCCO is of paramount importance. The obvious way to determine an absolute value for these rate constants is the approach of the HCCO concentration toward its stationary value. To achieve reasonably high spectrometer output signals for HCCO a relatively high primary reaction rate is required. Since raising the ethyne concentration might introduce interfering reactions with the fuel, it was preferred to increase the temperature to 535 K, ensuring a large enough value of k_1 .

As a consequence of the fairly high rate of reaction between C_2H_2 and O, a sizeable amount of oxygen atoms is converted into atomic hydrogen. This means that HCCO can react with both O and H:

HCCO + O
$$\rightarrow$$
 2CO + H $\Delta H = -102 \text{ kcal mol}^{-1}$ (7)

$$HCCO + H \rightarrow products \qquad (2)$$

(25) M. Schaekers, unpublished results.



Figure 3. Stern-Volmer plots of HCCO as a function of [H]/[O]: (A) $T = 285 \text{ K}, [C_2H_2]_0 = 4.4 \times 10^{-10} \text{ mol cm}^{-3}, [O]_0 = 2.0 \times 10^{-10} \text{ mol cm}^{-3};$ (B) $T = 535 \text{ K}, [C_2H_2]_0 = 1.2 \times 10^{-10} \text{ mol cm}^{-3}, [O]_0 = 8.7 \times 10^{-11} \text{ mol cm}^{-3}.$

Hence, under these circumstances, knowledge of k_2/k_7 is a prerequisite for deriving k_7 from an approach to steady state. The dependence of the stationary HCCO concentration on O and H concentrations follows the Stern-Volmer law

$$\frac{[C_2H_2]}{[HCCO]_{ss}} = \frac{k_7}{k_{1b}} + \frac{k_2}{k_{1b}} \frac{[H]}{[O]}$$
(I)

The ratio k_2/k_7 can be found from the ratio of slope to intercept of a $i_{(C2H2)}/i_{(HCCO)_{ss}}$ vs. [H]/[O] plot. In a reaction mixture at 285 K with [O]₀ = 2.0 × 10⁻¹⁰ and [C₂H₂]₀ = 4.4 × 10⁻¹⁰ mol cm⁻³ the species of interest were monitored as a function of the reaction time up to t = 10 ms. Under these conditions [H]/[O] ratios vary more than a factor of 3. The Stern–Volmer plot yielded a ratio $k_2/k_7 = 1.3 \pm 0.2$ (line A of Figure 3). A similar procedure, at T = 535 K, with [O]₀ = 8.7 × 10⁻¹¹ and [C₂H₂]₀ = 1.2 × 10⁻¹⁰ mol cm⁻³ resulted in $k_2/k_7 = 1.4 \pm 0.4$ (line B of Figure 3), indicating that reactions 2 and 7 have nearly the same activation energy.

A study of the effect induced by addition of molecular oxygen through a side inlet proved the reaction of HCCO with undissociated oxygen molecules which are normally present in the reaction system to be negligible.

Since the reaction of HCCO with H appears to be fast, it has to be taken into account when interpreting the approach of the HCCO concentration toward steady state in circumstances where a significant fraction of O is converted to H. As a consequence the usual approach-to-steady-state procedure cannot be applied. Instead, the first-order coupled differential equations describing the changes in concentration of the various species as a function of time have to be solved simultaneously by a numerical procedure. The reactions considered in this analysis are listed in Table III. The value of k_1 was determined from the measured O-atom profile; the rate of wall loss of H atoms was measured in a separate experiment. The shape of the HCCO profile is determined by k_2 and k_7 , the absolute magnitude of [HCCO] by k_{1b} . Hence relative signals suffice to derive k_2 and k_7 . Since the ratio k_2/k_7 is known, there is one parameter—say k_7 —that has to be adjusted such that the computed profile shape fits the experimental one.

The "best-fit" k_7 value is taken as that for which the "standard deviation" s(x)

$$s(x) = \{\sum_{i=1}^{n} (gx_i^* - x_i)^2 / (n-2)\}^{1/2}$$
(II)

passes through a minimum. Here, x_i is the relative HCCO signal at a reaction time t_i , x_i^* is the corresponding calculated HCCO concentration for a given k_7 , n is the number of measurements, and g is a scaling factor, chosen such that $\sum_i (gx_i^* - x_i)^2$ for the given k_7 is minimal:

$$g = \sum_{i=1}^{n} (x_i^* x_i) / \sum_{i=1}^{n} (x_i^*)^2$$
(III)

The confidence interval assigned to k_7 , in terms of Student's t, is approximated by²⁶

$$k_7 \pm t \{\sum_{i=1}^n (\partial k_7 / \partial x_i)^2 (s(x))^2 \}^{1/2}$$
 (IV)

TABLE III: Reaction System Considered for the Determination of k_7 at 535 K

reactions	adopted parameters p_j	$\partial k_7 / \partial p_j$	$(\partial k_7/k_7)/(\partial p_j/p_j)$
$C_2H_2 + O \rightarrow CH_2 + CO (1a)$	$k_1 = 1.25 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	-28.6	-0.33
$C_2H_2 + O \rightarrow HCCO + H (1b)$	$k_{1b}/k_1 = 0.7^a$	$-1.7 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	-0.11
$HCCO + O \rightarrow 2 CO + H (7)$	$k_7 = 1.1 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (best-fit value)		
$HCCO + H \rightarrow CH_2 + CO (2a)$	$k_{2a}/k_7 = 1.4$	$-2.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	-0.26
$CH_2 + O \rightarrow CO + 2 H (8)$	$k_8 = 8 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} b$	-0.09	-0.07
$CH_2 + H \rightarrow products (9)$	$k_9 = 6 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1 a}$	+0.01	+0.005
$H + wall \rightarrow products (10)$	$k_{10} = 40 \text{ s}^{-1}$	$+5.0 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	+0.02

"Estimate. ^bReference 22.



Figure 4. Approach of [HCCO] to steady state; T = 535 K, $[C_2H_2]_0 =$ $\begin{array}{l} 1.2 \\ 5.2 \\ \times 10^{-11} \\ \text{mol cm}^{-3}: \\ (\text{A}) \\ [\text{O}]_0 = 1.58 \\ \times 10^{-12}, \\ k_7 = (1.26 \\ \pm 0.22) \\ \times 10^{14}; \\ (\text{B}) \\ [\text{O}]_0 = 3.15 \\ \times 10^{-12}, \\ k_7 = (0.97 \\ \pm 0.06) \\ \times 10^{14}; \\ (\text{C}) \\ [\text{O}]_0 = 1.58 \\ \times 10^{-12}, \\ k_7 = (1.26 \\ \pm 0.22) \\ \times 10^{14}; \\ (\text{C}) \\ [\text{O}]_0 = 1.58 \\ \times 10^{-12}, \\ k_7 = (1.26 \\ \pm 0.22) \\ \times 10^{14}; \\ (\text{C}) \\ [\text{O}]_0 = 1.58 \\ \times 10^{-12}, \\ k_7 = (0.97 \\ \pm 0.06) \\ \times 10^{14}; \\ (\text{C}) \\ [\text{O}]_0 = 1.58 \\ \times 10^{-12}, \\ k_7 = (1.26 \\ \pm 0.22) \\ \times 10^{14}; \\ (\text{C}) \\ (\text{C})$ $4.75 \times 10^{-12}, k_7 = (1.15 \pm 0.12) \times 10^{14}; (D) [O]_0 = 4.75 \times 10^{-12}, k_7 =$ $(1.24 \pm 0.07) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Equation IV is arrived at by recognizing that the best-fit k_7 value, derived as outlined above, is a function of the HCCO signals x_i , each of which is treated as an independent quantity. The partial derivative $\Delta k_{\gamma}/\partial x_i$ was determined numerically by varying x_i while keeping all the remaining $x_{i\neq i}$ constant.

Four approach-to-steady-state experiments, carried out at T = 535 K, are shown in Figure 4. In each the initial $[C_2H_2]$ was 5.2×10^{-11} mol cm⁻³. The resulting best-fit values of k_7 are k_7 = $(1.26 \pm 0.22) \times 10^{14}$ (line A), $(0.97 \pm 0.06) \times 10^{14}$ (line B), $(1.15 \pm 0.12) \times 10^{14}$ (line C), and $(1.24 \pm 0.07) \times 10^{14}$ cm³ mol⁻¹ s^{-1} (line D) for initial concentrations of $[O]_0$ of respectively 1.58 $\times 10^{-12}$, 3.15×10^{-12} , 4.75×10^{-12} , and 4.75×10^{-12} mol cm⁻³. The above values result in a weighted mean value of $k_7 = (1.10)$ \pm 0.10) × 10¹⁴ cm³ mol⁻¹ s⁻¹.

Possible systematic errors due to the choice of the parameters $p_i(k_1, k_{1b}/k_1,...)$ in the numerical integration procedure were examined by means of a simple "brute force" sensitivity analysis. In this direct method it is assumed that a single variation Δp_i is, with some restrictions,²⁷ sufficient to calculate each $\partial k_7 / \partial p_j$. The resultant linear parametric sensitivity coefficients together with the relative values are listed in Table III. The parameters to which k_7 appears to be most sensitive are k_1 , k_{1b}/k_1 , and k_2/k_7 . The maximum systematic error induced in k_7 by the uncertainty of these parameters is about 10%. Taking for k_1 the value 0.85 \times 10^{12} cm³ mol⁻¹ s⁻¹ ²³ instead of 1.25×10^{12} would result in a best fit for $k_7 = 1.2 \times 10^{14}$ cm³ mol⁻¹ s⁻¹. Likewise, changing k_{1b}/k_1 from 0.7 to 0.3 increases k_7 to 1.2×10^{14} cm³ mol⁻¹ s⁻¹

TABLE IV: Ethyne and Ketyl Signals under Various Conditions

$[C_2H_2]_0/$			
mol cm ⁻³	$[O]_0/mol \ cm^{-3}$	$i_{C_2H_2}/mV$	$(i_{\rm HCCO})_{\rm ss}/\mu {\rm V}$
9.85×10^{-11}	1.17 × 10 ⁻¹¹	6.60	9.0
2.80×10^{-10}	2.11×10^{-11}	14.45	26.2
9.14×10^{-11}	1.15×10^{-11}	5.79	8.4
9.14×10^{-11}	1.09×10^{-11}	6.04	12.1
8.35×10^{-11}	9.92×10^{-12}	6.05	17.2
7.44×10^{-11}	9.35×10^{-12}	5.52	15.6
1.44×10^{-10}	9.09×10^{-12}	10.60	29.6
7.83×10^{-11}	9.31×10^{-12}	5.82	18.6
7.30×10^{-11}	8.67×10^{-12}	5.81	24.2
6.40×10^{-11}	8.04×10^{-12}	5.08	27.0
1.25×10^{-10}	1.35×10^{-11}	9.73	55.4
5.38×10^{-11}	6.76×10^{-12}	4.89	45.0
1.05×10^{-10}	6.05×10^{-12}	7.52	82.5
4.79×10^{-11}	6.02×10^{-12}	4.50	65.8
4.58×10^{-11}	6.50×10^{-12}	4.18	48.0
	$[C_2H_2]_0/ \mod cm^{-3}$ 9.85 × 10 ⁻¹¹ 2.80 × 10 ⁻¹⁰ 9.14 × 10 ⁻¹¹ 9.14 × 10 ⁻¹¹ 8.35 × 10 ⁻¹¹ 7.44 × 10 ⁻¹¹ 1.44 × 10 ⁻¹⁰ 7.83 × 10 ⁻¹¹ 7.30 × 10 ⁻¹¹ 7.30 × 10 ⁻¹¹ 1.25 × 10 ⁻¹⁰ 5.38 × 10 ⁻¹¹ 1.05 × 10 ⁻¹⁰ 4.79 × 10 ⁻¹¹ 4.58 × 10 ⁻¹¹	$\begin{array}{c c} [C_2H_2]_{0}/\\ mol\ cm^{-3} & [O]_{0}/mol\ cm^{-3} \\ \hline \\ 9.85\times10^{-11} & 1.17\times10^{-11} \\ 2.80\times10^{-10} & 2.11\times10^{-11} \\ 9.14\times10^{-11} & 1.15\times10^{-11} \\ 9.14\times10^{-11} & 1.09\times10^{-11} \\ 8.35\times10^{-11} & 9.92\times10^{-12} \\ 7.44\times10^{-11} & 9.35\times10^{-12} \\ 1.44\times10^{-10} & 9.09\times10^{-12} \\ 7.83\times10^{-11} & 9.31\times10^{-12} \\ 7.83\times10^{-11} & 8.04\times10^{-12} \\ 7.83\times10^{-11} & 8.04\times10^{-12} \\ 1.25\times10^{-10} & 1.35\times10^{-11} \\ 5.38\times10^{-11} & 6.76\times10^{-12} \\ 1.05\times10^{-10} & 6.05\times10^{-12} \\ 4.79\times10^{-11} & 6.50\times10^{-12} \\ \hline \end{array}$	$\begin{array}{c c} [C_2H_2]_{0}/\\ \hline mol\ cm^{-3} & [O]_0/mol\ cm^{-3} & i_{C_2H_2}/mV \\ \hline 9.85\times10^{-11} & 1.17\times10^{-11} & 6.60 \\ 2.80\times10^{-10} & 2.11\times10^{-11} & 14.45 \\ 9.14\times10^{-11} & 1.15\times10^{-11} & 5.79 \\ 9.14\times10^{-11} & 1.09\times10^{-11} & 6.04 \\ 8.35\times10^{-11} & 9.92\times10^{-12} & 6.05 \\ 7.44\times10^{-11} & 9.35\times10^{-12} & 5.52 \\ 1.44\times10^{-10} & 9.09\times10^{-12} & 10.60 \\ 7.83\times10^{-11} & 9.31\times10^{-12} & 5.81 \\ 6.40\times10^{-11} & 8.04\times10^{-12} & 5.08 \\ 1.25\times10^{-10} & 1.35\times10^{-11} & 9.73 \\ 5.38\times10^{-11} & 6.76\times10^{-12} & 4.89 \\ 1.05\times10^{-10} & 6.05\times10^{-12} & 4.50 \\ 4.58\times10^{-11} & 6.50\times10^{-12} & 4.18 \\ \end{array}$

It is worth noting that a conventional analytical approach-tosteady-state treatment of the data, disregarding HCCO removal by H, but allowing for O decay as observed, results in a k_7 value that is too high by a factor of 2, even though showing a narrow statistical distribution.

Under circumstances where relatively few hydrogen atoms are present (i.e., at low ethyne concentrations so that little oxygen is removed), it can be stated that the ketyl radical reacts solely with atomic oxygen, so that its stationary concentration is given bv

$$[\text{HCCO}]_{\text{ss}} = (k_{1\text{b}}/k_7)[\text{C}_2\text{H}_2] \tag{V}$$

This can be transformed into

$$\ln \frac{(i_{\rm HCCO})_{\rm ss}}{i_{\rm C_2H_2}} = C - (E_{\rm 1b} - E_{\rm 7})/RT \qquad (\rm VI)$$

In this equation C is a constant, E_{1b} and E_7 are the activation energies of reaction 1b and 7, respectively, i_{HCCO} and $i_{C_{2}H_{2}}$ are measured signals, with

$$\frac{(i_{\rm HCCO})_{\rm ss}}{i_{\rm C_2H_2}} = \frac{[\rm HCCO]_{\rm ss}(S_{\rm HCCO})_T}{[\rm C_2H_2](S_{\rm C,H_2})_T}$$
(VII)

In eq VI the sensitivity ratio $S_{\text{HCCO}}/S_{C_2H_2}$ is assumed independent of temperature on the grounds that the ratio $S_{C_2H_1}/S_{C_2H_2}$ was found to be constant within 6% from T = 285 to 540 K and that the change in sensitivity with temperature depends primarily on the molecular mass of the species; the mass of the stable compound C_3H_4 is nearly the same as that of HCCO.

The ketyl and ethyne signals at steady state have been determined in a temperature region between 285 and 535 K (Table IV). The appropriate plot (see Figure 5) yields an activation energy difference $(E_{1b} - E_7) = 2.6 \pm 0.3 \text{ kcal mol}^{-1}$. Since the Arrhenius plot of the ethyne plus O reaction shows no curvature in the temperature region concerned^{22,23} and because HCCO appears to be an important primary product, it can be stated that the activation energy E_{1b} for HCCO formation nearly equals the overall activation energy E_1 , which is 3.2 ± 0.16 kcal mol^{-1.22} These considerations result in an activation energy $E_7 = 0.6 \pm$ 0.3 kcal mol⁻¹. Combination with the directly measured value of k_7 at 535 K leads to the Arrhenius expression $k_7 = 1.93 \times 10^{14}$ $\exp(-300K/T)$ cm³ mol⁻¹ s⁻¹. In view of the way in which the

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Figure 5. Determination of $(E_7 - E_{1b})$ by plotting the left-hand side of eq VI as a function of 1/T.

above expression was obtained the statistical uncertainties are best derived from the expression

$$k_7 = (1.10 \pm 0.10) \times 10^{14} \exp \left[(300 \pm 150) \left(\frac{1}{535} - \frac{K}{T} \right) \right] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

At room temperature this results in $k_7 = (7.1 \pm 1.7) \times 10^{13}$ cm³ mol⁻¹ s⁻¹, 60 times higher than the value reported by Jones and Bayes.¹² The reason for this discrepancy is not clear yet, though it should be noted that the cited value was not derived from an approach of [HCCO] to the steady state as a function of time, but rather from the measured dependence of [HCCO] on the initial O-atom concentration in fuel-rich mixtures at a fairly large fixed reaction time, where important amounts of H atoms and other reactive intermediate species are present.

Knowing that reaction 7 is fast, it becomes clear that it is an important destruction route of HCCO. Since in the ethyne/O system nearly stoichiometric production of CO and H atoms is observed, these species must be the major products of the reaction

$$ICCO + O \rightarrow 2CO + H \quad \Delta H = -102 \text{ kcal mol}^{-1}$$
 (7)

Besides this main route, a small fraction might yield electronically

F

HCCO + O
$$\rightarrow$$
 HCO* + CO $\Delta H = -119 \text{ kcal mol}^{-1}$ (7a)

The reaction enthalpy given is for HCO in the ground electronic state. The reaction of HCCO with H is even faster; combination of k_7 and k_2/k_7 yields $k_2 = (9.2 \pm 2.6) \times 10^{13}$ cm³ mol⁻¹ s⁻¹ at T = 300 K. The relative importance of the various reaction paths is still uncertain and the ethyne oxidation system appears to be less suited for the determination of the branching ratio of reaction 2. Experiments with the C₃O₂/H system are now under way in order to establish whether the HCCO + H reaction is an important source of CH₂ radicals, which were already detected in preliminary work. If so, the ethyne oxidation mechanism is a rather complicated one in as much that the two primary products HCCO and CH₂ lead to interwoven reaction sequences.

Conclusion

Both the methylene and the ketyl radical were shown to be important primary products in the $C_2H_2 + O$ reaction; the branching ratio could not be established as yet. The reaction between HCCO and oxygen atoms was found to be much faster than previously reported, which implies that this reaction is one of the key processes in the ethyne oxidation. The above results also prove the reaction between ketyl radicals and atomic hydrogen to be fast. Furthermore, the constancy of the ratio k_2/k_7 at 285 and 535 K allows the conclusion that the HCCO + H reaction also is a low activation energy process (<1 mol⁻¹). Hence, this HCCO destruction path should be taken into account in modeling fast-flow and flame results—especially in fuel-rich mixtures. A further investigation is under way to determine the products of reaction 2, with a focus on the relative importance of CH₂ vs. C₂O formation (k_{2a}/k_{2b}).

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Registry No. C₂H₂, 74-86-2; HCCO, 55349-28-5; CH₂, 2465-56-7.

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