2247

Kinetics of the Reaction of Vinyl Radical with Molecular Oxygen

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The kinetics of the reaction $C_2H_3 + O_2 \rightarrow$ products (reaction 1) has been studied at temperatures 299–1005 K and He densities (3–18) x 10^{16} molecule cm^{-3} using laser photolysis/photoionization mass spectrometry. Rate constants were determined in time-resolved experiments as a function of temperature and bath gas density. The overall rate constant of reaction 1 is independent of pressure within the experimental range and can be described by the Arrhenius expression $k_1 = (6.92 \pm 0.17) \times 10^{-12} \exp((120 \pm 12 \text{ K})/T)$ cm^3 molecule^{-1} s^{-1}. Experimental results are compared with theoretical predictions, and implications for the mechanism of reaction 1 are discussed.

Introduction

Vinyl radicals are recognized as important intermediates in hydrocarbon combustion processes, with elementary reactions of C_2H_3 influencing both the rate and products of the overall combustion process. Although there is a growing body of evidence on the rate constants and products of vinyl reactions at room and slightly elevated temperatures,[1-7] the appropriateness of extrapolation of such results to the higher temperatures of combustion and flames has not yet been verified. The reaction of vinyl radicals with molecular oxygen

$$C_2H_3 + O_2 \rightarrow \text{products} \tag{1}$$
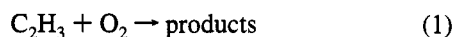
is particularly problematic.

The mechanism proposed by Baldwin and Walker[8] for reaction 1

$$C_2H_3 + O_2 \rightarrow HCO + H_2CO \tag{1a}$$
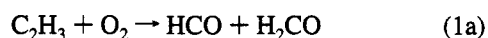
was confirmed by Gutman and co-workers,[1,2] who isolated reaction 1 for direct study at temperatures between 297 and 602 K and low pressures of helium (0.4–4.0 Torr). These studies detected HCO and H_2CO as the products of reaction 1 and determined a slightly negative temperature dependence of the reaction rate constant ($k_1 = (6.6 \pm 1.3) \times 10^{-12} \exp((126 \pm 50)K/T)$ cm^3 molecule^{-1} s^{-1}). The relatively high value of the room-temperature rate constant ($(1.06 \pm 0.21) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) determined by Gutman and co-workers was later corroborated by Krueger and Weitz[3] ($(1.0 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) and Fahr and Laufer[4] ($(6.7 \pm 2.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}).

Incorporation of reaction 1a and its associated Arrhenius parameters into combustion mechanisms had diverse effects on the agreement between modeled and experimental results. For example, Westmoreland et al.[9] found that inclusion of the products of reaction 1a in models of C_2H_2 flames resulted in improved simulation of the OH radical concentration. On the other hand, Hennessey et al.[10] report that incorporation of reaction 1a into their model of C_2H_6 flame chemistry is detrimental to the prediction of H_2CO concentrations, and Egolfopoulos et al.[11] reduced the rate constant determined by Slagle et al. by a factor of 4 in order to obtain closer agreement between experimentally and numerically determined laminar flame speeds in C_2H_4 flames.

The important role the reaction of vinyl radicals with O_2 plays in combustion prompted several theoretical studies of this reaction aimed at predicting the overall rate constant as well as the product branching ratios as a function of temperature. Westmoreland[12] and Bozzelli and Dean[13] applied quantum RRK analysis to predict the rate constants of several possible routes of reaction 1 over a wide range of pressures and temperatures, while Carpenter[14] studied the potential energy surface of the system using semiempirical and ab initio quantum chemical calculations.

The different rate parameters assigned to elementary steps in the models of the chemically activated system of reaction 1 resulted in significantly different predictions of the behavior of reaction 1 at high temperatures.[12,13] While the overall rate constant calculated by Bozzelli and Dean decreases only slightly with increasing temperature, Westmoreland predicts a strong decline of k_1 at $T > 600$ K, with values at 1000 K a factor of 4 lower than those at room temperature.
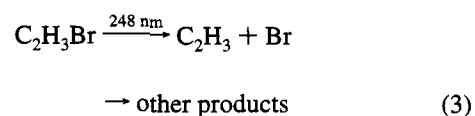
Because a change[15] in the design of the apparatus used by Slagle et al.[2] resulted in increased sensitivity, particularly at high temperatures, and because an improved wall-coating material, boron oxide, made it possible to extend the temperature range over which the vinyl + O_2 reaction could be studied, we have reinvestigated reaction 1 at temperatures up to 1005 K. The overall rate constants of reaction 1 were determined at temperatures 299–1005 K and bath gas (He) density (3–18) × 10^{16} molecule cm^{-3}. These experimental results are compared with the theoretical predictions and implications for the mechanism of reaction 1 are discussed herein.

Experimental Section

Vinyl radicals were produced by the pulsed, 193-nm laser photolysis of methyl vinyl ketone[6]

$$CH_3C(O)C_2H_3 \xrightarrow{193 \text{ nm}} C_2H_3 + \text{products} \tag{2}$$

or by the 248-nm laser photolysis of vinyl bromide

$$C_2H_3Br \xrightarrow{248 \text{ nm}} C_2H_3 + Br$$

$$\rightarrow \text{other products} \tag{3}$$

The decay of C_2H_3 was subsequently monitored in time-resolved experiments using photoionization mass spectrometry. Details of the experimental apparatus used have been described before.[15] In the current experimental setup, a quartz reactor coated with boron oxide was used. Neither the photolysis

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TABLE 1: Conditions and Results of Experiments To Measure k_1

T, K	[He], 10^{16} molecule cm^{-3}	[precursor], 10^{11} molecule cm^{-3}	[O$_2$], 10^{12} molecule cm^{-3}	k_4, s^{-1}	k_1,[a] 10^{-12} cm^3 molecule^{-1} s^{-1}
299	9.0	5.5	3.71−15.13	38.2	10.33 ± 0.54
299	9.0	11.7	4.74−15.09	66.7	10.92 ± 1.07
299	9.0	11.7	4.74−15.09	46.9	10.56 ± 0.72
399	9.0	4.5	6.25−21.63	31.5	9.01 ± 0.54
605	9.0	1.4	7.44−21.60	34.7	8.21 ± 0.55
705	6.0	5.0	2.03−18.89	36.1	7.99 ± 0.40
904	3.0	10.4	4.77−16.72	72.5	8.21 ± 0.83
904	6.0	4.8	2.87−24.00	40.4	7.90 ± 0.43
905	6.0	54.0[b]	5.33−19.85	44.7	8.54 ± 0.44
904	18.0	4.2	3.45−13.33	58.7	7.74 ± 0.58
904	18.0	4.2	3.45−13.33	54.3	7.81 ± 0.38
1005	6.0	54.0[b]	3.24−15.59	126.8[c]	7.65 ± 0.65

[a] All error limits are 1 σ. [b] 248-nm photolysis of C$_2$H$_3$Br was used for production of C$_2$H$_3$ radicals. 193-mn photolysis of methyl vinyl ketone was used in all other experiments. [c] Significant contribution from unimolecular decomposition.

wavelength nor the nature of the radical precursor had any observable influence on the kinetics of C$_2$H$_3$ radicals. Initial conditions (precursor concentration and laser intensity) were selected to provide low radical concentrations ($\leq 10^{11}$ molecule cm^{-3}), such that reactions between radical products had negligible rates compared to that of the reaction of vinyl radicals with molecular oxygen.

No information on the products of the vinyl + O$_2$ reaction at high temperatures could be obtained in this study. The combination of low concentrations, high background signals at the masses of interest, and rapid secondary reactions removing the possible reaction products from the system (e.g., HCO thermal decomposition) prevented the direct identification of the products of the C$_2$H$_3$ + O$_2$ reaction.

## Results

Experiments were conducted under pseudo-first-order conditions with [O$_2$] in the range 2.0×10^{12} to 2.4×10^{13} molecule cm^{-3}. The observed exponential decay of the C$_2$H$_3$ radical was attributed to reaction 1 and heterogeneous loss:

$$C_2H_3 \rightarrow \text{heterogeneous loss} \qquad (4)$$
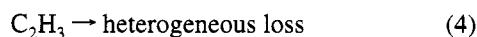
The vinyl ion signal profiles were fit to an exponential function ([C$_2$H$_3$]$_t$ = [C$_2$H$_3$]$_0$e$^{-k't}$) by using a nonlinear least squares procedure. In a typical experiment to determine k_1, the kinetics of the decay of C$_2$H$_3$ radicals was recorded as a function of concentration of molecular oxygen. Values of k_4 were determined in the absence of O$_2$. Values of k_1 were obtained from the slope of a linear plot of k' vs [O$_2$]. Experiments were performed to establish that the decay constants did not depend on the initial C$_2$H$_3$ concentration (provided that the concentration was kept low enough to ensure that radical−radical reactions had negligible rates in comparison to that of the reaction with O$_2$), the concentration of the radical precursor or the laser intensity, the nature of the precursor, and the laser wavelength−193 or 248 nm. The rate constants of reaction 1 were determined at $T = 299-1005$ K and [He] = $(3-18) \times 10^{16}$ atom cm^{-3}. The upper temperature limit of the experiments was determined by the onset of thermal decomposition of vinyl radicals. The conditions and results of these experiments are presented in Table 1. An example of a k' vs [O$_2$] plot is shown in Figure 1. The intercept at [O$_2$] = 0 corresponds to the rate of heterogeneous decay of C$_2$H$_3$ radicals, k_4.

The values of the bimolecular rate constant k_1 determined in this study are presented on an Arrhenius plot in Figure 2 together with data from earlier experimental and theoretical studies. The results of the current study yield the Arrhenius expression
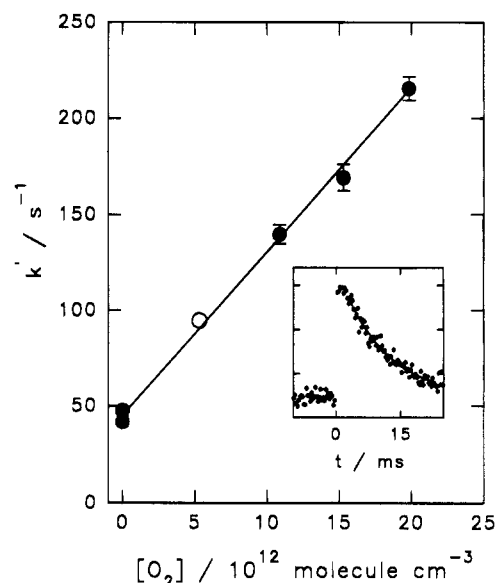

Figure 1. First order C$_2$H$_3$ decay rate k' vs [O$_2$]. The intercept at [O$_2$] = 0 corresponds to the rate of heterogeneous decay of C$_2$H$_3$ radicals. $T = 905$ K, [He] = 6.0×10^{16} atom cm^{-3}, [C$_2$H$_3$Br] = 5.4×10^{12} molecule cm^{-3}. The inset shows the recorded C$_2$H$_3$ decay profile for the conditions of the open circle: [O$_2$] = 5.33×10^{12} molecule cm^{-3}, $k' = 94.7 \pm 2.8$ s^{-1}.

$$k_1 = (6.92 \pm 0.17) \times 10^{-12} \exp((120 \pm$$
$$12 \text{ K})/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Discussion

The results of the current study are in excellent agreement with those of Slagle et al.[2] at temperatures 299−605 K. The room-temperature data also coincide with those of Park et al.[1] and Krueger and Weitz.[3] Although the k_1 value of Fahr and Laufer at room temperature is lower than those of refs 1−3 and the current study, the reported error limits overlap.

Westmoreland[12] and Bozzelli and Dean[13] analyzed the kinetics and product distribution of reaction 1 by modifications of the quantum RRK method applied to the chemical activation system. Both models[12,13] assume barrierless addition of C$_2$H$_3$ to O$_2$ forming a vibrationally excited C$_2$H$_3$OO adduct as the primary step of reaction 1. This adduct can either undergo further rearrangement via several possible channels to form the products of reaction 1, decompose back to reactants (C$_2$H$_3$ + O$_2$), or be stabilized by collisions with the bath gas. The final result of these models (overall rate constant and product branching ratio) depends on the interplay of these three processes. Both models predict the chemically activated cy-

Letters

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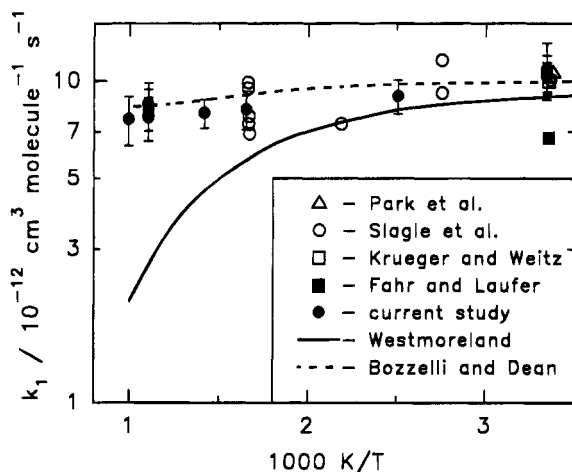
Figure 2. Experimental results and theoretical predictions for the temperature dependence of k_1 at low pressures. Symbols: experimental results (Park et al.;[1] Slagle et al.;[2] Krueger and Weitz;[3] Fahr and Laufer;[4] current study). Lines: theoretical calculations (Westmoreland[12] at 4 Torr of He, Bozzelli and Dean[13] at 7.6 Torr of N_2).

clization of the C_2H_3OO adduct leading to $HCO + H_2CO$ as final products to be the predominant channel at low temperatures (298–600 K) and pressures of several torr. However, due to different values of the rate parameters (preexponential factors and energy barriers) assigned to each of the many elementary steps included in each model, the predicted temperature and pressure dependencies of the branching fractions differ significantly under other conditions.

The difference between these two models which is most pertinent to the current experimental study concerns the temperature dependence of the overall rate constant at low pressures (Figure 2). The slight decline of k_1 with increasing temperature predicted by Bozzelli and Dean is in excellent agreement with the current experimental determinations. The model of Westmoreland, however, predicts a much stronger decrease in k_1 at temperatures above 600 K. The anticipated value at 1000 K and 4 Torr of He is 4 times lower than k_1 at room temperature and 3 times lower than that at 600 K. This prediction is in obvious contradiction with the experimental results of the current study (Figure 2). We discuss here the details of the above two models of reaction 1 which are most important for understanding the differences in predicted temperature dependencies.

In Westmoreland's model, the reverse decomposition of the C_2H_3OO adduct to $C_2H_3 + O_2$

$$C_2H_3OO \rightarrow C_2H_3 + O_2 \qquad (-1)$$
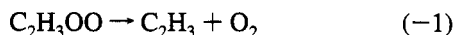
is assigned a high preexponential factor ($A_{-1} = 2 \times 10^{15}$ s^{-1}) and an activation energy of 41.5 kcal mol^{-1}, while all possible

channels of further reactive rearrangement of C_2H_3OO have relatively low preexponential factors ($9.6 \times 10^{11} - 2.1 \times 10^{12}$ s^{-1}). As a result, at high temperatures the reverse decomposition to reactants becomes the predominant channel for the C_2H_3OO adduct and the overall reaction rate constant decreases.

Bozzelli and Dean assign comparable preexponential factor values to reaction -1 ($A_{-1} = 5 \times 10^{14}$ s^{-1}) and to reaction 5

$$C_2H_3OO \rightarrow CH_2CHO + O \qquad (5)$$
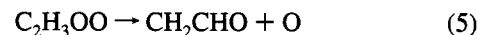
($A_5 = 3.3 \times 10^{14}$ s^{-1}, 2 orders of magnitude higher than the corresponding value assigned by Westmoreland), with the activation energy of reaction 5 being 3 kcal mol^{-1} lower than that of reaction -1. As a result, decomposition of the adduct to reactants (reaction -1) becomes less important and the overall rate constant k_1 decreases only slightly at high temperatures.

The fact that k_1 does not decrease sharply at temperatures up to 1005 K strongly supports the existence of some exit channel of the C_2H_3OO reaction capable of competing with reaction -1. In the model of Bozzelli and Dean[13] this role is performed by reaction 5. In fact, new ab initio calculations by Westmoreland et al.[16] support this possibility. They indicate a nearly barrierless addition of O atom to CH_2CHO to form C_2H_3OO (which implies a lower activation energy for reaction 5) and a higher preexponential factor for reaction 5 than assumed earlier in ref 12.

References and Notes

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