decisive factor in determining the structure.

From Figure 3 we also notice a linear relationship between $\Delta \nu_{C=0,2}$ and $\Delta \nu_{OH}$ for both I and II. This linear relationship indicates that both $\Delta \nu_{C=0,2}$ values of I and II are closely related to the OH proton acidity of alcohols. This is what we expected for I. For II, we consider $\Delta v_{C=0,2}$ as the summation of Δv^1 and $\Delta \nu^2$, where $\Delta \nu^1$ is the wavenumber shift due to the first hydrogen bonding or the formation of the 1:1 complex and $\Delta \nu^2$ is the shift due to the second hydrogen bonding. In our previous paper,¹ we determined Δv^1 for Cl₃-t-BuOH by resolving the spectrum obtained under the condition of the formation of only the 1:1 complex into non-hydrogen-bonded C=O and C=O of the 1:1 complex. The $\Delta \nu_{C=0,2}$ and $\Delta \nu^1$ values obtained were 24 and 21 cm⁻¹, respectively. By using the same procedure, we got 16.0 and 21.0 cm⁻¹ as the $\Delta \nu^1$ values for *t*-BuOH and Cl₃-*i*-PrOH. Thus, we obtained 2.0, 3.0, and 3.5 cm⁻¹ as the values of $\Delta \nu_2$ (= $\Delta \nu_{C=0,2} - \Delta \nu^1$) for *t*-BuOH, Cl₃-*t*-BuOH, and Cl₃-*i*-PrOH, respectively. Thus, we know that both Δv^1 and Δv^2 are dependent on the proton acidity of the alcohols, but Δv^1 contributes predominantly to the linear relationship between $\Delta \nu_{C=0,2}$ and the acidity of alcohol.

The formation of the 2:1 complex takes place after the formation of the alcohol-DMA 1:1 complex. As long as the DMA concentration is much higher than the alcohol concentration, only the formation of 1:1 complexes proceeds, and the 2:1 complex starts to form with increase in alcohol concentration. If we can analyze the absorption intensity of the non-hydrogen-bonded C=O band quantitatively, we can follow the formation process of I and II with a kinetic method. However, as seen from Figures 1 and 2, the peak of the non-hydrogen-bonded C=O band overlaps with the 1:1 complex and 2:1 complex bands in their highest wavenumber region. We cannot regard the absorbance of the peak as being proportional to the concentration of non-hydrogen-bonded DMA. Thus, we consider qualitatively the formation process of I and II as follows: As shown in Figures 1 and 2, the spectra pass an isosbestic point as long as only the formation of the 1:1 complex is taking place. We know from Figure 1 that the spectra deviate from the isosbestic point at the ratio $[Cl_2-i-PrOH]/[DMA] = 0.64$. This means that the formation of I starts at this ratio and that the equilibrium constant for the formation of I is comparable to the constant for the formation of the 1:1 complex. On the other hand, we know from Figure 2 that the spectra pass the isosbestic point up to the point of $[Cl_3-i-PrOH]/[DMA] = 1.2$, suggesting that the formation of the 1:1 complex proceeds predominantly up to the point where more than half of the total DMA molecules have changed into the 1:1 complex. We observed the same tendency in our previous work that the formation of II by Cl₃t-BuOH starts at $[Cl_3-t-BuOH]/[DMA] = 15$ after almost all the DMA molecules have been converted to the 1:1 complex. Accordingly, we can say that the equilibrium constant for the formation of II is much smaller than the constant for the formation of the 1:1 complex.

Though *i*-PrOH, Cl-*i*-PrOH, and Cl₂-*i*-PrOH studied in this work are much bulkier around the α -carbon than the primary alcohols studied in our previous work, our results show that these alcohols easily form I. Thus, we can reconfirm that the carbonyl oxygen of DMA has the potentiality of forming two hydrogen bonds like I, as long as the steric condition is satisfactory.

Registry No. DMA, 127-19-5; Cl-*i*-PrOH, 127-00-4; Cl₂-*i*-PrOH, 96-23-1; Cl₃-*i*-PrOH, 76-00-6; *i*-PrOH, 67-63-0; *t*-BuOH, 75-65-0.

Experimental and Theoretical Studies of the $C_2H_5 + O_2$ Reaction Kinetics

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The thermal reaction between C_2H_5 and O_2 , which yields both $C_2H_5O_2$ and $C_2H_4 + HO_2$, has been studied both experimentally and theoretically. The experiments were conducted in a heatable tubular reactor coupled to a photoionization mass spectrometer. C_2H_5 was produced by homogeneous 193- or 248-nm photolysis of suitable precursors. C_2H_5 decay and C_2H_4 growth profiles were recorded in time-resolved experiments. The measured reaction parameters include second-order rate constants for the loss of C₂H₅ (296–850 K) and the product branching ratio, $[C_2H_4]/([C_2H_5O_2] + [C_2H_4])$ (296–723 K). Buffer gas (primarily He) pressures from 0.5 to 15 Torr were used. The theoretical study involved modeling the kinetics of the reaction with a coupled mechanism, one in which the reactive routes both begin by the reversible formation of a chemically activated $C_2H_5O_2^*$ adduct. Collisional stabilization yields C₂H₂O₂ while rearrangement via a cyclic transition state leads to the formation of $C_2H_4 + HO_2$. Reactivation of $C_2H_5O_2$ was provided for. All the rate constants of the mechanism were calculated by using RRKM theory. Adjustable parameters that describe unknown features of the potential energy surface and the interaction of the buffer gas with the metastable adduct were required. This combined theoretical-experimental description of the C_2H_5 $+ O_2$ reaction quantitatively accounts for the behavior of this reaction over the full range of conditions that have been used in the current and all prior laboratory studies of the kinetics in this reaction. In particular, the mechanism change that occurs near 600 K is accurately described. The $C_2H_5 + O_2$ reaction kinetics has been cast in terms of a four-step mechanism which can easily be incorporated into combustion models. Analytical expressions for the rate constants of these four steps have been calculated by using the results of this study and are reported.

I. Introduction

The reactions of alkyl radicals (R) with molecular oxygen are important elementary steps in complex oxidation processes involving hydrocarbons.¹⁻⁵ Apparent changes that occur in the mechanisms of $R + O_2$ reactions (between 600 and 700 K at typical oxygen pressures) are directly responsible for changes in the properties of combustion processes as temperature increases, properties which include the ultimate stable products produced and the rate of the overall oxidation process itself.¹⁻⁹ For this

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reason, the kinetics of these elementary reactions have been extensively studied. Surprisingly, there is still significant uncertainty regarding the kinetics of these reactions, particularly regarding the elementary steps responsible for the mechanism changes that occur with increasing temperature.^{4,5,8-14} Up to about 600 K, $R + O_2$ reactions proceed mainly by a simple reversible addition process:

$$\mathbf{R} + \mathbf{O}_2 \rightleftharpoons \mathbf{R}\mathbf{O}_2 \tag{1}$$

At higher temperatures (typically above 700 K), this equilibrium strongly favors the reactants and therefore cannot by itself account for the consumption of alkyl radicals by O_2 which continues to occur at elevated temperatures. The increasing importance of olefins as products of combustion processes as temperature is increased (and the decreasing importance of hydroperoxides and aldehydes which are the most important low-temperature products) is the principal indication that the new high-temperature products of $R + O_2$ reactions are in fact these olefins.⁴⁻⁹

While the products of the $R + O_2$ reactions at high temperature are not in doubt, the kinetic step(s) responsible for their formation are.^{4,5} Two principal processes have been suggested. The first involves a direct H-atom metathesis, an elementary reaction with a small activation energy (20-40 kJ mol⁻¹) which proceeds in parallel with the addition process:

$$\mathbf{R} + \mathbf{O}_2 \rightarrow \mathbf{R}_{-H} + \mathbf{H}\mathbf{O}_2 \tag{2}$$

An activation energy of 20-40 kJ mol⁻¹ for reaction 2 has become accepted as that required to account for the mechanism change in $R + O_2$ reactions.^{6,7,15} Reactions 1 and 2 have been used by Knox and by Benson in 1965 to construct semiquantitative combustion models that account for the changing rates and product yields of hydrocarbon combustion processes as a function of temperature around the ceiling temperature (i.e., the temperature at which $[R] = [RO_2]$ in reaction 1 at equilibrium).^{6,7,15} Since these two studies were published, essentially all combustion modeling has been done using reactions 1 and 2 to represent the kinetics of $R + O_2$ reactions.^{2,16,17}

The second explanation offered for the changing $R + O_2$ mechanism involves olefin formation via a second decomposition channel of the RO₂ produced by the addition process^{4,5,11}

$$R + O_{2} = RO_{2}^{*} - R_{H}O_{2}H^{*} - R_{H} + HO_{2}$$
(3)
$$\downarrow^{[M]}_{*}$$

$$RO_{2}$$

At low temperatures and at modest pressures, RO₂ formation

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is dominant because only a small fraction of RO₂* proceeds on to $R_{-H} + HO_2$ each time the excited adduct is formed. However, at high temperatures, RO₂ is unstable, so it is continually formed and re-formed, and each time RO_2^* is re-formed it yields some $R_{-H} + HO_2$ until eventually there is complete conversion of R to R_{-H}.

Knowledge of the correct mechanism of $R + O_2$ reactions is extremely important in combustion modeling since the actual kinetic behavior of these key reactions under combustion conditions must still be inferred from laboratory studies that have been conducted under much milder conditions.^{2,16,17} The use of basically different high-temperature mechanisms (e.g., reaction 2 and mechanism 3) to extrapolate the kinetics of these reactions from the lower temperatures and pressures of laboratory studies to the harsher conditions of combustion processes can lead to very different predictions of high-temperature behavior. For example, reaction 2 predicts a $R + O_2$ rate constant that increases with temperature above 700 K while mechanism 3 can predict entirely the opposite behavior. Extrapolations to combustion temperatures (e.g., 2000 K) from the temperatures of laboratory studies (typically conducted below 800 K) can yield predicted rate constants as much as a factor of 100 apart depending on the mechanism chosen to represent the kinetics of $R + O_2$ reactions.

In spite of the widespread use of reaction 2 in combustion modeling, there is no direct evidence from laboratory studies (all of which have been conducted below 1000 K) that direct H-atom metathesis is the observed high-temperature $R + O_2$ mechanism. Until recently, the principal source of quantitative information of the high-temperature kinetics of $R + O_2$ reactions has been the large body of kinetic studies of these reactions by Baldwin and Walker (and co-workers) at Hull.^{8,9,13,14} While these investigations have provided phenomenological rate constants for $R + O_2$ reactions over narrow temperature ranges (typically near 750 K), they have not yielded the kind of information needed to discriminate between possible high-temperature mechanisms. This limitation has been repeatedly pointed out by the investigators themselves.^{8,9,18} In all the studies by Baldwin and Walker, equilibrium between R and RO2 is established quickly before there is significant consumption of R. Under these conditions the kinetic behavior of mechanism 3 resembles that of an elementary reaction, and its kinetic behavior in their experiments is indistinguishable from that expected from reaction 2 (i.e., the rate is proportional to both [R] and $[O_2]$, and there is complete conversion of R to R_{-H}).

Recently, studies of the kinetics of the $C_2H_5 + O_2$ reaction (the simplest $R + O_2$ reaction capable of undergoing a mechanism change of this type) have been conducted under conditions that are suitable for obtaining at least an indication of the correct mechanism. There are observations in these studies that suggest that the correct mechanism cannot be reaction 2. For example, in our laboratory, we have measured both the temperature (294-1000 K) and density dependence ((1-25) \times 10¹⁶ molecules cm⁻³) of the second-order $C_2H_5 + O_2$ rate constant as well as C_2H_4 yields at three temperatures.¹⁰ The observed kinetic behavior is consistent with the second high-temperature mechanism, reaction 3, but not with the first, reaction 2. This behavior includes a C_2H_5 $+ O_2$ rate constant which fails to increase above the ceiling temperature and a significant production of C₂H₄ at low temperatures and pressures, something which is inconsistent with the expected behavior of reaction 2 at low temperatures. (Comparable high C_2H_4 yields at ambient temperature have been reported by Plumb and Ryan,12 who have also noted the inconsistency of their measured C_2H_4 yields with those predicted from the Arrhenius expression for k_2 derived from poor high-temperature investigations of the kinetics of the $C_2H_5 + O_2$ reaction.) More recently, McAdam and Walker have measured ratios of the rate constants of the $C_2H_5 + O_2$ and $C_2H_5 +$ propionaldehyde reactions as a function of temperature, 593-753 K, and have confirmed that the $C_2H_5 + O_2$ reaction has a rate constant that decreases with in-

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creasing temperature in this temperature range.¹⁴

We have now conducted a more comprehensive investigation of the kinetics and mechanism of the $C_2H_5 + O_2$ reaction. It is a combined experimental and theoretical study directed at obtaining a more detailed and quantitative understanding of its kinetic behavior. A quantitative theoretical kinetic model based on mechanism 3 has been developed. It accounts not only for the new experimental observations of the kinetics of this reaction which are reported here but also for essentially all earlier observations of the kinetics of the $C_2H_5 + O_2$ reaction which have been reported by others over a wide range of conditions.

In this new study, emphasis was placed on obtaining kinetic information that would be most useful for establishing the mechanism of the $C_2H_5 + O_2$ reaction and for determining the important empirically derived molecular parameters in the theoretical kinetic model. Additional second-order rate constants were determined both below and above the ceiling temperature and over a wider density range than was covered in the initial study of this reaction in our laboratory.¹⁰ Yields of C_2H_4 were determined below the ceiling temperature as a function of both temperature and density. These experiments and the results obtained are presented in section II.

The detailed theoretical kinetic model based on mechanism 3 is described in section III. RRKM theory was used to obtain the rate constants for all the elementary steps in the mechanism. (Variational RRKM theory was used in the case of the initial addition process.) A special effort was made to incorporate current knowledge of relevant potential energy surfaces and of the structures and internal motions of reactants, intermediates, and transition states (obtained from results of ab initio calculations, spectroscopic studies, and the behavior of analogous systems). However, some empirically adjusted molecular parameters were required to complete the calculations. The ability of this theoretical model to reproduce the broad spectrum of kinetic observations that have been reported on the kinetics of the $C_2H_5 + O_2$ reaction is interpreted as strong evidence that the assigned mechanism is correct, at least up to 1000 K. In section IV, the theoretical model is used to obtain parametrized expressions for the rate constant of the $C_2H_5 + O_2$ reaction over a large range of temperatures and pressures which are suitable for use in combustion modeling. Section V presents a brief discussion of the direct abstraction channel (which was not observed). Section VI reviews the past experimental information for the reverse reaction of $C_2H_4 + HO_2$ and its implications for the current study of the forward reaction. A summary of all findings is given in section VII.

II. Experimental Study of the C₂H₅ + O₂ Reaction

Studies were conducted to obtain two kinds of kinetic information. First, experiments were performed to obtain extended knowledge of the density and temperature dependence of k_4 , the phenomenological rate constant for the loss of C_2H_5 in reaction 4:

$$C_2H_5 + O_2 \rightarrow \text{products}$$
 (4)

(The interpretation of k_4 in terms of a specific mechanism for the $C_2H_5 + O_2$ reaction is done in section III.) It was possible to determine k_4 both below 600 K (298-473 K) and above 740 K (750-850 K). In these low- and high-temperature ranges, the decay of C_2H_5 was exponential in the presence of an excess of O_2 and the decay constants were a linear function of $[O_2]$, thus making it possible to define and determine a second-order rate constant for the overall process represented by reaction 4. Between about 600 and 700 K, signs of the equilibrium, reaction 1, are apparent. C_2H_5 decays are not exponential. (The kinetics of the $C_2H_5 + O_2$ reaction in this particular temperature range was investigated earlier in our laboratory to obtain the equilibrium constant $K_p(T)$ for $C_2H_5 + O_2 \rightleftharpoons C_2H_5O_2$ and to determine the $C_2H_5-O_2$ bond energy.¹⁹) A second group of experiments was

conducted to obtain both the temperature and density dependencies of the C₂H₄ yield from reaction 4, $F(C_2H_4) = [C_2H_4]_f/[C_2H_5]_0$. Three temperatures below 600 K were chosen to cover the range of accessible temperatures (300–600 K) over which C₂H₅O₂ is essentially thermally stable under our experimental conditions. (Above about 700 K, where C₂H₅O₂ is thermally unstable, F-(C₂H₄) = 1.0 at all densities and temperatures because C₂H₅ is completely converted to C₂H₄.^{10,18})

A. Apparatus and Experimental Procedure. The experimental apparatus has been described previously.²⁰ Only a summary is presented here. Pulsed UV radiation from a Lambda Physik EMG 101E excimer laser (operated at 4-5 Hz) was directed along the axis of a heatable 1.05-cm-i.d. uncoated tubular quartz reactor. Gas flowing through the tube at 5 m s⁻¹ contained the C_2H_5 precursor (see below), O_2 (in varying amounts), and the carrier gas which was in large excess (primarily He). Gas was sampled through a 0.020- or 0.043-cm-diameter tapered hole in the wall of the reactor and formed into a beam by a conical skimmer before it entered the vacuum chamber containing the photoionization mass spectrometer. The reaction with the smaller orifice was used in the higher density experiments. As the molecular beam traversed the ion source, a portion was photoionized and then mass selected. The gas in the reactor was completely replaced between laser pulses. Temporal ion signal profiles were recorded from a short time before each laser pulse to 25 ms following the pulse by using a multichannel scaler. Data from 1000 to 12000 experiments were accumulated before the data were analyzed.

B. Photolytic Sources of C_2H_5 . Different C_2H_5 sources were used in the experiments to determine k_4 and $F(C_2H_4)$. In the experiments conducted to obtain the $C_2H_5 + O_2$ rate constants, direct photolysis of C_2H_5Br was employed:¹⁹

$$C_2H_5Br$$
 $\xrightarrow{248 \text{ nm}}$ C_2H_5 + Br (5a)
 C_2H_5Br $\xrightarrow{248 \text{ nm}}$ C_2H_4 + HBr (5b)

The photolysis, which involved using unfocused laser radiation, typically resulted in less than 1% decomposition of the C_2H_5Br . Approximately 50% of the photodecomposition proceeds by each of the two principal photodecomposition channels (5a and 5b) at this wavelength.

Measurements of C_2H_4 yields from reaction 4 required the use of a photolytic source of C_2H_5 which does not also produce significant amounts of C_2H_4 on UV photolysis. No precursor for C_2H_5 could be identified which has this property. Therefore, an indirect procedure was employed to produce C_2H_5 in the second group of experiments, those in which $F(C_2H_4)$ was determined. It involved the production of chlorine atoms by the photolysis of CCl_4 followed by the rapid reaction of these atoms with C_2H_6 :

$$\operatorname{CCl}_4 \xrightarrow{193 \text{ nm}} \operatorname{CCl}_3 + \operatorname{Cl} \tag{6}$$

$$Cl + C_2H_6 \rightarrow C_2H_5 + HCl$$
(7)

At the C_2H_6 concentrations used, chlorine atoms were rapidly converted to C_2H_5 (typically 0.2 ms). An analogous indirect source of C_2H_5 was employed in our earlier measurements of k_4 .¹⁰ Reaction 7 has also been used by others as a suitable source of C_2H_5 in prior studies of the kinetics and mechanism of reaction 4.^{12,21}

The use of 193-nm photolysis in the C_2H_4 yield experiments did not result in significant photodecomposition of O_2 . At the low laser fluences used and at the temperatures of the C_2H_4 yield experiments (<600 K), there was no detectable O-atom formation or other evidence of O_2 photolysis.

The C_2H_5 radicals produced by 248-nm photolysis contain an excess of internal energy. Under the conditions of our experiments,

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TABLE I:	Conditions	and Results	of Experiments	To Measure	the Over	rall Rate	Constant	of the	$C_{2}H_{5} +$	 O₂ Reaction 	1 (<i>k</i> 🗸	•)
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T, K	P, Torr	10 ⁻¹⁶ [M], molecules cm ⁻³	10 ⁻¹⁶ [He], molecules cm ⁻³	$10^{-13}[C_2H_5Br],$ molecules cm ⁻³	$10^{-14}[O_2],$ molecules cm ⁻³	k_{wali}, s^{-1}	$10^{13}k_4,$ cm ³ molecule ⁻¹ s ⁻¹	
298	0.894	2.89	2.47	4.47	0.28-1.20	56.0	16.8	
298	1.85	6.00	5.11	4.91	0.46-1.47	71.5	22.8	
296	3.69	12.0	10.1	4.82	0.22-1.00	101	32.0	
296	7.35	24.0	19.9	4.65	0.31-1.20	140	36.8	
385	2.40	6.02	5.12	4.88	0.31-1.72	50.2	11.8	
385	4.79	12.0	10.1	4.84	0.41-2.13	74.4	16.7	
385	9.62	24.1	20.6	4.91	0.34-1.57	92.4	24.0	
473	1.46	2.98	2.54	3.93	0.88-3.64	35.0	4.69	
473	2.98	6.08	5.18	4.15	0.66-2.90	37.0	6.23	
473	5.89	12.0	10.2	4.95	0.49-2.90	46.3	9.48	
473	11.8	24.2	20.0	4.57	0.46-1.78	63.2	13.8	
640	2.05	3.09	2.60	4.26	3.13-12.5	46.4	1.62ª	
640	4.01	6.05	5.13	9.44	3.03-12.1	33.0	1.35ª	
750	2.36	3.03	2.62	4.71	4.71-18.9	47.5	1.22	
750	4.70	6.06	5.15	9.48	4.71-18.6	38.5	1.08	
750	9.26	11.9	10.0	4.70	4.76-19.1	38.5	1.03	
750	14.0	18.1	15.6	4.50	4.85-16.7	34.0	1.11	
850	2.69	3.06	2.62	2.63	4.66-18.9	58.4	1.29	
850	5.34	6.60	5.13	3.40	4.79-20.2	67.4	1.16	
850	10.5	12.0	10.1	5.09	6.29-30.1	85.1	1.16	
850	15.8	18.0	15.5	4.97	10.5-41.1	108	1.08	

^a Decay constants not purely exponential but were fit to an exponential function to obtain a value of k'. Plot of k' vs $[O_2]$ was linear, and slope was used to obtain values of k_4 (see text). The k_4 values at 640 K are not to be regarded as genuine second-order rate constants.

 $C_2H_5^*$ has most probably relaxed to thermal equilibrium before any significant reaction has occurred. This conjecture is based on the presumption that $C_2H_5^*$ vibrational deactivation is at least as fast as that for $CH_3(\nu_3)$, a process that has been studied in detail.²² (Vibrational deactivation of C_2H_5 has not yet been quantitatively investigated.) The fact that the $C_2H_5 + O_2$ rate constants obtained with C_2H_5 produced by 248-nm photolysis of C_2H_5Br and a thermal source (reaction 7) agree also supports this conclusion.

C. Experimental Determinations of k_4 . Experiments to determine k_4 were conducted under pseudo-first-order conditions. O_2 was always in large excess. In a typical set of experiments to obtain k_4 , the exponential decay of C_2H_5 was recorded as a function of $[O_2]$. The temporal $C_2H_5^+$ ion-signal profile was fit to an exponential function, $[C_2H_5^+]_t = [C_2H_5^+]_0 \exp(-k't)$. The value of k_4 was obtained from the slope of a plot of k' vs $[O_2]$. The initial concentration of C_2H_5 , $[C_2H_5]_0$, was kept extremely low (typically 2×10^{11} molecules cm⁻³) to suppress radical-radical reactions including $C_2H_5 + C_2H_5$ recombination and disproportionation. That this condition was achieved was repeatedly verified by observing that the C_2H_5 decay constants did not depend on laser fluence (i.e., on $[C_2H_5]_0$). The conditions of these experiments and the results obtained are presented in Table I. A sample $C_2H_5^+$ ion signal profile is shown in Figure 1 together with an example of a k' vs $[O_2]$ plot from which one of the rate constants was determined. All the measured values of k_4 obtained in both this study and the earlier one¹⁰ together with theoretical calculations of k_4 (to be presented in the next section) are displayed in Figure 2.

The temperatures chosen to measure k_4 below 500 K (298, 385, and 473 K) were at or near some of the temperatures used in our prior investigation of the $C_2H_5 + O_2$ reaction.¹⁰ These new measurements extend the density range previously covered at these three temperatures. They also provide a test of the accuracy of the earlier determinations, ones that required the use of an indirect source of C_2H_5 instead of a direct one to measure k_4 and also that involved the use of an apparatus with a much lower detection sensitivity (by a factor of 20). As will be discussed in the next section, the agreement between the new and old measurements is good in the cases of the two lower temperatures. There is some disparity (on the order of 30%) between the 473 K rate constants reported in Table I and those obtained in the earlier study.

Near 640 K, the C_2H_5 decay was not purely exponential due to the detectable importance of the reverse reaction. To provide



Figure 1. First-order C_2H_5 decay constants (k') versus $[O_2]$ from the set of experiments conducted at 473 K. $[M] = 1.2 \times 10^{17}$ molecules cm⁻³. For conditions of the experiment, see Table I. Insert is actual data recorded at $[O_2] = 1.58 \times 10^{14}$ molecules cm⁻³ (k' = 192 s⁻¹). Solid point on plot is from the displayed data in the insert.

an additional test of the theoretical model, these decays were still fit to a simple exponential function. Since the exponential decay constants obtained from these fits were also linearly dependent on $[O_2]$, an effective value for k_4 could be calculated from a set of experiments in which $[O_2]$ was varied. Two sets of experiments were conducted at 640 K using different total gas densities to obtain values of " k_4 " that could be compared with theoretical values obtained from the kinetic model. The experimental results are included in Table I.

Above 700 K, the C_2H_5 decays profiles were again exponential in shape and the decay constants were still dependent on $[O_2]$, again permitting the determination of true second-order rate constants for reaction 4. The high-temperature behavior of reaction 4 was studied at two temperatures above 700 K not used before, 750 and 850 K. The results obtained are also presented

⁽²²⁾ Donaldson, D. J.; Leone, S. R. J. Phys. Chem. 1987, 91, 3128.



Figure 2. k_4 versus [He] for nine temperatures: theory (—) and experiment (\bullet , current investigation; Δ , Gutman et al. of ref 10; \bullet , Plumb and Ryan of ref 12).

in Table I. They are consistent with the previously determined values of k_4 obtained at 905 K.¹⁰

The carrier gas helium could not always be used in such a large excess that it was always the dominant collision partner of the $C_2H_5O_2^*$ adduct. At high temperatures, significant O_2 concentrations (approaching a mole fraction of 0.15) had to be employed because of the significant decrease in k_4 with increasing temperature. In order to conduct all these experiments using approximately the same "collision partner", the bath gas used was a mixture of He, N₂, and O₂. The He mole fraction was fixed at 0.85 in all experiments, and $X(N_2+O_2)$ was maintained at 0.15 by substituting N₂ for O₂ as the O₂ concentration was varied. (For simplicity, the carrier gas is referred to as He.)

The upper temperature limit of this study was determined by the increasing importance of competing loss processes involving C_2H_5 (particularly unimolecular decomposition) at more elevated temperatures.

D. Experimental Determinations of C_2H_4 Yields. Yields of C_2H_4 from reaction 4, $F(C_2H_4) = [C_2H_4]_f/[C_2H_5]_0$, were determined in experiments in which C_2H_5 was produced by reaction 7. The C_2H_6 concentrations (typically 8 × 10¹³ molecules cm⁻³) were chosen to obtain a rapid conversion of chlorine atoms to C_2H_5 . $[C_2H_5]_0$, the initial C_2H_5 concentration, was determined from measurements of the Cl-atom concentration following photolysis of CCl₄, and $[C_2H_4]_f$, the ultimate C_2H_4 concentration when reaction appeared complete, was obtained from direct observation of C_2H_4 concentration profiles up to a time of about 25 ms. By that observation time, C_2H_5 had completely reacted, and C_2H_4 appeared to have reached a constant value.

The initial Cl-atom concentrations were determined by conducting the CCl₄ photolysis in the presence of C_2H_3Br (with O_2 absent) and measuring the amount of C_2H_3Cl produced by the reaction

$$Cl + C_2H_3Br \rightarrow C_2H_3Cl + Br$$
 (8)

 C_2H_3Cl (and C_2H_4) ion signals were converted to concentrations by using measured sensitivity factors obtained from ion-signal measurements made using metered flows of these same molecules in the flow reactor. The use of reaction 8 as a titration for chlorine atoms has been shown to be quantitative at the reduced pressures used in this investigation.^{23,24} (The determination of the initial Cl-atom concentration by measuring the HCl yield of reaction 7 was not possible. HCl has an ionization potential too high to permit its detection with the photoionization mass spectrometer used.)

Some of the C_2H_3Br photodecomposed along with the CCl₄. Since none of the subsequent reactions of the photoproducts of C_2H_3Br yield C_2H_3Cl , this additional photolysis did not interfere with the determinations of $[C_2H_5]_0$.

The experiments conducted to determine $F(C_2H_4)$ employed higher values of $[C_2H_5]_0$ in order to increase $[C_2H_4]_f$ to levels that could be measured accurately. The O₂ concentrations used in these experiments were also higher not only to maintain O₂ in excess but also to assure that C_2H_5 reacted essentially exclusively with O₂ and was not lost to a significant degree either by recombination or by competing heterogeneous processes.

In preliminary experiments conducted using lower initial concentrations of C_2H_5 and O_2 , it was observed that no C_2H_4 was produced either by the photolysis process or during the brief time C_2H_5 was produced by reaction 7. The growth of C_2H_4 could not be monitored accurately under these conditions. However, it was still apparent that the C_2H_4 growth mirrored the behavior of the C_2H_5 decay as expected for a product of reaction 4.

Branching fractions obtained by using different initial concentrations of C_2H_5 (i.e., different initial Cl-atom concentrations) yielded the same values of $F(C_2H_4)$. This confirmed that radical-radical reactions (e.g., $C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6$ or CCl₃ + $C_2H_5 \rightarrow CCl_3H + C_2H_4$) and radical-atom reactions (e.g., C_2H_5 + $Cl \rightarrow C_2H_4 + HCl$) that occur during these experiments to a limited degree had negligible rates (i.e., they produced undetectable additional amounts of C_2H_4).

The conditions of the experiments to measure $F(C_2H_4)$ and the results obtained are presented in Table II and plotted in Figure 3 for room temperature and in Figure 4 for higher temperatures. Included in Figures 3 and 4 are the results of theoretical calculations of these yields which are discussed in the next section. Figure 3 also includes the measurements of Plumb and Ryan¹² made at room temperature. The current values obtained at this temperature are slightly greater than those obtained by Plumb

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TABLE II: Conditions and Results of Experiments To Measure the C ₂ H ₄ Product Branching Fraction	$F(C_2H_4)$) <u></u> "
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<i>T</i> , K	10 ⁻¹⁶ [He], molecules cm ⁻³	$10^{-15}[O_2],$ molecules cm ⁻³	10^{-13} [CCl ₄], molecules cm ⁻³	$10^{-12}[C_2H_5]_0,$ molecules cm ⁻³	$F(C_2H_4)$	$F(C_2H_4)_{av}^{b}$	
295	3.04	2.03	9.21	1.23	0.23		
296	6.19	1.73	7.98	1.62	0.15		
296	8.04	5.14	8.20	1.09	0.15		
296	8.04	5.02	15.6	1.95	0.17	0.16	
297	23.8	5.82	7.87	1.38	0.072		
296	24.1	2.37	17.0	2.39	0.093		
296	24.1	3.65	17.0	2.39	0.109	0.091	
373	2.97	2.80	11.4	1.37	0.37		
373	8.07	4.74	8.21	0.92	0.17		
373	24.0	4.32	7.93	1.26	0.093		
373	24.0	4.79	16.2	2.85	0.11	0.10	
473	2.98	1.87	8.58	1.22	0.55		
473	8.06	5.38	8.51	1.63	0.29		
473	23.5	1.65	16.5	2.15	0.21		
473	23.5	3.10	16.5	2.15	0.21	0.21	
573	3.00	3.09	8.92	0.466	0.63		
573	8.09	4.75	8.51	1.06	0.50		
573	8.09	6.47	8.52	1.41	0.46	0.48	
573	23.7	4.60	8.18	1.61	0.25		
573	23.7	4.79	17.0	4.29	0.24	0.24	
723	21.4	8.16	6.24	1.44	0.99		

^a In all experiments, $[C_2H_6] = (7-9) \times 10^{13}$ molecules cm⁻³, $[C_2H_3Br] = (0.5-1.0) \times 10^{14}$ molecules cm⁻³ (typically 1×10^{14}), and gas flow velocity = 4-5 m s⁻¹. ^b $F(C_2H_4)_{av}$ calculated and used when more than one determination of $F(C_2H_4)$ was made at a particular T and [M].



Figure 3. The C_2H_4 branching fraction at 298 K versus [He]: theory (-) and experiment (\blacksquare , current study; \square , Plumb and Ryan of ref 12; \triangle , Niki et al. of ref 21). See text for discussion of Niki et al.'s results.

and Ryan. However, the error limits of both studies generally overlap.

Three photoionization energies were used in these studies to monitor the different reactants and products with the mass spectrometer: 11.6 eV (C_2H_4 and C_2H_3Cl), 10.2 eV (C_2H_5Br and C_2H_3Br), and 8.9–9.1 eV (C_2H_5).

Gases were obtained from Linde (He, 99.995%; O_2 , 99.6%; N_2 , 99.998%), Matheson (C_2H_3Cl , 99.5%; C_2H_3Br , 99.5%; C_2H_6 , 99.9%; C_2H_4 , 99.5%), Fisher (CCl₄, 99.5%), and Aldrich (C_2H_5Br , >99%). He, O_2 , and N_2 were used as provided. The remaining compounds were degassed by using freeze-pump-thaw cycles.

III. Theoretical Study of the $C_2H_5 + O_2$ Reaction

A. Overview. In this section, a theoretical model for the $C_2H_5 + O_2$ reaction based on mechanism 3 is developed which quantitatively accounts for the observed kinetic behavior of this reaction over the full range of conditions that have been used to date in laboratory studies. This behavior includes the following: (1) the temperature and pressure dependence of the low-temperature (<550 K) rate constant (which is largely addition); (2) equilibrium constants ($C_2H_5 + O_2 \Longrightarrow C_2H_5O_2$) determined near the ceiling temperature ($\sim 600 \text{ K}$); (3) the temperature and pressure dependencies of the high-temperature (750–900 K) phenomenological rate constant; (4) the temperature and pressure dependencies of the C_2H_4 yield, particularly below the ceiling temperature



Figure 4. The C_2H_4 branching fraction at four temperatures versus [He]: theory (-) and experiment (\blacksquare).

perature where it depends on these variables.

The ability of this theoretical model to quantitatively account for all reported observations of the kinetic behavior of the C_2H_5 + O_2 reaction is interpreted as indicating that the mechanism used is the correct one, at least below 1000 K.

A direct H-atom abstraction process, reaction 2, must also occur to some extent even below 1000 K although it appears from the result of the current investigation to be of negligible importance below this temperature. This alternate reaction path is expected to have increasing importance with rising temperature and should, at some temperature above 1000 K, become a significant route leading to $C_2H_4 + HO_2$. Additional discussion of this route is presented in section V.

In Figure 5, the $C_2H_5 + O_2$ reaction coordinate used in the current theoretical study is shown schematically. It includes the stable species (C_2H_5 , O_2 , C_2H_4 , HO_2 , $C_2H_5O_2$, and $C_2H_4O_2H$) and transition states ($C_2H_5...O_2$, $..CH_2CH_2O_2...H.$, and $C_2H_4...O_2H$). The transition state $..C_2H_4O_2...H.$ indicates the ring structure in which an H atom partially bonds to both an O and a C atom to form a five-membered ring with a skeletal framework of -H-C-C-O-O-.

The mechanism used has been discussed in detail by Fish.¹¹ It begins by C_2H_3 addition to O_2 forming a metastable peroxy adduct. Subsequently, the adduct may either dissociate back to reactants, rearrange by rotating the $-O_2$ group about the newly formed $C-O_2$ bond in the adduct to form the ring transition state,



Reaction Path

Figure 5. A schematic representation of the potential energy along the reaction path for the assumed mechanism for the $C_2H_5 + O_2$ reaction. The theoretical calculations were insensitive to the dashed part of the path (subject to the conditions described in the text).

or become stabilized by collisions with the bath gas.

Passage through the " $CH_2CH_2O_2$ "H" transition state transfers H from the CH₃ group in the peroxy radical to the terminal oxygen atom. The metastable alkylhydroperoxy radical is formed as the $-O_2H$ group rotates back to its equilibrium position, and this isomerization is rapidly followed by decomposition of this excited intermediate into the ultimate reaction products, $C_2H_4 + HO_2$. $C_2H_5O_2$ may be reactivated and either return to reactants or proceed via the "CH₂CH₂O₂"H" transition state to the ultimate high-temperature products.

The elementary steps in mechanism 3 may conveniently be represented by the following processes:

$$C_2H_5 + O_2 \rightarrow C_2H_5O_2 \tag{4a}$$

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \tag{4b}$$

$$C_2H_5O_2 \rightarrow C_2H_5 + O_2 \qquad (-4a)$$

$$C_2H_5O_2 \rightarrow C_2H_4 + HO_2 \qquad (-4c)$$

Reactions 4a and 4b together account for the total rate of loss of C_2H_5 at lower temperatures where equilibrium effects are not important. Reactions 4a and -4a account for the equilibrium between C_2H_5 and $C_2H_5O_2$ which is important at higher temperatures. Reactions 4b and -4c represent the two routes to the ultimate products, one from addition-elimination and one from thermal dissociation of an already stabilized adduct. There are two other processes that could play a role under some experimental conditions, the reverse of reactions 4b and -4c. They are insignificant ones under the conditions that have been used to date in laboratory studies of the kinetics of the $C_2H_5 + O_2$ reaction. Values for these "rate constants" can be derived from the values of k_{4b} and k_{-4c} reported here and the known thermochemistry of reactants and products. The analysis of overall reactions in terms of the elementary processes such as (4a-4c) used here has been developed by Golden et al.^{25,26} and applied to a variety of reactions that proceed through a bound complex.

Each process can be characterized by a rate constant (bimolecular in the case of reactions 4a and 4b and unimolecular in the cases of reactions -4a and -4c) which is both pressure and temperature dependent. Because all these processes can occur simultaneously, a coupled kinetics model of mechanism 3 explicitly incorporating the rate constants of each process must be developed.

TABLE III: Reaction Enthalpies (in kcal mol⁻¹) of Critical Points along the $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ Reaction Path

_				_
	reaction	$\Delta H^{\circ}{}_{0}{}^{a}$	$\Delta H^{\circ}{}_{298}{}^{a,b}$	
	$C_2H_5 + O_2 \rightarrow C_2H_5O_2$	-32.9	-34.1	
	$C_2H_5 + O_2 \rightarrow \cdots CH_2CH_2O_2\cdots H\cdots$	-2.4	-3.9	
	$C_2H_5 + O_2 \rightarrow C_2H_4O_2H$	-21.9		
	$C_2H_5 + O_2 \rightarrow C_2H_4 \cdots O_2H$	-7.0		
	$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	-13.0		

 ${}^{a}\Delta H^{o}$ values are relative to $C_{2}H_{5} + O_{2}$. ^b The reaction enthalpy at 298 K is listed only for the two species whose frequencies and structures were developed.

This set of "reactions", their associated rate constants, and the coupled kinetics model provide a quantitative description of the kinetic behavior of the $C_2H_5 + O_2$ reaction which is well-suited for incorporation into models of combustion kinetics. In this theoretical study, analytical expressions are developed for k_{4a} to k_{-4c} . These expressions are presented and their development is discussed in section IV.

In sections IIIB and IIIC, the energetics, structures, and frequencies of the molecular species and transitions states that were used in the theoretical calculations are described. In section IIID, the RRKM calculations which use this information to obtain values for k_{4a} - k_{-4c} are presented. The coupled kinetics model of mechanism 3 (represented by reactions 4a to -4c and their theoretical rate constants), which was used to calculate observed properties of the $C_2H_5 + O_2$ reaction, is described in section IIIE. Optimum agreement between theory and experiment was obtained by varying unknown molecular parameters in the theoretical rate constant calculations. A comparison of the measured and optimum calculated properties of the $C_2H_5 + O_2$ reaction is presented in section IIIF. The theoretical study concludes in section IIIG with a discussion of the final values of the adjustable molecular parameters in the theoretical model.

B. Energetics of Stable Species and Transition States along the Reaction Coordinate. The reaction path shown in Figure 5 indicates the heats of formation of the stable species and the transition states that were used in the RRKM calculations of $k_{4a}-k_{-4c}$. These energies, expressed in terms of reaction enthalpies at 0 K (i.e., $\Delta H^o_0(C_2H_5 + O_2 \rightarrow \text{species})$, are presented in Table III.

The thermodynamic properties of stable species were obtained from the best available measurements or estimates. Accurate values for the heats of formation of C_2H_5 , O_2 , C_2H_4 , and HO_2 were taken from the literature²⁷⁻²⁹ and used without adjustment. That for $C_2H_5O_2$ was taken from the study of Slagle et al.¹⁹ (34.0 \pm 1.5 kcal mol⁻¹ at 0 K) but was varied in this theoretical study within the reported uncertainty limits to obtain optimum agreement between theory and experiment (particularly to reproduce the measured $C_2H_5 + O_2 \rightleftharpoons C_2H_5O_2$ equilibrium constants which were reported by these authors¹⁹). The heat of formation of $C_2H_4O_2H$ was estimated to be 11 kcal mol⁻¹ higher than that of $C_2H_5O_2$ based on the difference in estimated dissociation energies of $H-CH_2CH_2O_2$ and $C_2H_4OO-H.^{30}$

The heat of formation used for the transition state $C_2H_4 \cdot O_2H$ is based on an estimated 5–7 kcal mol⁻¹ activation energy for the addition of HO₂ to C_2H_4 suggested by Benson.⁷ (The value presumed in the current study is 6 kcal mol⁻¹.) This estimated addition barrier is consistent with an indirectly determined theoretical upper bound³¹ for O(¹D) addition to C_2H_4 of 9 kcal mol⁻¹. Because O(¹D) has a resonance energy which is not present in HO₂, the O(¹D) barrier is expected to be higher than that for addition of HO₂.

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The heat of formation of the cyclic transition state, "CH₂CH₂O₂"H", was treated as an unrestrained parameter, and the value indicated in Figure 5 (and presented in Table III) is that value which provides optimum agreement between theory and experiment.

Two features of the energetics along the reaction coordinate have major influences on the dynamic bottlenecks controlling the overall process $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$. The first involves the potential energy of the transition state C_2H_4 . O_2H . The use of a value that is below that of the "CH2CH2O2"H" transition state (3 kcal mol⁻¹ lower here) results in the irreversible formation of $C_2H_4 + HO_2$ once the ring transition state is formed. This irreversibility is further assured by the additional entropic bias favoring the formation of the C-O bond scission transition state from C₂H₄O₂H over the re-formation of a five-membered ring transition state. Given these transition-state energies, the theoretical rate constants calculated in the current study $(k_{4a}-k_{-4c})$ become independent of details of the potential energy surface after the ring transition state (the portion indicated by the dotted line in Figure 5).

McAdam and Walker have proposed a mechanism for the overall transformation $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ that has similarities as well as differences with the current one.¹⁴ On the basis of their recent observations that the high-temperature C_2H_5 + O₂ rate constant decreases slightly with increasing temperature,¹⁴ these authors have also concluded that $C_2H_4 + HO_2$ forms irreversibly from a $C_2H_5O_2^{\dagger}$ cyclic transition state. They have proposed a direct decomposition of this transition state into C₂H₄ + HO_2 along a reaction coordinate that does not involve the intermediate formation of a bound species like CH₂CH₂O₂H. While the quantitative description of the kinetics of the C_2H_5 + O_2 reaction in the forward direction is independent of the details of the reaction path beyond the $C_2H_5O_2^{\dagger}$ transition state, there are implications regarding the kinetics of the reverse reaction that are not. These are dealt with in section VI.

The second important feature of the potential energy surface is the absence of an energy barrier to forming the $C_2H_5O_2$ adduct. This absence is supported by both experimental and theoretical evidence. Munk et al.³² report a negative activation energy for the $C_2H_5 + O_2$ rate constant ($E_a = -1.0$ kcal mol⁻¹) at 1-atm total pressure in the temperature range 298-400 K. While some of this apparent negative activation energy is due to the fact that the reaction is not yet fully at the high-pressure limit at 1-atm pressure (see below), the significant negative temperature dependence of k_4 is evidence that the formation of $C_2H_5O_2$ proceeds along an attractive reaction coordinate.

There are also indications from studies of analogous systems that $R + O_2$ addition occurs without surmounting an energy barrier. Measurements³³ of the rate constant for $C_2H_3 + O_2$ over a 300 K temperature range under conditions that are comparable to the high-pressure limit indicate a slight negative activation energy of -0.25 kcal mol⁻¹. The C₂H₃ + O₂ rate constant at room temperature is about twice as large as that for $C_2H_5 + O_2$ reaction extrapolated to the high-pressure limit. Bayes³⁴ also finds that the high-pressure limiting rate constant for $(CH_3)_3CCH_2 + O_2$ has a negative activation energy

The absence of an $R + O_2$ addition barrier is also consistent with the best available ab initio calculation of the $H + O_2$ potential energy surface. Dunning et al.³⁵ found no energy barrier leading to the formation of HO₂

A variational form of RRKM theory was used to locate the C_2H_5 , O_2 transition state under both entropic and energetic constraints. The energetic constraint requires knowledge of the

potential energy along the addition portion of the reaction path. (In the discussion below, progress along the reaction path is measured by $R_{C-\Omega}$, the distance of the carbon-atom radical site in C_2H_5 to the closest O in O_2). There is no direct information on the potential energy along this portion of the reaction coordinate. It is likely to be a complicated function of distance due to several curve crossings involving excited states of neutral O_2 , interactions between the ionic $C_2H_5^+ + O_2^-$ and the neutral C_2H_5 $+ O_2$ surfaces (a situation which has been explored by Ruiz and Bayes³⁶), and a shallow van der Waals minimum which must lie along the adiabatic surface somewhere outside the curve-crossing region.

To construct an elaborate potential energy function that accounts for all these features would require extensive ab initio electronic structure calculations that are beyond the scope of this investigation. In this study, for the range of R_{C-O} values that are important in determining the properties of the variational transition state, a simple attractive function was used, the long-range attractive portion of the Morse oscillator function:

$$V(R_{\rm C-O}) \rightarrow -2D_e e^{-\beta(R_{\rm C-O}-R_e)} = A e^{-\beta R_{\rm C-O}} \quad (R_{\rm C-O} \rightarrow \infty) \quad (9)$$

Rather than using D_e , R_e , and β as three separate adjustable parameters in this theoretical study, we used β and the combined constant A.

C. Structures and Vibration Frequencies of Stable Species and Transition States along the Reaction Coordinate. In addition to the energetics, the RRKM calculation of the rate constant requires the structure and frequencies of three stable species (C_2H_5 , O_2 , $C_2H_5O_2$), one classical transition state (.. $CH_2CH_2O_2$..H.), and all configurations of the reactants along the reaction path from $C_2H_5 + O_2$ to $C_2H_5O_2$ (in order to locate the variational transition state C_2H_5 ...O₂). The structures and vibration frequencies used in the calculations are presented in Table IV. Their origins are discussed in this section. In addition, the reaction path degeneracies are reviewed.

1. Structure and Frequencies of Stable Species. The O₂ properties are well-known.28

The C_2H_5 and $C_2H_5O_2$ properties listed in Table V are described in detail by Wagner and Melius.³⁷ They either are directly measured values^{38,39} or were determined by using high-quality ab initio calculations.³⁹⁻⁴¹ The low value of the CH₃ internal rotation barrier in C₂H₅ permits this degree of freedom to be treated as a free rotation in the calculations.

The two internal rotations in $C_2H_5O_2$ are strictly neither free rotations nor harmonic torsions. Test calculations of the equilibrium constant K_{4a} show little difference in its value using a hindered rotor or a harmonic torsion model at temperatures below 1000 K (using the simplifying assumption that the C-O₂ internal rotation is rotomeric, i.e., the trans and gauche configurations are energetically equal). Consequently, the simpler harmonic torsional model was used in all the calculations. For one of the two internal rotations (the one involving the $C-O_2$ axis), this model is not likely to be accurate in the case of chemically activated, highly nonthermal $C_2H_5O_2^*$, where the average energy content of any mode is high. However, the errors introduced into the rate constant are probably too small to merit the complication of a more accurate treatment.

2. Structure and Frequencies of ...CH₂CH₂O₂...H... The properties of the ring transition state "CH2CH2O2"H" are derived from extended analogies with related systems. Its structure can be pictured as being formed by a sequence of two internal rotations of $C_2H_5O_2$ followed by distortion of the CH₃ under attack. First, internal rotation about the C-O bond moves the CCOO skeleton from a trans into a cis configuration. Two of the H atoms on the CH_3 end now have azimuthal angles with respect to the CCOO

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TABLE IV: Moments of Inertia (I_i) , Reduced Moments of Inertia for Internal Rotation (Ired), External and Internal Rotational Symmetry and Electronic Symmetry Numbers (sext, Sint, Selec), Rotomer Number $(s_{rotomer})$, Barriers to Internal Rotation (V_{rot}), Reaction Path Degeneracy, and Frequencies for O2, C2H5, C2H5O2, and ··C₂H₄O₂··H··^a

	O ₂	C₂H₅	$C_2H_5O_2$	••С₂Н₄- О₂••Н••
Selec	3	2	2	2
external rotation				
I_1	4.82	14.76	35.23	
I_2	11.65	22.39	111.86	62.50
I_3	11.65	24.11	120.37	90.89
Sext	2	1	1	1
frequency				
CH ₃ stretches				
out-of-plane		2987	2994	2994
in-plane		2842	2997	
sym		2920	2933	2933
CH ₂ stretches				
asym		3122	3016	3016
sym		3033	2961	2961
CH ₃ bends				
in-plane def		1440	1451	1451
out-plane def		1440	1389	1389
sym def		1366	1380	1380
out-plane rock		1025	1159	1159
in-plane rock		1138	1136	1136
CH ₂ bends				
scissors		1383	1474	1474
wag, pyramidal dist		540	1351	1351
twist		1242	1242	
rock		802	800	800
CCOO stretches				
O–O like	1580		1112	1112
C-C like		1175	1009	1009
C-O like			838	838
CCOO bends				
CCOO out-of-phase			499	499
CCOO in-phase			305	305
CHO				5 4 A
sym stretch				543
bend				160
asym stretch				16381
torsions or internal rotation				
C-CH ₃		1 1 1 1 1	2.75	
Ired		1.11° 4	2.75	
S _{int}		015	3	
V rot		141	3.3	
rot C. O		141	231	
$C = O_2$			7 7 2	
f red			3	
V srotomer			1 64	
rot //			920	
reaction path degeneracy			~ •	2

"Units are amu Å² for I_i and I_{red} , kcal mol⁻¹ for V_{rot} , and cm⁻¹ for frequencies. ^b Treated as a free rotor in the rate constant calculations. "Treated as a harmonic torsional mode in the rate constant calculations.

TABLE V: Values of the Final Set of Adjustable Constants Used in the **RRKM** Calculations

$\Delta H^{\circ}_{0}(C_{2}H_{5} + O_{2} \rightarrow C_{2}H_{5}O_{2}), \text{ kcal mol}^{-1}$	-32.9
A, kcal mol ⁻¹	500
β , Å ⁻¹	2.375
α , Å ⁻¹	1.340
$\Delta H^{\circ}_{0}(C_{2}H_{5} + O_{2} \rightarrow \cdots CH_{2}CH_{2}O_{2}\cdots H\cdots), \text{ kcal mol}^{-1}$	-2.4
$\nu_{\rm ring}$, cm ⁻¹	160
$\Delta E_{\rm tot}, {\rm cm}^{-1}$	-55

plane of $\pm 60^{\circ}$. A second internal rotation about the C-C bond reduces this azimuthal angle to 30° for one H atom (and increases the angle to 90° for the other) and brings the one H atom closer to the end O atom of the CCOO skeleton. The end C atom is now distorted into an sp² bonding configuration (with respect to the unbroken C-H and C-C bonds). The azimuthal angle of the

departing H atom is fixed at 30°. Now the H₂CC portion of the molecule lies in a common plane, and the departing H atom is perpendicular to that plane. When the C-H distance for the departing H atom is stretched from 1.08 to 1.48 Å, the H atom is equidistant from the end C and O atoms of the CCOO skeleton. This is the final structure which is adopted for the ring transition state. It is essentially an "envelope"-shaped five-membered ring with the C···H···O section of the ring being the "flap" of the envelope. Because this is a nonplanar structure, the reaction path degeneracy is 2 (for the cases of the flap up and the flap down).

The ring transition-state structure used is an approximation for the actual one, which is likely to have a somewhat more distorted configuration. The C---H distance of 1.48 Å is 0.1-0.2 Å longer than the calculated C...H distance in the abstraction transition state for $CH_4 + O^{42}$ or the migration transition states of HCO \rightarrow COH⁴³ and OCHCH \rightarrow OCCH₂.⁴⁴ This distance in the ring transition state would be less if the CCOO skeleton bond distances and angles or if the azimuthal out-of-plane angle of the H atom in the ring were relaxed from the values described above in a manner that does not change the potential energy significantly. Such distortions are due in part to the electronic structure of the terminal O atom. In either the cis or trans CCOO skeletal position, the radical orbital on the terminal O atom is expected to point out of the CCOO plane to minimize the repulsive overlap of the in-plane filled orbitals of that atom with the outof-plane filled orbitals of the inner O atom.⁴⁵ This results in a transition state in which the H atom being removed from the CH₃ group is out of the CCOO plane. However, there is an excited electronic state of $C_2H_5O_2$ for which the radical orbital is in-plane, which would allow a planar ring transition state. Accommodation of the strain in the "envelope" model and the electronic excitation in the terminal O would most probably lead to a distorted transition state. The resolution of such complexities is beyond the scope of this study.

Approximate values were used for the frequencies for the ring transition state. Most of these frequencies, i.e., the CH_2 and CH_3 stretch and bend frequencies, the C-C, C-O, and O-O stretch frequencies, and the CCO and COO bend frequencies, were taken to be those of $C_2H_5O_2$. The three remaining frequencies, a symmetric stretch, a bend, and an imaginary frequency, were estimated. The symmetric stretch and the imaginary frequency were taken from an ab initio electronic structure calculation⁴² of the CH₃...H...O transition state. Semiempirical studies by Cohen et al.46 indicate that these frequencies are consistent with the available rate constant measurements for $O(^{3}P)$ + alkane abstraction reactions. The CH3. H.O symmetric stretch frequency of 543 cm⁻¹ has a low value, as expected for the exchange of a light atom between two heavy ones.⁴⁷ The 1638-cm⁻¹ imaginary frequency of CH₃. H.O is similar to that for other H abstraction reactions.⁴⁸ The remaining C···H···O bend frequency is the most difficult to estimate. There are actually two bending motions for C...H...O in the ring, one corresponding to opening and closing the flap of the envelope and the other corresponding to a bending motion within the flap of the envelope. The assumption that the bend frequencies of CH₃, CCO, and COO are unchanged from $C_2H_5O_2$ is equivalent to fixing one of these two bend frequencies in C.-H.-O. However, in reality, the bend frequency of CH₃, and perhaps also of COO and CCO, is strongly coupled to the bending motion of C.-.H...O. The characterization of the coupling and the final bending motion is also beyond the scope of this study. Consequently, the one unassigned bend frequency, designated ν_{ring} , was made an adjustable parameter whose final value should be regarded as only an overall measure of the looseness or tightness

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of the ring transition state. Its optimum value is given in Table V together with the other properties of the ring transition state.

3. Structure and Frequencies of C_2H_5 . The C_2H_5 . O_2 . transition state must be variationally determined. In addition to the energetics, the variation of the structure and frequencies along the reaction path must also be described in order to calculate the addition rate constant. The Dunning et al. study³⁵ of the H + O₂ reaction found that the O-O distance changed very little along the reaction coordinate from reactants to the variational transition state, less than 2%. With this information and that of the theoretical study of the structure of C₂H₅O₂ as guides,⁴⁵ the equilibrium structures of O₂ and C₂H₅ were taken as unchanging along the reaction path to the variational transition state.

The CCO and COO angles of approach also need to be spec-ified. The Dunning et al.³⁵ calculations for HO₂ revealed that only a minor change occurs in the HOO angle with R (<15%) from the equilibrium value in HO₂ to the H-O₂ transition state. Again using the behavior of the HO₂ system as a guide (since no information is available on CCO and COO bond angle dependencies on R), these angles were fixed at their equilibrium values in $C_2H_5O_2$. All the moments of inertia for the free internal rotations are also regarded as independent of R, i.e., unchanged from their values in either C_2H_5 (for the CH₃ rotation) or $C_2H_5O_2$ (for the O_2 rotation). In summary, a reduction in R simply causes the structure of $C_2H_5\cdots O_2$ to become less extended.

A standard exponential switching function, governed by a parameter α , was used to connect reactant vibration frequencies with those of the adduct.⁴⁹ There are three adduct bending frequencies (symmetric and antisymmetric in-plane bends of the CCOO skeleton and a twist frequency of C(CH₃)H₂ relative to the C-O bond) that evolve into free rotations (zero frequencies) in the reactants. The switching function assumes that these three frequencies change exponentially with R. There is a fourth frequency that corresponds to internal rotation of O₂ about the C-O bond which was treated as a free rotor as discussed above.

4. Summary of Molecular Properties Used as Adjustable Parameters. The characterization of the potential energy surface involves the selection of six adjustable molecular parameters. There are three energy parameters that describe the long-range part of the potential: A and β which describe the energy on the minimum-energy path from $C_2H_5 + O_2$ to $C_2H_5O_2$ and α which describes the change in energy perpendicular to the minimumenergy path. There are two parameters that describe the ring transition state: $\Delta H_0^{\circ}(C_2H_5 + O_2 \rightarrow \cdots CH_2CH_2O_2\cdots H \cdots)$ (the height of the ring transition state relative to the reactants) and v_{ring} (a measure of the looseness of the transition state). Finally, there is one restricted energy, that of the $C_2H_5-O_2$ bond, $\Delta H^{\circ}_{0}(C_{2}H_{5} + O_{2} \rightarrow C_{2}H_{5}O_{2}).$

The experimental information available, although extensive, is not adequate to obtain unique values for all six parameters based on any best-fit criterion. Offsetting effects exist which produce comparable fits when certain variations of the parameters were used in the data-fitting exercises. The nature of some of these effects is discussed in section IIIG.

D. Calculations of $k_{4a}-k_{-4c}$. Chemically activated RRKM theory was used to calculate $k_{4a}-k_{-4c}$ using the energetics, structures, and frequencies described above. These calculations are of a standard form⁵⁰ using a direct count Beyer-Swinehart algorithm.⁵¹ Tunneling through an Eckhart barrier through the addition-elimination barrier is included.52 No explicit summation over total angular momentum states was done. Rather, an effective total angular momentum was used based on thermal averages of the external rotational energy.⁵⁰ The azimuthal external rotation associated with the smallest moment of inertia of the collision system was treated adiabatically.

The variational treatment of the C_2H_5 ... O_2 transition state was carried out canonically, rather than microcanonically.53 At each

temperature, the C₂H₅...O₂ transition state was found by minimizing the flux between the reactants and the adduct. This is equivalent to minimizing the high-pressure limit of the addition rate constant. Once selected, that transition-state configuration was used in the chemically activated RRKM calculations at that temperature.

The final feature of the RRKM calculation to be described is the treatment of the stabilization of $C_2H_5O_2^*$ by the buffer gas. In the experiments reported in section II, the buffer gas was primarily He (85%). The other collision partners present, N₂ and O_2 , have quenching properties close enough to that of He⁵⁴ that it is reasonable to presume that the quenching gas is entirely He. In view of the complexity of the reaction dynamics and the several unknown features of the potential energy surface, any rigorous inclusion of the quenching process in terms of a Master Equation model⁵⁰ is inappropriate. Hence, a modified strong collision approximation⁵⁵ was used in which a single "effective" bimolecular rate constant, $k_{\rm S}$, describes the rate of stabilization of C₂H₅O₂* by He. $k_{\rm S}$ is set to the gas kinetic rate constant, modified by a factor β' . The gas kinetic rate constant was calculated by using the Lennard-Jones parameters in ref 56 (with the known parameters for butane taken as the closest analogue to the unknown parameters for $C_2H_5O_2$). Through analytic expressions derived from master equation treatments of the collision effects,⁵⁵ the factor β' can be expressed as a function of temperature and the quantity $\langle \Delta E \rangle_{tot}$, the average total energy transferred by collisions with the buffer gas at temperature T. In the calculations below, $\langle \Delta E \rangle_{\rm tot}$ is treated as the adjustable collision efficiency parameter. There have been no prior determinations of its value.

E. The Couple Kinetics Model. The kinetic behavior of the $C_2H_5 + O_2$ reaction has been described in section IIIA in terms of four processes: reactions 4a, 4b, -4a, and -4c. These four "reactions" account for the behavior of mechanism 3 via coupled differential equations for the time dependence of species concentrations:

$$d[C_{2}H_{5}]/dt = -(k_{4a} + k_{4b})[O_{2}][C_{2}H_{5}] + k_{-4a}[C_{2}H_{5}O_{2}]$$

$$d[C_{2}H_{5}O_{2}]/dt = k_{4a}[O_{2}][C_{2}H_{5}] - (k_{-4a} + k_{-4c})[C_{2}H_{5}O_{2}]$$

$$(10)$$

$$d[C_{2}H_{4}]/dt = k_{4b}[O_{2}][C_{2}H_{5}] + k_{-4c}[C_{2}H_{5}O_{2}]$$

This coupled kinetics model can be solved analytically for O₂ in excess, i.e., $[O_2]$ constant. This was the condition of the current and former experiments whose results are modeled here. The solutions for C_2H_5 and C_2H_4 , the two species which were monitored, are the following:

$$[C_2H_5] / [C_2H_5]_0 = c_+ e^{-\lambda_+ t} + c_- e^{-\lambda_- t}$$
(11)

$$[C_2H_4] / [C_2H_5]_0 = d_+(1 - e^{-\lambda_+ t}) + d_-(1 - e^{-\lambda_- t})$$
(12)

where

$$\lambda_{\pm} = (\{k_{4a} + k_{4b}\}[O_2] + k_{-4a} + k_{-4c} \pm \theta)/2$$
(13)

$$c_{\pm} = (1 \pm \{(k_{4a} + k_{4b})[O_2] - k_{-4a} - k_{-4c}\}/\theta)/2 \quad (14)$$

$$\theta = (\{(k_{4a} + k_{4b})[O_2] - k_{-4a} - k_{-4c}\}^2 + 4k_{4a}[O_2]k_{-4a})^{1/2}$$
(15)

$$d_{\pm} = (k_{4b}[O_2]c_{\pm} \pm k_{4a}[O_2]k_{-4c}/\{\lambda_- - \lambda_+\})/\lambda_{\pm}$$
(16)

 $[C_2H_5]_0$ is the initial concentration of C_2H_5 . The RRKM calculations of $k_{4a} - k_{-4c}$ were used in the above solutions in an iterative manner to obtain a set of values for the adjustable parameters which optimized agreement between theory and experiment. In

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Figure 6. van't Hoff plot of the theoretical and experimental (from ref 19) equilibrium constant for the $C_2H_5 + O_2 \Rightarrow C_2H_5O_2$ reaction.

the iterative procedure, eq 11 and 12 were used to generate theoretical "data" for each of the experimental conditions used. The theoretical temporal concentration profiles were treated as were the experimental data in each of the experiments listed above. For example, k_4 was obtained from the slope of a straight-line fit to the dependence of the decay constant on $[O_2]$ where the decay constant at each value of [O₂] was determined by a least-squares fit of the corresponding $[C_2H_5]$ temporal profile to a single exponential. For another example, $F(C_2H_4)$ was obtained from eq 12 at approximately the same time (\sim 25 ms) and O₂ concentration as was used in the experiments. Only such explicit reproductions of the measurement procedure allow the calculations to accurately treat the equilibration between C_2H_5 and $C_2H_5O_2$ and to fully implement mechanism 3. The parameters were adjusted and the procedure was repeated until optimum agreement with experiment was achieved. The experimental results which were compared with theoretical predictions included the following: (1) values of k_4 and $F(C_2H_4)$ given in Tables I and II, (2) additional determinations of k_4 reported in ref 10, (3) equilibrium constants ($K_{4a} = k_{4a}/k_{-4a}$) reported in ref 19, and (4) the presumption (based on the evidence presented above) that the high-pressure limit for the addition rate constant has essentially no temperature dependence.

The above discussion has not dealt with C_2H_5 heterogeneous wall loss, a process which occurred to a measurable extent in all experiments listed in Table I and ref 10 and 19. The above formulation was easily modified to accommodate a wall reaction characterized by a rate constant k_{wall} by the following substitution

$$k_{4b}[O_2] \rightarrow k_{wall} + k_{4b}[O_2] \tag{17}$$

in eq 13-15. C_2H_5 wall loss can be viewed as another route that converts C_2H_5 to products without passing through a stabilized adduct. Since wall loss has no dependence on $[O_2]$, wall reactions yield an intercept in the linear fit of the first-order decay constants vs $[O_2]$ but do not alter the slope of the fitted line through the decay constants from which k_4 is obtained. C_2H_4 yield experiments were conducted under conditions where the wall reactions consumed a negligible fraction of C_2H_5 . Hence, no replacement of the $k_{4b}[O_2]$ term in eq 16 was required.

F. Comparison of Theoretical Calculations of the Kinetic Behavior of the $C_2H_5 + O_2$ Reaction with Experiment. 1. The Equilibrium Constant, K_{4a} . The simplest comparison between theory and experiment can be done with the equilibrium constant K_{4a} (equal to k_{4a}/k_{-4a}) for the process $C_2H_5 + O_2 \Longrightarrow C_2H_5O_2$, since no information about transition states is required. In Figure 6, the comparison between the theoretical and experimental determinations of K_{4a} is displayed. Agreement with the results of Slagle et al.¹⁹ is excellent. The theoretical value is very sensitive



Figure 7. k_4 versus inverse temperature at 1 atm of He buffer gas and in the high-pressure limit: theory (- or ---) and experiment (\Box , Munk et al. of ref 32; \bullet , Plumb and Ryan of ref 12).

to the value of one of the parameters, $\Delta H^o_0(C_2H_5O_2 \rightarrow C_2H_5 + O_2)$, the zero-point-corrected dissociation energy of the peroxy radical. The final value of this energy, 32.9 kcal mol⁻¹, is regarded as an accurate determination of this bond energy. Variations of ± 0.5 kcal mol⁻¹ to this value will cause the calculated K_{4a} to fall outside the range of uncertainty in the experimental values.

2. The High-Pressure-Limit $C_2H_5 + O_2$ Rate Constant, k^{∞}_4 . The next simplest comparison between theory and experiment is with the high-pressure limit rate constant which is obtainable from the determinations of k_4 below the ceiling temperature. (There have been no direct determinations of k^{∞}_4 since no studies of this reaction have been conducted above 1-atm pressure.) The calculations of k^{∞}_4 (which is equal to the high-pressure limit of k_{4a}) require only information about the reactants and the structure, frequencies and energetics of $C_2H_5\cdots O_2$ along that portion of the reaction coordinate where the variational transition state is located.

The comparison between theory and experiment is displayed in Figure 7. Comparisons can be made only with k_4 values obtained near the high-pressure limit, such as those reported by Munk et al.³² for a pressure of 1 atm, and with extrapolations of low-pressure determinations of k_4 to the high-pressure limit, such as were reported by Plumb and Ryan¹² (based on experiments conducted in the pressure range 1–10 Torr).

For comparison purposes, calculations of k_4 both at the highpressure limit and at 1 atm are shown in Figure 7. It is apparent from these calculations that the reaction is not yet at the highpressure limit at 1-atm pressure. The theoretical values of k_4 at 1-atm pressure are a factor of 1.5-2 higher than the values reported by Munk et al. and the extrapolated value of k_4^{∞} reported by Plumb and Ryan.

There are reasons to prefer the higher result of the theoretical study. First, agreement with the actual measured rate constants of Plumb and Ryan in the 1-10-Torr pressure region is excellent (see below). There is disagreement only with the extrapolation to high pressures. The Plumb and Ryan value of k^{∞}_4 was obtained by using a simple extrapolation function which is not expected to be as accurate a means for obtaining k^{∞}_4 as is the detailed RRKM calculation of the current investigation. Second, the determinations of Munk et al. are not direct but rather involve a data analysis which must take into account processes that compete with the $C_2H_5 + O_2$ reaction for the consumption of C_2H_5 . Neither the experiments themselves nor the data analysis is described in detail, so no particular source of experimental error can be suggested. The values of k_4 reported by Munk et al. at 1 atm display an anomalously steep decline with increasing temperature, 30% between 300 and 400 K. If one accepts the indications that k^{∞}_4 is essentially temperature independent, it would be difficult to devise a theoretical model that displays such a sharp temperature dependence of k_4 at 1-atm pressure. This suggests that the mechanism used to reduce the experimental results is not complete and the $C_2H_5 + O_2$ constants are not as accurate as reported.

The parameters that were adjusted to obtain the optimum value of k_4^{∞} are A, β , and α . The final values of these three parameters are given in Table V. While these parameter values are not unique, it is important to note that changing k_4^{∞} by as little as 20% noticeably reduces the agreement between theory and experiment for the pressure dependence of the rate constant.

3. The Pressure and Temperature Dependence of the C_2H_5 + O_2 Rate Constant, $k_4(T,M)$. The theoretical and measured rate constants for the loss of C_2H_5 in the $C_2H_5 + O_2$ reaction, k_4 , are displayed in Figure 2. Both the temperature and pressure dependencies are shown. Nine temperatures were studied from 296 to 904 K in the current and prior^{10,12} investigations. The pressure range (He buffer gas) is 0.4–16.0 Torr.

The experimental and theoretical results in Figure 2 show a change in the pressure dependence of k_4 as the temperature increases. The change in behavior occurs near 640 K, the transition temperature between the low- and high-temperature mechanisms. Below 640 K, experiment and theory display "typical" falloff behavior with the rate constant at a fixed temperature increasing with increasing pressure and with the rate constant at a fixed pressure decreasing with increasing temperature. Above 640 K, the rate constant is essentially independent of temperature and pressure. No significance is attributed to the pressure dependence of " k_4 " at 640 K.

The agreement between the theory and the experiments is very good. The root-mean-square (rms) relative error of the calculated rate constants (compared to the experimental values) provides a measure of the agreement. This error as a function of temperature ranges from 5% (at 385 K) to 36% (at 467 K), with an average value over the nine temperatures of 15%. The 36% disagreement at 467 K is anomalously large. For example, the rms relative error at 473 K, only 6 K higher in temperature, is 14%. The determinations of k_4 at these two temperatures near 470 K were obtained in different investigations conducted in our laboratory. The earlier determinations,¹⁰ which included those obtained at 467 K, are considered less accurate since detection sensitivity was over a factor of 20 lower than in the current study. However, experiments conducted in the former and current investigation at ambient temperature are in close agreement with each other as well as with the values reported by Plumb and Ryan.¹² (All the k_4 values obtained at 296 K are displayed in Figure 2.)

Below 640 K, $k_4 = k_{4a} + k_{4b}$, with a slight deviation from this equivalence at 580 K. At these lower temperatures, the value of the equilibrium constant is extremely low and there is no significant reaction of $C_2H_5O_2$ once it is formed. At 580 K, the equilibrium constant is large enough for back-reactions to be noticeable. At higher O_2 concentrations than were used to obtain k_4 , biexponential decays of C_2H_5 can be observed near 580 K.¹⁹

At 640 K, the back-reaction rate constant k_{-4a} is of the magnitude of the first-order rate constants $k_{4a}[O_2]$ and $k_{4b}[O_2]$ for the O₂ concentrations used in these experiments. Apparent k_4 values at 640 K were obtained by fitting single-exponential functions through the nonexponential radical decay profiles which result from this situation (as was done in the experiments performed at this temperature). In Figure 8, a theoretical C₂H₅ decay profile and the single-exponential fit to these "data" are displayed. In addition, a plot of the "decay constants" obtained in this manner from the simulated data vs $[O_2]$ is shown. From this plot the apparent values of k_4 at 640 K shown in Figure 2 were obtained. There is good agreement with the experimental "determinations".

The second insert in Figure 8 illustrates the necessity of including back-reactions in interpreting the data at 640 K. It includes theoretical values of k_4 which took the two decomposition reactions of $C_2H_5O_2$ into account (labeled multiple-pass) and those which did not (labeled single-pass).



Figure 8. Plot of the calculated dependence of the first-order decay constant versus $[O_2]$ at 640 K and a He pressure of 4.01 Torr. The top insert displays a superposition of the simulated data for $[O_2] = 0.89 \times 10^{15}$ molecules cm⁻³ and the single-exponential fit used to obtain the decay constant at that value of $[O_2]$. The lower insert shows the difference between the calculated value of k_4 (as a function of pressure) including (labeled multiple-pass) or excluding (labeled single-pass) the adduct dissociation reactions k_{-4a} and k_{-4c} . The values labeled by \blacksquare are the experimental values of " k_4 " found in Figure 2. Also the multiple-pass 2.

Significantly above 640 K, equilibrium between C_2H_5 and $C_2H_5O_2$ is rapidly established before there is significant depletion of C_2H_5 . Loss of C_2H_5 is thus due to reaction 4b with the equilibrium essentially maintained throughout the overall transformation of C_2H_5 into C_2H_4 . The value of k_4 is close to but higher than k_{4b} for the range of densities used in the current study. The maximum deviation is <20%. The deviation occurs because the equilibrium is not perfectly maintained.

The independence of k_4 on pressure for the three highest temperatures studied (750–904 K) is due in large part to the behavior of mechanism 3 at the densities used in the experimental studies considered here. At these higher temperatures, the metastable adduct $C_2H_5O_2^*$ predominantly undergoes unimolecular dissociation back to reactants. Over the range of densities used, the stabilization of the adduct is only a minor channel. Hence, the loss of $C_2H_5O_2^*$ via the addition-elimination channel competes almost exclusively with unimolecular decay back to reactants. The gradual decrease in k_{4b} with increasing density is almost perfectly compensated for by an increase in k_{-4c} with density which increases the yield of the ultimate products from the small fraction of $C_2H_5O_2^*$ which is collisionally stabilized.

The weak decrease in k_{4b} with increasing temperature is a consequence of the fact that the ring transition state barrier lies below the reactant potential energy. Unimolecular decay of $C_2H_5O_2^*$ back to reactants, with its loose transition state, competes more effectively with addition-elimination as temperature increases.

4. Pressure and Temperature Dependence of the $C_2H_4 + HO_2$ Branching Fraction, $F(C_2H_4)$. The final comparison is with the measured C_2H_4 branching fractions, $F(C_2H_4)$. Figure 3 displays this comparison for room-temperature determinations from the current study and from earlier investigations, i.e., the studies of Plumb and Ryan¹² and Niki et al.²¹ (Niki's measured value of $F(C_2H_4)$, made at 720-Torr total pressure, is so low they preferred to regard it as an upper limit.) The parameters in the theoretical calculations were adjusted to obtain optimum agreement of the calculated values at 25 ms with the current measured values (not only the ambient temperature values but also those obtained at three elevated temperatures).

It is important to note that the mechanism used in the theoretical calculations accurately predicts the large falloff in $F(C_2H_4)$ with increasing pressure. The extremely low branching fraction reported by Niki et al.²¹ obtained from experiments conducted at a density nearly 100 times greater than the densities used to obtain the parameters of the theoretical model is accurately reproduced by the theoretical model. Such a falloff is not expected if a direct H-atom metathesis reaction, reaction 2, is responsible for C_2H_4 production.¹²

Recently, Kaiser et al.⁵⁷ have measured $F(C_2H_4)$ at 298 K from 6.5 to 650 Torr. The buffer gas was either He or N₂. They observed essentially the same monotonic decrease of $F(C_2H_4)$ with increasing total pressure that is predicted by the theoretical model. The majority of the experiments conducted by Kaiser et al. involved the use of bath gases containing a higher fraction of O₂ or N₂ and lower fractions of He than were used in the current experiments. The small difference between the C₂H₄ yields reported here can be accounted for by an average 30% difference in bath-gas efficiencies for the respective gas mixtures used.

In Figure 4, the theoretical and experimental values of $F(C_2H_4)$ obtained at four temperatures are displayed. Agreement is good at all temperatures. The average rms absolute error between theory and experiment for the four temperatures studied below the ceiling temperature (where $F(C_2H_4)$ depends on density) is 0.06. This is only slightly higher than the estimated 0.05 uncertainty in the experimental determinations themselves.

For the three lowest temperatures in the figure, for a given value of [M], the branching fraction increases with temperature. This is due to the fact that as the temperature increases, the energy content of the $C_2H_5O_2^*$ increases, making it more difficult to stabilize by collision with M but easier to decay over the barrier to $C_2H_4 + HO_2$. However, for all three temperatures, the branching fraction will essentially go to zero with large enough increases in [M].

In contrast, the branching fraction for 723 K does not go to zero with increasing [M]. At this temperature, decomposition of $C_2H_5O_2$ is an important process. The establishment of an equilibrium between C_2H_5 and $C_2H_5O_2$ favoring the reactants provides repeated opportunities for $C_2H_5 + O_2$ to be converted into $C_2H_4 + HO_2$, the ultimate products. This results in a behavior which resembles that of an elementary reaction including complete conversion of C_2H_5 into C_2H_4 (resulting in a value of unity for $F(C_2H_4)$). This is the observed behavior at 723 K (and other temperatures above the ceiling temperature¹⁸) and of course is the theoretical prediction.

The theoretical branching fractions are a sensitive function not only of all the varied parameters described above but also of the two remaining ones, $\Delta H^{\circ}_{0}(C_{2}H_{5}O_{2} \rightarrow \cdots CH_{2}CH_{2}O_{2}\cdots H\cdots)$, the $C_{2}H_{5}O_{2}$ rearrangement barrier, and ν_{ring} , the measure of the looseness of the transition state that describes this rearrangement. The final values of these two parameters are also given in Table V. As will be discussed in section IIIG, these two parameters are partially coupled into an optimal range of correlated pairs of values. However, the temperature dependence of $F(C_{2}H_{4})$ tends to be more sensitive to ν_{ring} while the overall rate of reaction above the ceiling temperature, k_{4} , tends to be particularly sensitive to $\Delta H^{\circ}_{0}(C_{2}H_{5}O_{2} \rightarrow \cdots CH_{2}CH_{2}O_{2}\cdots H\cdots)$.

G. Discussion of Final Parameter Values. The values of the adjustable molecular parameters used to obtain the theoretical results in the prior part are now compared to values obtained in previous studies of the $C_2H_5 + O_2$ as well as other addition reactions. With one exception, the final values selected are not unique because comparable agreement between theory and experiment can be obtained when some pairs of parameters are changed (within limits) in a manner that produces compensating effects. These effects are also discussed in this section.

The uniquely determined parameter is $\Delta H^{\circ}_{0}(C_{2}H_{5} + O_{2} \rightarrow C_{2}H_{5}O_{2})$. A value of -32.9 ± 0.5 kcal mol⁻¹ is required to bring the theoretical and experimental equilibrium constants K_{4a} into agreement. With the calculated frequencies and moments of inertia, this value is equivalent to a dissociation enthalpy at 298 K, $\Delta H^{\circ}_{298}(C_{2}H_{5} + O_{2} \rightarrow C_{2}H_{5}O_{2})$, of 34.1 ± 0.5 kcal mol⁻¹. In the original report of the experimental results,¹⁹ Slagle et al. obtained a value of 35.2 ± 1.5 kcal mol⁻¹ at 298 K through a Third Law analysis using a calculated entropy of $C_{2}H_{5}O_{2}$ obtained from

unpublished results of Wagner and Melius on the structure of this peroxy radical. In the current theoretical study, the rotation of O_2 about the C-O bond in $C_2H_5O_2$ is treated as having three configurations of O_2 about the C-O bond that are equivalent in energy. (The reasons for this rotomeric model are discussed in ref 33.) In the entropy calculation used in Slagle et al., two of the three O_2 orientations were assumed to have energies high enough to be neglected. It is the entropy difference between these two rotations that is the origin of the 1 kcal/mol difference between the current value of $\Delta H^o_{298}(C_2H_5O_2 \rightarrow C_2H_5 + O_2)$ and that reported by Slagle et al.

The three parameters A, β , and α that describe the long-range approach of O₂ to C₂H₅ are correlated. The constraint on the theoretical study that k^{∞}_4 be temperature independent reduces these parameters to two in number since it fixes the ratio α/β . For the C₂H₅ + O₂ reaction, a value of 0.564 was required to achieve this temperature independence. A 10% variation in the value of this ratio produces a 25% change in k^{∞}_4 between 300 and 1000 K. In the final data-fitting exercise, α/β was kept fixed at the stated value. Comparable values of this ratio were required by Kobos et al.⁴⁹ to obtain theoretical agreement with measurements for other association reactions.

Changes in A and β were required to obtain agreement between theory and experiment only below the ceiling temperature. Above this temperature, k^{∞}_4 is no longer a meaningful rate constant to describe the overall chemical changes which occur in the C₂H₅ + O₂ reaction since C₂H₅ and C₂H₅O₂ are essentially in chemical equilibrium.

Appropriate changes in A and β in the same direction leave k^{∞}_{4} essentially unaltered. For example, a 5% increase in β coupled with a 25% increase in A (along with a small reoptimization in $\langle \Delta E \rangle_{tot}$) produces calculated values of k_4 that essentially preserved the agreement between theory and experiment (altering k^{∞}_{4} by less than 7%). While uncorrelated adjustments in A and β significantly affected the value of k^{∞}_{4} , they had less influence on calculated values of other observables.

The calculated values of the observables are not particularly sensitive to the values selected for A, β , and α in part because k^{∞}_4 and its temperature dependence have not been directly measured. Therefore, this study reveals relatively little about the potential energy surface in the region of the approach of C_2H_5 to O_2 . Nevertheless, the experimental results do indicate one qualitative feature about the long-range portion of the potential energy surface. If A and β were selected to be consistent with a Morse oscillator fit to the $C_2H_5-O_2$ dissociation energy, fundamental vibrational frequency, and equilibrium distance, then the resulting values of k^{∞}_4 would be on the order of 30 times larger than the observed values. The actual magnitude of k^{∞}_4 is consistent only with a much shallower and broader Morse potential. Such a shallow potential at the $C_2H_5-O_2$ distances of the variational transition state is consistent with a curve-crossing picture involving the ground, excited, and ionic states of O_2 .

The two parameters $\Delta H^{\circ}_{0}(C_{2}H_{5} + O_{2} \rightarrow \cdot CH_{2}CH_{2}O_{2} \cdot H \cdot \cdot)$ and ν_{ring} , which determine the ease of forming the ring transition state (leading to the ultimate products $C_{2}H_{4} + HO_{2}$), are also correlated. Below the ceiling temperature (at the densities of the experiments considered in this investigation), these parameters essentially determine only the $C_{2}H_{4}$ branching fraction. (There is a small influence on k_{4} .) Above the ceiling temperature the effect of these parameters is reversed. They have no effect on $F(C_{2}H_{4})$ whose value is always 1 but strongly influence the value of k_{4} (since reaction requires repeated attempts to form the ring transition state until $C_{2}H_{5}$ is completely converted into the ultimate products).

Changing both ring transition-state parameters in opposite directions in the appropriate proportion can yield comparable agreement between theory and experiment. For example, two sets of values of these parameters (30.5 kcal mol⁻¹, 160 cm⁻¹ or 30.0 kcal mol⁻¹, 250 cm⁻¹) yield essentially the same theoretical values of k_4 and $F(C_2H_4)$. More extreme correlated changes do not yield comparable agreement with experiment. Relatively low values of ν_{ring} are necessary to obtain the right temperature dependence

of the branching ratio. If ν_{ring} were assigned a value >500 cm⁻¹, no value of $\Delta H^o_0(C_2H_5 + O_2 \rightarrow \cdot\cdot CH_2CH_2O_2\cdot\cdot H\cdot\cdot)$ would restore the correct temperature dependence.

The final value of the last parameter, $\langle \Delta E \rangle_{tot}$, whose magnitude largely determines the falloff behavior of k_4 , can be compared with energy-transfer parameters determined for other systems. This parameter $\langle \Delta E \rangle_{tot}$ is only weakly correlated with all the others. For example, a 10% variation in $\langle \Delta E \rangle_{tot}$ can be compensated for by suitable, correlated changes in the other parameters. The value of $\langle \Delta E \rangle_{tot}$ for the $C_2H_5 + O_2$ reaction, -55 cm⁻¹, is somewhat below the range of values determined for other systems. Direct experimental measurements of $\langle \Delta E \rangle_{tot}$ for the bath gas He and six metastable adducts⁵⁴ have yielded values of -60 to -120 cm⁻¹. However, an RRKM analysis⁵⁸ of dissociation measurements of HCO indicates that a value of -45 cm⁻¹ is appropriate for that system.

The seven molecular parameters that were adjusted in the theoretical study of the kinetics of the $C_2H_5 + O_2$ reaction represent four basic pieces of information: the stability of the $C_2H_5O_2$ adduct $[\Delta H^o_0(C_2H_5 + O_2 \rightarrow C_2H_5O_2)]$, the probability of energy loss by $C_2H_5O_2^*$ ($\langle \Delta E \rangle_{tot}$), the high-pressure limit rate constant (k^{∞}_4) , and the effective barrier (energetic and entropic) between adduct and final products. The values of these four pieces of information indicate that the potential energy surface has an adduct well depth close to 33 kcal mol⁻¹, no effective barrier for the addition-elimination process, and a long-range $C_2H_5-O_2$ potential which is not consistent with the long-range behavior of the Morse oscillator potential which fits the correct $C_2H_5-O_2$ bond energy.

IV. Analytical Representation of k_{4a}/k_{-4c}

In this section analytical expressions for $k_{4a}-k_{-4c}$ are described which were obtained by using the theoretical calculations of their values.

The simple functional form of Gilbert et al.,⁵⁹ as recently modified,⁶⁰ was used to represent the recombination and dissociation rate constants k_{4a} , k_{-4a} , and k_{-4c} :

$$k_{4a}, k_{-4a}, k_{-4c} = \{k^{\infty}k_0[M]/(k^{\infty} + k_0[M])\}F_{cent}c$$
 (18)

where

$$c^{-1} = 1 + \{k_{\log}/(0.75 - 1.27F_{\log} - 0.14k_{\log})\}^{2}$$

$$F_{\log} = \log (F_{cent})$$

$$k_{\log} = \log (k_{0}[M]/k^{\infty}) - 0.4 - 0.67F_{\log}$$
(19)

The high- and low-pressure limiting values of the rate constants, k^{∞} and k_0 , respectively, were fit to the formula $A_i T^{n_i} e^{-T_i/T}$. The temperature dependence of F_{cent} is conveniently represented by the expression⁵⁹

$$F_{\text{cent}} = (1 - a)e^{-T/T^{***}} + ae^{-T/T^{*}} + e^{-T^{**}/T}$$
(20)

The functional representations of k_{4a} , k_{-4a} , and k_{-4c} each contain 10 constants: A_0 , n_0 , T_0 , A_{∞} , n_{∞} , T_{∞} , a, T^* , T^{**} , T^{***} .

 k_{4a} and k_{-4a} are related by the equilibrium constant $K_{4a} = k_{4a}/k_{-4a}$ which was fit to the expression $A_e T^{n_e} e^{-T_e/T}$. F_{cent} for both k_{4a} and k_{-4a} are then the same, and the remaining parameters (k_0 and k^{∞}) for these two rate constants are related via the constants in the equilibrium constant expression.

A different fitting function was required for k_{4b} , the overall rate constant for the addition-elimination process. A simple Lindemann description of the addition-elimination process would yield the following relationship:

$$k_{4b}/(k_{4a} + k_{4b}) = 1/\{1 + k_{\rm S}[M]/k_{\rm elim}\}\}$$
 (21)

where $k_{\rm S}$ is the bimolecular rate constant for stabilization of metastable $C_2H_5O_2^*$ by collisions with buffer gas M, and $k_{\rm elim}$ is the unimolecular decay constant for elimination of HO₂ from $C_2H_5O_2^*$. While this expression is qualitatively correct, it does

not accurately represent the results of the RRKM calculations. So a more complex fitting function was developed which retains some of the functional characteristics of the simpler expression yet provides a more accurate representation of the behavior of the addition-elimination process:

$$k_{4b}/(k_{4a} + k_{4b}) = 1/\{1 + \exp\{c_1c_3(T, [M]) + c_4(T)c_3(T, [M])^2\}\}^{c_2}$$
(22)

 c_1 and c_2 are simple constants, while c_3 and c_4 are temperature dependent:

$$c_{3}(T,[M]) = \log [M] - \{c_{31} + c_{32}T + c_{33}T^{2}\}$$
$$c_{4}(T) = c_{41} + c_{42}T + c_{43}T^{2}$$
(23)

A total of eight constants are required to describe $k_{4b}/(k_{4a} + k_{4b})$. Related expressions have been developed by Larson et al.²⁵

The parameters in the analytical expressions for $k_{4a}-k_{-4c}$ were obtained from fitting these expressions to a set of values of these rate constants determined by the RRKM calculations described above. (The final set of molecular parameters given in Table III were used.) These calculations covered an extended range of conditions which included those used in the current and prior investigations of the kinetics of this reaction. The theoretical data set includes rate constants determined at 13 temperatures: all the experimental temperatures (296, 373, 385, 467, 473, 573, 585, 640, 723, 750, 850, and 904 K) plus a higher one, 1000 K. At each temperature, rate constants were determined at eight pressures: 0.1, 0.3, 1, 3, 10 Torr; 0.1, 1, 10 atm. (Experiments covered the range 0.5-15 Torr.) The calculations were extended to 10 atm to cover the conditions of some combustion systems. The theoretical data set does not include either the low-pressure limit at low temperatures or the high-pressure limit at high temperatures. Therefore, the fitted high- and low-pressure functions $(k_0 \text{ and } k^{\infty})$ for k_{4a} , k_{-4a} , and k_{-4c} should be regarded only as fitting functions for the ranges of temperatures and pressures used in these calculations and not as actual expressions for the high- and low-pressure limit rate constants.

Fitting was done by minimizing the rms relative error between the theoretical rate constants in the data set and the values calculated from the above analytical expressions for the rate constants k_{4a} , k_{-4a} , and k_{-4c} and for the ratio $k_{4b}/(k_{4a} + k_{4b})$. The results are found in Table VI which also contains the parameter values for K_{4a} . In general, the fitting errors are quite small. This fit is noticeably worse for k_{-4c} than for any of the other rate constant expressions. For this constant, the larger errors occur at some of the higher temperatures where there is competition between the two dissociative channels characterized by k_{-4a} and k_{-4c} . The pressure broadening function, F_{cent} in eq 18, is apparently not flexible enough to represent this situation accurately. However, even in this case the rms error is only a little larger than 10%.

Since the kinetics of mechanism 3 involves combinations of all the $k_{4a}-k_{4c}$ rate constants (see eq 11 and 12), the individual fitting errors for each rate constant could add constructively, rather than randomly, to produce significant errors in the analytic representations of final observable quantities like the overall rate constant or the branching ratio. A systematic comparison of the theoretical calculations and the analytical expressions over a wide variety of temperatures, pressures, and oxygen concentrations shows this not to be the case. The rms error and maximum error for k_4 in these series of tests were approximately the average of the errors given in Table VI. Furthermore, under the experimental conditions, the agreement of the analytic representation of k_4 and $F(C_2H_4)$ with experimental measurements is comparable to the actual uncertainty of the experimental measurements. The analytic representation contained in Table VI and eq 18, 19, 22, and 23 are accurate representations of the kinetics of $C_2H_5 + O_2$ over the specified range of conditions.

V. Direct Abstraction Route of the $C_2H_5 + O_2$ Reaction

As discussed earlier, the theoretical model presented above contains no direct abstraction reaction, i.e., a reaction of C_2H_5 + O_2 that does not involve metastable adduct formation. At the

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TABLE VI: Least-Squares-Determined Parameters and Associated Relative Errors for the Analytic Representation of k44, k-44, k44, k-4c, and K44

parameter	k _{4a}	k_{-4a}	k_4c	parameter	k_{4b}/k_{4a}	parameter	K _{4a}	
A _∞	$3.67 (-14)^{b}$	6.17 (17)	6.92 (14)	<i>c</i> ₁	2.30	A,	5.96 (-32)	
n	0.772	-0.835	-0.634	C2	0.621	n,	1.607	
T_{∞}	-287	+17160	-15800	-		Ť,	-17450	
A_0	1.96 (-5)	3.29 (26)	2.04 (35)	<i>c</i> ₃₁	15.53			
n ₀	-8.24	-9.85	-12.86	C32	3.11 (-4)			
T ₀	+2150	+19600	-20100	<i>c</i> ₃₃	1.54 (-6)			
a	0.420	0.420	2.72	C41	0.367			
T*	183	183	220	C42	-7.09 (-4)			
T**	С	С	7270	C43	3.23 (-7)			
T***	1250	1250	с					
rel error, %								
rms	5.1	5.8	12.3		4.5		1.4	
max	12	15	39		11		2	

^a Units are cm³ molecule⁻¹ s⁻¹ for A_{∞} , cm⁶ molecule⁻² s⁻¹ for A_0 , cm³ molecule⁻¹ for A_e , and K for T_0 , T_{∞} , T_e , T^* , T^{**} , and T^{***} . ^bNumbers in parentheses are powers of 10. c Associated term in the fitting function is zero.

very least, the agreement of theory with experiment demonstrated here indicates that such a reaction is not necessary to explain the behavior of this reaction below 1000 K. In particular, it should be noted that the same rearrangement barrier and ring transition-state properties that were adopted to account for the pressure and temperature dependencies of the C2H4 yields at low temperatures (where the $C_2H_5 + O_2$ addition step is essentially irreversible) are also those needed to obtain the correct C_2H_5 + O_2 overall rate constants at high temperatures (where C_2H_5 + O_2 and $C_2H_5O_2$ are essentially in equilibrium).

A weaker argument for the absence of a significant abstraction route up to 1000 K can be made based on the experimental observations alone. To account for the observed temperature independence of k_4 between 750 and 950 K by a direct abstraction reaction would require that its rate constant have an activation energy no greater than 2 kcal mol⁻¹. Using this maximum activation energy (or any lower value), one would predict that there would have been a small but detectable C_2H_4 yield in the experiments conducted by Niki et al.²¹ and by Kaiser et al.⁵⁷ at ambient temperature and 1-atm pressure. However, none was observed. (The apparent pressure independence in $F(C_2H_4)$ observed by Plumb and Ryan¹² at the highest pressures of their study (see Figure 3) led them to conclude that they had observed the abstraction reaction. However, the measurements of $F(C_2H_4)$ at a much higher pressure by Niki et al.²¹ and by Kaiser et al.⁵⁷ reveal that this branching fraction has no apparent pressure-independent component.)

The conclusion that abstraction is a minor channel with a rate constant no larger than 10⁻¹³ cm³ molecule⁻¹ s⁻¹ at 1000 K is surprising. Such a low value would imply a relatively high barrier to abstraction. Experimental and theoretical studies⁴⁴ of H-atom abstraction reactions suggest that the reaction exothermicity of 11.5 kcal mol⁻¹ between $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ (see Table III) is consistent with a relatively low barrier ($\sim 5 \text{ kcal mol}^{-144}$) and a correspondingly large rate constant by 1000 K (considerably larger than 10⁻¹³ cm³ molecule⁻¹ s⁻¹). However, these studies all involve abstraction reactions that straightforwardly break one bond and form another. In the abstraction reaction $C_2H_5 + O_2 \rightarrow C_2H_4$ + HO₂, two bonds are broken and two bonds are formed. Not only the C-H bond in C₂H₅ but also the triplet-coupled radical orbitals on the two centers of O_2 (i.e., the double bond in O_2) must be broken to gain the double bond in C_2H_4 and the O-H bond in HO₂. Perhaps this leads to a higher than expected activation energy. There are essentially no detailed theoretical studies and only a few experimental studies of these more complicated abstraction reactions in combustion chemistry.

The most relevant previous experimental studies are those by Nesbitt et al.⁶¹ and Grotheer et al.^{62,63} on the reaction of CH₂OH $+ O_2$. The CH₂OH radical, which is isoelectronic with C_2H_3 . reacts rapidly with O_2 proceeding stoichiometrically to $H_2CO +$ HO₂. The two studies of this reaction indicate little or no pressure dependence at room temperature and a rate constant that decreases slightly with temperature between 300 and 500 K but increases by a factor of 2 between 500 and 700 K. These observations suggest a mechanism involving both addition and abstraction, but there are complications in the interpretation of the observations. First, since the CH₂OH + $O_2 \rightarrow H_2CO + HO_2$ reaction is more exothermic than the $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ reaction (by 5-10 kcal mol⁻¹), the barrier for rearrangement of the O_2CH_2OH adduct into products might be significantly lower than that for the rearrangement of the $C_2H_5O_2$ adduct. Were this the case, the $O_2CH_2OH \rightarrow H_2CO + HO_2$ reaction would proceed rapidly and the overall reaction would have a density-independent rate constant (at least over the range of conditions that have been used to study this reaction to date). Thus, the observed density independence of the $CH_2OH + O_2$ rate constant does not clearly indicate a direct abstraction route. Second, the observed increase in the rate constant between 500 and 700 K is relatively small (only a factor of 2) and could perhaps be accounted for by a temperature-dependent competition between the unimolecular dissociation channels of the metastable adduct. Such arguments are raised by Nesbitt et al. to explain their observation of an increasing rate constant for this reaction between 215 and 300 K.⁶¹ Thus, the temperature dependence is also not a conclusive indication of an abstraction route. Nonetheless, if the abstraction channel is actually indicated by the increasing rate constant at higher temperatures, then its activation energy ($\sim 5 \text{ kcal mol}^{-1}$) is somewhat higher than what would be expected⁴⁸ from simple abstraction reactions having this exothermicity.

VI. An Unresolved Issue Regarding the $C_2H_5 + O_2 \rightarrow C_2H_4$ + HO₂ Reaction

The lack of a temperature dependence of the high-temperature $C_2H_5 + O_2$ overall rate constant that was observed in the current investigation (or the slight negative activation energy that was reported by McAdam and Walker¹⁴) suggests that there is no energy barrier along the reaction coordinate from $C_2H_5 + O_2$ to $C_2H_4 + HO_2$ that is higher than the potential energy of the reactants. In the mechanism for this overall transformation that was used in the current investigation this is the situation. The potential energy barriers for the isomerization of C₂H₅O₂ as well as for the decomposition of CH2CH2O2H into the final products are both below that of the reactants.

Walker and co-workers have studied the kinetics of the overall process $HO_2 + C_2H_4 \rightarrow C_2H_4O + OH^{14,64}$ They interpret their results in terms of a two-step mechanism: HO_2 addition to C_2H_4

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to form $CH_2CH_2O_2H$ followed by an internal displacement of OH to form ethylene oxide. The large activation energy for the overall transformation (17 kcal mol⁻¹) is associated entirely with what the authors believe is the first and rate-determining step, the addition of HO_2 to C_2H_4 .

The barrier for HO₂ addition to C_2H_4 suggested by Walker and co-workers is 4 kcal mol⁻¹ above the potential energy of C_2H_5 + O₂. If this barrier does indeed exist, then the *reaction coordinate* leading from $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ given in Figure 5 cannot be correct for the reason presented above.

To reconcile the apparent disparity between the kinetics of the forward and reverse reactions created by the existence of a large barrier for HO₂ addition to C_2H_4 , McAdam and Walker have proposed that another reaction path must exist, and they have suggested that it might involve the direct formation of a cyclic quasi-stable structure (without the prior formation of $C_2H_5O_2$) which can either decompose back into $C_2H_5 + O_2$ or unimolecularly decompose into $C_2H_4 + HO_2$. This reaction path, which also would have no potential energy barriers higher than that of $C_2H_5 + O_2$, can account for the observed temperature dependence of the $C_2H_5 + O_2$ reaction without being inconsistent with the conclusion that there exists a high potential energy barrier between $CH_2CH_2O_2H$ and $C_2H_4 + HO_2$.

There is a difficulty with the new reaction path suggested by McAdam and Walker. Were it to exist, the $HO_2 + C_2H_4$ reaction would also proceed along it to a significant extent to form $C_2H_5 + O_2$ instead of exclusively by crossing the high-potential-energy barrier leading to the formation of $CH_2CH_2O_2H$ (followed by the subsequent formation of $C_2H_4O + OH$). No evidence of such behavior was observed by Walker and co-workers.^{14,64} Thus, incongruities between the observations and explanations of the kinetic behavior of the $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ reaction in the forward and reverse directions remain.

The formation of C_2H_4O from the $HO_2 + C_2H_4$ reaction must involve multiple steps. Were the two-step mechanism used by Walker and co-workers to interpret the kinetics of C_2H_4O formation from this reaction incomplete, incorrect conclusions could result regarding the activation energy of one part of the overall process. It would be useful to study the kinetics of epoxide formation from HO_2 + olefin reactions under different conditions, particularly in the absence of O_2 which can clearly bind to HO_2 olefin complexes as they are formed. Such additional information would help to clarify the kinetics of epoxide formation in these systems.

VII. Summary

The major results of the current experimental and theoretical study of the $C_2H_5 + O_2$ reaction are the following:

1. New determinations have been obtained as a function of temperature and density of the overall rate of loss of C_2H_5 and the branching fraction of the rate of formation of C_2H_4 over the overall rate of loss.

2. Theoretical calculations, employing RRKM theory, were used to calculate the four reaction rate constants involved in an addition mechanism for the $C_2H_5 + O_2$ reaction. This mechanism included the equilibration of the reactants with the adduct $C_2H_5O_2$ and its consequent effect on the overall kinetics. Molecular parameters and an energy-transfer parameter were adjusted to optimize agreement between the theoretical results and a wide range of experimental observations.

3. The theoretical model accurately accounts for all experimental observations which have been reported pertaining to the kinetics of the $C_2H_5 + O_2$ reaction including the temperature and pressure dependence of the overall rate constant, magnitude and temperature dependence of the $C_2H_5 + O_2 \rightleftharpoons C_2H_5O_2$ equilibrium constant, and the temperature and density dependence of the C_2H_4 branching fraction.

4. The success of the theoretical model to accurately account for the kinetic behavior of the $C_2H_5 + O_2$ reaction is interpreted as strong evidence that the addition mechanism used is the dominant one at temperatures below about 1000 K. A second mechanism involving direct abstraction must become important at some as yet unknown temperatures higher than 1000 K. The apparently small size of the abstraction rate constant at lower temperatures is surprising. However, this abstraction reaction is of an unusual type whose characteristics are poorly known.

5. The final values of the adjustable potential energy parameters indicate that (a) the dissociation energy of $C_2H_5O_2$ back to reactants is 32.9 ± 0.5 kcal mol⁻¹ (0 K), (b) the potential energy barrier for the $C_2H_5O_2$ rearrangement which leads to the products $C_2H_4 + HO_2$ is several kcal mol⁻¹ lower than the reactant energy, and (c) the long-range part of the $C_2H_5-O_2$ potential energy surface is a more slowly varying function of the $C_2H_5-O_2$ distance than is obtained from a Morse oscillator potential function containing the correct dissociation energy. This last feature is consistent with a curve-crossing model.

6. Analytical expressions have been obtained for the rate constants of a four-step mechanism that provides a comprehensive description of the kinetics of the $C_2H_5 + O_2$ reaction over a wide range of conditions. The expressions are derived from RRKM calculations of the same rate constants over the temperature range 300-1000 K and a buffer gas pressure range (He) of 0.1 Torr to 10 atm. These functions, along the the coupled kinetics model, provide a convenient and accurate analytic description of the kinetic behavior of the $C_2H_5 + O_2$ reaction over this broad range of conditions.

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