Oxidation of Propene in the Gas Phase

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Abstract

A series of laboratory and modelling experiments on the oxidation of propene in the gas phase has been undertaken to determine conditions which give high yields of propene oxide. The conditions under which the experiments were conducted were 505-549 K and up to 4 bar pressure. It is proposed that propene oxide is formed from propene by reaction with several peroxy radicals including HO₂ and CH₃CO₃. However, one of the more important radicals is hydroxypropylperoxy. Its reaction with propene, under these conditions

 $(107) \qquad \qquad \text{HOCH}_2\text{CHO}_2\text{CH}_3 + \text{C}_3\text{H}_6 \longrightarrow \text{HOCH}_2\text{CHO}\text{CH}_3 + \text{C}_3\text{H}_6\text{O}$

is more important than concerted decomposition to formaldehyde and acetaldehyde. @ 1995 John Wiley & Sons, Inc.

Introduction

This is the first of several articles concerned with our studies of the conversion of simple aliphatic alkenes to industrially-important oxygen-containing organic intermediates, in particular the production of epoxides in high yield.

The noncatalytic oxidation of alkanes in the gas phase has been the subject of numerous detailed studies over the last 70 years; in contrast, parallel experiments on alkenes have received much less attention [1]. This is strange since alkenes are important intermediates in the oxidation of the saturated hydrocarbons and such studies should help in the understanding of the mechanism of combustion. Further, oxygenated products from the alkene oxidation, such as carbonyls, epoxides, and unsaturated alcohols, are high value compounds of industrial importance.

There have been several key articles over the last 30 years describing the phenomological features of propene oxidation, for example, the change of product distribution between low (ca. 550 K) and higher (ca. 750 K) temperatures (for example, [2-9]), a negative temperature coefficient [3,6,8,10,11], and the characteristic autocatalytic behavior of hydrocarbon oxidation [2,7,9,11].

The oxidation products of propene are well established, particularly at low temperatures. Carbon monoxide is generally reported in greater yield than carbon dioxide [3,4,7] and the ratio becomes greater as the temperature increases [6,8,9]. Acetaldehyde and formaldehyde [2,7] are also major products but the yields fall as the temperature increases [8,9].

Acrolein has been reported as a product in some studies, varying widely in perceived importance [4,5,7], its formation appearing to be more favored at higher temperatures. The smaller hydrocarbons (for example, methane, ethane, ethene, and ethyne) as well as larger homologues, have been reported as products above ca. 630 K [7,12] and in significant amounts above 900 K [9,13].

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Surprisingly, in several studies, the presence or absence of propene oxide has not been the center of attention and it was not observed at all in some of the most detailed experiments (for example 4, 6), although it was detected in an early analytical study [14]. Nevertheless it has more recently been found that, under pressure, large concentrations of the epoxide are formed below 670 K [15].

For this work, a series of low temperature experiments (505-549 K), with fuel-rich mixtures were conducted to gain an understanding of the chemistry involved in the formation of propene oxide during propene oxidation, and to examine the variation in epoxide yield with experimental parameters (eg., temperature, pressure etc.)

The different accounts given of product formation, even for experiments under fairly similar conditions, obviously make for difficulties in postulating mechanisms. However, there have been in the last 10 years, two detailed computer modelling studies, one, by Wilk et al., at 530-740 K [16], the second, by Dagaut et al., over the range 900-1200 K [9], the former being based on earlier work concerning the oxidation of acetaldehyde [17].

The mechanism produced by Dagaut et al. is inappropriate for the experiments reported here, as it describes a higher temperature regime with peroxy species which are stable at lower temperatures, not well represented. That of Wilk et al. is fairly successful in explaining the observed product distribution in their studies and, in particular, the occurrence of the negative temperature coefficient. So the results reported here were initially simulated using a model that consisted mainly of the reactions from the mechanism of Wilk et al., [16] that would be important at low temperatures. However, this model significantly underestimated the yields of propene oxide and overestimated those of acetaldehyde and formaldehyde. Therefore the mechanisms involved in the formation of the main products, particularly propene oxide, were examined and a revised reaction scheme constructed, and tested on the results of Wilk et al., [16] and a wide range of conditions for our work.

Experimental

The experiments were performed in two static reaction vessels. Reactor 1 was constructed from Pyrex (volume 167 cm³, surface: volume ratio 1.00 cm⁻¹). Reactor 2 was constructed of steel and with the same dimensions.

Propene (Aldrich 99%+) was analyzed regularly prior to use. Impurities found were ethene and propane (0.1–0.5%) and no further purification was undertaken. Oxygen and nitrogen (BOC 99%+) were used without further purification. Oxygen was introduced into the reaction vessel first, followed by propene. Nitrogen, if needed, was then added. The start of the reaction was taken to be when the propene was introduced. Calculated diffusion times were less than 10 s, and thus mixing occurs on a timescale much shorter than any experiment. The rapid transport to the walls, along with the slow overall rate of reaction and the low ratio of $\Delta[C_3H_6]/[C_3H_6]$ ensured essentially isothermal behavior in the reactor.

The reaction was ended by the expansion of the mixture in the reaction vessel into the rest of the vacuum line (over approximately 1 s) giving a temperature of 340 K and an eight fold reduction in pressure. The decrease in pressure and temperature and increase in the surface to volume ratio ensured a rapid quenching of the reaction.

The bulk of the product analysis was by gas chromatography (Pye PU4500). Three columns were used, one packed with Carbosieve SII, (3m length, 3.1mm i.d.) using a TCD detector to determine oxides of carbon, the second with Tenax GC (2.5 m length,

3.1 mm i.d.) and a FID detector used to determine most of the other products. Propene oxide and acrolein and the hydrocarbons were not readily resolved on this column and better resolution was obtained on a GSQ capillary column (30 m length, 0.5 mm i.d.).

Concentrations of reactants and products were calibrated using standard samples and identification was by retention time and confirmed by GC-mass spectrometry (VG Analytical Autospec), for the following species: ethene, ethane, propene, butenes, butane, pentenes, pentane, hexenes, 1,5-hexadiene, methanol, acetaldehyde, propene oxide, acrolein, propionaldehyde, and acetone. Some minor products eluted after the hexenes, which could not be identified positively but appeared to be higher oxygenated compounds. Of the propene converted, less than 1% went to propane.

Formaldehyde and total peroxides were determined in solution, by allowing the reacted gases to flow into an evacuated vessel, where they were dissolved in water. Formaldehyde was determined colorimetrically using the Nash reagent (18) and peroxides by titration with sodium thiosulphate solution following addition of potassium iodide and dilute sulphuric acid. No peroxides were found (with a detection limit of 0.3 mbar), and we are currently trying to determine whether this results is valid or an artefact of the technique used. Standard errors for the product pressures and selectivities quoted are approximately 10%, except for the oxides of carbon at 20%.

The time dependence of the experimental and computed product yields are expressed in the figures as concentrations. However of more significance to the commercial manufacture of the epoxide are the product selectivities (the fraction of the propene reacting going to a particular product). The variations of selectivities of the major products at the end of the reaction are presented in tabular form. In the selectivity calculations, as the amount of propene consumed was generally small (<5%), the selectivities were based on the assumption that all the reacted propene appeared as products in the analyses performed.

The experiments reported here have been simulated using the numerical integration program CHEMSYS assuming constant volume and temperature and spatial uniformity throughout the reaction vessel. Rate constants for both forward and backward reactions are taken whenever possible from compilations of data. Where estimates for rate constants have been made full details are given (Appendix I). As only pressures near or above atmospheric were examined, the rate constants used were generally assumed to be pressure independent.

Results

Determining the effect of experimental parameters such as temperature or pressure on the system allows conditions to be optimized for maximizing selectivity of desired products. To this end, the dependence of propene autoxidation on the following parameters are reported in this article: (a) Temperature in the range of 505-549 K at 4.0 bar (Figures 1-3); (b) Pressures of 0.92 to 4.0 bar at 549 K (Figures 3-6); (c) Extent of reaction (Figures 7 and 8); and (d) Nature of surface (Figures 6 and 9).

The principal reaction products under the conditions used (fuel-rich mixtures; 505–549 K; up to 4.0 bar pressure) were formaldehyde, acetaldehyde, and propene oxide. Lesser amounts of carbon monoxide, carbon dioxide, acrolein, methanol, propanal, acetone, allyl alcohol, 1,5-hexadiene, and other alkanes and alkenes were found. The variation of product yields with temperature and pressure are expressed in terms of selectivities in Tables I and II.



Figure 1. Oxidation of propene at 505 K. The growth in product concentrations with time, 4.0 bar, $[C_3H_6]/[O_2]_{initial} = 19/1$, and reaction vessel 1.

The Effect of Temperature on the Overall Rate of Reaction and Product Distribution

The temperature was varied over the range 505-549 K using a standard set of conditions: reactor 1; 4.0 bar; and $[C_3H_6]/[O_2] = 19/1$ (Table I, Figures 1-3). On increasing the temperature under these conditions, of the major products, the selectivity of propene oxide decreases while those of formaldehyde and acetaldehyde



Figure 2. Oxidation of propene at 528 K. The growth in product concentrations with time, 4.0 bar, $[C_3H_6]/[O_2]_{initial} = 19/1$, and reaction vessel 1.



Figure 3. Oxidation of propene at 549 K. The growth in product concentrations with time, 4.0 bar, $[C_3H_6]/[O_2]_{initial} = 19/1$, and reaction vessel 1.



Figure 4. Oxidation of propene at 549 K. The growth in product concentrations with time, 3.0 bar, $[C_3H_6]/[O_2]_{initial} = 19/1$, and reaction vessel 1.



Figure 5. Oxidation of propene at 549 K. The growth in product concentrations with time, 1.8 bar, $[C_3H_6]/[O_2]_{initial} = 19/1$, and reaction vessel 1.



Figure 6. Oxidation of propene at 549 K. The growth in product concentrations with time, 0.92 bar, $[C_3H_6]/[O_2]_{initial} = 19/1$, and reaction vessel 1.



Figure 7. Oxidation of propene at 528 K. The variation of product selectivities with time, 4.0 bar, $[C_3H_6]/[O_2]_{initial} = 19/1$, and reaction vessel 1.



Figure 8. Oxidation of propene at 528 K. The variation of product selectivities with time, 4.0 bar, $[C_3H_6]/[O_2]_{initial} = 19/1$, and reaction vessel 1.



Figure 9. Oxidation of propene at 549 K. The growth in product concentrations with time, 0.92 bar, $[C_3H_6]/[O_2]_{initial} = 19/1$, and reaction vessel 2.

TABLE I. Oxidation of propene: Effect of temperature on product selectivities (%) at end of reaction. Simulated results in parenthesis. $[C_3H_6]/[O_2]_{initial} = 19/1$, total pressure 4.0 bar; and reaction vessel 1 (seasoned).

Temperature (K)	505	528	549
СО	4.9 (4.4)	4.7 (5.1)	4.7 (5.7)
CO_2	3.6 (5.5)	2.7 (5.3)	2.7(5.1)
нсно	8.6 (9.6)	7.7 (11.2)	10.9 (12.5)
CH ₃ CHO	16.4 (11.7)	17.0 (14.5)	20.3 (16.6)
C ₃ H ₆ O	46.1 (44.2)	39.2 (42.2)	37.2 (40.5)
$\Delta [C_3 H_6] / [C_3 H_6] (\%)$	3.6 (4.8)	5.3 (4.8)	4.8 (4.7)

TABLE II. Oxidation of propene: Effect of pressure of reactants on product selectivities (%) at the end of reaction. Simulated results in parenthesis. Temperature 549 K; $[C_3H_6]/[O_2]_{initial} = 19/1$, and reaction vessel 1 (seasoned).

Pressure (bar)	0.92	1.82	3.0	4.0
со	4.8 (7.2)	5.8 (6.4)	4.8 (6.0)	4.7 (5.7)
CO_2	3.6 (4.2)	4.1 (4.7)	3.1 (5.0)	2.7(5.1)
нсно	15.1 (15.7)	12.8 (14.2)	10.5 (13.1)	10.9 (12.5)
CH ₃ CHO	25.5 (23.2)	23.2 (19.7)	22.9 (17.9)	20.3 (16.6)
C ₃ H ₆ O	35.6 (33.5)	40.6 (37.3)	41.4 (39.2)	37.2 (40.5)
$\Delta [C_{3}H_{6}]/[C_{3}H_{6}](\%)$	3.7 (4.6)	4.3 (4.6)	4.2 (4.7)	4.8 (4.7)

increase. Of the minor products, the proportion of carbon dioxide to carbon monoxide decreases.

The Effect of Pressure on the Overall Rate of Reaction and Product Distribution

The effect of pressure has been examined in two ways while keeping other experimental parameters constant. In one series of experiments, a bath gas (nitrogen) was added. For example, adding 3.1 bar of bath gas (nitrogen) to a 46.7 mbar O_2 , 886 mbar C_3H_6 mixture at 549 K has no significant effect on the product distribution although the rate of reaction approximately doubles.

In the second set of experiments in which the pressure was increased while maintaining the gas mixture components in a constant ratio, a much larger effect on the rate of reaction was noted (Figures 3–6). In comparison with the effect on the overall rate, selectivities of the major products are little changed on increasing the pressure (Table II). The yields of acetaldehyde and formaldehyde decrease while those of the hydrocarbons increase. There is little effect on the yield of propene oxide on increasing the pressure.

Product Selectivity as a Function of the Extent of Reaction

The product selectivities vary with extent of reaction (Figures 7 and 8 describe the selectivities for one set of conditions, 528 K; 4.0 bar). The main observations are that, with extent of reaction, the selectivity of propene oxide, acetaldehyde acrolein and formaldehyde all decrease, while the selectivities of the hydrocarbons and methanol and the CO/CO_2 ratio increase.

The Effect of Altering the Surface of the Reaction Vessel on the Overall Rate of Reaction and Product Distribution

The dependence of the overall rate and product distribution in propene autoxidation on using "seasoned" or "cleaned" glass or steel for the reaction vessel walls was investigated. Cleaning the glass surfaces of the reactor leads to an increase in the rate of reaction but similar results were obtained with seasoned glass and metal reactors (Figures 6 and 9) (although the yields of carbon oxides increased slightly while those of propene oxide, acetaldehyde, and formaldehyde decreased slightly by using metal surfaces). After seasoning, the material used to make the surface does not appear to have a large effect on either the rate of reaction or the product distribution.

Discussion

The scheme initially constructed to simulate the results reported here consisted mainly of the reactions of the model of Wilk et al., [16] that would be significant at lower temperatures, but with a more complete representation of epoxidation reactions. This consisted of reactions 1 to 106 as well as appropriate peroxide decomposition and radical-radical reactions from the appendix, and with $k_{50} = 10^{16} \text{ sec}^{-1} \exp(104.6 \text{ kJ/mol } RT)$ [16]. However, for the fuel-rich experiments reported here, this initial model significantly underpredicted the propene oxide yield and overpredicted

those of acetaldehyde and formaldehyde, with the majority of the propene consumed by OH addition to propene (reaction 46), followed by O₂ addition (reaction 48) and decomposition of the $HOC_3H_6O_2$ adduct (reaction 50) giving acetaldehyde, formaldehyde, and reforming OH. For example, for the 528 K, 4 atm experiments (Table I), the predicted selectivities for propene oxide, acetaldehyde, and formaldehyde were 13%, 39%, and 19% respectively, compared with experimental values of 39%, 17%, and 8%.

Consequently an examination of the mechanisms forming the main products was undertaken and is presented here.

(i) Initiation. The initiation reaction between propene and oxygen is a highly endothermic process. The rate constant used has to be sensible but its precise value is not crucial to the model: the rate parameters were those of Stothard and Walker [19].

(1)
$$C_3H_6 + O_2 \longrightarrow C_3H_5 + HO_2$$

(*ii*) Propagation reactions leading to primary products. One of the problems faced using the model of Wilk et al. was the serious underestimate of propene oxide with fuel-rich conditions. Thus much of the work reported in this article is concerned with elucidating the reactions that lead to the formation of this important product.

Radicals can either add to or abstract a hydrogen atom from propene. With abstraction, either the allyl-H bond or the much stronger vinyl-H bond can be broken. Since higher temperatures (>800 K) were not investigated in this work, vinyl-H atom abstraction is ignored. The formula C_3H_5 represents the resonance stabilized allyl radical. Highly reactive radicals such as the hydroxy radical are thought predominantly to add to propene under the conditions used in these experiments [20]. They can add to propene at the terminal or nonterminal carbon atom, although since the resulting secondary alkyl (or alkyl-like) radical tends to be more stable than primary species, terminal addition dominates [21]. In this work, to simplify the scheme, only terminal addition is considered, although typically, identical molecular products result from nonterminal addition. The addition reaction is represented thus:

$$(46) C_3H_6 + OH \longrightarrow HOCH_2CHCH_3$$

The rate parameters determined by Tully and Goldsmith [20] were used in the model (Appendix 1). The resulting adduct is fairly unstable at elevated temperatures [16]. However, in the presence of even small quantities of oxygen, addition to form the corresponding peroxy radical will occur:

$$(48) \qquad \qquad \text{HOCH}_2\text{CHCH}_3 + \text{O}_2 \longrightarrow \text{HOCH}_2\text{CHO}_2\text{CH}_3$$

Wilk et al. have suggested that the so-called Waddington reaction [16] is the predominant fate for this radical:

$$(50) \qquad \qquad \text{HOCH}_2\text{CHO}_2\text{CH}_3 \longrightarrow \text{CH}_3\text{CHO} + \text{HCHO} + \text{OH}$$

However, we believe that there is an error in the A factor for reaction 50 used by Wilk et al. They give a value of 10^{16} s⁻¹ but in the work of Dechaux [22] which they quote, an A factor of 10^{13} s⁻¹, is given. Since the transition state for this reaction is cyclic,

there will be a decrease in entropy in going to the transition state, so the A factor will be somewhat smaller than the frequency factor $(3 \times 10^{13} \text{ s}^{-1})$. Walker et al. [23] quote a value of $1.3 \times 10^{12} \text{ s}^{-1}$ for the 1,5 p hydrogen transfer reaction in alkyl radicals and a similar value is used here $(1.0 \times 10^{12} \text{ s}^{-1})$ for A_{50} . For the low temperature (less than 550 K) experiments reported here, with the reduced value for A_{50} , it would be expected that the hydropropylperoxy radical lives long enough to react with propene to form an epoxide and the corresponding alkoxy radical in preference to decomposition:

(107)
$$HOCH_2CHO_2CH_3 + C_3H_6 \longrightarrow HOCH_2CHOCH_3 + C_3H_6O$$

We have included both reactions 50 and 107 in the overall scheme (Appendix I). At the temperatures used by Wilk et al. (>626 K) even with the reduced value for k_{50} , reaction 50 still remains dominant.

For temperature less than 550 K, in the presence of oxygen, hydroxy radical addition to propene (reaction 46) is largely irreversible. However at the higher temperatures of experiments used by Wilk et al., a significant fraction of the hydroxypropyl radicals decomposes back to propene and the hydroxy radical (reaction 47):

$$(47) \qquad \qquad \text{HOCH}_2\text{CHCH}_3 \longrightarrow \text{C}_3\text{H}_6 + \text{OH}$$

Indeed in their computer modelling, the value for A_{47} was adjusted to give a good agreement between the model and the experimental concentrations of acetaldehyde. Unfortunately, as their value for k_{50} was too fast, the "forced" rate constant for k_{47} was also too fast. A value for k_{47} calculated using group additivity theory [24] is used here which is approximately an order of magnitude lower than that used by Wilk et al. [16].

Alkoxy radicals are highly unstable and are thought to decompose under the conditions of our experiments to the largest alkyl (or equivalent) radical and an aldehyde or ketone, e.g.

$$(108) \qquad \qquad \text{HOCH}_2\text{CHOCH}_3 \longrightarrow \text{CH}_3\text{CHO} + \text{HOCH}_2$$

With oxygen present, the hydroxymethyl radical will react to form formaldehyde, the overall reaction being:

$$(109, 117, 122) \qquad \qquad \text{HOCH}_2 + \text{O}_2 \longrightarrow \text{HCHO} + \text{HO}_2$$

The hydroperoxy radical can react with propene to form further propene oxide and reform the hydroxyl radical to continue the radical chain:

$$HO_2 + C_3H_6 \longrightarrow OH + C_3H_6O$$

We used the rate parameters of Baldwin et al., for reaction 27 which were determined by a competitive method [25]. This simple explanation implies that in the early stages of the reaction, the main products are propene oxide, acetaldehyde, and formaldehyde with ratios of concentrations of 2:1:1 (or 6:2:1 in selectivity). However there are many other available reactions for the radicals, making the ratio only very approximate. Nevertheless, the reactions account for propene oxide, acetaldehyde, and formaldehyde being the main primary products from fuel-rich mixtures under the conditions of the experiments reported here. (*iii*) Propagation reactions leading to major secondary products. Carbon monoxide and carbon dioxide are formed in large concentrations. It is thought that their production is via the oxidation of primary products, particularly acetaldehyde and formaldehyde. These secondary reactions are important because the formation of the oxides of carbon entails a great release of heat, which necessarily determines the thermal stability of the system in more oxygen rich systems, and additional peroxy radicals can be formed which can increase further the yield of propene oxide. The two main reactions for the acetyl radical are to decompose or add an oxygen molecule:

(14)
$$CH_3CO \longrightarrow CH_3 + CO$$

(15)
$$CH_3CO + O_2 \longrightarrow CH_3CO_3$$

The acetylperoxy radical reacts very rapidly with alkenes to form the epoxide and under the conditions used in these experiments virtually all of it will react with propene [26]:

$$(22) \qquad \qquad CH_3CO_3 + C_3H_6 \longrightarrow CH_3 + CO_2 + C_3H_6O$$

Epoxidation of alkenes by peracyl species has not been considered in previous computer modelling studies of alkene oxidation [9,16,22]. The rate constant for reaction 15 is almost temperature independent [27] whereas the decomposition route has a large activation energy [28]. Therefore, increasing the temperature favors decomposition and hence reduces the ratio of yields of carbon dioxide to carbon monoxide and the selectivity of propene oxide. Further, as the reaction proceeds, the oxygen concentration decreases and the ratio of yields of carbon dioxide and carbon monoxide will also fall, as will the yield of propene oxide. Both results are observed (Table I and Figure 7).

(*iv*) Reactions leading to unsaturated products. Products such as acrolein, and 1,5hexadiene are formed in small quantities under all the conditions studied. They are thought to be formed via the resonance stabilized allyl radical produced by hydrogen atom abstraction from propene, for example:

$$(36) C_3H_6 + OH \longrightarrow C_3H_5 + H_2O$$

$$(28) C_3H_6 + HO_2 \longrightarrow C_3H_5 + H_2O_2$$

The allyl-allyl radical self-reaction gives 1,5-hexadiene [29]:

$$(219) 2C_3H_5 \longrightarrow C_6H_{10}$$

Acrolein is formed via the allylperoxy radical [16],

$$C_3H_5 + O_2 \longrightarrow C_3H_5O_2$$

which in turn yields the allyloxy radical, often via cross reactions with other peroxy radicals, for example,

(163)
$$C_3H_5O_2 + O_2C_3H_6OH \longrightarrow C_3H_5O + OC_3H_6OH + O_2$$

or when it reacts with propene, yielding further amounts of propene oxide:

$$(8) C_3H_5O_2 + C_3H_6 \longrightarrow C_3H_5O + C_3H_6O$$

The allyloxy radical can react with oxygen to yield acrolein [16],

(7)
$$C_3H_5O + O_2 \longrightarrow C_2H_3CHO + HO_2$$

or abstract a hydrogen atom to form allyl alcohol [16], for example:

$$(42) C_3H_5O + C_3H_6 \longrightarrow C_3H_5OH + C_3H_5$$

The low experimental ratio of unsaturated oxygenated products to radical addition products is indicative that most radicals undergo addition rather than abstraction reactions with propene under our conditions.

(v) Addition of allyl and other radicals to propene. The reaction of allyl with oxygen will always be much faster than with propene. However, as pointed out by Grigoryan et al., [7], the allylperoxy radical will tend to decompose back to allyl and oxygen without further reaction, above its ceiling temperature [30], allowing allyl addition to propene to become significant. Indeed any radical that adds to propene in preference to reaction with oxygen or abstraction from the alkene (or other product) can undergo a series of reactions similar to those described for OH addition, giving propene oxide, acetaldehyde, and formaldehyde as molecular products, e.g.

$$\begin{array}{cccc} X + C_{3}H_{6} & \longrightarrow & XCH_{2}CHCH_{3} & \stackrel{+O_{2}}{\longrightarrow} & XCH_{2}CHO_{2}CH_{3} & \stackrel{+C_{3}H_{6}}{\longrightarrow} \\ C_{3}H_{6}O + & XCH_{2}CHOCH_{3} & \longrightarrow & XCH_{2} + & CH_{3}CHO \end{array}$$

The resulting XCH₂ fragment typically gives formaldehyde, either by direct reaction with oxygen (eg., O_2 + HOCH₂), by decomposition (eg., X = RO where ROCH₂ \rightarrow R + HCHO) or by addition of oxygen to give a primary peroxy radical (eg., X = C_3H_5), with subsequent epoxidation and decomposition of the alkoxy radical:

$$XCH_2 + O_2 \longrightarrow XCH_2O_2 \xrightarrow{+C_3H_6} C_3H_6O + XCH_2O \longrightarrow X + HCHO$$

Reactions 123–146 in Appendix I detail this mechanism for the specific case of X = allyl. Grigoryan et al. [7] discussed the case of X = H, for which this radical addition mechanism is plausible, in that hydrogen will add to propene faster than to oxygen in fuel-rich experiments. However for the scheme in the Appendix, there is no significant source of hydrogen atoms, so hydrogen atom addition to propene is not considered to be significant for the experiments reported here.

Van Sickle et al. [31] suggested that in the liquid phase, peroxyalkyl radicals (formed by peroxy addition to propene) add oxygen in preference to decomposition to the epoxide, with this radical chain polymerization continuing until eventually an oxygen atom is lost from the free peroxy site, resulting in the "unzipping" of the $XC_3H_6O_2C_3H_6....C_3H_6O$ · species to form, for propene, large quantities of acetaldehyde and formaldehyde. That propene oxide is a major primary product suggests that this particular mechanism is not significant in the experiments reported here.

However, it should be pointed out that if the rate for the decomposition of hydroperoxyalkyl radicals to the epoxide and hydroxyl, suggested by Baldwin et al. [25] is accepted, oxygen addition to form hydroperoxyalkylperoxy radicals would be the most likely fate of HO_2 addition in both ours and in Wilk's experiments, e.g.,

		$A(dm^3, mol, s)$	$E(kJ mol^{-1})$	Reference
(a)	$HO_2 + C_3H_6 \rightarrow HO_2C_3H_6$	$1.3 imes10^9$	62.6	[25]
(b)	$HO_2C_3H_6 \rightarrow C_3H_6O + OH$	$\approx 10^{12}$	69	[25]
(c)	$\mathrm{HO}_2\mathrm{C}_3\mathrm{H}_6 +\mathrm{O}_2 o \mathrm{HO}_2\mathrm{C}_3\mathrm{H}_6\mathrm{O}_2$	$pprox 10^9$	-4.6	(as reaction 48)

For example at 550 K and 40 mbar of oxygen, oxygen addition (reaction c) is faster than decomposition to the epoxide (reaction b) by a factor of 8. However, in the absence of any experimental data for the rate of decomposition of hydroperoxyalkyl radicals, oxygen addition (reaction c) is ignored, with all the adduct assumed to decompose to the epoxide. We are currently investigating this problem.

(vi) Other reactions. The overall rate of reaction is partly controlled by radicalradical termination reactions, as they lead to a removal of chain carriers from the gas. Consequently a comprehensive representation of these reactions is given (reactions 157-226).

The scheme has also been used to model acetaldehyde-propene cooxidation experiments at pressures of 0.9 bar and pilot plant experiments at pressures of up to 55 bar [32]. The scheme worked well except at very high pressure (above 20 bar) when the formaldehyde concentrations were overestimated and formic acid was found in quantities such that

$$[\text{HCHO}] + [\text{HCO}_2\text{H}] \approx [\text{CH}_3\text{CHO}]$$

A possible explanation for this is that the very rapid addition reaction between hydroperoxy radicals and formaldehyde becomes significant. This reaction has been disregarded previously because the resulting peroxy radical is short lived. However, in the presence of high concentrations of propene, epoxidation can occur with the resulting alkoxy radical leading to formic acid. Reactions 109, 116–122 were added to the model to examine this submechanism.

Analysis of Model and Comparison with Experiment

To elucidate which are the key reactions during propene oxidation with the conditions used here, path analyses were conducted. Tables III-V gives an example (at 528 K, 4.0 bar pressure, 900 s, and 57% oxygen consumption). Of the reactions consuming propene, hydroxy, and hydroperoxy addition are the most significant (reactions 27 and 46). Summing over all the radicals present, addition to propene is faster than abstraction from propene by a factor of 4.4. Abstraction from propene is mostly by hydroxy or alkoxy radicals.

Reaction					(%)
46 27 31 107 36	$\begin{array}{c} OH\\ HO_2\\ C_2H_3CO_3\\ O_2C_3H_6OH\\ OH\\ OH \end{array}$	$\begin{array}{r} + \ C_{3}H_{6} \\ + \ C_{3}H_{6} \end{array}$	$ \begin{array}{l} \rightarrow C_3H_6OH \\ \rightarrow C_3H_6O \\ \rightarrow C_3H_6O \\ \rightarrow C_3H_6O \\ \rightarrow C_3H_6O \\ \rightarrow C_3H_5 \end{array} $	+ OH + C_2H_3 + CO_2 + OC_3H_6OH + H_2O	38.7 17.1 9.5 6.9 5.6
22 28 110 35 118 42	$CH_{3}CO_{3}$ HO_{2} $O_{2}C_{3}H_{6}OH$ $CH_{3}O$ $HOCH_{2}O_{2}$ $C_{3}H_{5}O$	$+ C_{3}H_{6}$ + $C_{3}H_{6}$ + $C_{3}H_{6}$ + $C_{3}H_{6}$ + $C_{3}H_{6}$ + $C_{3}H_{6}$	$ \rightarrow C_3H_6O \rightarrow C_3H_5 \rightarrow C_3H_5 \rightarrow C_3H_5 \rightarrow C_3H_6O \rightarrow C_3H_5 $	+ $CH_3 + CO_2$ + H_2O_2 + $HOC_3H_6O_2H$ + CH_3OH + $HOCH_2O$ + C_3H_5OH	5.2 4.2 3.5 2.9 1.9 1.7

TABLE III. Oxidation of propene: Relative rates of reactions consuming propene. $[C_3H_6]/[O_2]_{initial} = 19/1$, 4.0 bar, and 900 s. T = 528 K.

TABLE IV. Oxidation of propene: Relative rates of reactions consuming $O_2C_3H_6OH$. $[C_3H_6]/[O_2]_{initial} = 19/1$, 4.0 bar, and 900 s. T = 528 K.

Reaction					(%)
197	HO_2	$+ O_2 C_3 H_6 OH$	$\rightarrow O_2$	$+ HOC_3H_6O_2H$	20.7
107	C_3H_6	$+ O_2 C_3 H_6 OH$	$\rightarrow C_3 H_6 O$	$+ OC_3H_6OH$	17.9
115	C ₂ H ₃ CHO	$+ O_2 C_3 H_6 OH$	$\rightarrow C_2H_3CO$	$+ HO_2C_3H_6OH$	15.8
112	CH_3CHO	$+ O_2 C_3 H_6 OH$	$\rightarrow CH_3CO$	$+ HO_2C_3H_6OH$	10.1
110	C_3H_6	$+ O_2 C_3 H_6 OH$	$\rightarrow C_3H_5$	$+ HO_2C_3H_6OH$	9.0
199	$O_2C_3H_6OH$	$+ O_2C_3H_6OH$	$\rightarrow OC_3H_6OH$	$+ OC_3H_6OH + O_2$	7.9
159	C_3H_5	$+ O_2 C_3 H_6 OH$	$\rightarrow C_3H_5O$	$+ OC_3H_6OH$	6.9
111	HCHO	$+ O_2 C_3 H_6 OH$	\rightarrow HCO	$+ HO_2C_3H_6OH$	5.4
71	C_3H_6O	$+ O_2 C_3 H_6 OH$	$\rightarrow cC_3H_5O$	$+ HO_2C_3H_6OH$	3.1
50	$O_2C_3H_6OH$		\rightarrow CH ₃ CHO	+ HCHO + OH	2.2

TABLE V. Oxidation of propene: Relative rates of reactions forming propene oxide. . $[C_3H_6]/[O_2]_{initial} = 19/1$, 4.0 bar, and 900 s. T = 528 K.

Reaction					(%)
27	HO ₂	$+ C_3H_6$	$\rightarrow C_3H_6O$	+ OH	39.9
31	$C_2H_3CO_3$	$+ C_3H_6$	→C ₃ H ₆ O	$+ C_2 H_3 + CO_2$	22.2
107	O ₂ C ₃ H ₆ OH	$+ C_3H_6$	$\rightarrow C_3H_6O$	$+ OC_3H_6OH$	16.1
22	CH_3CO_3	$+ C_3H_6$	$\rightarrow C_3H_6O$	$+ CH_3 + CO_2$	12.1
118	$HOCH_2O_2$	$+ C_3H_6$	$\rightarrow C_3H_6O$	+ HOCH ₂ O	4.3
25	CH_3O_2	$+ C_3H_6$	$\rightarrow C_3 H_6 O$	$+ CH_3O$	2.1
113	CH_3CO_3H	$+ C_3H_6$	$\rightarrow C_3H_6O$	$+ CH_3CO_2H$	2.0
8	$C_3H_5O_2$	$+ C_3H_6$	$\rightarrow C_3H_6O$	$+ C_3H_5O$	1.2

The hydroxy radical, being highly reactive and nonselective, reacts predominantly (98.5%) with propene, with the addition reaction faster than abstraction by a factor of 6.8. With these conditions, hydroxy addition is largely irreversible, with less than 0.1% of the hydroxypropyl radicals decomposing back to propene and hydroxyl before oxygen addition occurs.

The rates of removal for the more significant reactions of $O_2C_3H_6OH$ are given in Table IV. Many abstract a hydrogen atom from the aldehydes present (31%) (reactions 111, 112, 115) with a significant fraction lost to the HO₂ termination reaction (21%). A significant fraction (33%) is converted directly to the alkoxy species OC_3H_6OH (and subsequently to acetaldehyde and formaldehyde) by either epoxidizing propene or by radical-radical reactions (reactions 107, 159, 199). Only 2.2% of $O_2C_3H_6OH$ is converted by concerted decomposition to the aldehydes (reaction 50), a tenth of that produced via the alkoxy species.

Virtually all of the propene oxide formed is by peroxy radical addition (Table V). Hydroperoxy radicals lead to much of the epoxide (40%) (reaction 27) with significant quantities (34%) formed by the peroxy species RCO_3 where R is C_2H_3 and CH_3 (reactions 22, 31). Although acetaldehyde is formed in larger concentrations than acrolein, the unsaturated peroxy species $C_2H_3CO_3$ is more significant than acetylperoxy in forming the epoxide, due to acrolein being much more reactive than acetaldehyde (in the model). Epoxidation by the hydroxypropylperoxy species form 16% of the epoxide (reaction 107).

The model in Appendix 1 reproduces much of the behavior observed in the experiments. Variation of the selectivities with temperature (Table I) for the main products, propene oxide, acetaldehyde, and formaldehyde, are well simulated with predicted yields of the correct magnitude and a decrease in the yield of epoxide and increase in that of aldehydes on increasing the temperature from 505 K to 549 K. Similarly, with variation of selectivites with pressure (Table II), the predicted yields of the main products are of the correct magnitude with the decreasing yields of the aldehydes with increasing pressure well represented.

Figures 1-6 give the time development of the main products for the experiments reported here. The agreement between model and experiment is generally acceptable at the end of the reaction (oxygen consumed). The overall rate of reaction is noticeably overpredicted by the model for the 0.9 bar experiments (Figures 6 and 9). As the rate of reaction increases significantly on adding bath gas or cleaning the reactor walls, it is possible that either radicals or branching agents are destroyed at the walls, the effect of this would be greater at lower pressure. The overall rate of reaction for the higher pressure experiments (Figures 1-5) is predicted to within a factor of 2, which is acceptable as no attempt has been made to "force" rate constants that affect the overall rate of reaction.

Variation of the product distribution with extent of reaction is most easily observed in terms of selectivity (Figures 7 and 8). The decrease in epoxide selectivity with time is successfully reproduced. However the decrease in acetaldehyde and formaldehyde is not reproduced although comparison of model and experimental selectivities is acceptable towards the end of the reaction. The selectivity of acrolein decreases markedly as the reaction proceeds which suggests that radical attack on acrolein is much faster than on acetaldehyde. This is consistent with the acyl-H bond strength being weaker for acrolein due to the resultant C_2H_3CO species being resonance stabilized by the adjacent double bond. In the early stages of the reaction, the product hydrocarbons consist mostly of 1,5hexadiene which is overpredicted for all the experiments reported here. As the rate for the self reaction has been accurately measured [29], it is possible that the rate for hydrogen abstraction from propene is slower in comparison with radical addition to propene than considered in the model. Towards the end of the reaction, other hydrocarbons such as pentenes and butenes become significant, suggesting that alkyl or alkenyl addition to propene is important when the oxygen concentration is low.

Experiments of Wilk et al. were also simulated to test the model under a wider range of conditions (Figure 10, $\phi = 0.8$, $T_{\text{initial}} = 626$ K, 0.78 bar). The model gave



Figure 10. Oxidation of propene. Computer simulation of results of Wilk et al. [8,16] using the reaction scheme reported in Appendix I (except for k_1 and k_2 as described in the text). $T_{\text{initial}} = 626 \text{ K}$, $\phi = 0.8$, and 0.78 bar.

no significant reaction over 1000 s when values for the rate constants for the initiation reaction and the corresponding reverse reaction $(k_1 \text{ and } k_2)$ of Walker et al. [19,33] were used. The model of Wilk et al. behaves in a similar way. They had adjusted the initiation rate to give agreement between model and experimental induction periods for the experiments at 626 K. The justification for this would be that surface initiation is significant. Therefore for the simulations in Figure 10 the rate constants k_1 and k_2 used by Wilk et al. were initially used (with A_1 subsequently reduced by \times 1.7). The computed concentrations are similar to the computed values of Wilk et al. and are in reasonable agreement with their experimental values.

From the computer modelling there are a number of differences between the experiments reported here and those of Wilk et al. First, at the higher temperatures of their experiments, a significant proportion of the hydroxypropylperoxy radicals either decompose to acetaldehyde, formaldehyde, and hydroxyl (reaction 50) or decompose progressively back to propene, oxygen, and hydroxyl (reactions 47 and 49) while these reactions are not significant for the lower temperatures of our experiments. Secondly in our experiments, the fuel is in vast excess over any product, and therefore highly reactive species such as OH react almost exclusively with the fuel and consumption of the more stable products such as the epoxide is insignificant. In the oxygen-rich experiments of Wilk et al. reactive products can build up to similar concentrations as the fuel causing a significant fraction of the hydroxy radicals to react with the products of the reaction.

Conclusion

The model reported here explains why, under the conditions used in these experiments, high yields of propene oxide are obtained during propene oxidation. There is a series of reactions between peroxy radicals and the fuel. The radicals include HO_2 , $CH_3O_2, C_3H_5O_2$, and $C_2H_3CO_3$. However, to explain the high yields of the oxide, two other radical reactions must play a significant rôle:

(22)
$$CH_3CO_3 + C_3H_6 \longrightarrow C_3H_6O + CH_3 + CO_2$$

$$(107) \qquad \qquad HOC_3H_6O_2 + C_3H_6 \longrightarrow C_3H_6O + HOC_3H_6O_2$$

The experimental evidence and the corresponding computer simulations suggest that the lower the temperature, the higher the yield of propene oxide, whereas increasing pressure has little direct effect. The model has been tested over a wide range of conditions: our present work, 505-549 K; 0.9-4.0 bar; $\phi = 86$, those used by Wilk et al. [16]; 626 K, 0.78 bar; $\phi = 0.8$ and those of pilot plant experiments using continuous, stirred, flow reactors 505-541 K; 16-55 bar; and $\phi = 30-39$ which will be described in a subsequent article [32]. Further, we are, at present, using the model to direct a series of cooxidation experiments to find conditions in which the yield of propene oxide is increased further.

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			[°] [°] [°]	$= A T^n \exp(-E_a/R)$	T): units (mol, dm ³	, s ⁻¹)	Ŀ	
					А	u	\mathbf{E}_{a}	Keterences and Footnotes
1	C_3H_6	$+ 0_{2}$	$>C_3H_5$	$+ HO_{2}$	1.95 E + 09,	0,	1.64 E + 02	[19]
5	C_3H_5	$+ HO_{2}$	$>C_3H_6$	+ 02	3.30 E + 09,	0,	0.00 E + 00	[33]
ŝ	C_3H_5	+ 02	$>C_{3}H_{5}O_{2}$		1.20 E + 07,	0,	-9.70 E + 00	[16]
4	$C_3H_5O_2$		$>C_3H_5$	+ 02	3.47 E + 14,	- 1.0 ,	6.65 E + 01	[16]
5 2	$C_3H_5O_2$	$+ C_3 H_6$	$>C_3H_5O_2H$	$+ C_3H_5$	1.00 E + 08,	0,	6.26 E + 01	$[34]^1$
9	$C_3H_5O_2H$	$+ C_3H_5$	$>C_{3}H_{5}O_{2}$	$+ C_3 H_6$	2.57 E + 07,	0,	6.28 E + 01	[16]
7	C_3H_5O	+ 02	$>C_2H_3CHO$	+ HO ₂	1.70 E + 08,	0,	7.40 E + 00	[16]
80	$C_3H_5O_2$	$+ C_3H_6$	$>C_3H_5O$	$+ C_3H_6O$	1.00 E + 08,	0,	5.96 E + 01	$[16]^2$
6	CH_3CHO	HO +	>CH ₃ CO	$+ H_2O$	2.35 E + 07,	0.73 ,	-4.66 E + 00	[35]
0	CH ₃ CHO	$+ HO_{2}$	>CH ₃ CO	$+ H_2O_2$	1.00 E + 09,	0,	4.99 E + 01	ę
Ξ	CH ₃ CO	$+ H_2O_2$	>CH ₃ CH0	$+ HO_2$	1.00 E + 09,	, o	5.90 E + 01	[36]
2	HCHO	HO +	>HCO	$+ H_2O$	9.63 E + 09,	0,	9.15 E - 01	[37]
3	HCHO	$+ HO_{2}$	>HCO	$+ H_2O_2$	1.00 E + 09,	0,	5.47 E + 01	n
4	CH ₃ CO		>CH ₃	+ CO	1.00 E + 13,	0,	7.36 E + 01	[28] ⁴
5	CH ₃ CO	$+ 0_{2}$	>CH ₃ CO ₃		6.00 E + 09,	0,	0.00 E + 00	[27] ⁴
16	HCO	+ M	H<	+ CO + M	2.50 E + 11,	0,	7.03 E + 01	[38]
17	HCO	+ 02	$>HO_2$	+ CO	3.00 E + 09,	0,	0.00 E + 00	[35]
18	CH_3CO_3	+ CH ₃ CHO	>CH ₃ CO ₃ H	+ CH ₃ CO	1.20 E + 08,	0,	2.06 E + 01	[17]
¹ A CH ₃ C epoxi ² Tl The t	5 was adjusted 22 attack on 2-r dation rate give ne epoxidation r hermochemical	to give a ratio of a nethylbut-1-ene, 2- s an extrapolated 1 ate constant for me analysis described	abstraction to epor- methylbut-2-ene, ratio of approxima thylperoxy plus pr in the first footn	kidation (k_5/k_8) of (and 2-3-dimethylbu tely 0.5 for propene opene of Wilk et al.	 1.5. Osborne et al. [1.2-ene. Using the e poxidation. Wilk [16] is used here for the methy trant for the methy. 	[34] measure correlation b et al.'s [16] ' r all alkyl an peroxy epoxi	d peroxide to epoxid etween ionization er value for E_5 was use d alkyl-like peroxy r_i dation of propene of	e ratios of 0.008 to 0.05 for lergy of the alkene and the d. adical epoxidation reactions.
				$\log_{10}(k) = 8.2 \pm 0$.4 - 60.8 kJ/mol h	T		

Appendix I: Propene Oxidation Reaction Scheme

The value of Wilk et al. [16] is within the estimated error of this calculation.

³ The rates of H atom abstraction from formaldehyde and acetaldehyde by peroxy radicals are all assumed equal to those for HO_2 [35]. The A factors have been reduced by $\times 3$ from the quoted value (within the estimated uncertainty) to give a better comparison between model and experiment. ⁴ The rate for acetyl decomposition k_{14} has been decreased by $\times 2$ while that for O₂ addition, k_{15} has been increased by $\times 2$ from the quoted values (within the estimated uncertainties), to improve the comparison between model and experiment.

OXIDATION OF PROPENE IN GAS PHASE

					А	u	E_{a}	References and Footnotes
19	CH_3CO_3	+ HCHO	>CH ₃ CO ₃ H	+ HCO	1.20 E + 08,	0,	2.06 E + 01	as 18
20	CH ₃ CO ₃ H	$+ CH_3CHO$	$> CH_3 CO_2 H$	$+ CH_3CO_2H$	2.00 E + 05,	, 0	4.18 E + 01	[39]
21	CH_3CO_3H	+ HCHO	$> CH_3CO_2H$	$+ HCO_2H$	2.00 E + 05,	, 0	4.18 E + 01	as 20
22	CH_3CO_3	$+ C_3 H_6$	$>C_3H_6O$	$+ CH_3 + CO_2$	1.70 E + 08,	0,	3.26 E + 01	[26]
23	Н	$+ 0_2 + M$	$> HO_2$	+ M	1.31 E + 12,	-0.8 ,	0.0	[35]
24	CH_3	$+ 0_{2}$	$>CH_3O_2$		1.20 E + 09,	0,	0.00 E + 00	[40]
25	CH_3O_2	$+ C_3H_6$	$>CH_3O$	$+ C_{3}H_{6}O$	1.00 E + 08,	0,	5.96 E + 01	2
26	CH_3O	+ 02	>HCHO	$+ HO_{2}$	4.30 E + 07,	0,	4.50 E + 00	[37]
27	HO_2	$+ C_3 H_6$	$>C_3H_6O$	H0 +	1.30 E + 09,	0,	6.26 E + 01	[25]
28	HO_2	$+ C_3H_6$	$>C_3H_5$	$+ H_2O_2$	3.20 E + 0.08	0,	6.26 E + 01	[16]
29	C_2H_3CHO	H0 +	$>C_2H_3CO$	$+ H_2O$	1.00 E + 10,	0,	0.00 E + 00	[16]
30	C_2H_3CO	$+ 0_{2}$	$>C_2H_3CO_3$		1.00 E + 09,	0,	0.00 E + 00	[16]
31	$C_2H_3CO_3$	$+ C_3H_6$	$>C_3H_6O$	$+ C_2 H_3 + CO_2$	1.70 E + 08,	0 ,	3.26 E + 01	as 22
32	CH ₃ CO ₃	$+ C_3H_6$	$>C_3H_5$	$+ CH_3CO_3H$	3.20 E + 08,	0,	6.26 E + 01	[16]
33	C_2H_3CHO	$+ HO_2$	$>C_2H_3CO$	$+ H_2O_2$	3.00 E + 09,	0,	3.94 E + 01	ũ
34	C_2H_3CO		$>C_2H_3$	+ CO	1.00 E + 13,	0,	9.62 E + 01	9
35	CH_3O	$+ C_3 H_6$	>CH ₃ OH	$+ C_3H_5$	0.68 E + 08,	0,	1.67 E + 01	$[16]^7$
36	$\rm C_3H_6$	H0 +	$>C_3H_5$	$+ H_2 O$	2.00 E + 10,	0,	1.28 E + 01	[20]
37	C0	HO +	>C02	+ H	2.24 E + 08,	0,	3.27 E + 00	[41]
38	C_2H_3CHO	$+ C_{3}H_{5}O_{2}$	$>C_2H_3CO$	$+ C_{3}H_{5}O_{2}H$	3.00 E + 09,	0,	3.94 E + 01	as 33
39	C_2H_3CO	$+ C_{3}H_{5}O_{2}H$	$>C_2H_3CHO$	$+ C_3 H_5 O_2$	2.51 E + 07,	, 0	4.23 E + 01	[16]
40	C_2H_3CHO	$+ CH_3O$	$>C_2H_3CO$	$+ CH_3OH$	1.15 E + 08,	0,	5.36 E + 00	as 92
41	CO	$+ HO_{2}$	>C02	+ 0H	1.51 E + 11,	0,	9.90 E + 01	[42]
42	C_3H_5O	$+ C_3 H_6$	$>C_3H_5OH$	$+ C_3 H_5$	1.35 E + 08,	0 ,	1.67 E + 01	as 35
43	C_3H_5OH	$+ C_3H_5$	$>C_{3}H_{5}O$	$+ C_3H_6$	6.76 E + 06,	0,	3.77 E + 01	[16]
5]	The rates for per	oxy radical abstra	ction from acrolein	a were adjusted to give	a reasonable com	oarison betv	veen the time dev	elopment of the model and

experimental acrolein concentrations (Fig. 8). The rate constant is approximately ×30 faster than from the acetaldehyde, which is consistent with the resulting C₂H₃CO radical being resonance stabilized by the adjacent double bond.

⁶ The activation energy is equal to the enthalpy change for the reaction [16]. The A factor is assumed analogous to the equivalent reaction for acetyl

(reaction 14). ⁷ Wilk et al.'s [16] estimate of k_{35} has been reduced by $\times 2$ to improve the comparison between model and experiment.

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Appendix I: (Continued)

						Α	u	E_{lpha}	References and Footnotes
44	CH_3	$+ C_{3}H_{5}O_{2}H$	>CH4	$+ C_3 H_5 O_2$		7.59 E + 08,	0,	5.36 E + 00	[16]
45	CH_3	$+ C_2 H_3 O_2 H$	>CH4	$+ C_2 H_3 O_2$		7.59 E + 08,	0,	5.36 E + 00	as 44
46	C_3H_6	H0 +	$>C_3H_6OH$			2.75 E + 09,	0,	-4.35 E + 00	[20]
47	C_3H_6OH		$>C_3H_6$	HO +		9.05 E + 14,	0,	1.26 E + 02	8
48	C_3H_6OH	+ 02	$>0_2C_3H_6OH$			1.00 E + 09,	0,	-4.60 E + 00	[16]
49	O ₂ C ₃ H ₆ OH		$>C_3H_6OH$	+ 02		3.24 E + 17,	$^{-1.0}$,	1.26 E + 02	[16]
50	$0_2 C_3 H_6 OH$		>CH ₃ CHO	+ HCHO	HO +	1.00 E + 12,	0,	1.20 E + 02	6
51	C_2H_3	$+ 0_{2}$	>HCHO	+ HCO		3.98 E + 09,	0,	-1.05 E + 00	[43]
52	C_3H_5OH	HO +	>C ₂ H ₃ CHOH	$+ H_2O$		3.98 E + 09,	0,	5.73 E + 00	10
53	C_3H_5OH	HO +	$>C_3H_5O$	$+ H_2O$		1.23 E + 10,	0,	1.36 E + 01	10
54	C_2H_3CHOH	+ 02	$>C_2H_3CHO$	$+ HO_2$		8.32 E + 08,	0,	0.00 E + 00	as 109
55	C_3H_6O	HO +	$>cC_3H_5O$	$+ H_2O$		2.00 E + 10,	0,	1.28 E + 01	[16]
56	$cC_{3}H_{5}O$	$+ H_2O$	$>C_3H_6O$	HO +		3.98 E + 04,	0,	3.01 E + 02	[16]
57	C_3H_6O	+ CH ₃	$>cC_3H_5O$	$+ CH_4$		1.58 E + 09,	0,	3.68 E + 01	[16]
58	$cC_{3}H_{5}O$	+ CH ₄	$>C_3H_6O$	$+ CH_3$		7.08 E + 09,	0,	1.14 E + 02	[16]
59	C_3H_6O	$+ HO_2$	$>cC_3H_5O$	$+ H_2O_2$		3.24 E + 08,	0,	6.23 E + 01	[16]
60	cC_3H_5O	$+ H_2O_2$	$>C_3H_6O$	$+ HO_2$		1.00 E + 08,	0,	6.28 E + 01	[16]
61	C_3H_6O	$+ C_3H_5$	$>cC_3H_5O$	$+ C_3 H_6$		7.94 E + 07,	0,	5.19 E + 01	[16]
62	cC_3H_5O	$+ C_3H_6$	$>C_3H_6O$	$+ C_3H_5$		1.00 E + 08,	, 0	6.28 E + 01	[16]
63	C_3H_6O	$+ C_2 H_3$	$>_{c}C_{3}H_{5}O$	$+ C_2 H_4$		3.02 E + 09,	0,	6.07 E + 01	[16]
64	cC_3H_5O	$+ C_2 H_4$	$>C_3H_6O$	$+ C_2 H_3$		1.00 E + 08,	0,	6.28 E + 01	[16]
^{8}k	47 has been det (CH ₃ CH · CH ₉ O	ermined from k_{46} (H) = 133.5 kJ/m	using an equilibri ol. C _n (CH ₃ CH · CH	ium constant ca 20H) = 86.4 J/i	lculated mol K. A	using Benson's ru un estimated error	in ΔH° (C	vith ΔS° (CH ₃ CH · ;H ₃ CH · CH ₂ OH) of	CH ₂ OH) = 308.8 J/mol K, 8 kJmol corresponds to an

Appendix I: (Continued)

4 , 2 00.4 J/1111 100.0 Ka/III01, Up/UII3UII 'UII2UII) Δn (Un3Un · Un2Un) = uncertainty in k_{47} of $\times 5$.

⁹ The value used here is an estimate. It is slightly slower than the rate for a 1,5p H transfer reaction estimated by Walker [23] at,

 $k_{1,5\ p} = 1.3 \times 10^{12}\ {
m sec}^{-1}\ {
m exp}\ (-113 {
m kJ/mol}\ RT)$

which is consistent with O—H bond being stronger than the primary C—H bond.

¹⁰ Assumed to be analogous to the corresponding reaction for methanol [49].

					А	u	E_a	References and Footnotes
65	C_3H_6O	$+ CH_{3}O$	$>cC_3H_5O$	$+ CH_3OH$	1.15 E + 08,	0,	7.87 E + 00	[16]
99	$c\mathrm{C_3H_5O}$	$+ CH_3OH$	$>C_3H_6O$	$+ CH_3O$	1.00 E + 07,	0,	6.28 E + 01	[16]
67	C_3H_6O	$+ CH_{3}O_{2}$	$>cC_3H_5O$	$+ CH_3O_2H$	1.58 E + 08,	0,	5.02 E + 01	[16]
68	cC_3H_5O	$+ CH_3O_2H$	$>C_3H_6O$	$+ CH_3O_2$	2.00 E + 07,	0,	4.60 E + 01	[16]
69	C_3H_6O	$+ C_{3}H_{5}O_{2}$	$>cC_3H_5O$	$+ C_{3}H_{5}O_{2}H$	1.58 E + 08,	0,	5.02 E + 01	[16]
70	$cC_{3}H_{5}O$	$+ C_3H_5O_2H$	$>C_3H_6O$	$+ C_3 H_5 O_2$	5.25 E + 06,	0,	4.60 E + 01	[16]
71	C_3H_6O	$+ 0_{2}C_{3}H_{6}OH$	$>cC_3H_5O$	+ HO ₂ C ₃ H ₆ OH	1.58 E + 08,	0,	5.02 E + 01	as 69
72	$cC_{3}H_{5}O$	+ HO ₂ C ₃ H ₆ OH	$>C_3H_6O$	+ 0 ₂ C ₃ H ₆ OH	5.25 E + 06,	0,	4.60 E + 01	as 70
71	$cC_{3}H_{5}O$		$> CH_2 CHOCH_2$		1.00 E + 11,	0,	4.18 E + 01	[16]
72	CH_2CHOCH_2		$>cC_3H_5O$		1.00 E + 10,	0,	2.09 E + 02	[16]
73	CH_2CHOCH_2		$>C_2H_3$	+ HCHO	1.00 E + 14,	0,	1.25 E + 02	[16]
74	C_2H_3	+ HCHO	>CH2CH0CH2		1.00 E + 07,	0,	2.09 E + 02	[16]
75	C_3H_5O	+ CO	$>C_3H_5$	+ CO ₂	1.58 E + 10,	0,	4.94 E + 01	11
92	$C_3H_5O_2$	+ HCHO	$>C_{3}H_{5}O_{2}H$	+ HCO	1.00 E + 09,	0,	5.47 E + 01	as 13
77	$C_3H_5O_2H$	+ HC0	$>C_{3}H_{5}O_{2}$	+ HCHO	2.51 E + 07,	0,	4.23 E + 01	[16]
78	$C_2H_3O_2$	+ HCHO	$>C_{2}H_{3}O_{2}H$	+ HCO	1.00 E + 09,	0,	5.47 E + 01	as 13
79	$C_2H_3O_2H$	+ HCO	$>C_{2}H_{3}O_{2}$	+ HCHO	2.51 E + 07,	0,	4.23 E + 01	as 77
80	CH_3O_2	+ HCHO	$> CH_3O_2H$	+ HCO	1.00 E + 09,	0,	5.47 E + 01	as 13
81	CH_3O_2H	+ HCO	$> CH_{3}O_{2}$	+ HCHO	2.51 E + 07,	0,	4.23 E + 01	as 77
82	C_3H_5O	+ HCHO	>C ₃ H ₅ OH	+ HC0	1.15 E + 08,	0,	5.36 E + 00	as 84
83	C_3H_5OH	+ HCO	$>C_3H_5O$	+ HCHO	3.02 E + 08,	0,	7.60 E + 01	as 85
84	CH_3O	+ HCHO	>CH ₃ OH	+ HC0	1.15 E + 08,	0,	5.36 E + 00	[16]
85	CH ₃ OH	+ HC0	$>CH_3O$	+ HCHO	3.02 E + 08,	0,	7.60 E + 01	[16]
86	CH ₃ CHO	$+ C_{3}H_{5}O_{2}$	>CH ₃ CO	$+ C_{3}H_{5}O_{2}H$	1.00 E + 09,	, 0	4.99 E + 01	as 10
87	CH_3CO	$+ C_{3}H_{5}O_{2}H$	>CH ₃ CHO	$+ C_{3}H_{5}O_{2}$	2.51 E + 07,	0,	4.23 E + 01	[16]
88	CH ₃ CHO	$+ CH_{3}O_{2}$	>CH ₃ CO	$+ CH_{3}O_{2}H$	1.00 E + 09,	0,	4.99 E + 01	as 10
89	CH ₃ CO	$+ CH_3O_2H$	>CH ₃ CHO	$+ CH_{3}O_{2}$	5.01 E + 06,	0,	4.23 E + 01	[16]
06	CH ₃ CHO	$+ C_{3}H_{5}O$	$>CH_3CO$	$+ C_3H_5OH$	1.15 E + 08,	0,	5.36 E + 00	as 84
91	CH ₃ CO	$+ C_3H_5OH$	>CH ₃ CHO	$+ C_{3}H_{5}O$	3.02 E + 08,	0,	7.60 E + 01	as 85
92	CH ₃ CHO	$+ CH_3O$	>CH ₃ CO	+ CH ₃ OH	1.15 E + 08,	0,	5.36 E + 00	[17]

¹¹ The rate is assumed analogous to the corresponding reaction for CH₃O [50].

Appendix I: (Continued)

					A	u	E_{a}	References and Footnotes
93	CH ₃ CO	$+ CH_3OH$	>CH ₃ CHO	$+ CH_3O$	3.02 E + 08,	0,	7.60 E + 01	[17]
94	C_2H_3CHO	$+ CH_3O_2$	$>C_2H_3CO$	$+ CH_3O_2H$	3.00 E + 09,	, 0	3.94 E + 01	as 33
95	C_2H_3CO	$+ CH_3O_2H$	$>C_2H_3CHO$	$+ CH_3O_2$	2.51 E + 07,	0 ,	4.23 E + 01	[16]
96	C_2H_3CHO	$+ CH_3CO_3$	$>C_2H_3CO$	$+ CH_3CO_2H$	1.20 E + 08,	, 0	2.06 E + 01	as 18
97	C_2H_3CO	$+ CH_3CO_3H$	$>C_2H_3CHO$	$+ CH_{3}CO_{3}$	2.00 E + 07,	, 0	4.18 E + 01	[16]
98	C_2H_3CHO	$+ CH_3CO_3H$	$>C_2H_3CO_2H$	$+ CH_3CO_2H$	2.00 E + 05,	, 0	4.18 E + 01	as 20
66	C_2H_3CHO	$+ C_{3}H_{5}O$	$>C_2H_3CO$	$+ C_3H_5OH$	1.15 E + 08,	0 ,	5.36 E + 00	as 84
100	C_2H_3CO	$+ C_3H_5OH$	$>C_2H_3CHO$	$+ C_3H_5O$	3.02 E + 08,	0,	7.60 E + 01	as 85
101	$C_3H_5O_2H$	H0 +	$>C_{3}H_{5}O_{2}$	$+ H_2 O$	3.24 E + 10,	, 0	4.18 E + 00	[16]
102	$C_3H_5O_2$	$+ H_2O$	$>C_{3}H_{5}O_{2}H$	H0 +	3.02 E + 10,	0,	1.37 E + 02	[16]
103	C_2H_3	$+ C_3 H_6$	$>C_2H_4$	$+ C_3H_5$	3.02 E + 09,	, 0	6.07 E + 01	[44]
104	C_2H_4	$+ C_3H_5$	$>C_2H_3$	$+ C_3 H_6$	7.94 E + 07,	0,	5.19 E + 01	[16]
105	C_2H_3	$+ C_3H_5O_2H$	$>C_2H_4$	$+ C_{3}H_{5}O_{2}$	2.00 E + 07,	0,	6.28 E + 01	[16]
106	C_2H_4	$+ C_{3}H_{5}O_{2}$	$>C_2H_3$	$+ C_{3}H_{5}O_{2}H$	7.08 E + 08,	0,	7.16 E + 01	[16]
107	$O_2C_3H_6OH$	$+ C_3 H_6$	$>0C_3H_6OH$	$+ C_{3}H_{6}O$	1.00 E + 08,	0,	5.96 E + 01	2
108	OC ₃ H ₆ OH		>CH ₃ CHO	$+ CH_2OH$	3.98 E + 14,	0,	7.20 E + 01	12
109	CH_2OH	+ 02	>HOCH ₂ O ₂		8.32 E + 08,	0,	0.00 E + 00	$[45]^{13}$
110	$O_2 C_3 H_6 OH$	$+ C_3 H_6$	$>C_3H_5$	$+ HO_2C_3H_6OH$	1.00 E + 08,	0,	6.26 E + 01	as 5
111	$O_2C_3H_6OH$	+ HCHO	>HCO	+ HO ₂ C ₃ H ₆ OH	1.00 E + 09,	0,	5.47 E + 01	as 13
112	$O_2C_3H_6OH$	$+ CH_3CHO$	>CH ₃ CO	$+ HO_2C_3H_6OH$	1.00 E + 09,	0,	4.99 E + 01	as 10
113	CH_3CO_3H	$+ C_3 H_6$	$>C_3H_6O$	$+ CH_3CO_2H$	3.20 E + 08,	0,	8.37 E + 01	[26]
114	C_3H_5O		$>C_2H_3CHO$	+ H	1.00 E + 14,	, 0	7.94 E + 01	[16]
115	$O_2C_3H_6OH$	$+ C_2 H_3 CHO$	$>C_2H_3CO$	$+ HO_2C_3H_6OH$	3.00 E + 09,	0,	3.94 E + 01	as 33
116	HO_2	+ HCHO	$>HO_2CH_2O$		7.23 E + 06,	0,	0.00 E + 00	13
117	HO_2CH_2O		$>HO_2$	+ HCHO	5.40 E + 13,	0,	0.00 E + 00	13
118	$HOCH_2O_2$	$+ C_3 H_6$	$>C_3H_6O$	+ HOCH ₂ O	1.70 E + 08,	0,	3.80 E + 01	13
119	$HOCH_2O$	$+ 0_{2}$	$>HCO_2H$	$+ HO_2$	4.30 E + 07,	0,	4.50 E + 00	¹³ as 26
12 T	The rate constant.	is assumed analogo	us to the correspondi	ing reaction for <i>i</i> -C _o H	"O [51]			

Appendix I: (Continued)

¹³ These reactions explicitly include short-lived species formed by HO₂ addition to HCHO and O₂ addition to CH₂OH. The rate constants are estimates based on the experimental study of the HO₂ + HCHO reaction and calculations of Veyret et al. [52]. Activation energy for the epoxidation by HOCH₂O₂ is assumed to be midway between that for CH₃CO₃ and CH₃O₂.

						А	u	E_{a}	References and Footnotes
120	$HOCH_2O$	$+ C_3 H_6$	>HCHO	$+ H_2O$	$+ C_{3}H_{5}$	1.35 E + 08,	0,	3.50 E + 01	13
121	HO_2CH_2O		>H0CH ₂ O ₂			8.60 E + 12,	0,	6.80 E + 00	13
122	$HOCH_2O_2$		$>HO_2CH_2O$			2.47 E + 12,	0,	7.48 E + 01	13
123	C_3H_5	$+ C_3 H_6$	$>C_{6}H_{11}$			2.70 E + 07,	0,	8.00 E + 01	14
124	C_6H_{11}		$>C_3H_5$	$+ C_3 H_6$		3.00 E + 13,	0,	1.33 E + 02	14
125	C_6H_{11}		$> CH_3 c C_5 H_8$			3.90 E + 12,	0,	5.50 E + 01	15
126	C_6H_{11}	$+ C_3 H_6$	$>C_{6}H_{12}$	$+ C_3H_5$		3.84 E + 08,	0,	3.02 E + 01	16
127	$CH_3cC_5H_8$	$+ C_3H_6$	$> CH_3 c C_5 H_9$	$+ C_3H_5$		3.84 E + 08,	0,	3.02 E + 01	as 126
128	C_6H_{11}	$+ 0_{2}$	$>C_6H_{11}O_2$			1.00 E + 10,	0,	0.00 E + 00	17
129	$C_6H_{11}O_2$	$+ C_3 H_6$	$>C_3H_6O$	$+ C_6H_{11}O$		1.00 E + 08,	0,	5.96 E + 01	2
130	$C_6H_{11}O$		>CH ₃ CHO	$+ C_4H_7$		6.30 E + 14,	0,	6.40 E + 01	18
131	C_4H_7	+ 02	$>C_4H_7O_2$			4.50 E + 09,	0,	0.00 E + 00	17
132	$C_4H_7O_2$	$+ C_3 H_6$	$>C_3H_6O$	$+ \ C_4 H_7 O$		1.00 E + 08,	0,	5.96 E + 01	2
133	C_4H_7O		$>C_3H_5$	+ HCHO		4.00 E + 13,	0,	7.99 E + 01	18
134	$C_6H_{11}O_2$	$+ C_3 H_6$	$>C_6H_{11}O_2H$	$+ C_3H_5$		1.00 E + 08	0,	6.26 E + 01	as 5
135	$C_4H_7O_2$	$+ C_3H_6$	$>C_4H_7O_2H$	$+ C_3H_5$		1.00 E + 08,	0,	6.26 E + 01	as 5
136	$C_6H_{11}O_2$	$+ CH_3CHO$	$> C_6 H_{11} O_2 H$	$+ CH_3CO$		1.00 E + 09,	0,	4.99 E + 01	as 10
137	$C_4H_7O_2$	$+ CH_3CHO$	$> C_4 H_7 O_2 H$	$+ CH_3CO$		1.00 E + 09,	0,	4.99 E + 01	as 10
138	$C_6H_{11}O_2$	+ HCHO	$> C_6 H_{11} O_2 H$	+ HCO		1.00 E + 09,	0,	5.47 E + 01	as 13
139	$C_4H_7O_2$	+ HCHO	$>C_4H_7O_2H$	+ HCO		1.00 E + 09,	0,	5.47 E + 01	as 13
140	$C_6H_{11}O$	$+ 0_{2}$	$>C_{6}H_{10}O$	$+ HO_2$		9.03 E + 06,	0,	1.66 E + 00	19
141	C_4H_7O	+ 02	$>C_3H_5CHO$	$+ HO_2$		1.70 E + 08,	0,	7.31 E + 00	19
¹⁴ 7 (50 ke	Thermochemical J/mol for loss of	calculation with ΔH_1 resonance energy in	23 = 55.3 kJ/mol allyl [24] plus 30	and $\Delta S_{123} =$ kJ/mol for a	- 151J/mol ddition of	K, with ΔS° (C _s alkyl to alkene [2]	H ₅ C ₅ 21]).	$(H_6)^{\dagger} = \Delta S^{\circ} (C_6 H)$	f_{11}) and $E_{123} = 80 \text{ kJ/mol}$

¹⁵ Thermochemical calculation assuming a strain energy of 26 kJ/mol (cyclopentene) and an activation energy of secondary alkyl addition to the terminal

carbon in 1-alkenes of 29 kJ/mol (i- $C_3H_7 + 1-C_4H_8$) [21], and $\Delta S_{125} = -16J/mol K$.

¹⁶ Assumed analogous to the corresponding reaction of $i \cdot C_3H_7$ [53]. ¹⁷ Assumed analogous to O₂ addition to 2-butyl and *n*-butyl for reactions 128 and 131 [1]. ¹⁸ Assumed analogous to the decomposition of CH₃CHO $\cdot C_2H_5$ [1, p300] and $n \cdot C_4H_9O$ for reactions 130 and 133. ¹⁹ Assumed analogous to the corresponding reactions for $i \cdot C_3H_7O + O_2$ [37] and $n \cdot C_3H_7O + O_2$ [54] for reactions 140 and 141.

Appendix I: (Continued)

						А	u	E_{a}	References and Footnotes
142	$C_{6}H_{11}O$	$+ C_3H_6$	>C ₆ H ₁₁ OH	$+ C_3H_5$		1.35 E + 08,	0,	1.67 E + 01	as 35
143	C_4H_7O	$+ C_3 H_6$	$>C_4H_7OH$	$+ C_{3}H_{5}$		1.35 E + 08,	0,	1.67 E + 01	as 35
144	C_4H_7	$+ C_3H_6$	$>C_4H_8$	$+ C_{3}H_{5}$		1.40 E + 08,	0,	3.68 E + 01	20
145	$C_{6}H_{11}O_{2}$	$+ C_2 H_3 CHO$	$>C_6H_{11}O_2H$	$+ C_2 H_3 CO$		1.00 E + 09,	0,	4.99 E + 01	as 33
146	$C_4H_7O_2$	$+ C_2 H_3 CHO$	$>C_4H_7O_2H$	$+ C_2 H_3 CO$		1.00 E + 09,	0,	4.99 E + 01	as 33
147	$C_3H_5O_2H$		$>C_3H_5O$	HO +		4.00 E + 15,	0,	1.81 E + 02	as 148
148	CH_3O_2H		$>CH_3O$	HO +		4.00 E + 15,	0,	1.81 E + 02	[46]
149	$HO_2C_3H_6OH$		H0<	$+ 0C_3H_6O_3$	Н	4.00 E + 15,	0,	1.81 E + 02	as 148
150	$C_6H_{11}O_2H$		$>C_6H_{11}O$	HO +		4.00 E + 15,	0,	1.81 E + 02	as 148
151	$C_4H_7O_2H$		$>C_4H_7O$	HO +		4.00 E + 15,	0,	1.81 E + 02	as 148
152	H_2O_2	+ M	+0<	- HO +	+ M	1.20 E + 14,	0,	1.90 E + 02	[35]
153	CH ₃ CO ₃ H		>CH ₃	+ CO ₂	HO +	4.00 E + 15,	, 0	1.67 E + 02	[47]
154	CH_3CO_3		>CH ₃ CO	$+ 0_{2}$		2.88 E + 16,	-1.0,	1.56 E + 02	[16]
155	CH_3O_2		>CH ₃	+ 02		6.12 E + 13,	0,	1.14 E + 02	21
156	$C_2H_3CO_3$		$>C_2H_3CO$	+ 02		4.37 E + 18,	-1.0,	1.55 E + 02	[16]
157	C_3H_5	$+ HO_{2}$	$>C_3H_5O$	HO +		8.91 E + 09,	0,	0.00 E + 00	[16]
158	C_3H_5	$+ CH_3O_2$	$>C_3H_5O$	$+ CH_3O$		3.80 E + 08,	0,	-5.02 E + 00	as 160
159	C_3H_5	$+ O_2 C_3 H_6 OH$	$>C_3H_5O$	$+ 0C_3H_6O_3$	Н	3.80 E + 08,	0,	-5.02 E + 00	as 160
160	$C_3H_5O_2$	$+ C_{3}H_{5}$	$>C_3H_5O$	$+ C_3H_5O$		3.80 E + 08,	0,	-5.02 E + 00	[16]
161	CH_3O_2	$+ CH_{3}O_{2}$	>CH ₃ O	+ CH ₃ O	$+ 0_{2}$	4.80 E + 08,	0,	7.10 E + 00	$[48]^{22}$
162	CH_3O_2	$+ CH_{3}O_{2}$	>CH ₃ OH	+ HCHO	$+ 0_{2}$	3.20 E + 06,	0,	-8.80 E + 00	[48]
163	$O_2C_3H_6OH$	$+ C_3H_5O_2$	$>0C_3H_6OH$	$+ C_{3}H_{5}O$	$^{+}0_{2}$	9.51 E + 07,	0,	3.87 E + 00	as 178
164	$O_2C_3H_6OH$	$+ CH_{3}O_{2}$	$>0C_3H_6OH$	$+ CH_3O$	$+ 0_{2}$	9.51 E + 07,	0,	3.87 E + 00	as 178
165	$C_3H_5O_2$	$+ CH_3O_2$	$>C_3H_5O$	$+ CH_{3}O$	$^{+}0_{2}$	9.51 E + 07,	, 0	3.87 E + 00	as 178
166	C_3H_5O	$+ CH_3O + O_2$	$>C_{3}H_{5}O_{2}$	$+ CH_{3}O_{2}$		2.00 E + 07,	0 ,	0.00 E + 00	[16]
167	HO_2	$+ HO_{2}$	$>H_{2}O_{2}$	$^{+}$ 0 ²		1.32 E + 08,	0,	-5.00 E + 00	[37]
168	$C_3H_5O_2$	$+ HO_2$	$>C_{3}H_{5}O$	HO +	$^{+}0_{2}$	1.00 E + 09,	0,	0.00 E + 00	[16]
169	CH_3O_2	$+ HO_{2}$	>CH30	HO +	$+ 0_{2}$	1.00 E + 09,	0,	0.00 E + 00	[16]
20 A	ssumed analogor	is to the correspondi	ng reaction for C	H ₃ [38].					
^{21}k	$_{155}$, k_{228} , and k_{25}	²⁹ has been determine	ed from k_{24} , k_{128} ,	and k_{131} us:	ing calcul	ated equilibrium (constants	[30].	
$^{22}\mathrm{T}$	he rate constant	for self reactions is	defined by the ra	tte equation,	d[X]/dt =	$= -2k[\mathbf{X}]^2$			

Appendix I: (Continued)

OXIDATION OF PROPENE IN GAS PHASE

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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-1.09 E + 01 as 174		1.63 $E + 02$ as 175	-1.09 E + 01 [16]	$\begin{bmatrix} 0 \\ 1 \end{bmatrix} \qquad \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 $	1.63 E + 02 [16]	-4.40 E + 00 [37]	-4.40 E + 00 as 176	3.87 E + 00 23	-3.01 E + 00 23	3.87 E + 00 as 178	-3.01 E + 00 as 179	3.87 E + 00 as 178	-3.01 E + 00 as 179	3.87 E + 00 as 178	-3.01 E + 00 as 179	-3.01 E + 00 as 179	3.87 E + 00 as 178	3.87 E + 00 as 178	3.87 E + 00 as 178	3.87 E + 00 as 178	3.87 E + 00 as 178	3.87 E + 00 as 178	-1.09 E + 01 as 174	-1.09 E + 01 as 174	-5.02 E + 00 as 160	-5.02 E + 00 as 160	-1.09 E + 01 as 174	3.87 E + 00 as 178	3.87 E + 00 as 178	3.87 E + 00 as 178
c	, S	, 0	, 0	, 0	Ċ	, ,	0 0	, 0	0,	0,	0,	0,	0 [,]	0,	0,	0 ,	0,	, 0	, 0	0 ,	0,	, 0	, 0	0,	0 ,	, 0	0 ,	0 ,	, 0	0 ,	0 ,	, 0
1 00 12 1 00	1.00 ± 103	1.00 E + 09,	4.57 E + 07,	3.02 E + 09,	4.57 E + 07	4.01 E + 01,	3.02 E + 09,	1.70 E + 09,	1.70 E + 09,	9.51 E + 07,	2.83 E + 06,	9.51 E + 07,	2.86 E + 06,	9.51 E + 07,	2.83 E + 06,	9.51 E + 07,	2.83 E + 06,	2.83 E + 06,	9.51 E + 07,	9.51 E + 07,	9.51 E + 07,	9.51 E + 07,	9.51 E + 07,	9.51 E + 07,	4.57 E + 07,	4.57 E + 07,	3.80 E + 08,	3.80 E + 08,	4.57 E + 07,	9.51 E + 07,	9.51 E + 07,	9.51 E + 07,
	+ 02	$+ 0_{2}$	+ 02	$+ HO_2$	- - -	+ 02	$+ HO_{2}$	$+ 2CO_2 + O_2$	$+ 2CO_2 + O_2$	$+ C_{3}H_{5}O + O_{2}$	$+ C_3H_5OH + O_2$	$+ C_6 H_{11} O + O_2$	$+ C_6 H_{10} O + O_2$	$+ C_4 H_7 O + O_2$	$+ C_3H_5CHO + O_2$	$+ C_4 H_7 O + O_2$	$+ C_3H_5CHO + O_2$	+ C_4H_7OH + O_2	$+ C_3 H_5 O + O_2$	$+ C_3 H_5 O + O_2$	$+ 0C_{3}H_{6}OH + O_{2}$	$+ \text{ OC}_3\text{H}_6\text{OH} + \text{O}_2$	$+ CH_3O + O_2$	$+ CH_3O + O_2$	+ 02	+ 02	$+ C_3 H_5 O$	$+ C_3H_5O$	+ 02	$+ CH_3 + CO_2 + O_2$	+ $OC_3H_6OH+O_2$	$+ C_2 H_3 + CO_2 + O_2$
11 07	>U2H4	>CH ₃ CO ₃ H	$>C_{3}H_{5}O_{2}H$	$>C_{3}H_{5}O_{2}$	J O°H∪<	∕∪п302п 2 0	$> CH_3O_2$	$> 2CH_3$	$> 2C_2H_3$	$>C_3H_5O$	$>C_2H_3CHO$	$>C_6H_{11}O$	$>C_{6}H_{11}OH$	$>C_4H_7O$	$>C_4H_7OH$	$>C_6H_{11}O$	$>C_6H_{11}OH$	$>C_{6}H_{10}O$	$>C_6H_{11}O$	$>C_4H_7O$	$>C_6H_{11}O$	$>C_4H_7O$	$>C_{6}H_{11}O$	$>C_4H_7O$	$>C_6H_{11}O_2H$	$>C_4H_7O_2H$	$>C_6H_{11}O$	$>C_4H_7O$	$>HO_2C_3H_6OH$	$>0C_3H_6OH$	$>0C_3H_6OH$	$>0C_3H_6OH$
	+ HU2	$+ HO_2$	$+ HO_2$	$+ 0_{2}$	т нО. + НО.	+ nu2	$+ 0_{2}$	$+ CH_{3}CO_{3}$	+ C ₂ H ₃ CO ₃	$+ C_{3}H_{5}O_{2}$	$+ C_3 H_5 O_2$	$+ C_6H_{11}O_2$	$+ C_6H_{11}O_2$	$+ C_4H_7O_2$	$+ C_4H_7O_2$	$+ C_4H_7O_2$	$+ C_4H_7O_2$	$+ C_4 H_7 O_2$	$+ C_{3}H_{5}O_{2}$	$+ C_{3}H_{5}O_{2}$	$+ 0_2 C_3 H_6 OH$	$+ O_2 C_3 H_6 OH$	$+ CH_{3}O_{2}$	$+ CH_{3}O_{2}$	$+ HO_2$	$+ HO_2$	$+ C_3H_5$	$+ C_3H_5$	+ O ₂ C ₃ H ₆ OH	$+ CH_3CO_3$	$+ O_2 C_3 H_6 OH$	$+ C_{2}H_{3}CO_{3}$
11 0	C2H3	CH_3CO_3	$C_3H_5O_2$	$C_3H_5O_2H$	CH.O.	CD302	CH_3O_2H	CH_3CO_3	$C_2H_3CO_3$	$C_3H_5O_2$	$C_3H_5O_2$	$C_{6}H_{11}O_{2}$	$C_6H_{11}O_2$	$C_4H_7O_2$	$C_4H_7O_2$	$C_{6}H_{11}O_{2}$	$C_6H_{11}O_2$	$C_6H_{11}O_2$	$C_6H_{11}O_2$	$C_4H_7O_2$	$C_{6}H_{11}O_{2}$	$C_4H_7O_2$	$C_6H_{11}O_2$	$C_4H_7O_2$	$C_6H_{11}O_2$	$C_4H_7O_2$	$C_{6}H_{11}O_{2}$	$C_4H_7O_2$	HO_2	$O_2C_3H_6OH$	$O_2C_3H_6OH$	$0_2 C_3 H_6 OH$
021	T/0	171	172	173	174	1 / 1	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200

 $^{23}\operatorname{Assumed}$ analogous to the corresponding for $\operatorname{C_2H_5O_2}$ [48].

Appendix I: (Continued)

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(Continued)	
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Appendix	

					Α	u	E_{a}	References and Footnotes
201	$O_2C_3H_6OH$	+ HOCH ₂ O ₂	>0C ₃ H ₆ OH	$+ \text{HOCH}_2\text{O} + \text{O}_2$	9.51 E + 07,	, 0	3.87 E + 00	as 178
202	HO_2	+ HOCH ₂ O ₂	>TERM		4.57 E + 07,	0,	-1.09 E + 01	24 as 174
203	$C_3H_5O_2$	+ O ₂ C ₃ H ₆ OH	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
204	$C_3H_5O_2$	+ CH ₃ O ₂	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
205	$C_3H_5O_2$	$+ C_6H_{11}O_2$	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
206	$C_3H_5O_2$	$+ C_4H_7O_2$	>TERM		2.86 E + 06	0,	-3.01 E + 00	24
207	$C_3H_5O_2$	+ HOCH ₂ O ₂	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
208	$O_2C_3H_6OH$	$+ CH_{3}O_{2}$	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
209	$O_2C_3H_6OH$	$+ C_6 H_{11} O_2$	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
210	$O_2 C_3 H_6 OH$	$+ C_4H_7O_2$	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
211	$O_2C_3H_6OH$	+ HOCH ₂ O ₂	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
212	CH_3O_2	+ CH ₃ O ₂	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
213	CH_3O_2	$+ C_6H_{11}O_2$	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
214	CH_3O_2	$+ C_4H_7O_2$	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
215	CH_3O_2	+ HOCH ₂ O ₂	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
216	$C_6H_{11}O_2$	+ $HOCH_2O_2$	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
217	$C_4H_7O_2$	+ HOCH ₂ O ₂	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
218	$HOCH_2O_2$	+ HOCH ₂ O ₂	>TERM		2.86 E + 06,	0,	-3.01 E + 00	24
219	C_3H_5	$+ C_3H_5$	$>C_{6}H_{10}$		1.02 E + 10,	0,	-1.25 E + 00	[29]
220	CH_3	$+ C_3H_5$	$>C_4H_8$		1.00 E + 10,	0,	0.00 E + 00	25
221	C_2H_3	M+ H+	$>C_2H_4$	+M	2.00 E + 11,	0,	0.00 E + 00	[16]
222	C_3H_5	$+ C_{6}H_{11}$	$>C_{9}H_{16}$		1.00 E + 10,	0,	0.00 E + 00	25
223	C_3H_5	+ $CH_3cC_5H_8$	$>C_{9}H_{16}$		1.00 E + 10,	0,	0.00 E + 00	25
224	C_6H_{11}	$+ C_{6}H_{11}$	$>C_{12}H_{22}$		1.00 E + 10,	0,	0.00 E + 00	25
225	C_6H_{11}	$+ CH_3cC_5H_8$	$>C_{12}H_{22}$		1.00 E + 10,	0,	0.00 E + 00	25
226	$CH_3cC_5H_8$	$+ CH_3cC_5H_8$	$>C_{12}H_{22}$		1.00 E + 10,	, 0	0.00 E + 00	25
227	$CH_3cC_5H_8$		$>C_{6}H_{11}$		2.33 E + 0.8,	, 0	2.89 E + 01	15
228	$C_{6}H_{11}O_{2}$		$>C_6H_{11} + O_2$		1.20 E + 15,	0,	1.19 E + 02	21
229	$C_4H_7O_2$		$>C_4H_7 + O_2$		4.31 E + 14,	0,	1.13 E + 02	21
230	CH_2OH	$+ C_3H_5$	$>C_4H_7OH$		1.00 E + 10,	,0	0.00 E + 00	25
24] to th: ^{25 E}	Permination reac at for the C ₂ H ₅ latimate.	tions for peroxy rad D2 self reaction [4	licals that have not 8].	been explicitly given are i	included without de	fining th	e products, with a	rate constant corresponding

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