# Formation of $C_3H_6$ from the Reaction $C_3H_7 + O_2$ and $C_2H_3Cl$ from $C_2H_4Cl + O_2$ at 297 K

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The generation of conjugate olefins from the reactions of propyl (reaction 1) or chloroethyl (reaction 2) radicals with O<sub>2</sub> has been investigated as a function of total pressure (0.4-700 Torr) at 297  $\pm$  2 K. The experiments were carried out by UV irradiation of mixtures of propane (or ethyl chloride), Cl<sub>2</sub>, and O<sub>2</sub> to generate alkyl radicals. Propylene from reaction 1 was measured by FTIR spectroscopy, while vinyl chloride from reaction 2 was monitored by both FTIR and gas chromatographic analysis. At pressures where the formation of propylperoxy radicals is near the high-pressure limit, the propylene yield from reaction 1 was inversely dependent on total pressure ( $Y_{C3H6} \propto P^{-0.68 \pm 0.03}$ ), proving that it is formed via rearrangement of an excited propylperoxy adduct that can also be stabilized by collision. The vinyl chloride yield decreased from  $0.3 \pm 0.1\%$  at 1 Torr to <0.1% at 10 Torr. Because the formation of chloroethylperoxy radicals is in the fall-off region over this pressure range, the vinyl chloride yield cannot be ascribed unambiguously to an addition-elimination process. The propylene yield from reaction 1 is 2-4 times smaller than the ethylene yield from  $C_2H_5 + O_2$  over the pressure range 0.4–100 Torr, while the vinyl chloride yield from reaction 2 is 40 times smaller between 1 and 10 Torr. This is consistent with more efficient stabilization of the excited propylperoxy relative to the ethylperoxy adduct caused by the presence of additional vibrational modes. The markedly smaller ambient temperature vinyl chloride yield from reaction 2 may result from a combination of more efficient stabilization resulting from the lower frequency of the C-Cl bond and reduction of the C-H bond reactivity upon Cl substitution.

### Introduction

Detailed experiments<sup>1-5</sup> and calculations<sup>6-9</sup> have been carried out on the reaction of ethyl radicals with O<sub>2</sub> over the past decade. This body of work has shown that at low to moderate temperatures the reaction proceeds via an excited adduct that can either isomerize and decompose to form  $C_2H_4 + HO_2$  or be stabilized by collisions to form C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>. Prior to this work on the mechanism of the  $C_2H_5 + O_2$  reaction, it was typically assumed that the production of C<sub>2</sub>H<sub>4</sub> at elevated temperature occurred by H atom abstraction from C<sub>2</sub>H<sub>5</sub> with a significant activation energy rather than via addition-elimination with little or no activation energy. Thus, a better understanding of this type of reaction is important to the modeling of combustion processes. A similar reaction channel is likely to be active during the oxidation of other alkyl radicals, as inferred by Slagle et al.<sup>10</sup> from the time dependence of  $C_3H_6$  generation during the reaction of O2 with n-propyl radicals at 635 K and 4 Torr total pressure. However, no experiments have been performed as a function of pressure at ambient temperature to verify conclusively the formation of propylene through an excited adduct.

The experiments presented here examine the oxidation of propyl and chloroethyl radicals at 297 K,

$$C_3H_7 + O_2 \rightarrow \text{products}$$
 (1)

$$C_2H_4Cl + O_2 \rightarrow \text{products}$$
 (2)

as a function of total pressure. Particular attention is paid to the pressure dependence of the yields of  $C_3H_6$  and  $C_2H_3Cl$ . The formation of  $C_3H_6$  in a pressure-dependent reaction at ambient temperature near the high-pressure limit of the reaction 1, which is reached below 1 Torr,<sup>10,11</sup> would be a clear indication of a channel that passes through an excited adduct:

$$C_3H_7 + O_2 \rightarrow C_3H_7O_2^* \rightarrow C_3H_6 + HO_2$$
(1a)

$$C_3H_7O_2^* + M \rightarrow C_3H_7O_2 + M$$
(1b)

Similar reaction channels can be written for reaction 2:

$$C_2H_4Cl + O_2 \rightarrow C_2H_4ClO_2^* \rightarrow C_2H_3Cl + HO_2 \quad (2a)$$

$$C_2H_4ClO_2^* + M \rightarrow C_2H_4ClO_2 + M$$
(2b)

The experiments were performed by UV irradiation of mixtures of propane (or ethyl chloride), chlorine, and oxygen. The consumption of reactants by Cl atoms via reactions 3 and 4,

$$Cl_{2} + h\nu \rightarrow Cl + Cl$$

$$Cl + C_{3}H_{8} \rightarrow C_{3}H_{7} + HCl$$
(3)

$$Cl + C_2H_5Cl \rightarrow C_2H_4Cl + HCl$$
(4)

and the formation of products were monitored by FTIR spectroscopy for the propyl radical experiments and by both FTIR and gas chromatography (GC) in the case of the chloroethyl radical. These results extend the data base obtained for the ethyl radical to include a larger hydrocarbon radical and to include an ethyl radical containing a C–Cl bond to explore substituent effects on olefin formation via excited adducts. No estimation of the  $C_3H_6$  yield from the individual, isomeric 1- and 2-propyl radicals or vinyl chloride yield from the 1- and 2-chloroethyl radicals was possible in these experiments.

### Experiment

The FTIR system<sup>12</sup> used to study reactions 1 and 2 consisted of a Mattson Instruments Inc. Sirius 100 FT-IR spectrometer

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TABLE 1: Yield of  $C_3H_6$  from the Reaction  $C_3H_7 + O_2^a$ 

expt	P (Torr)	[C <sub>3</sub> H <sub>8</sub> ] <sub>0</sub> (mTorr)	[Cl <sub>2</sub> ] <sub>0</sub> (mTorr)	[O <sub>2</sub> ] <sub>0</sub> (Torr)	$C_3H_6^b$ yield (%)
А	0.38	22.5	7.4	0.35	$9.7 \pm 1.5$
В	0.49	45.0	15.5	0.43	$9.2 \pm 0.8$
С	0.49	44.7	7.4	0.43	$9.3 \pm 0.8$
D	0.52	89.4	7.7	0.42	$7.8\pm0.8$
Е	0.52	46.3	7.3	0.00	<1
F	1.07	94.6	14.5	0.96	$5.2 \pm 0.3$
G	10	905	129	9.0	$1.21 \pm 0.1$
Н	20	910	132	19.0	$0.76\pm.07$
Ι	100	1830	312	97.8	$0.22 \pm .04$
J	700	910	130	699	< 0.13

<sup>*a*</sup> All data were obtained using the FTIR technique. <sup>*b*</sup> Corrected for secondary consumption and formation of 1- and 2-chloropropane.

interfaced to a 140 L, 2 m long, evacuable Pyrex chamber surrounded by fluorescent BLB lamps. White-type multiple reflection optics were mounted in the reaction chamber to provide a total path length of 26.6 m for the IR analysis beam. The spectrometer was operated at a resolution of  $0.25 \text{ cm}^{-1}$ . Infrared spectra were derived from 32 coadded interferograms. Reagents and products were quantified by fitting reference spectra of the pure compounds to the observed product spectra using integrated absorption features. Reference spectra were obtained by expanding known volumes of the reference materials into the long path-length cell. C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>5</sub>CHO, CH<sub>3</sub>-COCH<sub>3</sub>, 1-C<sub>2</sub>H<sub>5</sub>OH, 2-C<sub>2</sub>H<sub>5</sub>OH, C<sub>2</sub>H<sub>3</sub>Cl, and C<sub>2</sub>H<sub>5</sub>Cl were identified and quantified using features over the wavelength ranges 850-950, 1200-1600, 800-1800, 900-1300, 800-1500, 800-1000, and 900-1350 cm<sup>-1</sup>, respectively. Systematic uncertainties associated with quantitative analyses using these reference spectra are estimated to be <10%. Experiments were performed at 0.4-700 Torr by irradiating mixtures of  $C_3H_8$ (or  $C_2H_5Cl$ ),  $Cl_2$ , and  $O_2$ .

Consumption of  $C_3H_8$  and formation of products were determined after each of several successive irradiations for a single reactant mixture. Typically, 5–20% of the initial  $C_3H_8$  concentration was consumed by reaction with Cl atoms. The yields of the products were then determined from the slopes of plots of product concentration vs  $C_3H_8$  consumed. Corrections were made for secondary consumption of the products by Cl using known rate constants:  $C_2H_5CHO$  (1.1 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>);<sup>13</sup> 1-C<sub>3</sub>H<sub>7</sub>OH (1.4 × 10<sup>-10</sup>);<sup>13,14</sup> 2-C<sub>3</sub>H<sub>7</sub>-OH (8.6 × 10<sup>-11</sup>);<sup>14</sup> C<sub>3</sub>H<sub>6</sub> (pressure dependent<sup>15</sup>);  $C_3H_8$  (1.43 × 10<sup>-10</sup>).<sup>16</sup>

The second system, used only to study reaction 2, consisted of a cylindrical, 80 cm<sup>3</sup> Pyrex reactor 20 cm in length. It was irradiated by a single Sylvania F6T5 BLB fluorescent lamp, whose intensity peaks at 360 nm. The reactants were premixed in a separate flask, and the reactor was filled to the desired pressure. The mixture was then irradiated for a predetermined time after which the contents of the reactor were analyzed by gas chromatography (GC) using flame-ionization detection; consumption of C<sub>2</sub>H<sub>5</sub>Cl varied from 35% to >90%. There was no discernible impact of degree of consumption on the measured rate constant ratios.

Initial conditions for the study of reaction 1 using the FTIR apparatus are presented in Table 1. Table 2 presents the conditions for reaction 2 using both FTIR and GC techniques. Also included in the tables are the olefin yields derived at each pressure. As described above, the FTIR data were obtained from several successive irradiations during each experiment, and error limits including both statistical  $(2\sigma)$  and systematic uncertainties are quoted for each ratio. Only single points are available for each GC experiment.

TABLE 2: Yield of  $C_2H_3Cl$  from the Reaction  $C_2H_4Cl + O_2{}^a$ 

expt	P (Torr)	[C <sub>2</sub> H <sub>5</sub> Cl] <sub>0</sub> (mTorr)	[Cl <sub>2</sub> ] <sub>0</sub> (mTorr)	[O <sub>2</sub> ] (Torr)	$\begin{array}{l} [C_2H_5Cl] / \\ [C_2H_5Cl]_0 \end{array}$	C <sub>2</sub> H <sub>3</sub> Cl <sup>c</sup> yield (%)
a b c d $e^b$ f <sup>b</sup> g h i j k	$ \begin{array}{r} 1.05\\ 1.04\\ 1.03\\ 1.08\\ 1.1\\ 2.4\\ 10.2\\ 10.5\\ 10.4\\ 10.6\\ 10.7\\ \end{array} $	8.7 8.7 8.8 260 210 84 85 85 96 96	$ \begin{array}{c} 10.5 \\ 10.5 \\ 10.5 \\ 10.6 \\ 62 \\ 67 \\ 100 \\ 102 \\ 102 \\ 110 \\ 110 \\ 110 \end{array} $	$\begin{array}{c} 1.03\\ 1.02\\ 1.01\\ 1.06\\ 0.80\\ 2.2\\ 10\\ 10.3\\ 10.1\\ 10.4\\ 10.5\\ \end{array}$	0.62 0.31 0.026 0.33 0.73 0.65 0.64 0.43 0.075 0.60 0.33	$\begin{array}{c} 0.25\\ 0.29\\ 0.22\\ 0.5\pm 0.2\\ <0.2\\ <0.1\\ <0.1\\ <0.1\\ <0.1\\ <0.08\end{array}$

<sup>*a*</sup> All data obtained using the GC technique unless noted otherwise. <sup>*b*</sup> Obtained using FTIR technique. <sup>*c*</sup> Corrected for secondary consumption.<sup>24</sup>



**Figure 1.** Plot of  $C_3H_6$  formed, corrected for secondary consumption by Cl, as a function of  $C_3H_8$  consumed via  $O_2$  reaction with propyl radicals using FTIR analysis. Data for runs G, H, and I in Table 1 are shown.

## Results

 $C_3H_7 + O_2$ . Figures 1 and 2 present plots of  $C_3H_6$  formation versus propane consumption via reaction with O<sub>2</sub> for representative data spanning the full range of total pressures tested. The propylene concentrations have been corrected for secondary consumption by Cl atoms using the rate constants presented above. The corrections ranged from 1 to 2% at 0.5 Torr to 5-10% at 100 Torr. In addition, corrections have been applied to the C<sub>3</sub>H<sub>8</sub> consumed to account for the fact that a small amount of the propyl radicals formed in reaction 3 react with molecular chlorine to form propyl chlorides rather than with O<sub>2</sub>. This correction was calculated from the measured ratio of the rate constants for reaction of 2-propyl radicals with Cl<sub>2</sub><sup>17</sup> relative to that with  $O_2^{11}$  ( $k_{C12}/k_{O2} = 4$ ). Although measurements for 1-propyl radicals are not available, the ratio for 1-propyl was assumed to be identical with that for 2-propyl radicals. This assumption is reasonable based on recent measurements for 1-butyl and 2-butyl radicals in which the rate constant ratio for Cl<sub>2</sub> reaction relative to that for O<sub>2</sub> reaction was observed to be identical for both isomers (=3).<sup>16</sup> Formation of propyl chlorides accounts for 15% of the total C<sub>3</sub>H<sub>8</sub> consumption for run B in Table 1 and less than 7% for all other experiments.

In all cases, the corrected concentration of  $C_3H_6$  increases linearly with  $C_3H_8$  consumption, indicating that  $C_3H_6$  is a primary product and that unwanted secondary reactions are absent. Run E in Table 1 was performed in the absence of  $O_2$ ,



Figure 2. Plot of  $C_3H_6$  formed, corrected for secondary consumption by Cl, as a function of  $C_3H_8$  consumed via  $O_2$  reaction with propyl radicals using FTIR analysis. Data for runs C and F in Table 1 are shown.

and no  $C_3H_6$  is observed. This proves that  $C_3H_6$  is formed by a reaction of  $C_3H_7$  with  $O_2$ . Runs A–D were performed at different initial reactant concentrations at nearly the same initial pressure. The fact that the  $C_3H_6$  yields from these experiments are identical within experimental error indicates that unknown reactions with reactants do not affect the results significantly.

Figure 3 presents the yields of all measurable products for experiment G at 10 Torr. The major products are oxygenated species formed from the 1- and 2-propyl radicals produced by reaction 3. These oxygenated products are formed by reactions involving alkylperoxy and alkoxy radicals such as the following (plus cross reactions between 1- and 2-peroxypropyl radicals):

$$\begin{aligned} 1-C_{3}H_{7}(\text{ or } 2-C_{3}H_{7}) + O_{2} &\rightarrow 1-C_{3}H_{7}O_{2} \text{ (or } 1-C_{3}H_{7}O_{2}) \\ 1-C_{3}H_{7}O_{2} + 1-C_{3}H_{7}O_{2} &\rightarrow 1-C_{3}H_{7}O + 1-C_{3}H_{7}O + O_{2} \\ &\rightarrow C_{2}H_{5}CHO + n-C_{3}H_{7}OH + O_{2} \\ 1-C_{3}H_{7}O + O_{2} &\rightarrow C_{2}H_{5}CHO + HO_{2} \\ 1-C_{3}H_{7}O_{2} + HO_{2} &\rightarrow 1-C_{3}H_{7}OOH + O_{2} \\ 2-C_{3}H_{7}O_{2} + 2-C_{3}H_{7}O_{2} &\rightarrow 2-C_{3}H_{7}O + 2-C_{3}H_{7}O + O_{2} \\ &\rightarrow (CH_{3})_{2}CO + i-C_{3}H_{7}OH + O_{2} \\ 2-C_{3}H_{7}O + O_{2} &\rightarrow (CH_{3})_{2}CO + HO_{2} \\ 2-C_{3}H_{7}O_{2} + HO_{2} &\rightarrow 2-C_{3}H_{7}OOH + O_{2} \end{aligned}$$

No standard FTIR spectra were available for the hydroperoxides. Therefore, the yield of hydroperoxides was estimated from the broad residual IR feature centered near 3600 cm<sup>-1</sup>, which is characteristic of both CH<sub>3</sub>OOH and C<sub>2</sub>H<sub>5</sub>OOH and represents the sum of 1- and 2-C<sub>3</sub>H<sub>7</sub>OOH. The total hydroperoxide concentration was estimated from the average of the integrated absorption coefficients of CH<sub>3</sub>OOH and C<sub>2</sub>H<sub>5</sub>OOH in our reference library, which differ by only 20% and have nearly identical spectral shape. The concentration of 1-C<sub>3</sub>H<sub>7</sub>-Cl could not be measured because its intensity was below the detectability limit. We estimate its concentration from the



Figure 3. Product yields, corrected for secondary consumption by Cl, plotted as a function of total  $C_3H_8$  consumed for run G in Table 1.



**Figure 4.**  $C_3H_6$ ,  $C_2H_4$ , and  $C_2H_3Cl$  yields, corrected for secondary consumption by Cl, formed by alkyl radical reactions with  $O_2$  for  $C_3H_7 + O_2$ ,  $C_2H_5 + O_2$ , and  $C_2H_4Cl + O_2$ , respectively. Olefin yields are plotted as a function of total pressure. A downward arrow attached to a point indicates an upper limit. Open symbols are obtained by FTIR; filled symbols for  $C_2H_3Cl$  are determined by GC.

known yield of 1- and 2-propyl radicals from reaction 3 [43% and 57%, respectively<sup>16</sup>] and the measured 2-chloropropane yield. The carbon balance (=108 ± 8)% is satisfactory, particularly in light of the fact that the hydroperoxide concentration was not calibrated directly. The ratio of the sum of the products that can be identified as arising from 1-propyl radicals (propionaldehyde, 1-propanol, 1-chloropropane) to that from 2-propyl radicals (acetone, 2-propanol, and 2-chloropropane) is 1-propyl/2-propyl =  $1.04 \pm 0.16$ . The ratio determined in ref 16 is  $0.75 \pm 0.07$ . The two values deviate by somewhat more than the combined experimental errors. However, data for the individual hydroperoxides are not available, and these species represent 23% of the total products. Thus, overall, the agreement in the ratio of 1- to 2-propyl radical products with the ratio from ref 16 is reasonable.

All measurements of the yield of  $C_3H_6$  from reaction 1 are presented in Figure 4 as a function of total reactor pressure over the range 0.4–100 Torr. At 700 Torr, the  $C_3H_6$  yield is below the detectability limit of 0.1%. The  $C_3H_6$  yield displays a negative pressure dependence that is proportional to  $P^{-(0.68\pm0.03)}$ over the entire pressure range. This dependence is similar to that observed for the corresponding ethyl radical reaction,  $P^{(-0.8\pm0.1).3}$  As noted earlier, the overall rate of reaction 1 is essentially independent of pressure for pressures above 0.5 Torr.<sup>10,11</sup> Therefore, the negative pressure dependence of the  $C_3H_6$  yield from reaction 1 cannot result from competition between a pressure-dependent O<sub>2</sub> addition channel to form propylperoxy radicals and a pressure-independent abstraction channel to form  $C_3H_6 + HO_2$ . Instead, these pressure-dependent data are consistent with  $C_3H_6$  formation via an excited adduct as deduced for the ethyl + O<sub>2</sub> reaction.

To obtain a direct comparison of the ethylene yield from reaction 5

$$C_2H_5 + O_2 \rightarrow \text{products}$$
 (5)

to the propylene yield from reaction 1, the yield of ethylene from reaction 5 was remeasured at several pressures. These results are also plotted in Figure 4. The ethylene yields are approximately 25-30% higher than those in ref 3 for pressures of 10 Torr and below. The data at 150 Torr agree very well with measurements presented at this pressure in refs 3 and 5. Thus, the ethylene yield data taken over a period of 6 years agree satisfactorily within the  $\pm 15\%$  data scatter of the measurements.

The yield of propylene from reaction 1 is a factor of 2-4times smaller that of ethylene from the  $C_2H_5 + O_2$  reaction over the pressure range studied. We do not believe that this difference can be ascribed to a difference in C-H bond strengths in these radicals, since the strength of the secondary C-H bond in the excited propylperoxy radical adduct will be weaker than the primary bond in ethylperoxy. Thus, excited 1-propylperoxy radicals should form propylene via intramolecular H atom abstraction from the secondary C-H bond at a rate that is at least 2/3 the rate for ethylene from excited ethylperoxy radicals based on the number of available H atoms. Excited 2-propylperoxy radicals might be expected to produce propylene at twice the rate that is observed for ethylene production during the reaction of ethyl radicals with O<sub>2</sub> because there are six available H atoms in the two adjacent methyl groups instead of three. Thus, based on these arguments, the propylene yield from reaction 1 might be expected to be larger than the ethylene yield from reaction 5, opposite to the trend observed.

A plausible explanation for the reduced olefin generation from propyl radicals may lie in the larger number of vibrational modes available in the propylperoxy radicals. These additional modes can lead to more efficient stabilization of the excited adduct via reaction 1b, reducing its steady-state concentration. This will decrease the rate of formation of  $C_3H_6$  via reaction 1a relative to generation of  $C_2H_4$  from an excited  $C_2H_5O_2$  adduct. The addition of Cl to  $C_3H_6$  in the low-pressure regime is a factor of 30 larger than that for Cl addition to ethylene,<sup>15</sup> illustrating the increased stabilization efficiency for the excited chloropropyl relative to chloroethyl radicals. Increased stabilization may also occur for propylperoxy relative to the ethylperoxy radicals.

 $C_2H_4Cl + O_2$ . The chloroethyl radical is formed in our experiments by reactions 4a and 4b:

$$Cl + C_2H_5Cl \rightarrow CHClCH_3 + HCl (82\%)$$
 (4a)

$$Cl + C_2H_5Cl \rightarrow CH_2ClCH_2 + HCl(18\%)$$
 (4b)

The 1-chloroethyl radical is the major product from reaction 4 with a yield of 82%.<sup>18,19</sup> The rate constants measured by absolute and relative rate methods are  $k_4 = [(8.04 \pm 0.57) \times$ 

 $10^{-12}$ ]  $^{20}$  and [(8.7  $\pm$  1.0)  $\times$   $10^{-12}$ ]  $^{19}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. The rate constants for reactions 4a and 4b are 9 and 40 times smaller than that of Cl + C<sub>2</sub>H<sub>6</sub> (=(5.9  $\pm$  0.5)  $\times$  10<sup>-11</sup>),  $^{21}$  indicating a much lower reactivity for the H atoms in ethyl chloride, caused by the presence of the Cl atom as discussed by Tschuikow-Roux et al.<sup>22</sup>

Table 2 presents the experimental conditions and measured yields of vinyl chloride from reaction 2 using both FTIR and GC detection. For this reaction, the measured olefin yield is near the detection limit and the estimated uncertainties are large for both experimental techniques. Measured yields or upper limits to the yields of vinyl chloride for pressures between 1 and 10 Torr are presented in Figure 4. The yield does exhibit a negative dependence on pressure, decreasing from  $0.3 \pm 0.1\%$ at 1 Torr to <0.1% at 10 Torr, but the data are not sufficiently precise to determine the magnitude of this pressure dependence accurately. In this case, the presence of a negative pressure dependence does not verify the presence of vinyl chloride formation via an excited peroxy adduct. This is because reaction 2 is not at its high-pressure limit over this pressure range, decreasing by a factor of 3 between 10 and 1 Torr of He diluent.<sup>23</sup> Thus, even if vinyl chloride is formed by H atom abstraction from the 1-chloroethyl radical, the yield would decrease by a factor of 3 over this pressure range, which is consistent with the observed pressure variation of the vinyl chloride yield to within its large error limits. However, the vinyl chloride yield from reaction 2, which represents an upper limit to the yield via an excited adduct, is much smaller than the olefin yields from the reactions of  $O_2$  with ethyl (reaction 5) or propyl (reaction 1) radicals by factors of 40 and 10, respectively, at 1 Torr total pressure.

A portion of the decrease in the yield of vinyl chloride from an excited chloroethylperoxy adduct might result from the lower vibrational frequency of the C-Cl bond, which can increase the stabilization efficiency of the adduct as discussed above for propylperoxy radicals. However, the low-pressure-limiting rate constant for Cl addition to vinyl chloride is only 3 times faster than that for Cl addition to ethylene.<sup>24</sup> On the basis of the results for this exothermic addition reaction, it would seem unlikely that increased stabilization can explain the entire factor of 40 decrease in olefin yield from reaction 2 relative to that of reaction 5. The decreased rate of intramolecular H atom abstraction from the CH<sub>3</sub> group of the 1-chloroethylperoxy radical, which is the predominant radical formed from reaction 4, may result in large part from the reduced reactivity of the C-H bonds in this group relative to those in the ethylperoxy radical. That these C-H bonds are less reactive is shown by the fact that the rate constant for H atom abstraction by Cl from ethyl chloride at the 2 position is a factor of 20 slower than for abstraction from a methyl group in CH<sub>3</sub>.

#### Discussion

The propylene yield from reaction 1

$$C_3H_7 + O_2 \rightarrow C_3H_7O_2^* \rightarrow C_3H_6 + HO_2$$
(1a)

$$C_3H_7O_2^* + M \rightarrow C_3H_7O_2 + M$$
(1b)

exhibits a strong inverse dependence on total pressure at ambient temperature  $[Y_{C3H6} \propto P^{-0.68\pm0.0.03}]$  over the pressure range 0.4– 700 Torr where reaction 1 is at its high-pressure limit. This observation confirms that propylene is formed via rearrangement and decomposition of an excited propylperoxy adduct (reaction 1a) that competes with the stabilization reaction 1b to form the propylperoxy radical. This result is similar to that observed previously for the ethylene yield from the reaction of ethyl radicals with O<sub>2</sub> [ $Y_{C2H4} \propto P^{-0.8\pm0.1}$ ] and substantiates the suggestion that high-temperature propylene generation from reaction 1 arises from an excited adduct rather than via H atom abstraction. The exponent of the pressure dependence is similar for both ethyl and propyl radicals, but the total olefin yield for reaction 1 is 2-4 times smaller than for that of ethyl radicals with O<sub>2</sub>. As discussed above, it is likely that the reduced olefin yield results from the more efficient stabilization of the propylperoxy radical adduct that is expected to result from the additional vibrational degrees of freedom for propylperoxy relative to ethylperoxy radicals. These experiments confirm the suggestion, made on the basis of time-dependent, high-temperature data, that propylene is formed via an excited adduct rather than hydrogen abstraction.<sup>10</sup>

Because the yield of vinyl chloride from reaction 2 is small, a precise determination of the pressure dependence of the formation of vinyl chloride was not possible:

$$C_2H_4Cl + O_2 \rightarrow C_2H_4ClO_2^* \rightarrow C_2H_3Cl + HO_2 \quad (2a)$$

$$C_2H_4ClO_2^* + M \rightarrow C_2H_4O_2 + M$$
(2b)

The vinyl chloride yield has a negative pressure dependence, but because reaction 2b is in the fall-off region under the conditions of these measurements, the pressure-dependent data cannot determine whether the formation of  $C_2H_3Cl$  occurs via an excited adduct or by H atom abstraction. However, the measured  $C_2H_3Cl$  yield does represent an upper limit to the contribution of reaction 2a. The  $C_2H_3Cl$  yield is smaller than the olefin yields from reactions of ethyl and propyl radicals with  $O_2$  by factors of 40 and 20, respectively. We believe that this large reduction in yield is caused by a combination of increased stabilization of the excited adduct by the lower frequency C–Cl bond and by the reduction in reactivity of the C–H bonds in the chloroethylperoxy radicals.

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