Formation of C_3H_6 from the Reaction $C_3H_7 + O_2$ between 450 and 550 K

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The generation of C_3H_6 from the reaction $C_3H_7 + O_2$ (1) has been investigated as a function both of temperature (450−550 K) at constant density (5.5×10^{18} molecules/cm^3) and of pressure (55−550 Torr) at 490 K. The experiments were carried out by UV irradiation of mixtures of C_3H_8, Cl_2, and O_2 to generate propyl radicals. C_3H_8, C_3H_6, and C_3H_7Cl were monitored by gas chromatographic analysis. The propylene yield is 0.7% at 450 K. Based on these measurements and previous data at 298 K, the propylene yield has an apparent activation energy which is less than 2.5 kcal mol^{-1} below 450 K. Beginning near 450 K, the yield increases rapidly with an apparent activation energy of ∼32 kcal mol^{-1}, similar to previous observations on the generation of C_2H_4 from the reaction $C_2H_5 + O_2$. At 490 K, the propylene yield from reaction 1 depends inversely on total pressure ($Y_{C_3H_6} \propto P^{-0.6}$) between 55 and 550 Torr, while the overall value of k_1 has a much smaller pressure dependence ($P^{0.18}$). These observations show that above 450 K propylene is formed via reaction 1 through an excited propylperoxy adduct which can be stabilized by collision as was observed at 298 K.

Introduction

Detailed experiments[1−5] and calculations[6−9] have been carried out on the reaction of ethyl radicals with O_2 over the past decade. This body of work has shown that at low to moderate temperatures the reaction proceeds via an excited adduct which can either isomerize and decompose to form $C_2H_4 + HO_2$ or be stabilized by collisions to form $C_2H_5O_2$. Temperature-dependent measurements[5] have shown that the yield of ethylene from this reaction has a very weak temperature dependence ($E_a \leq 1$ kcal mol^{-1}) at temperatures below that (450 K) at which the O_2 addition reaction begins to be reversible. Above this temperature, the ethylene yield increases rapidly.

Recent experiments have determined the propylene yield from reaction 1

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

as a function of total pressure at 298 K.[10] The C_3H_6 yield showed a strong inverse pressure dependence at ambient temperature over a pressure range ($P = 0.5−100$ Torr) within which the addition reaction to form $C_3H_7O_2$ is near its high-pressure limit. As discussed in refs 5 and 10, this is a clear indication of a channel that passes through an excited adduct rather than an abstraction reaction:

$$C_3H_7 + O_2 = C_3H_7O_2{}^* = C_3H_6 + HO_2 \qquad (1a)$$

$$C_3H_7O_2{}^* + M = C_3H_7O_2 + M \qquad (1b)$$

Note that if reaction 1 is not near its high-pressure limit and olefin formation is not its major channel, the presence of a pressure-dependent olefin yield does not exclude the existence of an abstraction channel. For example, if reaction 1b is at its low-pressure limit and C_3H_6 is formed via abstraction (which is pressure independent), then the C_3H_6 yield would show an inverse dependence on pressure. This occurs because the olefin yield depends on the rate of the abstraction reaction relative to that of the addition process to form $C_3H_7O_2$. Thus, as the pressure decreases, the rate of (1b) decreases, increasing the olefin yield even if formed via a pressure-independent abstraction channel.

The present publication extends this previous study of reaction 1 to include elevated temperatures (450−550 K) in order to determine whether the propyl radical shows the onset of rapid olefin generation in this temperature range as was observed for the $C_2H_5 + O_2$ reaction. No estimation of the C_3H_6 yield from the individual, isomeric 1- and 2-propyl radicals is possible in these experiments.

Experiment

The experimental apparatus consists of a cylindrical, 80 cm^3, Pyrex reactor, 20 cm in length, enclosed in a tube oven. The reactor was irradiated by a single Sylvania F6T5 BLB fluorescent lamp, whose intensity peaks at 360 nm. The reactants, containing C_3H_8, Cl_2, O_2, and N_2, were premixed in a separate flask, and the reactor was filled with the mixture to the desired pressure. UV irradiation dissociates Cl_2 to form Cl atoms. The Cl atoms subsequently react with C_3H_8 to form 1- and 2-propyl radicals which cannot be distinguished from one another in these experiments:

$$Cl_2 + h\nu = 2Cl$$

$$Cl + C_3H_8 = C_3H_7 + HCl$$

These reactions provide the source of propyl radicals for the study of reaction 1.

The mixture was irradiated for a predetermined time after which the entire contents of the reactor were analyzed by gas chromatography (GC) using flame-ionization detection; consumption of C_3H_8 varied from 6% to 40%. There was no discernible impact of degree of consumption on the measurements. For the experiments in which propylene yields were determined, the mixtures contained 10500 ppm of C_3H_8 and 18 000 ppm of Cl_2, with the balance O_2. Limited measurements of the yields of 1- and 2-chloropropane were carried out with

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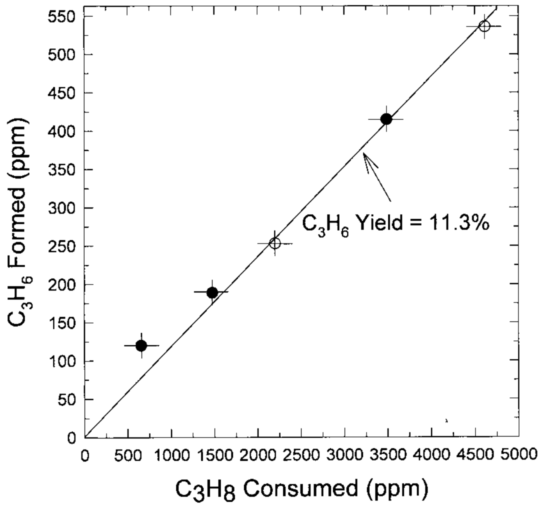

Figure 1. Plot of C_3H_6 formed as a function of C_3H_8 consumed via O_2 reaction with propyl radicals at 512 ± 2 K and 290 Torr. Error limits are shown as lines through the individual points. Open and closed symbols were obtained on separate days. The slope is the "apparent" yield uncorrected for the occurrence of reaction 2; see text. Initial mixture: 10 900 ppm of C_3H_8; 17 900 ppm of Cl_2; balance O_2.

a mixture containing 10 500 ppm of C_3H_8, 18 200 ppm of Cl_2, and 318 000 ppm of O_2 with N_2 balance.

TABLE 1: Yields (in ppm) of Chloropropanes at 490 K[a]

P (Torr)	C_3H_8 consumed	1-C_3H_7Cl	2-C_3H_7Cl	k_1/k_2
550	1660	95	155	0.32
61	1840	160	270	0.19
550	2226	155	285	0.23
275	2045	155	295	0.20
275	3574	260	470	0.22
61	1883	185	325	0.16

[a] Initial concentrations: 10 600 ppm of C_3H_8; 18 200 ppm of Cl_2; 318 000 ppm of O_2; N_2 balance.

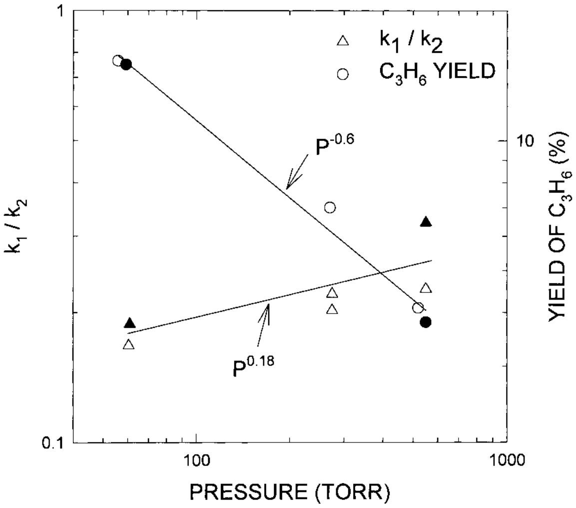

Figure 2. Rate constant ratio (k_1/k_2) presented as a function of total pressure at 490 K (triangles, left axis). Filled and open symbols obtained on different days. Initial mixture for k_1/k_2 experiments: 10 600 ppm of C_3H_6; 18 200 ppm of Cl_2; 318 000 ppm of O_2, balance N_2. Pressure dependence of line = $P^{0.18}$. Yield of C_3H_6 plotted as a function of total pressure at 490 K (circles, right axis). Initial mixtures for C_3H_6 measurements: A (open circles) 10 600 ppm of C_3H_6, 18 200 ppm of Cl_2, 318 000 ppm of O_2, balance N_2; B (filled circles) 10 400 ppm of C_3H_6, 18 000 ppm of Cl_2, balance O_2. Pressure dependence of line = $P^{-0.6}$.

Results

Figure 1 shows the C_3H_6 mole fraction as a function of the C_3H_8 consumed for five experiments on two separate days with different percentages (6−43%) of C_3H_8 consumption at 512 K and 290 Torr total pressure. To within the experimental error, the yield is essentially independent of the percentage of C_3H_8 consumed. This indicates that any uncertainty associated with secondary consumption of C_3H_6 is of the order of the measurement error at this temperature, and no correction for secondary consumption of C_3H_6 has been applied to the measured yields throughout this publication. The Cl + C_3H_6 rate constant (k_3) has not been measured at 512 K. However, at 298 K[11] and a density of 5.5×10^{18} cm^{-3}, $k_3 = 1.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which is slightly larger than that of Cl + C_3H_8 (=1.4×10^{-10}).[12] Because k_3 will decrease as the temperature increases at constant density, the above value of k_3 represents an upper limit to its value at 512 K. Based on these rate constants at 298 K, this correction should be <20%, consistent with the data in Figure 1 in which any correction is of the order of the data scatter.

However, the apparent 11% yield in Figure 1 should be corrected for the formation of small yields of 1- and 2-chloropropane via reaction 2:

$$C_3H_7 + Cl_2 = C_3H_7Cl + Cl \tag{2}$$

since this channel does not involve reaction with oxygen. The yields of the chloropropanes were measured at 490 K; results from experiments at three pressures on two separate days are presented in Table 1. These tabulated yields have been corrected for a small amount of secondary consumption (≤15%) of the chloropropanes by Cl atoms using rate constants determined previously at 298 K.[12] The rate constants at 298 K for reaction of Cl with 1- and 2-chloropropane are fast (4.8×10^{-11} and 20×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively) and will not have a large temperature dependence.

As discussed in the Introduction, to verify that the propylene is being formed via an excited adduct, the pressure dependence of k_1 must be known. The pressure dependence of k_1 can be determined directly from the ratio k_1/k_2 because reaction 2 will have no pressure dependence. The ratio k_1/k_2 can be calculated from the total yield of the chloropropanes (Y_{RCl}), from which can be calculated the total yield of products from O_2 reaction ($1 - Y_{RCl}$) assuming that propyl radicals react only with O_2 or Cl_2, using the known ratio of Cl_2 to O_2 in the initial mixture:

$$k_1/k_2 = \{[Cl_2]/[O_2]\}\{(1 - Y_{RCl})/Y_{RCl}\}$$

The measured ratios are presented in Table 1 and plotted in Figure 2. There is a small increase (50 ± 15%) in the rate constant ratio as the pressure increases by a factor of 10. Because the rate constant for an abstraction reaction such as (2) will not be pressure dependent, this increase must result from a small increase in the rate constant of reaction 1, which is near to but not quite at its high-pressure limit over the pressure range studied at 490 K. The rate constant, k_2, for isopropyl radical reaction with Cl_2 has been measured at 490 K (=4.1×10^{-11} cm^3 molecule^{-1} s^{-1}).[13] Assuming that the rate constant for the *n*-propyl radical reaction with Cl_2 is similar to this value, $k_1 \approx 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 550 Torr, a value which is typical of O_2 addition to alkyl radicals in the high-pressure limit.

The measured rate constant ratio, k_1/k_2, plotted in Figure 2 as a function of pressure at 490 K, can be used to estimate the correction to the apparent C_3H_6 yields caused by reaction 2.

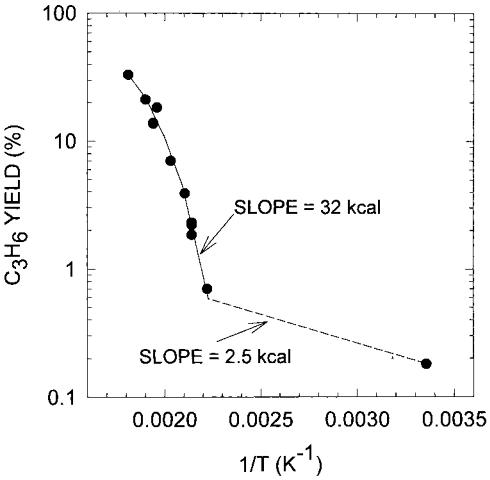

Figure 3. Plot of percentage yield of C_3H_6 as a function of $1/T$ at a constant density [$(5.5 \pm 0.5) \times 10^{18}$ molecules cm^{-3}]. Initial mixture: 10 500 ppm of C_3H_6; 18 000 ppm of Cl_2; balance O_2.

This correction is small (6−9% depending on total pressure) for the ratio $[O_2]/[Cl_2] = 54$ used in the C_3H_6 determinations and has been applied to all C_3H_6 yields presented in the following discussion. The ratio k_1/k_2 is assumed constant over the experimental temperature range.

Figure 3 presents the yields of C_3H_6 (corrected for C_3H_7Cl formation) determined over the temperature range 450−550 K in the current experiments at a total gas density of $(5.5 \pm 0.5) \times 10^{18}$ molecules cm^{-3} of O_2. Also included in Figure 3 is the C_3H_6 yield at this density measured at 298 K in the earlier experiments.[10] The data show a temperature dependence similar to that observed for the ethylene yield from $C_2H_5 + O_2$. For temperatures between 298 and 450 K, the rate of increase in propylene yield is small. No data are available for intermediate temperatures in this range in contrast to the ethyl radical data because the C_3H_6 yield is too small to be measured by the GC in the presence of a large C_3H_8 signal.

Beginning near 450 K, the C_3H_6 yield increases sharply, reaching 35% at 550 K. Again, this observation is similar to that for $C_2H_5 + O_2$. In the ethyl radical case, data obtained in the intermediate temperature range showed that the apparent activation energy for ethylene generation was ≤1 kcal/mol. This value is consistent with the data for reaction 1 presented in Figure 3, for which any activation energy must be less than 2.5 kcal/mol as shown by the line connecting the 298 and 450 K data. At temperatures above 450 K, the propylene yield increases with an apparent initial activation energy of approximately 32 kcal/mol. As demonstrated by chemical kinetic model calculations for the $C_2H_5 + O_2$ reaction in ref 5, this rapid increase in C_3H_6 likely occurs because the reaction forming $C_3H_7O_2$ becomes reversible and can return to reactants ($C_3H_7 + O_2$) above this temperature on the time scale of the experiments. Because of this reversibility, multiple passes through the excited adduct occur, each pass having a small probability of forming C_3H_6. Therefore, the C_3H_6 yield increases above that observed at lower temperature for a single pass. The apparent initial activation energy of approximately 32 kcal/mol is also of the order of the heat of reaction for isopropyl radicals with O_2 to form $C_3H_7O_2$ (=37.8 kcal/mol).[14] This is consistent with the suggestion that the reversibility of reaction 1 plays an important role in the rapid increase of the propylene yield for temperatures above 450 K.

As discussed in ref 10, the formation of propylene from reaction 1 at 298 K must occur via an excited propylperoxy adduct rather than by direct H atom abstraction from propyl radicals. Because reaction 1b is at its high-pressure limit for pressures greater than 1 Torr at ambient temperature, if abstraction were the source of the olefin formation at 298 K, no pressure dependence would be present. However, a strong negative pressure dependence was observed, consistent with a competition between reactions 1a and 1b at 298 K.

To verify that this is also the case at elevated temperature, measurements of the propylene yield were made as functions of pressure (55−550 Torr) at 490 K; the results are presented in Figure 2. The C_3H_6 yields in Figure 2 were obtained at two initial O_2 concentrations; the yield is independent of O_2 as expected. The yield of propylene is strongly pressure dependent, decreasing by a factor of 4 over this pressure range. This represents a $P^{-0.6}$ pressure dependence, similar to the $P^{-0.68}$ observed at 298 K. As discussed above, the rate constant ratio k_1/k_2 increases by approximately 50 ± 15%, indicating that k_1 increases by 50% over this pressure range ($P^{0.18}$). These two sets of results show that propylene cannot be formed primarily by abstraction at 490 K because the pressure dependence of reaction 1 is much smaller than that observed for propylene generation. Therefore, it is likely that, over the entire temperature range studied, propylene arises from the decomposition of an excited propylperoxy radical (reaction 1a). This observation is consistent with conclusions drawn for the ethyl radical at elevated temperature.[6]

Conclusions

Mixtures of C_3H_8, O_2, and Cl_2 have been irradiated with 350 nm UV light to form C_3H_7 radicals, which subsequently react with O_2. The C_3H_6 yields from the $C_3H_7 + O_2$ reaction were measured at pressures between 55 and 550 Torr and temperatures from 450 to 550 K. The C_3H_6 yield depends inversely ($P^{-0.6}$) on the total pressure at 490 K, a temperature at which reaction 1 shows a much smaller pressure dependence ($P^{0.18}$). This observation shows that the propylene is formed through an excited propylperoxy radical at this temperature as has been observed previously at 298 K.[10]

The temperature dependence of the propylene yield is similar to that observed for ethylene formed in the $C_2H_5 + O_2$ reaction, which also is generated through an excited peroxy intermediate.[5] Between 298 and 450 K, the propylene yield increases slowly with an apparent activation energy <2.5 kcal mol^{-1}. Beginning near 450 K, the C_3H_6 yield increases sharply with an apparent activation energy of approximately 32 kcal. This behavior is ascribed to the onset of reversibility in reaction 1, allowing repeated opportunity for C_3H_6 formation with each passage through the excited peroxy intermediate. These results are similar to the temperature dependence observed for $C_2H_5 + O_2$, demonstrating that the influence of excited peroxy radicals in low to intermediate temperature oxidation is not restricted to ethyl radicals.

Note Added in Proof. Because of temperature nonuniformity along the cylinder axis (see ref 5), the average absolute reactor temperature is estimated to be accurate to ±2%; relative temperatures are uncertain to ±0.5%. At 520 K, the C_3H_6 yield in the absence of O_2 is <10% of that observed with O_2 present, verifying that the C_3H_6 is formed by reaction with O_2 as required by reaction 1.

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