Pressure Dependence of the Reaction $Cl + C_3H_6$

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The rate constant for the reaction $Cl + C_3H_6(k_1)$ has been measured relative to that of $Cl + C_2H_6$ over the range 0.3-700 Torr in N₂ at 298 K. UV irradiation was used to generate Cl atoms in mixtures of C_3H_{63} C₂H₆, Cl₂, and N₂ in two different reactors using FTIR or GC analysis. The yields of the two major products, allyl chloride (3-C₃H₅Cl) and 1,2-dichloropropane were measured. k_1 decreases by a factor of 5 between 700 and 1 Torr. Below 1 Torr, the rate constant becomes independent of pressure. The results indicate that k_1 is a composite of three reaction channels, each having a different pressure dependence. Measurement of the yield of 1,2-dichloropropane, the final product formed from the addition of Cl to C_3H_{6} , at each pressure allows a determination of the rate constant (k_{1a}) for the addition of Cl to C_3H_6 . Assuming a typical center broadening factor ($F_c = 0.6$), the high- and low-pressure limiting constants are calculated to be $k_{1a}(\infty) = (2.7)$ ± 0.4) $\times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ and $k_{1a}(0) = (4.0 \pm 0.4) \times 10^{-28}$ cm⁶ molecule⁻² s⁻¹. The pressure dependence of the yield of 3-C₃H₅Cl indicates that the allyl radical is likely formed by both abstraction and addition-elimination channels. The rate constant of the abstraction reaction from the methyl radical in C_3H_6 is $(2.3 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. At pressures below 10 Torr, the rate constant for formation of the allyl radical increases by 50%, and this is ascribed to an addition-elimination process. Relative rate constant ratios were also measured for Cl atom reactions with allyl chloride (k_6) and 1,2-dichloropropane (k_7) relative to C_3H_6 , C_2H_5Cl , or CH_3Cl to correct the product yield experiments for secondary consumption. The observed values of k_6/k_1 are 0.75 for total pressures of 10–700 Torr, 0.44 at 1 Torr, and 0.33 at 0.4 Torr. On the basis of the relative rate measurements $k_7 = (3.9 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 1-700 Torr.

Introduction

The kinetics of Cl atom reactions with hydrocarbons have been a topic of considerable interest.¹⁻⁴ Most measurements have been performed using saturated hydrocarbons and represent determinations of rate constants for hydrogen abstraction reactions. Ethylene⁵ and acetylene^{5,6} are the only two hydrocarbons for which the addition of atomic chlorine to a carboncarbon multiple bond has been studied in detail as a function of total pressure. We present here results of an experimental study of the pressure dependence of the reaction of Cl atoms with propylene. These experiments include measurement of the overall rate constant relative to that of the reaction of Cl atoms with ethane in N₂ diluent and a determination of the yields of the two major products (vinyl chloride and 1,2-dichloropropane) formed by reaction of alkyl radicals with Cl₂:

$$\mathrm{Cl} + \mathrm{C}_{3}\mathrm{H}_{6}\left(+\mathrm{M}\right) =$$

$$CH_3CHClCH_2$$
 (or CH_3CHCH_2Cl) (+M) (1a)

$$Cl + C_3H_6 = CH_2CHCH_2 + HCl$$
(1b)

$$Cl + C_2H_6 = C_2H_5 + HCl$$
 (2)

Such a study permits a determination of the effect of additional internal degrees of freedom on the low-pressure limiting rate constant for addition of chlorine atoms to double bonds by comparing the rate constant of reaction 1a to that of ethylene, a smaller olefin. In addition, the rate constant of the abstraction reaction from the methyl group in propylene (reaction 1b) was measured.

Experiment

Two experimental setups were used; both have been described previously. The first system⁷ consisted of a Mattson Instruments

Inc. Sirius 100 FTIR spectrometer 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 cm⁻¹. Infrared spectra were derived from 32 co-added 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. C₃H₆, C₂H₆, 1,2-C₃H₆Cl₂, 3-C₃H₅Cl, CH₃Cl, and C₂H₅Cl were identified and quantified using features over the following wavelength ranges: 800-1700, 780-860, 600-1500, 650-1600, and 650-1350 cm⁻¹, respectively. Systematic uncertainties associated with quantitative analyses using these reference spectra are estimated to be <10%. The second system consisted of a spherical, 1-L, Pyrex reactor which 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.

The rate of reaction 1 was measured relative to the abstraction reaction of Cl atoms with C_2H_6 (reaction 2, $k_2 = (5.9 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹).⁶ Experiments were performed over the pressure range 0.3–700 Torr by irradiating mixtures of C_3H_6 , C_2H_6 , and Cl_2 in N_2 diluent.

In the FTIR experiments, the consumptions of C_3H_6 and the reference compound were determined after each of several successive irradiations for a reactant mixture. Typically, 30–90% of the initial reactant concentration was consumed. The relative rate constants (e.g. k_1/k_2) were then obtained from the

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Figure 1. Plot of the consumption of propylene relative to that of ethane at four total pressures using the FTIR system. Open symbols = N_2 diluent; filled symbols = air diluent. Rate constant ratios, k_1/k_2 : 0.85 ± 0.05 at 1.26 Torr; 1.29 ± 0.10 at 5 Torr; 2.34 ± 0.12 at 50 Torr; 4.54 ± 0.21 at 700 Torr.

TABLE 1: Initial Conditions for FTIR and GC Measurements of k_1

P (Torr)	$\frac{[C_{3}H_{6}]}{[C_{3}H_{6}]_{0}}$	$[Cl]_{ss}^{a}$ (cm^{-3})	Cl ₂ (mTorr)	[C ₃ H ₆] ₀ (mTorr)	[C ₂ H ₆] ₀ (mTorr)	k_1/k_2
0.33^{b}	0.27	5×10^7	25.1	8.7	8.4	0.67
0.7^{c}	0.8 - 0.2	3×10^9	252	76.0	28.1	0.80 ± 0.05
1.2^{c}	0.9 - 0.2	5×10^9	240	76.0	38.5	0.85 ± 0.05
1.01^{b}	0.29	4×10^7	15.5	6.2	5.4	0.86
5.0^{c}	0.9-0.3	3×10^9	240	76.0	34.0	1.29 ± 0.10
10.2^{b}	0.65	$1.6 imes 10^8$	160	51.9	51.9	1.5
50.0°	0.9 - 0.5	3×10^{9}	220	76.0	45.4	2.34 ± 0.12
126 ^b	0.26	1.3×10^8	2000	640	640	3.07
620^{b}	0.72	7×10^7	725	363	210	4.65
700 ^c	0.96 - 0.60	7×10^8	187	76.0	35.1	4.54 ± 0.21

 a Steady state Cl atom concentration calculated from the time dependence of the C_2H_6 decrease. b GC data. c FTIR data.

slopes of plots of $\ln\{[C_3H_6]_0/[C_3H_6]_t\}$ vs $\ln\{[C_2H_6]_0/[C_2H_6]_t\}$ over the consumption range. In all cases, straight lines were obtained extending through the origin, indicating the absence of unwanted secondary reactions. Data for the FTIR experiments are shown in Figure 1 for several pressures. At 700 Torr of total pressure, measurements were performed using N₂ (open circles) or air (filled circles) diluents. As seen in Figure 1, the results obtained using N₂ or air diluent are indistinguishable, suggesting that neither products nor intermediate radicals affect the results.

During the GC measurements, the experiment was ended at a chosen time and the contents were analyzed; consumptions of C_3H_6 varied from 15 to 80%. There was no discernable impact of the degree of consumption on the measured rate constant ratios.

Initial reactant concentrations varied substantially between the FTIR and GC experiments, providing verification that the measured rate constants do not depend on mixture composition. Examples of selected initial conditions studied by FTIR and GC are presented in Table 1 for data obtained over the pressure range 0.3-700 Torr. Also included in the table are the rate constant ratios derived at each pressure. As described above, the FTIR data were obtained from several successive irradiations during each experiment, and a statistical error (2σ) for each ratio is quoted. Only single points are available for each GC experiment (see Table 1).



Figure 2. Plot of the rate constant ratio k_1/k_2 as a function of total pressure.

Results

Determination of k_1 **.** Figure 2 presents measurements of k_1/k_2 as a function of total pressure obtained using both GC and FTIR techniques. The results for both techniques agree over the full pressure range. There have only been two previous measurements of k_1 , both near 1 atm. Our ratio at 700 Torr (4.56 ± 0.13) can be compared to that determined for propylene relative to *n*-butane (1.24 ± 0.037) at 760 Torr by Atkinson and Aschmann.⁸ Using the rate constant ratio derived recently for *n*-butane relative to ethane ($k_{n-butane}/k_{ethane} = (3.76 \pm 0.20)$,⁴ Atkinson and Aschmann's measurement can be converted to ethane as reference (= 4.66 ± 0.30), in excellent agreement with our measurement. The second measurement of k_1 was also made relative to *n*-butane and yields a slightly higher ratio when corrected to ethane as the reference species (5.39 ± 0.37).⁹

As shown in Figure 2, the rate constant ratio k_1/k_2 depends on pressure, decreasing as the pressure decreases. Because k_2 is independent of pressure, as shown by absolute rate measurements spanning the pressure range 1-60 Torr,^{2,4,10,11} the decrease in the rate constant ratio results from the expected fall off in the rate constant of the addition reaction, k_{1a} . The fall off in the rate constant ratio relative to ethane for the addition of Cl to both ethylene and acetylene continues to the lowest pressures attainable within experimental error.⁵ For example, the rate constant ratios for ethylene and acetylene relative to ethane at 1 Torr are 200 and 300 times smaller than at 700 Torr, respectively. For propylene, k_1/k_2 is only 5.5 smaller at 1 Torr than at 700 Torr (see Figure 2), indicating that the decrease in the rate constant for the reaction of Cl with propylene is much less pronounced over this pressure range than is observed for either ethylene or acetylene. Part of the reason for the smaller pressure dependence is the presence of an exothermic ($\Delta H = -17$ kcal mol⁻¹), pressure-independent, abstraction channel (1b) for propylene which does not exist for either ethylene or acetylene. This channel dominates reaction 1 at lower pressures, causing k_1/k_2 to approach an asymptote.

Product Yields from Reaction 1. On the basis of the above interpretation of the pressure dependence of the rate constant ratio, the product yields should change markedly as the pressure changes. At high pressures, the addition reaction dominates and the major product should be CH₂ClCH₂ClCH₃ (1,2-dichloropropane) formed by reactions 3 and 4. Reactions 3 and

 $CH_2CICHCH_3 + Cl_2 = CH_2CICHCICH_3 + Cl \qquad (3)$

$$CH_2CHClCH_3 + Cl_2 = CH_2ClCHClCH_3 + Cl \qquad (4)$$

4 should be fast, based on the typical rates of exothermic reactions of alkyl radicals with molecular chlorine ($k \approx (0.2-5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹), and will be the dominant sink for the chloropropyl radicals formed by reaction 1a. At low pressures, reaction 1b will become significant and the major product will be CH₂ClCH=CH₂ (allyl chloride) formed by reaction 5. The rate constant k_5 has been measured¹² over the

$$CH_2CHCH_2 + Cl_2 = CH_2ClCH = CH_2 + Cl \qquad (5)$$

temperature range 487–693 K. Using the Arrhenius expression derived from these data, $k_5(298 \text{ K}) = 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Reaction 5 is much slower than typical alkyl radical reactions with Cl₂. The reaction of allyl radicals with O₂ has a substantially faster rate constant (=1.6 × 10⁻¹³ at 2.8 Torr [348 K]¹³ and 6 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ at 700 Torr [298 K]¹⁴) than that of the reaction of allyl radicals with Cl₂. Therefore, in the determination of k_{1b}/k_1 by measuring the allyl chloride yield, oxygen must be carefully excluded so that reaction 5 is the major reaction channel for allyl radicals.

During the determination of product yields, the measured yield of a product must be corrected for secondary consumption of that product by Cl after it is formed. To make this correction, the rate constants for the reactions of $3-C_3H_5Cl$ (allyl chloride) and $1,2-C_3H_6Cl_2$ with Cl atoms were determined by the relative rate technique using both the FTIR and GC methods.

The rate constant of the reaction of allyl chloride with Cl atoms,

$$Cl + CH_2ClCH = CH_2 = products$$
 (6)

was measured relative to k_1 at five pressures between 0.4 and 700 Torr. The GC experiments were performed in N2 diluent, and corrections were made to account for allyl chloride formation from C_3H_6 . The ratio of the initial C_3H_6 to that of allyl chloride was ≈ 0.05 , and these corrections were always small (<5% of the allyl chloride consumption). The FTIR experiments were performed in air, and no correction was necessary since the allyl radical formed in reaction 1b reacts with O_2 rather than Cl_2 . The values of k_6/k_1 determined in these experiments are presented in Figure 3. Above 10 Torr the ratio is essentially independent of pressure because, as will be shown later, reaction 1 is dominated by the addition channel in this pressure range. This should be the case for reaction 6 also, and both the absolute values and the pressure dependence of the rate constants for these addition reactions are very similar above 10 Torr. However, below 10 Torr, k_6/k_1 decreases with pressure. This indicates that the rate constant for the abstraction reaction from the chloromethyl group in allyl chloride is likely to be smaller than that of the methyl group in propylene. As a result, k_6 continues to decrease as the pressure is decreased from 10 to 0.4 Torr rather than approaching the asymptote of reaction 1. This is consistent with the previous observation that ethyl chloride reacts much more slowly with Cl than does ethane. The rate of hydrogen atom abstraction from the chlorinated methyl group in ethyl chloride is 4.5 times slower than attack at one of the methyl groups in ethane.¹⁵ By analogy, the rate constant for H atom abstraction from the chloromethyl group in allyl chloride might be expected to be substantially smaller than that from the methyl group in propylene, consistent with the data in Figure 3.



Figure 3. Plot of the rate constant ratio k_6/k_1 as a function of total pressure.

TABLE 2: Product Yields

pressure (Torr)		$\frac{[C_{3}H_{6}]}{[C_{3}H_{6}]_{0}}$	carbon balance (%)	3-C ₃ H ₅ Cl yield ^a (%)	1,2-C ₃ H ₆ Cl ₂ yield ^a (%)
700	FTIR	0.99-0.4	91 ± 6	8.1 ± 0.6	83 ± 5
640	GC	0.19	95.5	8.4	87.1
220	GC	0.30	93.6	10.9	82.8
220	GC	0.53	100.3	11.9	88.4
105	GC	0.38	97.6	15.3	82.3
100	FTIR	0.88 - 0.6	106 ± 6	16.9 ± 1.2	89 ± 5
93	GC	0.56	101.5	14.0	87.5
30	FTIR	0.63 - 0.4	109 ± 8	28 ± 3	81 ± 5
10.7	GC	0.18	89.5	34.7	54.8
10.2	FTIR	0.83 - 0.5	110 ± 9	43 ± 4	67 ± 5
1.46	FTIR	0.96 - 0.5	104 ± 9	71 ± 6	33 ± 3
1.0	GC	0.52	87.6	66.7	20.9
1.0	GC	0.20	95.8	75.3	20.5
0.4	GC	0.40	94.1	82.8	11.3
0.3	GC	0.67	91.6	84.1	7.5

^{*a*} The product yields presented in this table are the yields obtained after correcting the measured concentrations for secondary consumption by Cl atoms.

The rate constant for reaction of Cl atoms with 1,2dichloropropane (k_7) was determined using the relative rate technique with both GC and FTIR systems. The GC experiments were carried out in N2 at 1 Torr relative to C3H6, yielding the ratio k_7/k_1 (1 Torr) = 0.093 \pm 0.04. On the basis of the data in Figure 2 and this ratio, $k_7 = (4.6 \pm 2) \times 10^{-12} \text{ cm}^3$ molecule 1 s⁻¹. The FTIR experiments were performed at 700 Torr in N₂ using either CH₃Cl ($k_8 = 4.9 \times 10^{-13}$) or C₂H₅Cl $(k_9 = 8.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ as reference species. The rate constant ratios determined in these experiments were $k_7/k_8 = 7.3 \pm 0.5$ and $k_7/k_9 = 0.51 \pm 0.04$. The values of k_7 calculated from these ratios are $(3.6 \pm 0.3) \times 10^{-12}$ and $(4.1 \pm$ $(0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Thus, the GC and FTIR measurements agree and show that there is no pressure dependence to k_7 , as expected. The FTIR data are more precise, and the best estimate of k_7 is $(3.9 \pm 0.6) \times 10^{-12}$. This value was used to correct for the small secondary consumption of $1,2-C_3H_6Cl_2$ in the following product studies.

Table 2 presents product yields from reaction 1 measured at pressures between 0.3 and 700 Torr. These yields have been corrected for secondary consumption using a chemical kinetic mechanism based on reactions 1 and 3–7 using the rate constant ratios measured above. Two representative FTIR data sets are presented in Figure 4. The raw data are shown as filled symbols,



Figure 4. Product partial pressures measured at two total pressures of N_2 diluent as a function of propylene consumed ($[C_3H_6]_0 = 72$ mTorr). Data were obtained using the FTIR system. Filled triangles = raw data for allyl chloride; open triangles = allyl chloride corrected for secondary consumption by Cl atoms.

while the open symbols present the yields of products after correction for secondary consumption. After correcting for secondary consumption, the product concentrations increase linearly with increasing C_3H_6 consumption. Each GC entry in Table 2 represents a single determination of the product yields. The average carbon recovery in the GC experiments is 95 ± 4%, while that for the FTIR data, determined from the slope of plots similar to those in Figure 4, is $104 \pm 7\%$. The carbon balances do not depend on the extent of C_3H_6 consumption for either FTIR or GC experiments, suggesting that the correction for secondary consumption of products is being made correctly.

Because the carbon recovery is, within experimental error, essentially 100%, the product yields for each data point in Table 2 were normalized to 100% total yield, and these normalized yields are presented in Figure 5 for both FTIR and GC data. As postulated in the discussion of the measurement of k_1 presented earlier, the product yields change markedly with total pressure. At high pressure, the addition reaction 1a dominates and 1,2-C₃H₆Cl₂ is the principal product, reaching a yield of 92% at 700 Torr. At low pressure, 3-C₃H₅Cl is the primary product with a yield of 92% at 0.3 Torr. This shows that reaction 1b dominates at low pressures and is indeed the reason why the rate constant ratio k_1/k_2 approaches an asymptote at low pressure.



Figure 5. Yields of $3-C_3H_5Cl$ and $1,2-C_3H_6Cl_2$ as a function of total pressure of N₂ diluent. Open symbols = GC system; filled symbols = FTIR system.



Figure 6. Values of k_{1a} and k_{1b} plotted as a function of the total pressure. Open symbols = GC system; filled symbols = FTIR system.

Determination of k_{1a} and k_{1b} . The values of the overall rate constant k_1 can be determined at any pressure from the rate constant ratios in Figure 2 and the known value of k_2 (=5.9 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹). By multiplying the yield of either 3-C₃H₅Cl or 1,2-C₃H₆Cl₂ at each measured pressure by the value of k_1 at that pressure, the rate constants for the individual channels, k_{1b} and k_{1a} , can be determined. These rate constants are plotted in Figure 6.

The rate constant for the addition reaction (triangles) falls off rapidly as the pressure decreases, as has been observed for Cl atom addition to ethylene or acetylene. All measured rate constants for the addition reaction were fitted using the Troe expression represented by eqs 6.1 and 6.3-6.6 in the reference of Gilbert et al.¹⁶ Two fits were performed, using center broadening factors of either 0.6 or 0.45. The solid line through the triangles in Figure 6 was obtained using the common approximation¹⁷ $F_{\text{cent.}} = 0.6$ and the resulting low- and highpressure limiting rate constants ($k_{1a}(0) = (4.0 \pm 0.4) \times 10^{-28}$ cm⁶ molecule⁻² s⁻¹; $k_{1a}(\infty) = (2.7 \pm 0.4) \times 10^{-10} \text{ cm}^3$ molecule $^{-1}$ s $^{-1}$). This fits the limited data set reasonably well, although some deviation occurs at the highest pressure leading to a slight underprediction for $P \approx 700$ Torr. Reducing $F_{\text{cent.}}$ to 0.45 $(k_{1a}(0) = (4.7 \pm 0.4) \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}; k_{1a}(\infty)$ = $(3.4 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$, results in a somewhat better fit to the data points as shown by the dashed line. A similar improvement in fitting the data when using a value of $F_{\text{cent.}}$ smaller than 0.6 was also noted in studies of the Cl atom addition to ethylene or acetylene.⁵ However, in all

cases, the improvement upon reducing the value of $F_{\text{cent.}}$ is of the order of the experimental error. Changing the value of $F_{\text{cent.}}$ from 0.6 to 0.45 increases the calculated values of $k_{1a}(0)$ and $k_{1a}(\infty)$ only slightly more than the stated experimental errors.

The low-pressure rate constant for the addition of Cl to C_3H_6 is approximately 30 times faster than the low-pressure limiting rate constant for ethylene (=1.4 × 10⁻²⁹ cm⁶ molecule⁻² s⁻¹ for $F_{\text{cent.}} = 0.6$). This shows that a larger molecule such as C_3H_6 , containing more low-frequency vibrational modes, distributes the excess energy from the addition reaction more efficiently within the molecule, resulting in a large increase in the low-pressure addition rate constant.

 $k_{1a}(\infty)$ is close to the gas kinetic limit and indistinguishable from that of ethylene (=3.2 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for $F_{\text{cent.}} = 0.6$) within the uncertainty of the determinations. Such behavior is not surprising since there should be little steric hinderance in the approach of the Cl atom to the II bond in either molecule.

For pressures > 100 Torr, $k_{1b} = (2.3 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (circles in Figure 6). This value is very similar to that for H atom abstraction from methyl groups in alkanes $(3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$. If reaction channel 1b to form the allyl radical is purely an abstraction process, no pressure dependence would be expected. While k_{1b} does not change dramatically over the factor of 2000 pressure range studied, it does increase by approximately 50% as the pressure decreases from 100 to 10 Torr (from a value of 2.3×10^{-11} (200–700 Torr) to 3.7×10^{-11} (<30 Torr). While this change is small, it is observed in both GC and FTIR experiments and is greater than the experimental uncertainty.

We suggest that this observation may result from the existence of two possible channels for allyl radical generation within reaction 1b. The first channel, represented by the rate constant measured at pressures > 200 Torr, arises from direct hydrogen abstraction at the methyl group in propylene. This rate constant is independent of pressure, as expected for a metathesis reaction.

The second channel becomes apparent only at pressures < 100 Torr. We believe that this arises from an addition elimination process (reaction A) in which a Cl atom adds to the double bond to form an activated complex (C₃H₆Cl*), from which HCl can be eliminated.

$$C_{3}H_{6} + CI \xrightarrow{k_{1a}(\infty)} C_{3}H_{6}CI^{*} \xrightarrow{k_{E}} C_{3}H_{5} + HCI \qquad (A)$$

$$\downarrow^{(M)} C_{3}H_{6}CI$$

On the basis of a Lindemann analysis of the pressure dependence of such a reaction, the overall rate constant (k) for C₃H₅ formation by elimination from the activated complex is

$$\frac{d[C_3H_5]}{dt} = k[C_3H_6][Cl]$$

where $k = k_{1a}(\infty) / \left[\frac{k_R + k_M[M]}{k_E} + 1\right]$

Formation of the allyl radical by this type of reaction will have an inverse pressure dependence, as has been observed for the addition—elimination reaction leading to the formation of ethylene from $C_2H_5 + O_2$.¹⁸ Near the high-pressure limit, the activated complex is stabilized efficiently by third-body collisions. In this pressure region, the rate of the HCl elimination reaction is small and inversely dependent on total pressure. At low pressures, the elimination reaction becomes increasingly important. At sufficiently low pressure, the stabilization channel to form the C₃H₆Cl radical becomes insignificant. In this pressure regime, the apparent rate constant for allyl formation from the elimination channel reaches a constant value determined by the rate constants for HCl elimination (k_E), elimination of Cl from the activated complex to return to the reactants (k_R), and the high-pressure limiting rate constant ($k_{1a}(\infty)$):

$$k = k_{1b}(P < 10$$
Torr $) - k_{1b}(P > 200$ Torr $) = k_{1a}(\infty) / \left[\frac{k_{\rm R}}{k_{\rm E}} + 1\right]$

Substituting the measured values of $k_{1b}(P < 10) = 3.7 \times 10^{-11}$, $k_{1b}(P > 200) = 2.3 \times 10^{-11}$, and $k_{1a}(\infty) = 2.7 \times 10^{-10} \text{ cm}^3$ molecule⁻¹ s⁻¹ gives $k_{\text{R}}/k_{\text{E}} = 18$.

Conclusions

The rate constant (k_1) for the reaction of Cl atoms with C₃H₆ has been measured as a function of pressure in relative rate experiments, using either FTIR or GC detection in two different reactors. The results of the two experimental techniques yield indistinguishable results, suggesting the absence of significant systematic errors.

At high pressure (>100 Torr), the primary product observed following UV irradiation of Cl₂/C₃H₆/N₂ mixtures is 1,2dichloropropane with a yield in excess of 85%, indicating that addition of a Cl atom to the double bond (k_{1a}) is the major reaction channel. On the basis of the measured values of k_1 and the 1,2-dichloropropane yield as a function of pressure, the high [$k_{1a}(\infty) = (2.7 \pm 0.4) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹] and low pressure [$k_{1a}(0) = (4.0 \pm 0.4) \times 10^{-28}$ cm⁶ molecule⁻² s⁻¹] limiting rate constants have been calculated assuming that $F_{cent.} = 0.6$. Because of the additional vibrational degrees of freedom, the low-pressure limiting rate constant for propylene is approximately 30 times larger than that for Cl addition to C₂H₄.

At low pressure (<10 Torr), allyl chloride is the major product (yield 75-90%), indicating that as the addition reaction rate slows, removal of an H atom from the CH_3 group in C_3H_6 is the dominant channel. Measurement of the product yields over the full pressure range studied (0.3-700 Torr) permits calculation of the pressure dependence of the rate constant for this channel (k_{1b}) . Three different pressure regimes were identified for k_{1b} . Within the experimental uncertainties, there was no discernable effect of total pressure on k_{1b} over the ranges 0.3-100 Torr ($k_{1b} = 3.7 \times 10^{-11}$) and 200–700 Torr ($k_{1b} = 2.3 \times 10^{-11}$) 10^{-11}). In contrast, k_{1b} increased by approximately 50% as the total pressure was decreased from 100 to 10 Torr. We suggest that this increase in the rate constant at lower pressure indicates that the allyl radical may be formed by two processes: (1) a pressure independent direct abstraction; (2) an additionelimination process which depends inversely on the total pressure.

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