Chemistry of the Cyclopentoxy and Cyclohexoxy Radicals at Subambient Temperatures

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The Cl-atom initiated oxidation mechanisms of both cyclopentane and cyclohexane have been studied as a function of temperature using an environmental chamber/FTIR technique. The oxidation of cyclohexane leads to the formation of the cyclohexoxy radical, the chemistry of which is characterized by a competition between ring-opening (R5) and reaction with O_2 (R6) to form cyclohexanone. The yield of cyclohexanone is shown to increase with decreasing temperature, and a rate coefficient ratio $k_6/k_5 = (1.3 \pm 0.3) \times 10^{-27} \exp(5550 \pm 1100/T)$ cm^3 molecule^{-1} is obtained. The energy barrier to ring-opening is estimated to be 11.5 ± 2.2 kcal/mol. The dominant fate of the cyclopentoxy radical, formed in the Cl-atom initiated oxidation of cyclopentane, is ring-opening under all conditions studied here (230−300 K, 50−500 Torr O_2), with only a minor contribution from the O_2 reaction at the lowest temperatures studied. The barrier to ring-opening for the cyclopentoxy radical is probably less than 10 kcal/mol.

Introduction

The alkanes, including the cycloalkanes, are released into the atmosphere from a variety of anthropogenic sources.[1,2] Their oxidation leads to the formation of secondary pollutants (e.g., ozone, aldehydes, ketones, aerosols), and thus contributes to the degradation of air quality in and around urban regions. Numerous laboratory investigations of the oxidation rates and mechanisms of the atmospheric oxidation of the cycloalkanes have been carried out.[3−12] Like other hydrocarbon species, the atmospheric oxidation of the cycloalkanes is initiated by their reaction with OH which, in the presence of O_2, leads to the production of cycloalkylperoxy radicals. In and near urban areas, the chemistry of these peroxy species will be dominated by their reactions with NO, leading in part to the formation of organic nitrates,[3,4] and in part to the formation of cycloalkoxy radicals. The subsequent chemistry of the cycloalkoxy radicals, which determines the stable products of the oxidation, may involve reaction with O_2 to form the corresponding cycloalkanone, decomposition by ring opening, or isomerization by 1,5-hydrogen shifts.[3,9,11,12] The behavior of the cyclohexoxy radical has been shown to be quite different from that of the cyclopentoxy or cycloheptoxy radicals.[3,6−9,11] In the case of cyclohexoxy, reaction with O_2 (to form cyclohexanone) is competitive with ring-opening under ambient conditions (cyclohexanone yield 25−35%).[3,6−9,11] However, in the case of the cyclopentoxy or cycloheptoxy species, increased ring strain leads almost exclusively to ring-opening and hence to very small yields (<5%)[3,6−8] of the cycloalkanone. Products obtained following ring-opening have been identified in the case of cyclohexane,[11] and include a series of multi-functional aldehydes, alcohols, and nitrates. Although not yet observed, similar species are expected to be obtained in high yield from the oxidation of cyclopentane and cycloheptane.

In this study, the behavior of both the cyclohexoxy and cyclopentoxy radicals are examined at temperatures below ambient. A quantitative determination of the competition between ring-opening and reaction with O_2 for these species allows for the determination of the Arrhenius parameters for the ring opening reactions. As part of this work, yields of organic nitrates as a function of temperature in the oxidation of both cyclopentane and cyclohexane are estimated.

Experimental Section

All experiments were conducted in a 2-m long, 47-liter stainless steel chamber, which is interfaced to a BOMEM DA3.01 Fourier Transform infrared spectrometer.[13,14] The chamber is equipped with Hanst-type multipass optics which provided an IR analysis beam path length of 32.6 m. Chilled ethanol (from a NESLAB Model EX-250HT cooler) was circulated around the cell to control the temperature, which was constant to ±1.0 K, as monitored by eight thermocouples along the length of the cell.

Most experiments involved the photolysis of mixtures of Cl_2 (Linde, 0.1−1 Torr), cyclopentane or cyclohexane (Aldrich, 12−120 mTorr), NO (Linde, 0−25 mTorr), O_2 (U.S. Welding, UHP, 10−700 Torr), and N_2 (boil-off from LN_2 dewar, U.S. Welding, 0−700 Torr) at a total pressure of 700−750 Torr. Minor components of the gas mixtures were flushed into the cell with N_2 from smaller calibrated volumes. A cw Xe-arc lamp, filtered to provide radiation between 235 and 400 nm, was used for photolysis of the gas mixtures, and the temporal profiles of the parent cycloalkane and its oxidation products were monitored by FTIR spectroscopy. The FTIR spectra were recorded over the range of 800−3900 cm^{-1} at a spectral resolution of 1 cm^{-1}, and were obtained from the co-addition of 100−250 scans. Quantification of the cycloalkanes and cycloalkanones was done by comparison with standard spectra (obtained in the presence of 1 atm air) of known quantities of these species.

Results and Discussion

Cyclohexane. The first set of experiments involved the irradiation of mixtures of Cl_2, cyclohexane, NO, O_2, and N_2 at a total pressure of 700 Torr, with the O_2 pressure varied from 150 to 600 Torr. Major reactions are expected to be as follows:

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$$Cl_2 + h\nu \rightarrow Cl + Cl \quad (1)$$

$$Cl + c{-}C_6H_{12}\ (+ O_2) \rightarrow c{-}C_6H_{11}O_2 + HCl \quad (2)$$

$$c{-}C_6H_{11}O_2 + NO \rightarrow c{-}C_6H_{11}ONO_2 \quad (3a)$$

$$\rightarrow c{-}C_6H_{11}O + NO_2 \quad (3b)$$

$$c{-}C_6H_{11}O_2 + NO_2 \leftrightarrow c{-}C_6H_{11}OONO_2 \quad (4, -4)$$

$$c{-}C_6H_{11}O \rightarrow \text{ring-opening products} \quad (5)$$

$$c{-}C_6H_{11}O + O_2 \rightarrow c{-}C_6H_{10}O\ (\text{cyclohexanone}) + HO_2 \quad (6)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (7)$$

$$OH + c{-}C_6H_{12}\ (+O_2) \rightarrow c{-}C_6H_{11}O_2 + H_2O \quad (8)$$

Although isomerization of the $c{-}C_6H_{11}O$ radical via a 1,5-H shift is feasible, this reaction pathway has been shown to be of negligible importance, likely due to the geometric constraints imposed by the ring system.[11] Products obtained from the oxidation of cyclohexane included cyclohexanone and formic acid (identified by comparison to standard spectra), as well as cyclohexyl nitrate ($c{-}C_6H_{11}ONO_2$) and cyclohexyl peroxynitrate ($c{-}C_6H_{11}OONO_2$), which were identified by virtue of characteristic absorption features (1280 and 1666 cm^{-1} for the nitrate, and 1300 cm^{-1} for the peroxynitrate).[12]

Before the competition between (R5) and (R6) can be properly assessed, the presence of the peroxynitrate and nitrate species needs to be properly accounted for in the analysis. Yields of the peroxynitrate, obtained using the absorption cross sections of Platz et al.,[12] were found to be dependent on the initial [NO] and on the extent of reaction, but typically increased from zero early in an experiment to about 10% toward the end of an experiment. This is expected, since the $[NO_2]/[NO]$ ratio increases with time, increasing the importance of (R4) relative to (R3). All yields of cyclohexyl nitrate and cyclohexanone reported below have been corrected for the formation of the cyclohexyl peroxynitrate (that is, they are determined relative to the difference between the cyclohexane consumed and the peroxynitrate formed).

An experiment was run to determine the thermal stability of the cyclohexyl peroxynitrate species at room temperature. In this experiment, a mixture of Cl_2 (140 mTorr), cyclohexane (17 mTorr), NO (10 mTorr), O_2 (400 Torr), and N_2 (300 Torr) was irradiated until NO was no longer detectable in the IR spectra ([NO] < 0.2 mTorr), and measurable amounts (1.5 mTorr) of the peroxynitrate species had built up. The photolyzed mixture was then allowed to sit in the dark, and the concentration of the cyclohexyl peroxynitrate was monitored. Its temporal profile was characterized by an early rapid decay (of order $10^{-3}\ s^{-1}$), followed by a slow steady first-order decay, $k = 7 \times 10^{-5}\ s^{-1}$. This reaction system is characterized by thermal decomposition and reformation of the cyclohexyl peroxynitrate, reactions (4, −4), and reaction of the cyclohexyl peroxy radical with NO (R3) and with itself, reaction 9:

$$c{-}C_6H_{11}O_2 + c{-}C_6H_{11}O_2 \rightarrow 2c{-}C_6H_{11}O + O_2 \quad (9a)$$

$$\rightarrow c{-}C_6H_{10}O + c{-}C_6H_{11}OH + O_2 \quad (9b)$$

Simulations (using Acuchem)[15] of the system showed that the initial rapid decay of the cyclohexyl peroxynitrate was due to consumption of the residual NO by the peroxy radicals. Once the NO was completely titrated away, the observed first-order loss rate of the cyclohexyl peroxynitrate was determined by a competition between (R9) and (R4). Using data for the rate coefficient of (R9) from Rowley et al.,[6,7] the rate coefficient for (R{−4}) was adjusted in the model to best match the observed data. A first-order rate coefficient of 7 ± 2 s^{-1} for thermal decomposition of the peroxynitrate species is obtained, in reasonable agreement with measurements made by Zabel and co-workers (5 s^{-1}).[16]

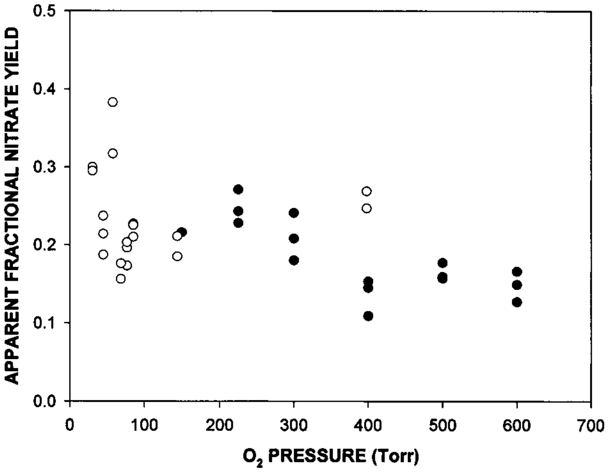


Figure 1. Plot of the apparent nitrate yield as a function of O_2 partial pressure in the photolysis of Cl_2/cyclohexane/NO/O_2/N_2 mixtures at 700 Torr total pressure. Open circles, 273 K; Filled circles, 296 K.

Concentrations of cyclohexyl nitrate were obtained by assuming a peak absorption cross section at 1284 cm^{-1} of $1.8 \times 10^{-18}\ cm^2\ molecule^{-1}$, by analogy to methyl nitrate.[17] A determination of the cyclohexyl nitrate yield is complicated by the likelihood of the formation of other organic nitrate species from the reaction of NO with various peroxy radicals formed after ring-opening,[12] which is most prevalent at low O_2 partial pressures. A plot of the apparent nitrate yield as a function of $[O_2]$ at 296 K is shown in Figure 1. As seen from the figure, the apparent nitrate yield decreases slightly with increasing $[O_2]$ until a constant value is reached at 400 Torr. The cyclohexyl nitrate yield, obtained from an average of all data at $[O_2] \geq$ 400 Torr, is 15 ± 4%. This value is in excellent agreement with previously reported cyclohexyl nitrate yields (9.0 ± 4.4%,[3] 16.0 ± 1.5%,[4] 16.5 ± 2.1%,[11] 16 ± 4%[12]). The increase in apparent nitrate yield at low $[O_2]$ indicates that additional nitrates are being produced from peroxy radicals formed after ring-opening (a series of straight-chain, partially oxygenated C_6 species).

A similar procedure was used to obtain the cyclohexyl nitrate yield at temperatures of 273 and 261 K. For the 273 K data, experiments with O_2 partial pressures in excess of 60 Torr were used in the analysis (see Figure 1), while at 261 K a series of experiments was conducted at a partial pressure of 500 Torr O_2 to cleanly evaluate the cyclohexyl nitrate yield. Values obtained were 21 ± 6%, and 18 ± 7%. Thus, the cyclohexyl nitrate yield shows a fairly weak dependence on temperature (albeit over a small temperature range, and with a substantial uncertainty).

Following a proper accounting of the nitrate and peroxynitrate formation, examination of the competition between (R5) and (R6) can be done from an analysis of the dependence of the cyclohexanone yield on $[O_2]$. From the reaction scheme above, it can be seen that the yield of cyclohexanone (Y) is given by:

$$Y = \alpha\, k_6[O_2]/\{k_5 + k_6[O_2]\} \quad (A)$$

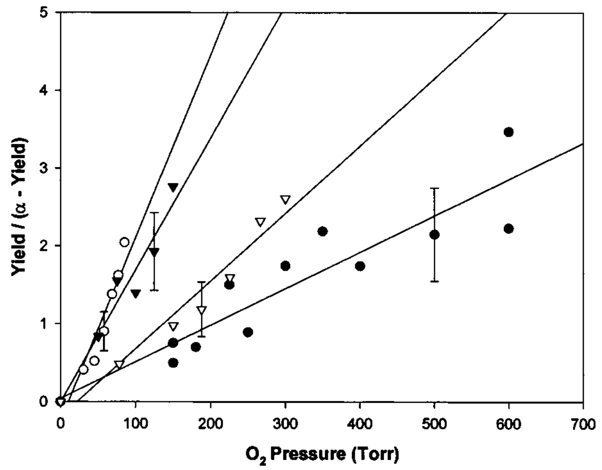


Figure 2. Plots of Yield/(α−Yield) vs O_2 partial pressure in the photolysis of Cl_2/cyclohexane/NO/O_2/N_2 mixtures at 700 Torr total pressure, where Yield refers to the yield of cyclohexanone and (1−α) is the cyclohexyl nitrate yield (see text for details). Filled circles, 296 K; Open triangles, 288 K; Filled triangles, 280 K; Open circles, 273 K.

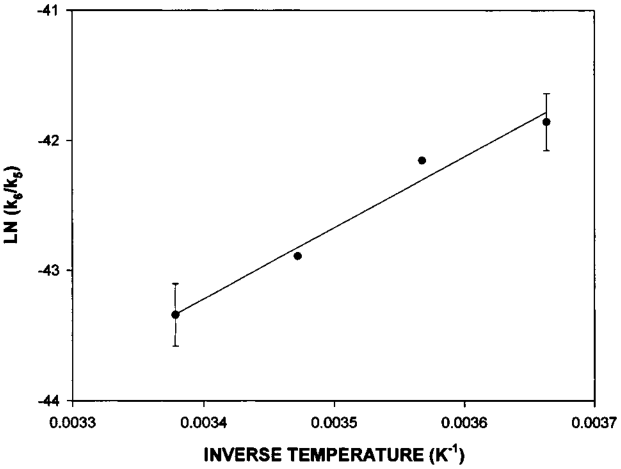


Figure 3. Rate coefficient ratio k_6/k_5 plotted in Arrhenius form.

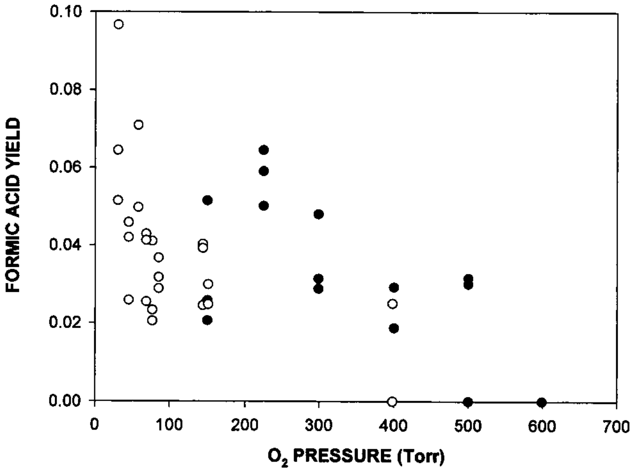


Figure 4. Formic acid yield as a function of O_2 partial pressure in the photolysis of Cl_2/cyclohexane/NO/O_2/N_2 mixtures at 700 Torr total pressure. Filled circles, 296 K; Open circles, 273 K.

where (1 − α) is defined as the cyclohexyl nitrate yield from (R3), $k_{3a}/(k_{3a} + k_{3b})$, which was assumed to increase from 16% at 296 K to 20% at 273 K. Rearrangement of (A) yields the following relationship:

$$Y/(\alpha - Y) = k_6[O_2]/k_5 \qquad (B)$$

Thus, the slope of plots of Y/(α −Y) as a function of the O_2 partial pressure at a given temperature yields values for the rate constant ratio, k_6/k_5. Data obtained at temperatures ranging from 273 to 296 K are shown in Figure 2. The rate coefficient ratio obtained at 296 K is $k_6/k_5 = (1.5 \pm 0.4) \times 10^{-19}$ cm^3 molecule^{-1}, in very good agreement with the value recently reported by Platz et al.,[12] $(1.2 \pm 0.2) \times 10^{-19}$ cm^3 molecule^{-1}, and with the estimate of Rowley et al.,[6] 2×10^{-19} cm^3 molecule^{-1}. The cyclohexanone yield in 1 atm air obtained from our data (calculated from eq A) is then 36 ± 6%, which agrees well with previous studies performed in air in which cyclohexanone yields of 23 ± 13%,[3] 32 ± 4%,[11] and 35 ± 4%[9] were reported.

Rate coefficient ratios obtained at the four temperatures studied are plotted in Arrhenius form in Figure 3. As expected, the ratio k_6/k_5 increases sharply with decreasing temperature, owing to the strong temperature dependence to the endothermic decomposition (R5). A nonweighted linear least-squares fit to the data yields $k_6/k_5 = (1.3 \pm 0.3) \times 10^{-27} \exp(5550 \pm 1100/T)$ cm^3 molecule^{-1}, where the uncertainty in the A-factor ratio reflects the uncertainty in the room-temperature value. While measurements of k_6 are not presently available, its value can be estimated to be $1.5 \times 10^{-14} \exp(-200/T)$ cm^3 molecule^{-1} s^{-1},[18] which leads to $k_5 = (1.2 \pm 0.3) \times 10^{13} \exp(-5750 \pm 1100/T)$ s^{-1}. Thus, we estimate that ring-opening of the cyclohexoxy radical, (R5), occurs with a barrier of 11.5 ± 2.2 kcal/mol.

It is clear from the above experiments that ring-opening is a significant fate of the cyclohexoxy radical at room temperature, and becomes of little or no importance at the lower temperatures of the upper troposphere. Some previously identified ring-opening products,[11] including $HC(O)(CH_2)_4CH_2ONO_2$ and $HC(O)CH_2CH(OH)CH_2CH_2CHO$, could not be uniquely identified in our study, though carbonyl-type absorptions near 1740 cm^{-1} are clearly evident in the product spectra. Formic acid was also observed in small yield in most, but not all product spectra. Closer examination of the data revealed that the formic acid yields increased with decreasing O_2 partial pressures, indicating that it may be originating from chemistry occurring after ring-opening (see Figure 4). For example, at 296 K, formic acid yields varied from about 5−6% at 100−200 Torr O_2, to ≤2% at 500−600 Torr O_2. At 273 K, yields of HCOOH were about 3% for O_2 greater than 100 Torr, and increased sharply (though with considerable scatter) at lower O_2. At 261 K, in the presence of 500 Torr O_2, (where ring-opening should not occur to any extent), formic acid yields were immeasurably small (<0.8%). Recent studies in our laboratory[19] indicate that formic acid may be obtained from the reaction of R−CHOH radicals (where R is any relatively large organic fragment) with O_2:[20]

$$R{-}CHOH + O_2 \rightarrow R{-}CHO + HO_2 \qquad (10a)$$

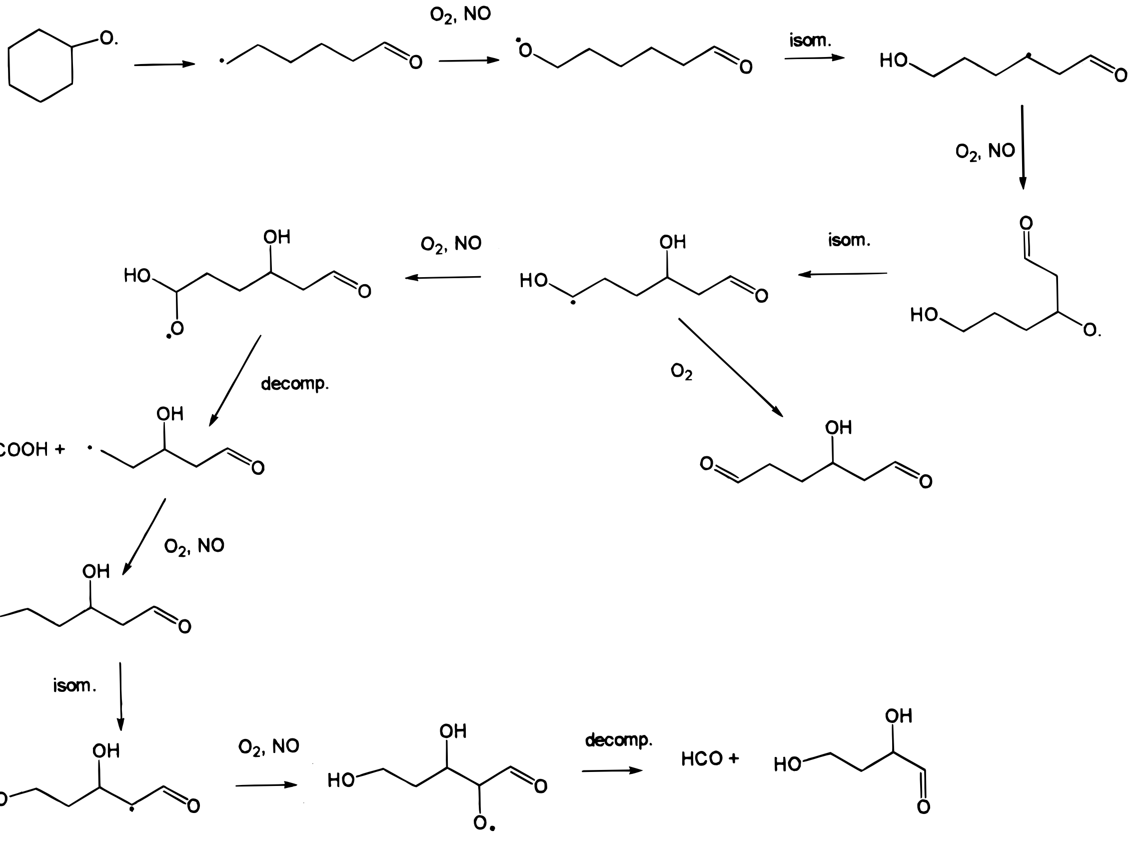
$$\rightarrow RCH(OH)O_2 \qquad (10b)$$

$$RCH(OH)O_2 + NO \rightarrow RCH(OH)O + NO_2 \qquad (11)$$

$$RCH(OH)O \rightarrow R + HCOOH \qquad (12)$$

As shown by Aschmann et al.,[11] such a radical is formed from ring-opening, see Reaction Scheme 1. Formic acid was also

SCHEME 1: Chemistry Occurring Subsequent to Ring-Opening of the Cyclohexoxy Radical, Showing a Possible Route to Formic Acid Formation; Formation of Organic Nitrates and Peroxynitrates Omitted for Clarity



among the products reported by Takagi et al.,[3] though their yields are somewhat larger than ours. Takagi et al.[3] also report rather large (40% by mol) yields of formaldehyde, which we did not observe in our experiments (yield < 10%), and acetylene (5% yield). While the acetylene is too weak an absorber to be excluded as a minor product in our experiments, it is extremely unlikely to be a product of cyclohexane oxidation. It is apparent that acetylene (as well as CH_2O and to a certain extent HCOOH) were artifacts in the Takagi et al.[3] experiments.

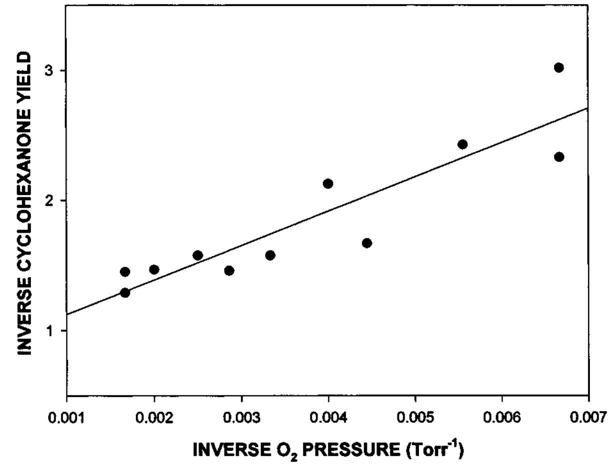


Figure 5. Plot of the inverse of the cyclohexanone yields versus the inverse O_2 partial pressure in the photolysis of Cl_2/cyclohexane/$NO/O_2/N_2$ mixtures at 700 Torr total pressure and 296 K.

Finally, we note that chemical activation has recently been shown to be important in the chemistry of certain alkoxy radicals, when formed from the exothermic reaction of the corresponding peroxy radicals with NO.[21−24] In these cases, a measurable fraction of the alkoxy radicals are born with an energy in excess of the barrier to their decomposition, and thus decompose on a time scale that is short compared with collisions. In cases where chemical activation is significant, plots of the inverse yield of the O_2 reaction product (in this case cyclohexanone) versus the inverse $[O_2]$ show intercepts significantly greater than unity.[21] As noted by Platz et al.,[12] and confirmed by the work carried out here (see Figure 5), there is apparently no large chemical activation effect in the case of cyclohexoxy radicals. Chemical activation has been shown to be important in cases where the barrier to decomposition is of order 9 kcal/mol or less, somewhat less than the 11−12 kcal/mol barrier determined herein for cyclohexoxy decomposition. Note that the average amount of energy imparted to the alkoxy fragment is typically about 10 kcal/mol (although with a wide distribution),[22] somewhat below the measured decomposition barrier. In addition, the large size of the cyclohexyl system may act against the occurrence of decomposition due to chemical activation. First, the peroxynitrite complex initially formed in (R3) is likely fairly long-lived and is thus likely to suffer some collisional deactivation before decomposition to products. Furthermore, the RRKM lifetime of the hot alkoxy species is likely to be considerably longer than previously studied systems, and the likelihood of collisional deactivation is again enhanced.

Cyclopentane. Initial experiments involved the photolysis of mixtures of Cl_2 and cyclopentane in O_2/N_2 mixtures, with the O_2 partial pressure varied from 50 to 700 Torr, at a total pressure of 700 Torr. Major reactions are expected to be as follows, where RO_2 are organic peroxy radicals formed after ring opening:

$$\mathrm{Cl_2 + h\nu \rightarrow Cl + Cl} \tag{1}$$

$$\mathrm{Cl + c{-}C_5H_{10}(+O_2) \rightarrow c{-}C_5H_9O_2 + HCl} \tag{13}$$

$$\mathrm{c{-}C_5H_9O_2 + c{-}C_5H_9O_2 \rightarrow c{-}C_5H_9O + c{-}C_5H_9O + O_2} \tag{14a}$$

$$\mathrm{\rightarrow c{-}C_5H_8O + c{-}C_5H_9OH + O_2} \tag{14b}$$

$$\mathrm{c{-}C_5H_9O_2 + HO_2 \rightarrow c{-}C_5H_9OOH + O_2} \tag{15}$$

$$\mathrm{c{-}C_5H_9O_2 + RO_2 \rightarrow c{-}C_5H_9O + RO + O_2} \tag{16a}$$

$$\mathrm{\rightarrow molecular\ products\ (incl.\ cyclopentanone)} \tag{16b}$$

$$\mathrm{c{-}C_5H_9O + O_2 \rightarrow c{-}C_5H_8O\ (cyclopentanone) + HO_2} \tag{17}$$

$$\mathrm{c{-}C_5H_9O + M \rightarrow CH_2(CH_2)_3CHO + M} \tag{18}$$

As in the work of Rowley et al.,[7] products identified in experiments conducted at room temperature were cyclopentanone and glutaric dialdehyde. Cyclopentanol, observed in the work of Rowley et al.,[7] could not be detected in our experiments due to its weak absorption features, but can be assumed to have a yield similar to that of cyclopentanone. The cyclopentanone yield was found to be 11 ± 3%, independent of the O_2 partial pressure. Although our yield is somewhat lower than the value of 18 ± 1% reported by Rowley et al.,[7] the lack of an O_2 dependence to the cyclopentanone yield nevertheless indicates that its formation is predominantly from (R14b) and (R16b), and that reaction with O_2 (R17) is not important for the cyclopentoxy radical. That is, at room temperature, the decomposition of the $c{-}C_5H_9O$ radical (R18) dominates its chemistry, even in the presence of 700 Torr O_2.

Absorption cross sections for glutaric dialdehyde are not available, and thus its absolute yield cannot be obtained. However, based on an approximate peak absorption cross section for the carbonyl band of 5×10^{-19} cm^2 molecule^{-1} (by analogy to other carbonyl species studied in our reaction chamber), a yield of order 20% can be estimated. Regardless of the exact yield of the glutaric dialdehyde, the important fact is that its yield was found to be independent of O_2. Since it is likely to originate from the chemistry of the peroxy radical formed after ring-opening, (R18),

$$\mathrm{CH_2(CH_2)_3CHO + O_2 \rightarrow O_2CH_2(CH_2)_3CHO} \tag{19}$$

$$\mathrm{2O_2CH_2(CH_2)_3CHO \rightarrow 2OCH_2(CH_2)_3CHO + O_2} \tag{20a}$$

$$\mathrm{\rightarrow HC(O)(CH_2)_3CHO + HOCH_2(CH_2)_3CHO + O_2} \tag{20b}$$

$$\mathrm{OCH_2(CH_2)_3\,CHO + O_2 \rightarrow HC(O)(CH_2)_3CHO + HO_2} \tag{21}$$

$$\mathrm{OCH_2(CH_2)_3CHO + M \rightarrow isomerization,\ decomposition} \tag{22}$$

the lack of an O_2 dependence to its yield is again indicative of the unimportance of (R17) in the chemistry. Furthermore, the independence of the glutaric dialdehyde yield on O_2 indicates that (R22) is dominant over (R21) under these conditions (as expected),[9,25] and that the majority of the dialdehyde originates from (R20b). Yields of CO, CO_2, and CH_2O were all less than 5%, indicating that they are not significant products of chemistry occurring after ring-opening. Thus, it is likely that a very complex set of multi-functional products arises following ring-opening, as a result of the peroxy radical self-reactions (such as R20b) and of isomerization of the C5 oxy radical (R22).

Similar experiments were conducted at lower temperatures (260 and 238 K). The yield of cyclopentanone increased substantially with decreasing temperature (25% at 260 K, and 43% at 238 K), indicating an increase in the branching ratios of the molecular channels of (R14b) and/or (R16b), but was still found to be independent of O_2 at a given temperature. However, firm conclusions on the competition between (R17) and (R18) are difficult to make owing to the preponderance of the formation of molecular products in the peroxy radical self-reactions at these low temperatures. Glutaric dialdehyde was observed at low temperature, but was found to be lost in the chamber on a time scale of a couple of minutes, presumably via heterogeneous processes.[7]

To further investigate the competition between (R17) and (R18) at low temperature, similar experiments to those just described were conducted in the presence of NO (initial concentrations of 16−24 mTorr). In these experiments, reactions of the cyclopentylperoxy radicals (and other organic peroxy species) will be dominated by their reaction with NO, e.g.:

$$\mathrm{c{-}C_5H_9O_2 + NO \rightarrow c{-}C_5H_9O + NO_2} \tag{23a}$$

thus eliminating the possibility of direct cyclopentanone production from peroxy radical chemistry. However, as was the case in the cyclohexane experiments, added complications arise from the formation of organic nitrates (including cyclopentyl nitrate) and at higher conversions, when the $[NO_2]/[NO]$ ratio increases, organic peroxynitrates:

$$\mathrm{c{-}C_5H_9O_2 + NO + M \rightarrow c{-}C_5H_9ONO_2 + M} \tag{23b}$$

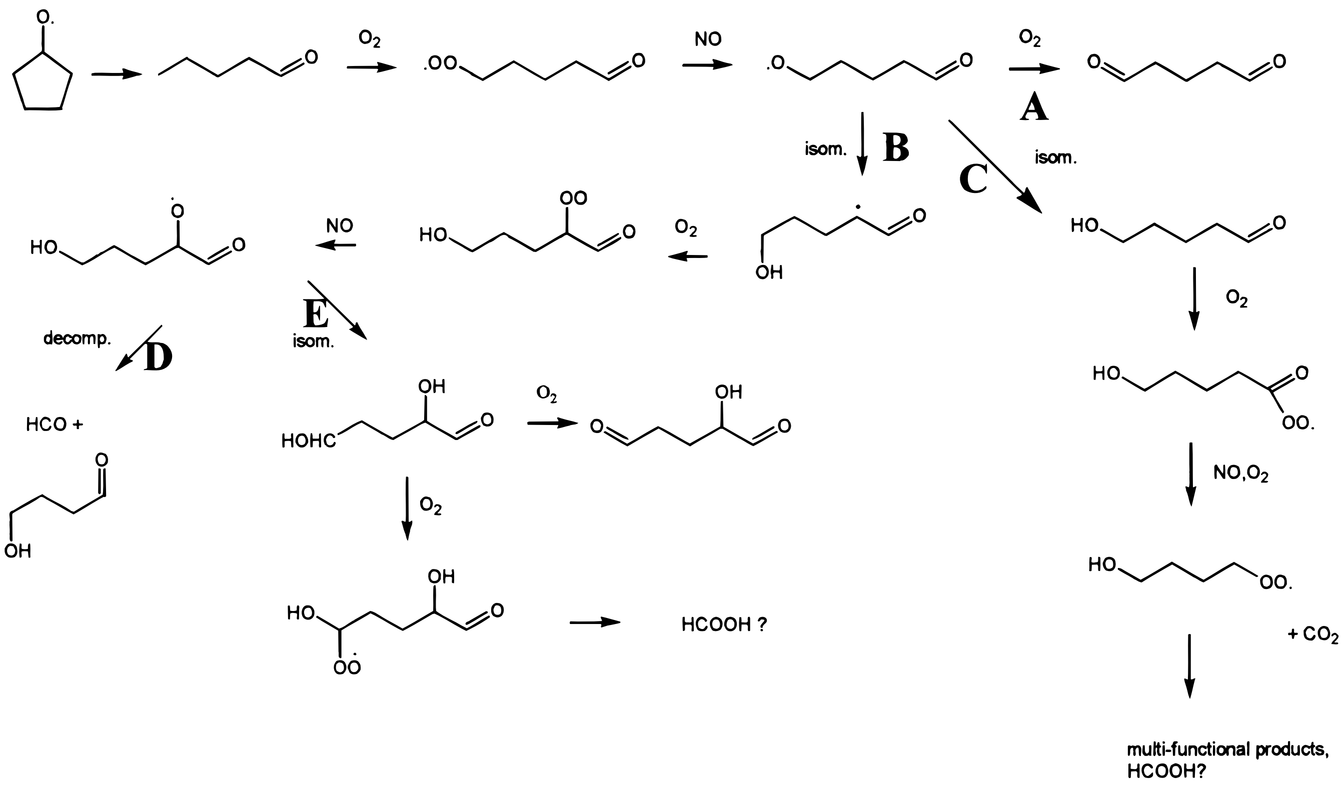
$$\mathrm{c{-}C_5H_9O_2 + NO_2 + M \rightarrow c{-}C_5H_9O_2NO_2 + M} \tag{24}$$

Organic nitrates were indeed found in these experiments, as evidenced by the observation of absorption features at 1280 and 1665 cm^{-1}. Assuming a 296 K peak absorption cross section at 1280 cm^{-1} of 1.8×10^{-18} cm^2 molecule^{-1}, again by analogy to CH_3ONO_2,[17] the overall nitrate yield is estimated to be 12 ± 5% at 296 K, similar to the previous estimate of Takagi et al., 13%. This value provides an upper limit to the cyclopentyl nitrate yield from (R23b), since there is a likelihood of nitrate production from peroxy radicals formed after ring-opening. Takagi et al.,[3] using GC analysis, assigned a yield of only 5% to the cyclopentyl nitrate, which is considerably lower than the cyclohexyl nitrate yield of 15% discussed above. Assuming a 10% increase in the peak absorption cross section of the organic nitrate species at 1284 cm^{-1} due to the lower temperature, a total nitrate yield of 21 ± 5% is estimated at 230 K.

At higher cyclopentane conversions, absorption features centered at 1295 and 1715 cm^{-1} appeared, consistent with the formation of cyclopentyl peroxynitrate. To assess the contribution of the cyclopentyl peroxynitrate to the chemistry, a calibrated reference spectrum was generated from the photolysis of Cl_2 (400 mTorr) in the presence of cyclopentane (75 mTorr) and NO_2 (20 mTorr), conditions which should lead to near-100% formation of the peroxynitrate. Absorption cross sections of 1.3×10^{-18} cm^2 molecule^{-1} at 1295 cm^{-1}, and 2.0×10^{-18} cm^2 molecule^{-1} at 1715 cm^{-1} were determined, consistent with values for other peroxynitrates, including cyclohexyl peroxynitrate.[12] For peroxynitrate concentration estimates below ambient temperature, the 1295 cm^{-1} peak absorption cross section was assumed to vary inversely with temperature, and to reach a value of 1.5×10^{-18} cm^2 molecule^{-1} at 230 K.

Experiments involving the photolysis of $Cl_2/c{-}C_5H_{10}/NO/O_2/N_2$ mixtures were conducted at temperatures of 296 K to 230 K, with the O_2 partial pressure varied from 100 to 500 Torr

SCHEME 2: Chemistry Occurring Subsequent to Ring-Opening of the Cyclopentoxy Radical; Formation of Organic Nitrates and Peroxynitrates Omitted for Clarity



at all temperatures studied. The competition between (R17) and (R18) was determined from the ratio of the observed cyclopentanone concentration to the amount of cyclopentoxy radical formed, which is in turn defined as the amount of cyclopentane consumed less the estimated cyclopentyl nitrate (assumed to be 5% at 296 K, and 8% at 230 K, based on the Takagi et al.[3] data) and cyclopentyl peroxy nitrate produced (as described above). While the actual values assumed for the cyclopentyl nitrate yields make little difference on the conclusions that follow regarding the competition between (R17) and (R18), we do note that these cyclopentylnitrate yields do seem lower than expected, based on previous studies on *n*-pentane,[25] *n*-hexane,[25] and cyclohexane (see earlier).

No cyclopentanone was observed in experiments conducted at room temperature, with O_2 partial pressures of 150 to 700 Torr, indicating a yield of $< 0.5\%$. In similar experiments, conducted at 300 K in 1 atm air, Takagi et al.[3] reported a cyclopentanone yield of 0.2%, consistent with our measured upper limit. Other products observed in our experiments were CO (29% yield) and CO_2 ($10 \pm 5\%$ yield), which likely result from chemistry of the radical obtained following ring-opening, $CH_2(CH_2)_3CHO$, see Reaction Scheme 2. The observation of significant yields of CO point to the probable importance of isomerization of the $OCH_2(CH_2)_3CHO$ radical, and eventual elimination of HCO. In fact, the observation of measurable CO yields indicates that HCO elimination (reaction D of Scheme 2) is able to compete effectively with isomerization (reaction E), a process that is anticipated to be rapid ($\approx 10^7$ s^{-1}).[26] It is also interesting to note that CO is observed in the presence of NO_x, but not in its absence. The reason for this observation may be due to the large yield of molecular products that are obtained in the consecutive peroxy radical self-reactions that occur in the NO_x-free experiments, which reduces the yield of each successive oxy radical, and hence the final CO yield.

The origin of the CO_2, observed in the NO_x experiments, but not in the NO_x-free experiments, is not immediately evident. One possibility, shown as reaction C of Scheme 2, involves the transfer of the weak aldehydic H-atom of the $\cdot OCH_2(CH_2)_3$-CHO radical via a seven-membered transition state.

Formic acid was consistently observed in these NO_x experiments, with a yield of order 2%, considerably lower than the 7.5% yield reported by Takagi et al.[3] and lower than was observed in the cyclohexane system under conditions where substantial ring-opening occurred. The production of the formic acid could occur after Reaction (E) of Scheme 2. The reduced formic acid yield relative to the cyclohexane system is likely a result of the occurrence of HCO elimination (Reaction D), a reaction not available in the cyclohexoxy case. Some formic acid may also be generated in conjunction with CO_2 formation.

As was the case for cyclohexane oxidation, Takagi et al.[3] also observed formaldehyde (44% molar yield) and acetylene (17.5% molar yield) as products of the OH-initiated oxidation of cyclopentane in the presence of NO. These species were not observed in our experiments, and are very likely artifacts.

The lack of cyclopentanone formation in these experiments confirms that reaction with O_2 is not an important fate of the cyclopentoxy radical at room temperature; its chemistry is clearly dominated by decomposition, which will lead to a number of multi-functional C4 and C5 straight chain species in conjunction with the observed CO and CO_2. It is possible that some of the cyclopentoxy ring-opening is occurring as a result of chemical activation,[21−24] but the importance of this process cannot be determined using the current experimental methodology.

In experiments conducted at lower temperature (260, 250, 240, and 230 K), cyclopentanone was observed in small yields, which increased with decreasing temperature and increasing O_2 (see Table 1 for a summary). The highest cyclopentanone yield

TABLE 1: Product Yields (Molar %) Measured in the Cl-Atom Initiated Oxidation of Cyclopentane, as a Function of Temperature and O_2 Concentration, in the Presence and Absence of NO_x[a]

temp (K)	no NO_x	with NO_x present			
	cyclopentanone	CO	cyclopentanone (100 Torr O_2)	cyclopentanone (500 Torr O_2)	CO_2
230		10	7	11	9
240	42	10	2.9	5.5	9
250		11	2	5	11
260	25	17	0.7	1.7	12
300	10	28	<0.5	<0.5	11

[a] Yields were independent of O_2, unless otherwise indicated.

measured was 11%, at 230 K and an O_2 partial pressure of 500 Torr. The observation of only small yields of cyclopentanone under these conditions indicates that reaction with O_2 (R18) is of only minor importance in the chemistry of cyclopentoxy radicals throughout the entire range of conditions present in the troposphere. Yields of CO were found to decrease with decreasing temperature (see Table 1), from a value of about 30% at room temperature to values near 10% at 230−240 K. The decreasing CO yield may result from a decrease in the rate of the isomerization of the $HC(O)CH_2CH_2CH_2CH_2O$ radical (reaction B of Scheme 2) relative to its reaction with O_2 (reaction A), and/or to an increase in the rate of reaction (E) relative to that of reaction (D).

Discussion

The data presented above show that, at ambient temperature, the chemistry of the cyclohexoxy radical is characterized by a competition between reaction with O_2 and ring-opening. Because of the fairly substantial barrier to ring opening (about 12 kcal/mol), the importance of this process decreases rapidly with temperature, such that the O_2 reaction will dominate the atmospheric chemistry of cyclohexoxy at temperatures below about 270 K. In contrast, the dominant fate of the cyclopentoxy radical at all temperatures relevant to atmospheric chemistry will be ring-opening. As first discussed by Takagi et al.,[3] the added ring strain in the C_5 system lowers the enthalpy of the ring-opening, leading to an approximate 100-fold increase in the rate coefficient for cyclopentoxy ring-opening compared to that for cyclohexoxy.

Methods for the estimation of the rate coefficients for the various reactions of alkoxy radicals (reaction with O_2, decompositions, and isomerizations) have been developed by Atkinson and co-workers.[11,18,26,27] For decomposition reactions, rate coefficient estimates are obtained by first assuming an A-factor of 2×10^{14} s^{-1}, multiplied by the reaction degeneracy. The activation energy (E_d, in kcal/mol) is then estimated from the following formula: $E_d = (2.4{*}\mathrm{IP} - 8.1) + 0.36\Delta H_d$, where IP is the ionization potential of the leaving group (in eV), and ΔH_d is the enthalpy of the decomposition (in kcal/mol). Using this methodology for the cyclohexoxy radical leads to an Arrhenius expression for (R5) of $k_5 = 4 \times 10^{14} \exp(-6730/T)$ s^{-1}, which can be compared to our experimentally determined value of $k_5 = 1.2 \times 10^{13} \exp(-5750/T)$ s^{-1}. Over the temperature range covered by our experiments (260−300 K), the two expressions agree very well, generating values for k_5 that agree to within 20% (approximately the uncertainty in our experimental data). However, the data obtained herein open up the possibility that the cyclohexoxy ring-opening process is characterized by a lower A-factor and lower energy barrier than previously believed. Similarly low A-factors ($\approx 10^{13}$ s^{-1}), with activation energies below the estimated[26] values, have recently reported for the decomposition reactions of *tert*-butoxy[28] and ethoxy[29] radicals.

Firm conclusions regarding the energetics of cyclopentoxy radical ring-opening are more difficult to obtain, owing to the dominance of the ring-opening over the O_2 reaction, and thus the difficulty in obtaining definitive temperature-dependent values for the rate coefficient ratio, k_{17}/k_{18}. Further complications arise from the possible influence of chemical activation effects[21−24] in the chemistry of the cyclopentoxy species. Approximate Arrhenius parameters for the ring-opening reaction can be estimated from our low-temperature data, however, under the initial assumption that the degree of decomposition due to chemical activation is minimal. The data presented in Table 1 indicate that for conditions of high O_2 (500 Torr) and low temperature (230 K), the decomposition reaction rate still exceeds that of reaction with O_2 by about an order of magnitude, and thus must be of order 1×10^6 s^{-1}. Assuming an A-factor of about 1×10^{13} s^{-1}, as was obtained for the cyclohexoxy ring-opening reaction, leads to an energy barrier to ring-opening for the cyclopentoxy radical of about 7−8 kcal/mol. Assuming a higher A-factor, 2×10^{14} s^{-1} as suggested by Atkinson,[18] leads to an activation energy of about 9 kcal/mol. Even with a very high (70%) occurrence of cyclopentoxy decomposition by chemical activation, these barrier estimates would only increase by about 1 kcal/mol. Thus, even the highest probable decomposition barrier implied by the data obtained in our study (10 kcal/mol) falls somewhat below the 11−12 kcal/mol that is obtained using the estimation methods outlined above. The data obtained regarding the thermodynamics of the cyclopentoxy radical chemistry support the general conclusion alluded to above, that decomposition barriers and A-factors for alkoxy radical decomposition reactions are lower than previously believed.

Conclusions

The Cl-atom oxidation of cyclohexane and cyclopentane have been studied over a range of conditions relevant to atmospheric chemistry. The chemistry of the cyclohexoxy radical is governed by a competition between reaction with O_2 (R6) and ring-opening (R5), with $k_6/k_5 = (1.3 \pm 0.3) \times 10^{-27} \exp(5550 \pm 1100/T)$ cm^3 $molecule^{-1}$. Reaction with O_2 will dominate the chemistry at the temperatures encountered in the middle to upper troposphere. In contrast, ring-opening is the major fate of the cyclopentoxy radical under all conditions relevant to the troposphere. The energy barrier to ring-opening for the cyclopentoxy radicals, < 10 kcal/mol, and possibly for the cyclohexoxy radical as well, are lower than values currently estimated.

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