Reactions of OH Radicals with $C_6 - C_{10}$ Cycloalkanes in the Presence of NO: Isomerization of $C_7 - C_{10}$ Cycloalkoxy Radicals

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ABSTRACT: Rate constants have been measured for the reactions of OH radicals with a series of C_6-C_{10} cycloalkanes and cycloketones at 298 ± 2 K, by a relative rate technique. The measured rate constants (in units of 10^{-12} cm³ molecule⁻¹ s⁻¹) were cycloheptane, 11.0 ± 0.4; cyclooctane, 13.5 ± 0.4; cyclodecane, 15.9 ± 0.5; cyclohexanone, 5.35 ± 0.10; cycloheptanone, 9.57 ± 0.41; cyclooctanone, 15.4 ± 0.7; and cyclodecanone, 20.4 ± 0.8, where the indicated errors are two least-squares standard deviations and do not include uncertainties in the rate constant for the



reference compound *n*-octane. Formation yields of cycloheptanone from cycloheptane ($4.2 \pm 0.4\%$), cyclooctanone from cyclooctane ($0.85 \pm 0.2\%$), and cyclodecanone from cyclodecane ($4.9 \pm 0.5\%$) were also determined by gas chromatography, where the molar yields are in parentheses. Analyses of products by direct air sampling atmospheric pressure ionization mass spectrometry and by combined gas chromatography—mass spectrometry showed, in addition to the cycloketones, the presence of cycloalkyl nitrates, cyclic hydroxyketones, hydroxydicarbonyls, hydroxycarbonyl nitrates, and products attributed to carbonyl nitrates and/or cyclic hydroxynitrates. The observed formation of cyclic hydroxyketones from the cycloheptane, cyclooctane and cyclodecane reactions, with estimated molar yields of 46%, 28%, and 15%, respectively, indicates the occurrence of cycloalkoxy radical isomerization. Potential reaction mechanisms are presented, and rate constants for the various alkoxy radical reactions are derived.

INTRODUCTION

Alkanes, including cycloalkanes, comprise \sim 60% of reformulated gasolines in California and \sim 40% of nonmethane volatile organic compounds emitted in vehicle exhaust.^{1,2} In the atmosphere, acyclic and cyclic alkanes react dominantly with hydroxyl (OH) radicals, by H-atom abstraction from the various C–H bonds to form alkyl radicals (R[•]), which rapidly react with O₂ to form alkyl peroxy (RO₂[•]) radicals.³

$$OH + RH \rightarrow H_2O + R^{\bullet}$$
(1)

$$R^{\bullet} + O_2 + M \rightarrow RO_2^{\bullet} + M$$
(2)

In the presence of NO, RO_2^{\bullet} radicals react with NO via two channels, to form alkyl nitrates (RONO₂) or an alkoxy radical (RO[•]) plus NO₂:³

$$\mathrm{RO}_2^{\bullet} + \mathrm{NO} + \mathrm{M} \rightarrow \mathrm{RONO}_2 + \mathrm{M}$$
 (3a)

$$\mathrm{RO}_2^{\bullet} + \mathrm{NO} \rightarrow \mathrm{RO}^{\bullet} + \mathrm{NO}_2$$
 (3b)

Under atmospheric conditions, alkoxy radicals react by unimolecular decomposition, unimolecular isomerization (generally through a six-member transition state), and by reaction with O_{2i} ^{3,4} note that not all of these potential reactions may be feasible for a given alkoxy radical. There is now a semiquantitative or better understanding of the relative importance of these three processes for acyclic alkoxy radicals, such as those formed from acyclic alkanes.^{3,4} However, there are few data available concerning the importance of isomerization of cycloalkoxy radicals formed from cycloalkanes.⁵⁻⁸ The potential reactions of the cyclohexyl peroxy radical leading to first-generation products are shown in Scheme 1,⁶ which assumes, consistent with observations,⁶ that isomerization of the HC(O)CH₂CH₂CH₂CH₂CH₂O[•] alkoxy radical dominates over its decomposition and reaction with O₂. Hence for cyclohexane the potential products (with molecular weights, MW, in parentheses) are cyclohexyl nitrate (MW 145) from reaction 3a; cyclohexanone (MW 98) from the O₂ reaction; cyclic C₆-hydroxynitrate (MW 161) and cyclic C₆-hydroxyketone (MW 114) from the isomerization reaction; and C_6 -carbonyl nitrate (MW 161), C₆-hydroxycarbonyl nitrate (MW 177), and C₆-hydroxydicarbonyl (MW 130) from the decomposition reaction. Homologous products occur for other cycloalkanes (with the product molecular weights increasing by 14 mass units per additional CH₂ group in the cycloalkane).

As expected because the chair configuration of the cyclohexoxy radical is preferred, isomerization of the cyclohexoxy radical has been shown to be of no importance,⁶ and to date the only reported study of the reactions of >C₆ cycloalkoxy radicals is that of Tagaki et al.⁵ for OH + cycloheptane. Lim and Ziemann⁹ have studied aerosol formation from the OH radical-initiated reactions of a series of cycloalkanes and observed products in the aerosol phase that were consistent with the occurrence of cycloalkoxy

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Scheme 1. Potential Reactions of the Cyclohexyl Peroxy Radical^a



^{*a*}It is assumed that, after isomerization of the cyclohexoxy radical, the resulting 4-hydroxycyclohexoxy radical will undergo a rapid second isomerization. Potential first-generation products are shown in boxes. See ref 6.

radical isomerizations during the OH radical-initiated reactions of cyclododecane and cyclopentadecane.

In this work, we have investigated the products formed from the reactions of OH radicals with cyclohexane, cycloheptane, cyclooctane, and cyclodecane, specifically with regard to the occurrence of cycloalkoxy radical isomerization. As part of this study, we have also measured rate constants for the reactions of OH radicals with cycloheptane, cyclooctane, cyclodecane, cyclohexanone, cycloheptanone, cyclooctanone, and cyclodecanone at 298 \pm 2 K.

EXPERIMENTAL METHODS

All experiments were carried out in a 7000 L Teflon chamber equipped with two parallel banks of black lamps for irradiation, at 298 \pm 2 K and 735 Torr of purified air. While the majority of experiments were carried out in dry purified air, in several experiments 3.3 \times 10¹⁷ molecules cm⁻³ of water vapor was added to the chamber [corresponding to ~50% relative humidity (RH)]. OH radicals were generated from the photolysis of CH₃ONO at wavelengths >300 nm, and NO was included in the reactant mixtures to avoid formation of O₃ and hence of NO₃ radicals.

Kinetic Experiments. Rate constants for the reactions of OH radicals with cycloheptane, cyclooctane, cyclodecane, cyclohexanone, cycloheptanone, cyclooctanone, and cyclodecanone were measured by a relative rate method, in which the relative disappearance rates of the organic compounds and a reference compound (whose rate constant for reaction with OH radicals is reliably known) were measured in the presence of OH radicals.

$$OH + organic \rightarrow products$$
 (4)

$$OH + reference compound \rightarrow products$$
 (5)

Providing that the only loss process for the organic and reference compound were by reaction with OH radicals, then

$$\ln\left(\frac{\left[\text{organic}\right]_{t_0}}{\left[\text{organic}\right]_t}\right) = \frac{k_4}{k_5} \ln\left(\frac{\left[\text{reference compound}\right]_{t_0}}{\left[\text{reference compound}\right]_t}\right) \quad (I)$$

where $[\text{organic}]_{t_0}$ and $[\text{reference compound}]_{t_0}$ are the concentrations of the organic and reference compound, respectively, at time t_0 ; $[\text{organic}]_t$ and $[\text{reference compound}]_t$ are the corresponding concentrations at time t; and k_4 and k_5 are the rate constants for reactions 4 and 5, respectively. The initial reactant

concentrations (in molecule cm⁻³) were CH₃ONO and NO, ~2.4 × 10¹⁴ each; and organic and reference compound, ~2.4 × 10¹³ each. *n*-Octane was used as the reference compound, apart from experiments with cycloheptane, which coeluted with *n*octane on the gas chromatographic column used. The rate constant for cycloheptane was therefore determined relative to that for cyclooctane. Irradiations were carried out at 20% of the maximum light intensity for up to 16–27 min, resulting in up to 28–67% of the initially present organic or reference compound being consumed by reaction.

The concentrations of the organics and reference compounds were measured during the experiments by gas chromatography with flame ionization detection (GC-FID). Gas samples of 100 cm³ volume were collected from the chamber onto Tenax-TA adsorbent, with subsequent thermal desorption at ~205 °C onto a 30 m DB-1701 megabore column, initially held at -40 °C and then temperature-programmed to 250 °C at 8 °C min⁻¹. During each experiment, the following GC-FID analyses were conducted: at least two replicate analyses prior to reaction, one analysis after each of three irradiation periods, and a replicate analyses of the cycloalkanes, cycloketones, and *n*-octane showed that the measurement uncertainties were typically <3%.

Product Studies. Analyses by Gas Chromatography. OH radical-initiated reactions of cycloheptane, cyclooctane, and cyclodecane were carried out to measure the formation yields of the corresponding cycloketones, with reactants and products being collected onto Tenax solid adsorbent and analyzed by GC-FID as described above. The initial concentrations (molecule cm⁻³) of CH₃ONO, NO, and cycloalkane were ~2.4 × 10^{14} , ~2.4 × 10^{14} , and (2.20–2.41) × 10^{13} , respectively. Irradiations were carried out at 20% of the maximum light intensity for up to 3–24 min.

An additional series of CH₃ONO-NO-air irradiations of cyclohexane (dry), cycloheptane (dry and at 50% RH), cyclooctane (dry), cyclodecane (dry), cyclooctane + cyclodecane (50% RH), and cyclohexane + cycloheptane + cyclooctane + cyclodecane (dry and at 50% RH) were carried out, with a single irradiation period. GC-FID analyses of the cycloalkanes and of their cycloketone products were conducted as described above. For the analysis of cyclohexane, gas samples were also collected into a 100 cm³ all-glass gastight syringe and transferred via a 1 cm³ gas sampling loop onto a 30 m DB-5 megabore column initially held at -25 °C and then temperature-programmed at $8 \,^{\circ}\text{C} \,^{-1}$. Samples were also collected, starting immediately after the lights were turned off, for 60 min at 15 L minby use of an XAD resin-coated denuder, further coated with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) prior to sampling to derivatize carbonyls to their oximes, and extracted as described previously.¹⁰ The extracts were analyzed by combined gas chromatography-mass spectrometry in both positive chemical ionization (PCI GC-MS) and negative chemical ionization (NCI GC-MS) modes and by GC-FID, with all analyses using 30 m DB-5 columns. The GC-MS analyses used an Agilent 5973 mass-selective detector operated in the scanning mode with methane as the reagent gas. Each carbonyl group derivatized to an oxime adds 195 mass units to the compound's molecular weight (MW), and methane-PCI gives characteristic protonated molecules $([M + H]^+)$ and smaller adduct ions at $[M + 29]^+$ and $[M + 41]^+$. In addition, hydroxycarbonyls have characteristic $[M + H - H_2O]^+$ fragment ions.

Analyses by API-MS/MS. CH₃ONO-NO-cycloalkane-air irradiations were carried out during which the chamber contents



Figure 1. Plots of eq I for reactions of OH radicals with (\triangle) cyclooctane and (\Box) cyclodecane, with *n*-octane as the reference compound. Data are from three experiments for each cycloalkane.

were sampled through a 25 mm diameter, 75 cm length, Pyrex tube at ~20 L min⁻¹ directly into the atmospheric pressure ionization (API) MS source. The operation of the API-MS in the MS (scanning) and MS/MS [with collision-activated dissociation (CAD)] modes has been described previously.^{6,11} Both positive and negative ion modes were used in this work. In positive ion mode, protonated water hydrates $[H_3O^+(H_2O)_n]$ generated by the corona discharge in the chamber diluent air were responsible for the formation of protonated molecules $([M + H]^+)$, water adduct ions $[M + H + H_2O]^+$, and protonated homo- and heterodimers,¹¹ while in negative ion mode, O_2^{-7} , NO_2^{-7} , and NO_3^{-7} ions were responsible for formation of adduct ions.¹¹

The initial concentrations (molecule cm⁻³) were CH₃ONO, \sim 4.8 × 10¹³; NO, \sim 4.8 × 10¹³; and cycloalkane, \sim 2.4 × 10¹³. The reactant mixtures were irradiated for 3–15 min at 20% of maximum light intensity, resulting in 14–35% consumption of the initially present cycloalkane as measured by GC-FID; note that experiments were carried out at low extents of reaction (14–19%) for each cycloalkane.

Chemicals. The chemicals used, and their stated purity levels, were cyclohexane (99.9+%), cycloheptane (98%), cyclooctane (99+%), cyclodecane (samples of 95% and 98% purity were used), cyclohexanone (99.8%), cycloheptanone (99%), cyclo-octanone (99%), cyclodecanone (97%), and *n*-octane (99+%), from Aldrich; *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (99+%), from Lancaster; cyclohexyl nitrate, from Fluorochem, Inc.; and NO (\geq 99.0%), from Matheson Gas Products. Methyl nitrite was prepared as described by Taylor et al.¹² and stored at 77 K under vacuum.

RESULTS AND DISCUSSION

Kinetic Experiments. The experimental data from CH₃O-NO-NO-organic-reference compound-air irradiations are plotted in accordance with eq I in Figures 1–3, and the rate constant ratios k_4/k_5 obtained from least-squares analyses of these data are given in Table 1. The rate constant ratios k_4/k_5 (*n*-octane) are placed on an absolute basis by use of a value of $k_5(n$ -octane) = 8.11×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298 K,³



Figure 2. Plot of eq I for reactions of OH radicals with cycloheptane, with cyclooctane as the reference compound. Data are combined from three experiments.



Figure 3. Plots of eq I for reactions of OH radicals with (\triangle) cyclohexanone, (\Box) cycloheptanone, (\bigcirc) cyclooctanone, and (∇) cyclodecanone, with *n*-octane as the reference compound. Data are from three experiments for each cycloketone.

and the resulting rate constants k_4 are also given in Table 1. The rate constant for cycloheptane was measured relative to that for cyclooctane, and the measured rate constant ratio is placed on an absolute basis by use of our measured rate constant for OH + cyclooctane (Table 1).

As shown in Table 2, our rate constant for cycloheptane agrees with that of Jolly et al.¹³ within the combined experimental uncertainties, and our rate constants for cycloheptane and cyclooctane agree to within 10% with those of Behnke et al.,¹⁴ Donahue et al.,¹⁵ Wilson et al.,¹⁶ and Sprengnether et al.¹⁷ Our rate constant for cyclohexanone is 16% lower than the absolute rate constant measured by Dagaut et al.¹⁸ The rate constant per CH₂ group in cycloheptane, cyclooctane, and cyclodecane is

Table 1. Rate Constant Ratios k_4/k_5 and Rate Constants k_4 for Reactions of OH Radicals with a Series of Cycloalkanes and Cycloketones at 298 \pm 2 K

reactant	ref compd	$k_4/k_5^{\ a}$	$10^{12} imes k_4^{\ b}$ (cm ³ molecule ⁻¹ s ⁻¹)
cycloheptane	cyclooctane	0.817 ± 0.005	11.0 ± 0.4
cyclooctane	<i>n</i> -octane	1.66 ± 0.04	13.5 ± 0.4
cyclodecane	<i>n</i> -octane	1.96 ± 0.05	15.9 ± 0.5
cyclohexanone	<i>n</i> -octane	0.660 ± 0.012	5.35 ± 0.10
cycloheptanone	<i>n</i> -octane	1.18 ± 0.05	9.57 ± 0.41
cyclooctanone	<i>n</i> -octane	1.90 ± 0.08	15.4 ± 0.7
cyclodecanone	<i>n</i> -octane	2.52 ± 0.09	20.4 ± 0.8

^{*a*} At 298 ± 2 K. Indicated errors are two least-squares standard deviations. Estimated overall uncertainties are ±6% or two least-squares standard deviations, whichever is largest. ^{*b*} Placed on an absolute basis by use of rate constants $k_5(OH + n\text{-}octane) = 8.11 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ 3} \text{ and } k_5(OH + cyclooctane}) = (1.35 \pm 0.04) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this work). A rate constant ratio of $k_4(OH + cycloheptane)/k_5(OH + n\text{-}octane}) = 1.36 \pm 0.04$ is obtained from $k_4(OH + cycloheptane)/k_5(OH + n\text{-}octane}) = [k_4(OH + cycloheptane)/k_5(OH + cyclooctane})][k_4(OH + cyclooctane)].$

 Table 2. Comparison of Rate Constants Measured in the

 Present Work with Literature Data

$10^{12} imes k_4$				
$(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	<i>T</i> (K)	ref		
	Cycloheptane			
13.1 ± 2.1	298 ± 2	13		
11.8 ± 0.2^a	300	14		
12.0 ± 0.3	300	15		
10.4^{b}	298	16		
11.0 ± 0.4	298 ± 2	this work		
	Cyclooctane			
13.7 ± 0.3^a	300	14		
13.4 ± 0.4	300	15		
14.1 ± 1.4	298	17		
13.5 ± 0.4	298 ± 2	this work		
Cyclohexanone				
6.39 ± 0.51	298	18		
5.35 ± 0.10	298 ± 2	this work		

^{*a*} Relative rate determination, relative to a series of organics. The rate constants used¹⁴ for these organics (*n*-butane, *n*-hexane, *n*-octane, 2,2,3,3-tetramethylbutane, 2,2,4-trimethylpentane, and hexafluorobenzene) were 8–11% higher than recent recommendations for *n*-butane, *n*-hexane, *n*-octane, 2,2,3,3-tetramethylbutane, and 2,2,4-trimethylpentane,³ and 30% higher than the 300 K rate constant of McIlroy and Tully¹⁹ for hexafluorobenzene. ^{*b*} Relative rate determination. Rate constants were measured over the temperature ranges 300–404 K and 312–408 K relative to *n*-hexane and cyclohexane, respectively, and the cited 298 K value is that calculated by Wilson et al.¹⁶ from their Arrhenius expression.

constant, at $(1.62 \pm 0.13) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 ± 2 K, and is a factor of 1.4 higher than the rate constant per CH₂ group in cyclohexane $(1.16 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K)³ and marginally higher than the rate constant per CH₂ group bonded to two other CH₂ groups in the *n*-alkanes, of

Table 3. Observation of Anticipated Products from OH Radical-Initiated Reactions of Cyclohexane, Cycloheptane, Cyclooctane, and Cyclodecane^a

	observed in API-MS positive (pos) or negative (neg) ion mode, ^b and/or in PCI and/or NCI GC-MS analyses of PFBHA-coated denuder extracts			
products	cyclohexane	cycloheptane	cyclooctane	cyclodecane
cycloalkyl nitrates	API pos			
(N6-N10)	PCI and NCI GC-MS ^c	PCI and NCI GC-MS ^c	PCI and NCI GC-MS ^c	PCI and NCI GC-MS ^c
cycloketones (K6–K10)	API pos	API pos ^e	API pos ^e	API pos
	PCI and NCI GC-MS ^d	PCI and NCI GC-MS ^d	PCI and NCI GC-MS ^d	PCI and NCI GC-MS ^d
carbonyl-nitrates and/or	API pos and neg	API pos and neg	API pos and neg	API neg
cyclic hydroxynitrates		PCI and NCI GC-MS ^f	PCI and NCI GC-MS ^f	
(ON6-ON10)				
cyclic hydroxyketone	not observed	API pos and neg	API pos and neg	API pos and neg
(HC7-HC10)		PCI and NCI GC-MS ^g	PCI and NCI GC-MS ^g	PCI and NCI GC-MS ^g
hydroxydicarbonyls	API pos and neg	API pos and neg	API pos and neg	API pos and neg
hydroxycarbonyl nitrates	API pos and neg	API pos and neg	API pos and neg	API neg

^a See Scheme 1 and also Figure 5. ^b Unless noted otherwise, API-MS/MS spectra were also analyzed. ^c Cyclohexyl nitrate was confirmed by matching the retention time and mass spectrum with those of an authentic standard. Retention times for the cyclohexyl-, cycloheptyl-, cyclooctyl-, and cyclodecyl nitrates were: 10.9, 13.7, 16.1, and 19.8 min, respectively. Molecular ions were not observed with either NCI or PCI mode, but the spectra were readily identifiable. The characteristic spectra in NCI mode included a large m/z 46 $[NO_2]^-$ fragment (base peak in the cyclohexyl and cycloheptyl nitrates), large $[M - H_2 - NO_2]^-$ fragments (base peak in the cyclooctyl and cyclodecyl nitrates) and smaller $[M - NO_2]^-$ ion fragments. In PCI mode the $[M + H - HNO_3]^+$ fragment was present in all spectra (base peak in cyclohexyl, cycloheytl, and cyclooctyl nitrates), as were $[M + H - HNO_2]^+$ fragments and $[M + H - H_2 - HNO_3]^+$ ions (base peak in cyclodecyl nitrate).^d Cycloketones were confirmed by matching retention times and mass spectra with the oximes of authentic standards. The PCI spectra were similar to those of many carbonyl oximes with strong $[M + H]^+$ ions and weaker adduct ions at $[M + 29]^+$ and $[M + 41]^+$ and a fragment ion of $[M + H - 198]^+$ (see, for example, spectrum A in Figure 6). The retention times of the cyclohexanone, cycloheptanone, cyclooctanone, and cyclodecanone oximes were 19.6, 21.3, 22.4, and 24.9 min, respectively. In NCI mode, no molecular ions were present, but $[M - HF]^-$ fragments were observed. The low yield of cyclooctanone (K8 in Figure 5) relative to the other cycloketones is consistent with the GC-FID analyses of samples collected onto Tenax solid adsorbent (see Table 4). e Identified from presence of $[M + H]^+$ ion peaks at m/z 113 (cycloheptanone) and m/z 127 (cyclooctanone; see Figure 4); no API-MS/MS spectra taken.⁴ In NCI mode (not shown), in addition to the cycloalkyl nitrates, the m/z 46 ion chromatogram of the cyclohexane, cycloheptane, cyclooctane, and cyclodecane reaction whose PCI TIC is shown in Figure 5 showed two additional large peaks. If the base peaks in the spectra of these two products $(m/z \ 127 \ and \ m/z \ 141)$ are attributed to $[M - H_2 - H_2 - H_2]$ NO2] fragments, these spectra would be of nitrates of MW 175 and 189, respectively, consistent with carbonyl nitrates or cyclic hydroxynitrates of molecular formulas C₇O₄NH₁₃ and C₈O₄NH₁₅, respectively. ^gSpectra attributed to the oximes of the C₇-cyclic hydroxyketone (see spectrum B in Figure 6) and the C₈- and C₁₀-cyclic hydroxyketones were observed in PCI mode with strong $[M + H - H_2O]^+$ fragments characteristic of the oximes of hydroxycarbonyls.²² The retention times were 24.8, 25.7, and 27.7 min, respectively. In NCI mode, no molecular ions were present, but $[M - HF]^$ fragments were observed. Consistent with the API-MS data, no hydroxycyclohexanone was observed.

 $(1.45 \pm 0.03) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K by use of the recommended 298 K rate constants for the C₄-C₁₀ *n*-alkanes.³

For the cycloketones, the rate constant ratios k(OH + C_n -cycloketone)/k(OH + C_n -cycloalkane) increase monotonically with increasing carbon number, *n*, with values of 0.77 (n = 6, for 6.97×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298 K for OH + cyclohexane³), 0.87 ± 0.05 (n = 7), 1.14 ± 0.07 (n = 8), and 1.28 ± 1.28 0.07 (n = 10). For the linear ketones, H-atom abstraction from the C–H bonds on the β -carbon (i.e., two carbons from the C=O group) is enhanced (β -activation) and this is proposed to be due to formation of a hydrogen-bonded transition state.^{18,20} In addition to β -enhancement, the structure-reactivity estimation method of Kwok and Atkinson²¹ has H-atom abstraction from C–H bonds of the neighboring (α) group being slightly deactivated. On the basis of literature rate constants for cyclopentanone,¹⁸ cyclopentane,³ and cyclohexane³ and those measured here for the C_7-C_{10} cycloalkanes and C_6-C_{10} cycloketones, it appears that β -activation is absent in cyclopentanone,¹⁸ cyclohexanone,¹⁸ and cycloheptanone but becomes present in cyclooctanone and cyclodecanone. Thus, the rate constants for OH + cyclooctanone and cyclodecanone estimated by the Kwok and Atkinson approach with β -activation²¹ (1.49 × 10⁻¹¹ and $1.77 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹, respectively) are in good agreement with the measured values, being only 3% and 13% lower, respectively. In contrast, the estimated rate constants including β -activation²¹ for cyclohexanone and cycloheptanone are factors of 2.3 and 1.4 higher than our measured values, respectively.

Identification of Products. Products were identified from API-MS and GC-MS analyses, and Table 3 gives the compound classes observed from these two complementary analysis techniques. In positive ion mode, API-MS and API-MS/MS analyses of the OH + cyclohexane reaction gave results in agreement with our previous study.⁶ The API-MS spectra for the four cycloalkane reactions were analogous, and Figure 4 shows the positive and negative ion spectra for the cyclooctane reaction (see the figure caption for peak assignments). GC-MS analyses were carried out for reactions of the individual cycloalkanes as well as for combinations, including all four cycloalkanes. Because of the possibility of cyclization of the cyclic hydroxyketones to their bicyclic hemiacetals with subsequent dehydration,²² experiments were carried out in purified air at \sim 50% relative humidity as well as in dry purified air. Figure 5 shows a PCI GC-MS total ion chromatogram (TIC) from an experiment with all four cycloalkanes present at 50% relative humidity, and details of the product identifications are given in the footnotes to Table 3. Labeled in

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Figure 4. API-MS spectra of an irradiated CH₃ONO-NO-cyclooctaneair mixture. The products identified were cyclooctanone (MW 126), C₈-cyclic hydroxyketone (MW 142), C₈-hydroxydicarbonyl (MW 158), C₈-carbonyl nitrate and/or cyclic hydroxynitrate (MW 189), and C₈hydroxycarbonyl nitrate (MW 205). Top: positive ion spectrum. Based on positive ion API-MS/MS analyses, the ion peak assignments (m/z)are 125, $[142 + H - H_2O]^+$; 127, $[126 + H]^+$; 141, $[158 + H - H_2O]^+$; $143, [142 + H]^+; 157, [158 + H - H_2]^+; 159, [158 + H]^+; 161, [142 + H]^+; [142$ $+ H_2O$]⁺; 172, [189 + H - H₂O]⁺; 190, [189 + H]⁺; 208, [189 + H + H_2O]⁺; 226, [189 + H + 2 H_2O]⁺; 283, [158 + 142 + H - H_2O]⁺; 285, $[142 + 142 + H]^+$; 299, possibly $[158 + 142 + H - H_2]^+$; and 332, [142 + 189 + H]⁺. Bottom: negative ion spectrum. Based on negative ion API-MS/MS analyses, the ion peak assignments (m/z) are 174, [142 + O₂]⁻; 188, [142 + NO₂]⁻; 190, [158 + O₂]⁻; 204, [158 + NO₂]⁻; 218, [158 + 60]⁻; 220, [158 + NO₃]⁻; 235, [189 + NO₂]⁻; 249, [189 + 60]⁻; 251, [189 + NO₃]⁻; 265, [205 + 60]⁻; 267, [205 + NO₃]⁻; and 298, [189 + 109]⁻. The ion peaks at m/z 148 and 202 could not be readily assigned.

Figure 5 are C_{8^-} and C_{10} -cycloalkyl nitrates (N8 and N10); C_{6^-} , C_{7^-} , C_{8^-} , and C_{10} -cycloketones (K6, K7, K8, and K10); and C_{7^-} , C_{8^-} , and C_{10} -cyclic hydroxyketones (HC7, HC8, and HC10), together with C_{7^-} and C_{8^-} oxygenated nitrates (ON7 and ON8; presumably carbonyl nitrates). As shown in the PCI GC-MS TIC and mass spectra in Figure 6 for the cycloheptane reaction, the mass spectra of the oximes of the cycloketones (see, for example, spectrum A in Figure 6) have ions at $[M + H]^+$, $[M + C_2H_5]^+$, $[M + C_3H_5]^+$ and $[M + H - 198]^+$ (where M is the oxime and 198 is $C_6F_5CH_2OH$), while the oximes of the products ascribed to the cyclic hydroxyketones (see, for example, spectrum B in Figure 6) have an additional intense fragment ion at $[M + H - H_2O]^+$.

API-MS and GC-MS analyses both show evidence for the formation of cyclic hydroxyketones from the cycloheptane, cyclooctane, and cyclodecane reactions, in contrast to the cyclohexane reaction where the C₆-cyclic hydroxyketone was not observed (Table 3 and Figure 5). That the cyclic hydroxyketone from the cyclohexane reaction is not formed is in agreement with our previous study, using API-MS in positive ion mode, of the OH + cyclohexane and cyclohexane- d_{12} reactions.⁶ The only other potential product isomeric to the cyclic hydroxyketone from the OH + C_n -cycloalkane reactions would be the ring-opened dicarbonyl HC(O)(CH₂)_{n-2}CHO formed after reaction of the HC(O)(CH₂)_{n-2}CH₂O[•] alkoxy radical with O₂.



Figure 5. PCI GC-MS total ion chromatogram (TIC) of an extract of a PFBHA-coated denuder sample from an irradiated CH₃ONO–NO– cyclohexane–cycloheptane–cyclooctane–cyclodecane–air mixture at \sim 50% relative humidity. The labeled peaks are C₈- and C₁₀-cycloalkyl nitrates (N8 and N10); C₆-, C₇-, C₈-, and C₁₀-cycloketones (K6, K7, K8, and K10); C₇-, C₈-, and C₁₀-cyclic hydroxyketones (HC7, HC8, and HC10); and C₇- and C₈-oxygenated nitrates (ON7 and ON8; presumably carbonyl nitrates).

However, for $n \ge 7$, isomerization of $HC(O)(CH_2)_{n-2}CH_2O^{\bullet}$ alkoxy radicals is expected to dominate over the O₂ reaction by at least a factor of 70,⁴ consistent with the lack of observation of $HC(O)CH_2CH_2CH_2CH_2CHO$ from cyclohexane and of the deuterated analogue from cyclohexane- d_{12} .⁶ Both the positive and negative ion API-MS spectra were consistent with the presence of C₇-, C₈-, and C₁₀- cyclic hydroxyketones of formula $C_nH_{2n-2}O_2$, and there was no evidence for dioximes of C_ndicarbonyls in the PCI GC-MS analyses of the extracts of PFBHA-coated denuder samples.

Positive and/or negative ion API-MS showed evidence for hydroxydicarbonyls and hydroxycarbonyl nitrates (Table 3 and Figure 4). However, while both of these compound classes might be expected to derivatize with PFBHA, no product peaks in PCI GC-MS analyses could be attributed to these compounds.

Quantification of Products. Formation yields of cycloheptanone, cyclooctanone, and cyclodecanone for the OH radicalinitiated reactions of cycloheptane, cyclooctane, and cyclodecane, respectively, were measured by GC-FID analyses of samples collected onto Tenax solid adsorbent from CH₃O-NO-NO-cycloalkane-air irradiations. The cycloketones also react with OH radicals, and hence the measured concentrations were corrected to take into account reaction with OH radicals as described previously,²³ using the rate constants measured here for the cycloalkanes and cycloketones (Table 1). The cyclodecane samples contained a small amount of cyclodecanone (\sim 0.7% and \sim 0.35% for the 95% and 98% stated purity samples, respectively), and the initial presence of cyclodecanone was also taken into account in the data analysis. The maximum values of the multiplicative correction factors, which increase with the rate constant ratio k(OH + cycloketone)/k(OH + cycloalkane) and with the extent of reaction,²³ were 1.32 for formation of cycloheptanone from cycloheptane, 1.58 for formation of cyclooctanone from cyclooctane, and 1.59 for formation of cyclodecanone from cyclodecane. Plots of the amounts of the cycloketones





Figure 6. Top: PCI GC-MS total ion chromatogram (TIC) of an extract of a PFBHA-coated denuder sample from an irradiated CH₃O-NO-NO-cycloheptane-air mixture. The peak assignments are N7, cycloheptyl nitrate; 1, mono-oximes of molecular weight (MW) 72 carbonyl or dicarbonyl; ON7, C7-carbonyl nitrate or cyclic hydroxynitrate of MW 175; K7 (A), oxime of cycloheptanone; HC7 (B), oxime of MW 128 hydroxycarbonyl of formula C7H12O2; 2, dioximes of MW 72 dicarbonyl; 3, mono-oxime of MW 142 carbonyl; and 4, dioximes of MW 86 dicarbonyl. Bottom panels, PCI mass spectra of peaks A (K7) and B (HC7). Peak A (cycloheptanone, confirmed by GC retention time and mass spectral matching with an authentic standard introduced into the chamber and sampled and analyzed in the same manner as the reaction products) exhibits $[M + H]^+$ and smaller adduct ions at $[M + 29]^+$ and $[M + 41]^+$ and with an $[M + H - 198]^+$ fragment ion, and peak B exhibits $[M + H]^+$, smaller adduct ions at $[M + 29]^+$ and $[M + 41]^+$, and intense $[M + H - H_2O]^+$ and $[M + H - 198]^+$ fragment ions.

formed, corrected for reaction with OH radicals, against the amounts of cycloalkanes reacted are shown in Figure 7, and the formation yields obtained from least-squares analyses of these data are listed in Table 4. To our knowledge, these are the first reported formation yields of cyclooctanone from cyclooctane and for cyclodecanene from cyclodecane. For cycloheptanone formation from OH + cycloheptane, Takagi et al.⁵ reported a yield of $3.1 \pm 0.8\%$, which, although lower, is in agreement with our value of $4.2 \pm 0.4\%$ within the combined experimental uncertainties.

Because 1,4-hydroxycarbonyls require derivatization prior to GC analysis,²² GC-FID quantification of the cyclic hydroxyketones was carried out on the extracts from PFBHA-coated denuder samples collected from OH + cycloalkane reactions, using the cycloketone formed in the reaction as an internal standard. Peaks were identified by matching the FID chromatogram with the PCI GC-MS TIC, and the ratios of peak areas of oximes of cyclic hydroxyketones compared to those of cycloketones were determined. Small differences in the FID response factors for the oximes of the various cycloketones and cyclic hydroxyketones were taken into account by use of effective carbon numbers calculated from the data in Scanlon and Willis²⁵ and Nishino et al.²⁶ Secondary reactions of the cycloketones and

Figure 7. Plots of the amounts of (\bigcirc) cycloheptanone, (\triangle) cyclooctanone, and (\Box) cyclodecanone formed, corrected for reaction with OH radicals (and, for cyclodecanone, for the presence of small amounts of cyclodecanone in the cyclodecane samples used; see text), against the amounts of cycloheptane, cyclooctane, and cyclodecane reacted. Data are combined from six experiments (cycloheptane and cyclooctane) or three experiments (cyclodecane). The data for cyclodecanone have been displaced vertically by 1.0×10^{11} molecules cm⁻³ for clarity.

cyclic hydroxyketones were taken into account as described above, by use of estimated rate $constants^{21,27}$ for the reactions of OH radicals with C7-, C8-, and C10-cyclic hydroxyketones of 27.2 \times 10⁻¹², 28.6 \times 10⁻¹², and 31.4 \times 10⁻¹² cm³ molecule⁻¹ s⁻¹, respectively. While these estimated rate constants for the cyclic hydroxyketones are subject to significant uncertainty, the reactions with GC-FID quantification of the denuder extracts were all carried out with \leq 21% consumption of the initially present cycloalkane. This resulted in maximum multiplicative correction factors for the C7-, C8-, and C10-cyclic hydroxyketones of 1.29, 1.23, and 1.26, respectively, which can be compared to the maximum multiplicative correction factors for the C₇-, C₈-, and C₁₀-cycloketones of 1.10, 1.12, and 1.16, respectively. Thus, at the relatively low extents of reaction employed for these experiments, the ratios (correction factor for C_n -cyclic hydroxyketone/correction factor for C_n -cycloketone) were ≤ 1.17 , and uncertainties in the rate constants for the cyclic hydroxyketones resulted in only small uncertainties in the correction factors.

Our experimental data are presented in Table 5, and the resulting formation yields for the cyclic hydroxyketones are given in Table 4. While the ratio of formation yield of C₁₀-cyclic hydroxyketone relative to that of cyclodecanone appeared to increase upon going from dry air to air at ~50% relative humidity, the relative yields of C₇-, C₈-, and C₁₀- cyclic hydroxyketones when all four cycloalkanes were reacted together were essentially identical in dry air and in air at ~50% relative humidity. It should also be noted that aerosol formation from the cyclodecane reaction⁹ could, in conjunction with the chamber walls, lead to losses of the cyclic hydroxyketone.

Fates of C_6 -, C_7 -, C_8 -, and C_{10} -Cycloalkoxy Radicals. As shown in Scheme 1, cycloalkoxy radicals can react with O_2 to form the cycloketone, isomerize to ultimately form either a cyclic

Table 4. Cycloketones and Cyclic Hydroxyketones Observed from OH + Cycloalkane Reactions in the Presence of NO and Their Formation Yields

	cycloketone		cyclic hydroxyketone	
cycloalkane	observed by	yield (%) ^a	observed by	yield $(\%)^b$
cyclohexane	Tenax; denuder; ^c API	34 ± 4^d	not detected	
cycloheptane	Tenax; denuder; ^c API	4.2 ± 0.4	denuder; API	46
cyclooctane	Tenax; denuder; ^c API	0.85 ± 0.2	denuder; API	28
cyclodecane	Tenax; denuder; ^c API	4.9 ± 0.5	denuder; API	15

^{*a*} Unless noted otherwise, from this work. Indicated errors are two least-squares standard deviations of the slopes of the plots shown in Figure 7, combined with estimated uncertainties in the GC-FID response factors for the cycloalkane and its cycloketone product of \pm 5% each. ^{*b*} From the yield data presented in Table 5, using the data from the experiment with all four cycloalkanes present in air at 50% relative humidity (which is in excellent agreement with the relative yields of cycloheptanone, cyclooctanone, and cyclodecanone from the experiment with all four cycloalkanes present carried out in dry air). ^{*c*} Observed as oximes. ^{*d*} Average \pm two standard deviations of the literature room-temperature cyclohexanone yields from OH + cyclohexane carried out in air at atmospheric pressure in the presence of NO of 35.4 \pm 4.2%, ²⁴ 32.1 \pm 3.5%, ⁶ 33 \pm 6%, ⁷ and 36 \pm 6%. ⁸

Table 5. Measured Ratios of Formation Yields of Cyclic Hydroxyketones to Those of the Corresponding Cycloketones and Resulting Formation Yields of Cyclic Hydroxyketones

	$(cyclic hydroxyketone yield/cycloketone yield)^a$		cyclic hydroxyketone molar yield (%)			5)
cycloalkane	dry	\sim 50% RH	dry		\sim 50% RH	
cycloheptane	12.4	11.4	52 ^{<i>a,b</i>}	$(49)^{c,d}$	48 ^{<i>a,b</i>}	46 ^{<i>c</i>,<i>e</i>}
cyclooctane	36	41^f	$31^{a,b}$	$28^{c,d}$	$35^{b_{i}f}$	28 ^{<i>c</i>,<i>e</i>}
cyclodecane	1.8	2.8^{f}	$9^{a,b}$	15 ^{c,d}	$14^{b,f}$	15 ^{<i>c</i>,<i>e</i>}

^{*a*} From experiments with a single cycloalkane present, unless noted otherwise. ^{*b*} From ratio of (cyclic hydroxyketone yield/cycloketone yield), placed on an absolute basis by use of the cycloketone yields measured here and listed in Table 4. ^{*c*} From experiments in which all four cycloalkanes were present. ^{*d*} Because of the small, and uncertain, amount of cyclohexane reacted, the cyclic hydroxyketone data for cycloheptane, cyclooctane, and cyclodecane reactions are placed on an absolute basis by use of a C₇-cyclic hydroxyketone yield of 49% (the average of the two yields derived relative to cycloheptanone formation and that derived relative to cyclohexanone formation at ~50% relative humidity). ^{*c*} Relative to a yield of cyclohexanone from OH + cyclohexane of 34% (Table 4). ^{*f*} From experiment with cyclooctane + cyclodecane. Based on the amounts of cyclooctane and cyclodecane reacted and the GC-FID peak areas of the oximes of the cyclic hydroxyketones, then after correction for reaction with OH radicals and for slight differences in the GC-FID response factors, the C₁₀-cyclic hydroxyketone yield = 0.52 × C₈-cyclic hydroxyketone yield.

hydroxynitrate (minor) or a cyclic hydroxyketone (major), and decompose to form primarily a carbonyl nitrate, a hydroxycarbonyl nitrate, and a hydroxydicarbonyl. In addition, the initial cycloalkyl peroxy + NO reaction leads, in part, to formation of the cycloalkyl nitrate (Scheme 1). Our product data in Table 4 can therefore be used to derive rate constants for the isomerization and decomposition reactions. At room temperature and atmospheric pressure of air, the formation yield of cyclohexyl nitrate from OH + cyclohexane is $16 \pm 2\%$,^{6-8,28} essentially identical to the 2-hexyl nitrate and 3-hexyl nitrate yields from the 2- and 3-hexyl peroxy + NO reactions of 14.0% and 15.8%, respectively.¹¹ For the cycloheptane, cyclooctane, and cyclodecane reactions, we can therefore use the formation yields of alkyl nitrates from the reactions of secondary alkyl peroxy radicals with NO calculated from the expression given by Arey et al.,¹¹ and these are given in Table 6, together with measured formation yields of cycloketones (O2 reaction) and cyclic hydroxyketones (isomerization reaction). The remaining fraction of the overall reaction products is then assumed to be that corresponding to decomposition of the cycloalkoxy radicals; note that this does not take into account the small amount of cyclic hydroxynitrate expected to be formed after the isomerization reaction (this will increase the overall fraction of the reaction proceeding by isomerization by a factor of \sim 1.2 or less, since hydroxynitrate formation yields in the *n*-alkanes appears to be significantly lower than alkyl nitrate yields¹¹). By use of the formation yields of

cycloketones and cyclic hydroxyketones listed in Table 4 and the calculated (by difference) yields of decomposition products, and equating these to the relative reaction rates of cycloalkoxy radicals with O₂, isomerization, and decomposition, respectively, rate constant ratios of $k_{isomerization}/k_{O_2}[O_2]$ and $k_{decomposition}/k_{O_2}[O_2]$ $k_{O_2}[O_2]$ are obtained (Table 6) from $\tilde{k}_{isomerization}/k_{O_2} =$ (yield of cyclic hydroxyketone)/(yield of cycloketone) and k_{decomposition}/ k_{O_2} = (yield of decomposition products, obtained by difference)/(yield of cycloketone). The overall uncertainties in these rate constant ratios are likely to be a factor of \sim 2. These rate constant ratios can be placed on an absolute basis if it is assumed that the rate constants for the reactions of cycloalkoxy radicals with O₂ are independent of ring size and identical to those for reactions of simple acyclic alkoxy radicals with O₂, which appear to be essentially identical irrespective of the alkoxy radical.⁴ We use the recommended rate constant for reaction of simple acyclic alkoxy radicals with O₂ of $k_{O_2} = 9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K,⁴ corresponding to $k_{O_2}[O_2]$ = 4.5×10^4 s⁻¹ at 298 K and 735 Torr of air. The resulting rate constants $k_{\text{isomerization}}$ and $k_{\text{decomposition}}$ are given in Table 6; note that the data for cyclohexane are from previous literature studies.^{6-8,24,28}

Based on literature data,²⁹ the ring-strain energy for simple $\geq C_6$ -cycloalkanes increases from zero for cyclohexane to 6.4 kcal mol⁻¹ for cycloheptane and 9.9 kcal mol⁻¹ for cyclooctane, maximizes at 12.8 kcal mol⁻¹ for cyclononane, and then

	cyclohexane	cycloheptane	cyclooctane	cyclodecane
cycloalkyl nitrate (%)	16 ± 2^a	19^b	23^b	31^{b}
cycloketone ^c (%)	34 ± 4^d	4.2 ± 0.4	0.85 ± 0.2	4.9 ± 0.5
cyclic hydroxyketone ^c (%)	not detected	46	28	15
decomposition products ^e (%)	50 ± 5	31	48	49
$k_{\text{isomerization}}/k_{\text{O}_2}[\text{O}_2]$		11	33	3.1
$k_{\text{isomerization}}^{f}(s^{-1})$		$5.0 imes 10^5$	$1.5 imes 10^6$	$1.4 imes 10^5$
$k_{\rm decomposition}/k_{\rm O_2}[{\rm O_2}]$	1.47 ± 0.23	7.4	56	10
$k_{\text{decomposition}}^{f}(s^{-1})$	$(6.6\pm1.1)\times10^4$	$3.3 imes10^5$	$2.5 imes 10^6$	$4.5 imes 10^5$
$\Delta H_{\rm decomposition}^{g}$ (kcal mol ⁻¹)	7.3	2.2	-2.5	-5.1

Table 6. Product Molar Yields from OH + Cycloalkanes in the Presence of NO at 298 \pm 2 K and 735 Torr of Air, Together with Estimated Rate Constants for Cycloalkoxy Radical Isomerization and Decomposition

^{*a*} Average ± two standard deviations of the literature room temperature and atmospheric pressure cyclohexyl nitrate yields of $16.0 \pm 1.5\%$,²⁸ $16.5 \pm 2.1\%$,⁶ $16 \pm 4\%$,⁷ and $15 \pm 4\%$.⁸ ^{*b*} Calculated from the following expression: yield (%) = 3.81n - 7.3 derived for reactions of secondary alkyl peroxy radicals + NO, where *n* = carbon number.¹¹ ^{*c*} This work (from Table 4), unless noted otherwise. ^{*d*} Average ± two standard deviations of the literature room-temperature cyclohexanone yields from OH + cyclohexane carried out in air at atmospheric pressure in the presence of NO of $35.4 \pm 4.2\%$,²⁴ $32.1 \pm 3.5\%$,⁶ $33 \pm 6\%$,⁷ and $36 \pm 6\%$.⁸ ^{*e*} By difference. ^{*f*} The rate constant ratios of $k_{isomerization}/k_{O_2}[O_2]$ and $k_{decomposition}/k_{O_2}[O_2]$ are placed on an absolute basis with the assumption that $k_{O_2} = 9 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ at 298 K,⁴ corresponding to $k_{O_2}[O_2] = 4.5 \times 10^4$ s⁻¹ at 298 K and 735 Torr of air. ^{*g*} Calculated from measured or estimated heats of formation of cyclic alcohols and linear aldehydes,²⁹ with the assumptions of C–H (in a CH₃ group) and O–H bond dissociation energies of 101 and 104 kcal mol⁻¹, respectively.³⁰

decreases with increasing ring size to 12.6 kcal mol⁻¹ for cyclodecane and 4.4 kcal mol-1 for cyclododecane.²⁹ As expected because of the effect of ring strain,^{5,6,8} decomposition rate constants for the strained cycloalkanes cycloheptane, cyclooctane, and cyclodecane are significantly higher than that for the nonstrained cyclohexane (the calculated enthalpies of decomposition are also listed in Table 6), although the correlation between decomposition rate constant and $\Delta H_{
m decomposition}$ is only approximate. In particular, the decomposition rate constant we obtain for cyclodecoxy radicals (Table 6) is about an order of magnitude lower than that expected from a linear correlation of log ($k_{\text{decomposition}}$) versus $\Delta H_{\text{decomposition}}$ for the cyclohexoxy, cycloheptoxy, and cyclooctoxy radicals. It is possible that the rate constant for cyclodecoxy + O_2 is significantly higher than the value we assume [the other, unlikely explanation would be that our measured cyclodecanone formation yield from OH + cyclodecane is significantly too high; the derived yield of decomposition products is already 49% (Table 6) and obviously could only increase modestly]. Losses of C₁₀-cyclic hydroxyketone to the chamber walls or aerosol, leading to our measured C10-cyclic hydroxyketone formation yield being an underestimate, would increase $k_{\text{isomerization}}/k_{O_2}$ and decrease $k_{\text{decomposition}}/k_{O_2}$ k_{O_2} , and so would not explain the apparently low decomposition rate constant we derive for cyclodecoxy radicals. Additional studies to measure rate constants for the reactions of cycloalkoxy radicals with O_2 as a function of ring size are clearly warranted.

The rate constants derived for the cycloheptoxy, cyclooctoxy, and cyclodecoxy radical isomerizations (Table 6) can be compared to that for isomerization of a linear alkoxy radical, $RCH_2CH_2CH_2CH_2CH(O^{\bullet})R'$ via a 1,5-H shift with a sixmember transition state, of $\sim 4 \times 10^6 \text{ s}^{-1}$ at 298 K.⁴ The rate constants for the cycloheptoxy and cyclodecoxy radical isomerizations are an order of magnitude lower than that for linear alkoxy radicals, suggesting the presence of additional steric and/ or energy barriers. In contrast, the rate constant we derive for isomerization of the cyclooctoxy radical is similar to that expected for a linear, nonstrained, alkoxy radical, suggesting little or no additional energy barrier in the transition state over that for linear alkoxy radicals.

CONCLUSIONS

Analyses of OH + cycloheptane, cyclooctane, and cyclodecane reactions show the presence of products attributed to cyclic hydroxyketones, which can arise after cycloalkoxy radical isomerization. The occurrence of cycloalkoxy radical isomerization has not previously been observed directly but has recently been inferred from aerosol-phase products.⁹ For the cycloheptane, cyclooctane, and cyclodecane reactions studied here, cycloalkoxy radical isomerization appears to be an important process that needs to be included in detailed chemical models for cycloalkane atmospheric degradations.

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