

# Photooxidation of C<sub>5</sub>-C<sub>7</sub> Cycloalkanes in the NO-H<sub>2</sub>O-Air System

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Photooxidation of C<sub>5</sub>-C<sub>7</sub> cycloalkane-NO-H<sub>2</sub>O-air systems was investigated. Reaction products were analyzed by FID gas chromatography (GC), GC/MS, and FT IR. Cycloalkanone and cycloalkyl nitrate were observed to form as undegraded products. Among the C<sub>5</sub>-C<sub>7</sub> cycloalkanes, the ratios of cycloalkyl nitrate produced to cycloalkane consumed were nearly equal (0.05-0.1), while marked variations were observed in the ratios of cycloalkanone produced to cycloalkane consumed (0.0016, 0.23, and 0.031 for C<sub>5</sub>, C<sub>6</sub>, and C<sub>7</sub> cycloalkanes, respectively). These differences were explained by the ring rupture of cycloalkane ring, assuming that the extent of the ring rupture process depends on the strain energy of the cycloalkane ring. Cycloalkanone and cycloalkyl nitrate were minor product except for cyclohexanone, which amounted 20-30% of cyclohexane consumed. Formaldehyde was observed as a ring rupture product (3-9% of cycloalkane consumed). Major products were unidentified carbonyls produced by ring cleavage reactions. These carbonyls amounted to about 45% of cycloalkane consumed. Formation of carbonyls and formaldehyde could be explained by the ring cleavage decomposition of the vibrationally hot cycloalkyloxy radicals.

## Introduction

Analysis of the reaction products of the photooxidation of the hydrocarbon-NO-H<sub>2</sub>O-air system is one of the widely accepted methods used to understand the reaction mechanisms occurring in photochemical air pollution. This method has been used to report on the photooxidation processes of alkanes,<sup>1-7</sup> alkenes,<sup>8-10</sup> and aromatic hydrocarbons.<sup>11-16</sup> In this study, the photooxidation processes of cyclopentane, cyclohexane, and cycloheptane were investigated in cycloalkanes-NO-H<sub>2</sub>O-air systems in order to clarify the following three questions:

(1) What kinds of products are produced in the photooxidation of cycloalkanes? Formation of cycloalkanone and cycloalkyl nitrate is expected from the reaction of O<sub>2</sub>, NO, and NO<sub>2</sub> with the cycloalkyl radical which is produced by hydrogen atom abstraction by OH radicals or oxygen atoms, O(<sup>3</sup>P).

(2) Are there marked differences in the products pro-

duced from C<sub>5</sub>-C<sub>7</sub> cycloalkanes?

(3) Does a ring rupture reaction occur in the photooxidation of cycloalkanes? Cleavage of the aromatic ring was found in the photooxidation of toluene,<sup>12,17</sup> xylene,<sup>15,16</sup> and mesitylene.<sup>18</sup>

## Experimental Section

The Pyrex cylindrical reaction chamber (240 mm i.d., 1660 mm length, and 67 dm<sup>3</sup> volume), oil-free pumping system, and xenon short-arc light source (500 W) have been described previously.<sup>13,14,16</sup> Experimental conditions were as follows: cycloalkane, 1-20 ppm; NO, 1-7 ppm, H<sub>2</sub>O 60-80% relative humidity; and air, 1 atm. Procedures for the mixing of gases and the sampling of the reaction products were also the same as described previously.<sup>13,14,16</sup> Analyses of the reaction products were made by GC, GC/MS, and GC/PIMS<sup>16,19</sup> with a 3-m column of 5% SE-30 on Shimalite-W. Cycloalkyl nitrates used as the standard samples were synthesized<sup>20</sup> as follows: Cyclopentyl nitrate was prepared by the nitration of cyclopentyl alcohol in a mixture of nitric acid and sulfuric acid at low temperature (-20 °C). Cyclohexyl and cycloheptyl nitrates were prepared by the reaction of the bromide salt of these compounds with silver nitrate in acetonitrile solvent.

Reaction products were also analyzed by a Nicolet 7199 long-path FT IR spectrometer. In this case, photooxidation was carried out in another reactor, which will be described in detail in a later publication.<sup>17</sup> Briefly, the reaction chamber is a stainless steel cylinder, 500 mm i.d., 3550 mm long, and 0.79 m<sup>3</sup> in volume. The inner wall of the chamber is coated by FEP-Teflon. The chamber is bakable to 80 °C and evacuable to 1 × 10<sup>-6</sup> torr. An eight-mirror multireflection cell is set in the chamber. The base path between multireflection mirrors is 3000 mm and the number of reflection is 69, giving a total path length of 210.8 m. Fourteen black lights (40 W, Toshiba FL 40S BLB) set on the inner wall of the chamber were used as

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TABLE I: Ratios of Cycloalkanone and Cycloalkyl Nitrate Produced to Cycloalkane Consumed for the Various Experimental Conditions

initial concn, ppm		$\Delta$ [cycloalkanone] $-\Delta$ [cycloalkane], ( $\pm$ %)	$\Delta$ [cycloalkyl nitrate]/ $-\Delta$ [cycloalkane], ( $\pm$ %)	final	total
cycloalkane	NO			cycloalkane unreacted, %	irrdn time, min
Cyclopentane					
7.8	1.2	0.00052 (90)	0.029 (30)	80	478
9.2	2.4	0.00098 (110)	0.042 (40)	89	429
8.1	6.1	0.00175 (70)	0.049 (25)	88	483
2.8	5.7	0.00400 (130)	0.069 (25)	92	360
1.3	6.3	0.00158 (40)	0.036 (30)	69	434
		av 0.00159 $\pm$ 0.00152	av 0.045 $\pm$ 0.015		
Cyclohexane					
9.5	1.2	0.44 (50)	0.163 (30)	97	343
9.3	2.5	0.14 (30)	0.054 (45)	86	360
8.7	6.2	0.18 (20)	0.079 (40)	90	358
2.9	6.1	0.14 (50)	0.057 (50)	82	341
0.8	6.1	0.23 (30)	0.095 (60)	88	305
		av 0.23 $\pm$ 0.13	av 0.090 $\pm$ 0.044		
Cycloheptane					
8.8	0.8	0.031 (20)	0.039 (20)	95	309
7.9	2.3	0.024 (15)	0.037 (30)	89	306
8.8	5.5	0.041 (20)	0.047 (15)	87	296
3.0	5.6	0.025 (20)	0.054 (40)	73	335
1.0	5.4	0.025 (15)	0.061 (20)	73	322
20.0	5.8	0.039 (30)	0.063 (15)	84	342
		av 0.031 $\pm$ 0.008	av 0.050 $\pm$ 0.011		

the photooxidation light source. The effective light intensity as measured by the primary photodecomposition rate of  $\text{NO}_2$  was  $0.22 \text{ min}^{-1}$ .

### Results and Discussion

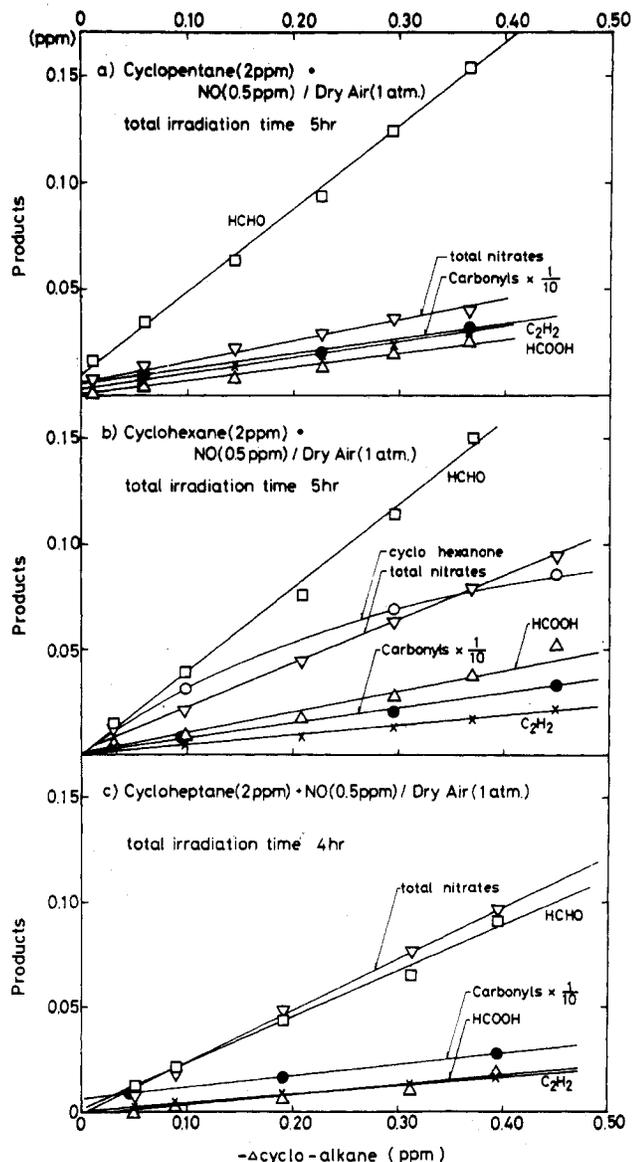
Three major products were observed in the photooxidation of each  $\text{C}_5$ - $\text{C}_7$  cycloalkane by the FID GC analysis. One product appeared with a shorter retention time than cycloalkane. This low-boiling-point product was thought to be produced by the ring cleavage of cycloalkane. The other two products appeared at a longer retention time than cycloalkane. These two products were identified as cycloalkanone and cycloalkyl nitrate by the GC/MS and GC/PIMS. In the case of cyclohexane, mass spectra of the low-boiling-point product observed showed only one signal at  $m/e$  58 when GC/PIMS by Ar resonance lines (11.83 and 11.62 eV)<sup>19</sup> was used. Mass spectra by GC/EIMS with 70-eV electron impact could not be measured because of the interference from the large background of water which was initially contained in the gas mixture. If the signal at  $m/e$  58 is the signal of the parent ion, the low-boiling-point product might be glyoxal, acetone, or propionaldehyde. The formation of acetone and propionaldehyde from cyclohexane is highly unlikely. Therefore, glyoxal is the most probable low-boiling-point product measured by the GC/PIMS. The low-boiling-point product observed by the FID GC may not be glyoxal, because glyoxal is not sensitive to FID GC. Therefore at least two low-boiling-point products were observed by GC/PIMS and FID GC. Two high-boiling-point products were identified as cyclohexanone and cyclohexyl nitrate by comparison with a reference mass pattern and GC retention time from standard samples. Both cyclohexanone and cyclohexyl nitrate increased linearly with irradiation time. Values of the ratio of cycloalkanone and cycloalkyl nitrate formed to cycloalkane consumed under the various experimental conditions were calculated and are listed in Table I ( $\Delta$ [cycloalkanone]/ $-\Delta$ [cycloalkane] and  $\Delta$ [cycloalkyl nitrate]/ $-\Delta$ [cycloalkane]). Each value is the mean value of 7-9 measurements during one experiment. Total irradiation time and the final reactant (cycloalkane) conversion are also shown in Table I. The values were calculated from

the peak area of the FID GC peak for each product and the sensitivities of these product to the FID GC which were measured by standard samples.

As shown in Table I, a significant difference was observed in the yield of cycloalkanone among  $\text{C}_5$ - $\text{C}_7$  cycloalkanes. Values for  $\Delta$ [cycloalkanone]/ $-\Delta$ [cycloalkane] differed by two orders of magnitude between cyclopentane and cyclohexane. In the case of cyclopentane, the formation of cyclopentanone appears to show a dependence on [NO]. However, the dependence may be insignificant, considering the scatter of the results. (In this case, signals for cyclopentanone were very small on the FID gas chromatogram and error limits ( $\pm$ ) on the measurements of the FID GC peak area of cyclopentanone were about 100%.)

On the other hand, the amounts of cycloalkyl nitrates produced are not remarkably different for each  $\text{C}_5$ - $\text{C}_7$  cycloalkane.

Table I also shows that cycloalkanone and cycloalkyl nitrate are not major products except when cyclohexane is used. In order to determine what compounds are major products, we analyzed the photooxidation products with the long-path FT IR spectrometer. In this case, since the large amount of water disturbed the measurements, photooxidation was carried out in the cycloalkane-NO-dry air system. Carbonyls, nitrates,  $\text{H}_2\text{CO}$ ,  $\text{HCOOH}$ ,  $\text{C}_2\text{H}_2$ , and a small amount of  $\text{CH}_4$  were observed as the photooxidation products. The ratios of each product formed to cycloalkanes consumed were calculated and plotted in Figure 1 a-c. In this case, the concentrations of products ( $\text{H}_2\text{CO}$ ,  $\text{HCOOH}$ ,  $\text{C}_2\text{H}_2$ ) were calculated by using the absorption coefficients of each product. The concentration of total nitrate was calculated by using the average absorption coefficients for  $\text{CH}_3\text{ONO}_2$  and  $\text{C}_2\text{H}_5\text{ONO}_2$  ( $\epsilon = 1.25 \times 10^{-2} \text{ torr}^{-1} \text{ cm}^{-1}$  at  $863 \text{ cm}^{-1}$ , which corresponds to the O- $\text{NO}_2$  stretching mode). The concentration of total carbonyls was calculated as monocarbonyl compounds by using the average integrated absorbance of the C=O stretching, which was estimated from the absorbances of various carbonyl compounds,  $(\text{CH}_3)_2\text{CO}$ ,  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{COOH}$ ,  $(\text{CH}_3\text{CO})_2\text{O}$ ,  $(\text{CH}_3\text{CO})(\text{HCO})\text{O}$ ,  $c\text{-C}_5\text{H}_8\text{O}$ , and  $c\text{-C}_6\text{H}_{10}\text{O}$  (the integrated absorbance used was  $0.374 \text{ cm}^{-2} \text{ torr}^{-1}$  per a C=O stretching mode at  $\sim 1780 \text{ cm}^{-1}$ ).  $\text{H}_2\text{CO}$



**Figure 1.** Photooxidation products measured by long-path FT IR are plotted against the cycloalkane consumed. Values for the carbonyls (except H<sub>2</sub>CO, HCOOH, and cyclohexanone) should be multiplied by 10.

and HCOOH are not included in with the total carbonyls (contributions of H<sub>2</sub>CO and HCOOH to the absorption  $\sim 1780\text{ cm}^{-1}$  were subtracted). All of the above absorption coefficients and absorbances were determined in this reactor by use of the reference samples. Since the absorption of cyclohexanone was observed separately from other carbonyls in the case of cyclohexane, both of cyclohexanone and other carbonyls except cyclohexanone, H<sub>2</sub>CO, and HCOOH are plotted separately in Figure 1b.

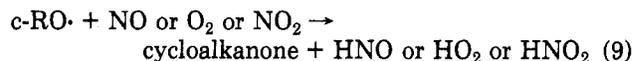
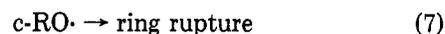
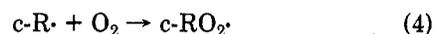
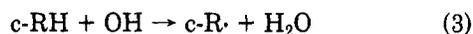
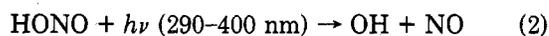
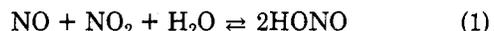
From the slopes shown in Figure 1a-c, the ratios of total nitrates formed to cycloalkane consumed are 0.13, 0.22, and 0.25 for cyclopentane, cyclohexane, and cycloheptane, respectively. Since these total nitrates do not consist of only cycloalkyl nitrates, values are consistent with the results in Table I. The value of the ratio of the cyclohexanone produced to the cyclohexane consumed (0.15-0.25) agreed well with the results in Table I. Results in Figure 1a-c show that carbonyls are the major products in the photooxidation of cycloalkanes.

Figure 2 shows the absorption spectra of carbonyls produced in the photooxidation of cyclopentane (a), cy-

cloheptane (b), and cyclohexane (c). Large absorptions by the C=O stretching of the carbonyl compounds ( $1700\text{--}1850\text{ cm}^{-1}$ ) were observed beneath the strong absorption by water. Below these spectra, the reference spectra of cyclopentanone (a), cycloheptanone (b), and cyclohexanone (c) are shown. As shown in Figure 2, only in the case of cyclohexane (c) can a large absorption by cyclohexanone be seen. This absorption by cyclohexanone is shown as a shaded area in Figure 2c. The remaining absorption, subtracting the absorption of cyclohexanone, is shown in Figure 2d. This remaining absorption corresponds to the absorption by other carbonyls except cyclohexanone. In the case of cyclopentane and cycloheptane, no significant absorptions by cyclopentanone and cycloheptanone were observed. These results are consistent with the results shown in Table I (the amounts of cyclopentanone and cycloheptanone formed are very small).

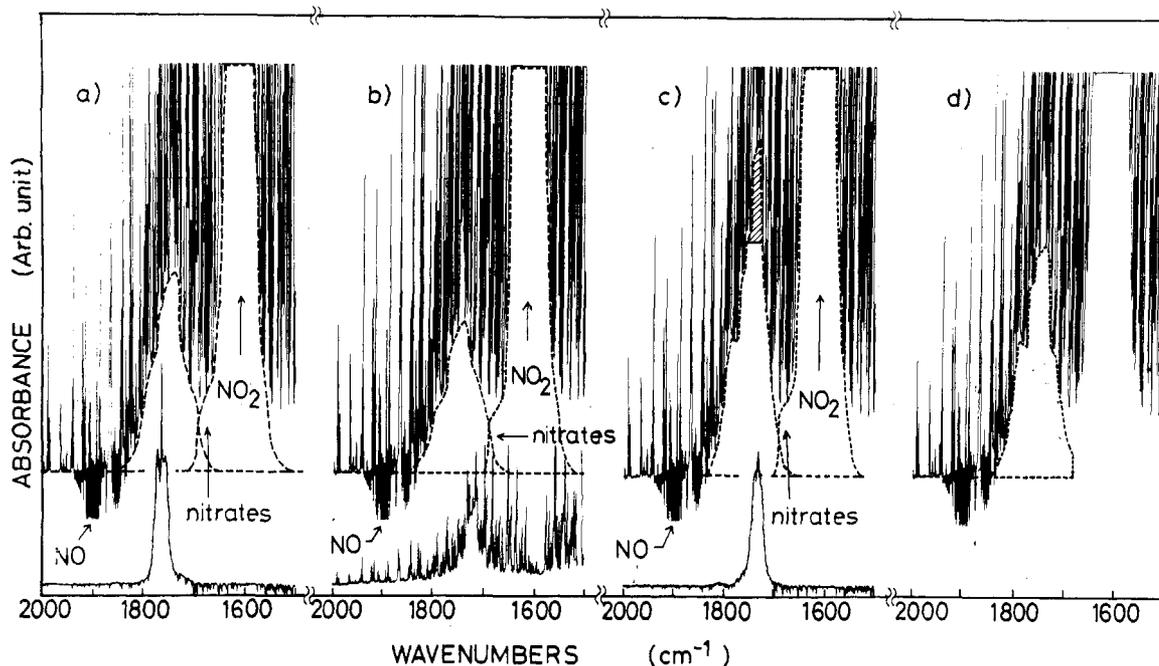
The absorption spectra of carbonyls are broad. This fact means that several carbonyl compounds were produced or that dicarbonyls were produced. Yields of the products are calculated and listed in Table II. In this case, the yields were normalized to number of carbon atoms in order to estimate the carbon balance among the products. As shown in Table II, HCOOH and C<sub>2</sub>H<sub>2</sub> are minor products and H<sub>2</sub>CO amounted to 3-9% of the cycloalkane consumed. In addition carbonyls produced through the cleavage of the cycloalkane ring are major products. Methods to estimate the number of carbon atoms used to normalize the carbonyls and nitrate yields will be discussed later.

In the NO-H<sub>2</sub>O-air system, the reaction of cycloalkane should be initiated mainly by OH radicals produced by the photodecomposition of HONO.<sup>21</sup> The reaction of OH radicals with cycloalkane (c-RH) starts with the abstraction of a hydrogen atom to form cycloalkyl radicals (c-R $\cdot$ ). Processes to form cycloalkanone and cycloalkyl nitrate might be as follows:



Cycloalkyl nitrates are produced by reactions 6 or 8. Figure 3 shows the concentration of NO, NO<sub>2</sub>, and O<sub>3</sub> plotted against the irradiation time for the photooxidation of cyclopentane. Time profiles for these molecules were quite similar in the cases of cyclohexane and cycloheptane. As shown in Figure 3, although most of the NO is converted into NO<sub>2</sub> in the latter half of the experiment, the concentration of nitrates increases in proportion to the decrease of cycloalkane (see Figure 1a). Since the formation rate of nitrates is not proportional to the concen-

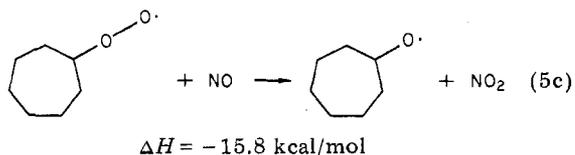
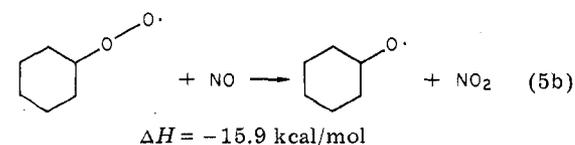
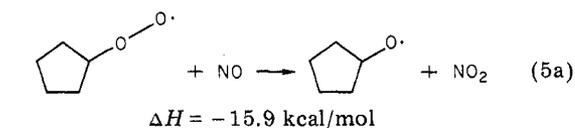
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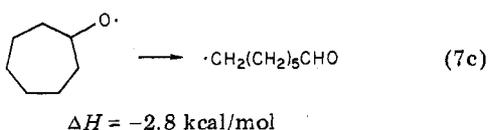
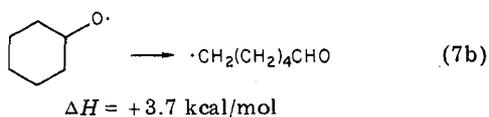
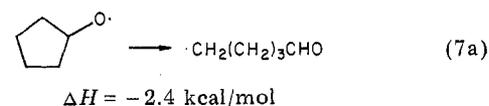
**Figure 2.** Long-path FT IR absorption spectra of carbonyls produced in the photooxidation of cyclopentane (a), cycloheptane (b), and cyclohexane (c). The lower spectra are the reference spectra of cyclopentanone (a), cycloheptanone (b), and cyclohexanone (c). The cyclohexanone absorption is shown by the shaded area in (c). This absorption was subtracted and the remaining absorption is shown in (d).

tration of  $\text{NO}_2$ , reaction 6 might be important as well as reaction 8, as suggested by Darnall et al.<sup>4</sup>

The ring cleavage reaction, reaction 7, might occur by the decomposition of a vibrationally hot cycloalkyloxy radical produced by reaction 5:



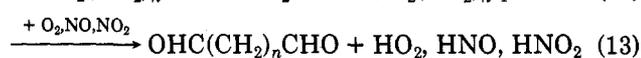
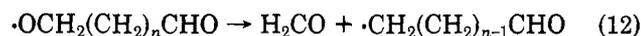
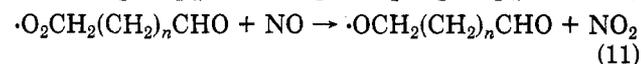
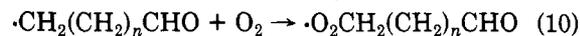
and, for example



where the values of heat of formation of cycloalkyloxy radicals, cycloalkyloxy radicals, and  $\cdot\text{CH}_2(\text{CH}_2)_n\text{CHO}$  radicals were calculated<sup>22</sup> by the group additivity rule of

free radicals.<sup>23</sup> The vibrationally hot cycloalkyloxy radicals have 18.3, 12.2, and 18.6 kcal/mol for  $\text{C}_5$ – $\text{C}_7$  cycloalkyl, respectively, in excess of that necessary to cause ring cleavage. Therefore, the unimolecular decomposition rate for reaction 7 should be faster in  $\text{C}_5$  and  $\text{C}_7$  than in  $\text{C}_6$ . In addition the differences in  $\Delta H$  among  $\text{C}_5$ – $\text{C}_7$  in reaction 7 result from the strain energies of the cycloalkane rings. Ring cleavage, reaction 7, competes with reactions 8 and 9. The  $\Delta H$  value for reaction 9 is 33–36 kcal/mol in excess, independent of the number of carbon atoms in the cycloalkane. Therefore, the larger yield of cyclohexanone than cyclopentanone and cycloheptanone in reaction 9 can be explained by the strain energy of the cycloalkane ring. On the other hand, the yields of cycloalkyl nitrates are not affected by the number of carbon atoms in the cycloalkane. This result supports the importance of reaction 6 rather than reaction 8 as a route to form cycloalkyl nitrates.

The  $\cdot\text{CH}_2(\text{CH}_2)_n\text{CHO}$  radicals produced by reaction 7 can be decomposed to smaller fragments:



(22)  $\Delta H_f^\circ$  of cycloalkyloxy radicals were deduced to be -5.9, -17.0, and -15.4 kcal/mol for  $\text{C}_5$ – $\text{C}_7$  cycloalkanes, respectively, from group additivity tables and ring correction values; e.g.,  $\Delta H_f^\circ[\text{cyclopentylperoxy radical}] = [\text{C}(\text{C})_2(\text{H})(\text{O})] + 4[\text{C}(\text{C})_2(\text{H})_2] + \text{ring correction} = -5.9 \text{ kcal/mol}$ .  $\Delta H_f^\circ$  of  $\cdot\text{CH}_2(\text{CH}_2)_n\text{CHO}$  radicals were deduced to be -8.3, -13.3, and -18.2 kcal/mol for  $n = 3, 4, \text{ and } 5$ , respectively; e.g.,  $\Delta H_f^\circ[\cdot\text{CH}_2(\text{CH}_2)_3\text{CHO}] = [\text{C}(\text{C})(\text{H})_2] + 2[\text{C}(\text{C})_2(\text{H})_2] + [\text{C}(\text{H})_2(\text{C})(\text{CO})] + [\text{CO}(\text{C})(\text{H})] = -8.3 \text{ kcal/mol}$ . In the cases of cycloalkylperoxy radicals, first,  $\Delta H_f^\circ$  of cycloalkyl-OOH molecules were deduced to be -41.6, -52.7, and -51.2 kcal/mol for  $\text{C}_5$ – $\text{C}_7$ , respectively. The bond dissociation energy of  $\text{ROO-H}$  was estimated to be 90 kcal/mol from  $\text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}$  and  $\text{HOOH} \rightarrow \text{HO}_2 + \text{H}$ . From these values,  $\Delta H_f^\circ$  values for cycloalkylperoxy radicals were calculated to be -3.7, -14.8, and -13.3 kcal/mol for  $\text{C}_5$ – $\text{C}_7$ , respectively.

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TABLE II: Yields of Products at  $-\Delta[\text{cycloalkane}] = 0.20$  ppm

	carbonyls <sup>a</sup>	cyclo- alkanone	nitrates <sup>b</sup>	H <sub>2</sub> CO	HCOOH	C <sub>2</sub> H <sub>2</sub>	total
Cyclopentane							
yield, ppm	0.20		0.026	0.088	0.014	0.018	
carbon no. to normalize	2.2/5		4.7/5	1/5	1/5	2/5	
normalized yield, ppm	0.088		0.024	0.018	0.003	0.007	
% to 0.20 ppm	44		12	9.0	1.5	3.5	70
Cyclohexane							
yield, ppm	0.16	0.054	0.044	0.080	0.021	0.010	
carbon no. to normalize	2.6/6	6/6	5.6/6	1/6	1/6	2/6	
normalized yield, ppm	0.069	0.054	0.041	0.013	0.004	0.003	
% to 0.20 ppm	43	27	20	6.5	2.0	1.5	100
Cycloheptane							
yield, ppm	0.17		0.049	0.045	0.009	0.009	
carbon no. to normalize	3.2/7		6.8/7	1/7	1/7	2/7	
normalized yield, ppm	0.078		0.048	0.006	0.001	0.003	
% to 0.20 ppm	45	24	3.2	0.6	1.3	74	

<sup>a</sup> Carbonyls except H<sub>2</sub>CO, HCOOH, and cyclohexanone (measured by the absorption of the C=O stretching mode). <sup>b</sup> Total nitrates (measured by the absorption of the O-NO<sub>2</sub> stretching mode).

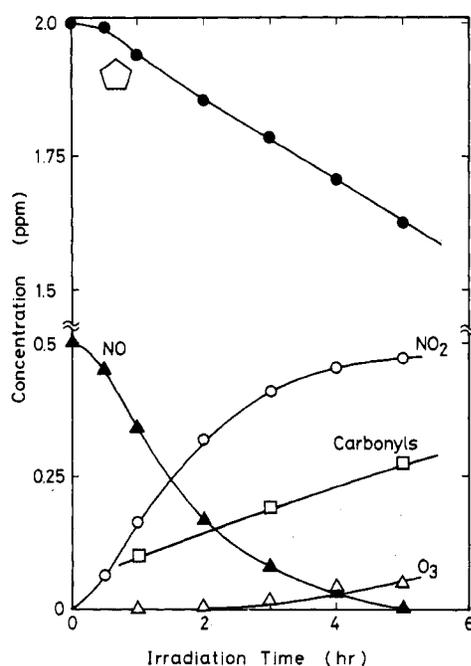
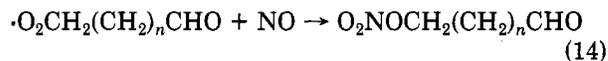


Figure 3. Concentrations of NO, NO<sub>2</sub>, O<sub>3</sub>, cyclopentane, and carbonyls are plotted against the irradiation time. The experimental conditions are the same as the conditions in Figure 1a.

A vibrationally hot  $\cdot\text{OCH}_2(\text{CH}_2)_n\text{CHO}$  radical produced in reaction 11 has about 8 kcal/mol in excess to decompose to  $\text{H}_2\text{CO} + \cdot\text{CH}_2(\text{CH}_2)_{n-1}\text{CHO}$ , reaction 12. The  $\cdot\text{CH}_2(\text{CH}_2)_{n-1}\text{CHO}$  radicals produced in reaction 12 decompose to  $\cdot\text{CH}_2(\text{CH}_2)_{n-2}\text{CHO} + \text{H}_2\text{CO}$  by the same processes as reactions 10-12, and finally decompose to glyoxal,  $(\text{CH}-\text{O})(\text{CHO})$ . As shown in Table II, the ratios of the absolute yield of H<sub>2</sub>CO to carbonyls are 0.44:1, 0.50:1, and 0.26:1 for C<sub>5</sub>-C<sub>7</sub> cycloalkane, respectively. If the carbonyl compounds observed are dicarbonyl compounds, e.g.,  $\text{OHC}(\text{CH}_2)_n\text{CHO}$ , as shown in reaction 13, the integrated absorption coefficient for the C=O stretching band should be doubled. In such a case, above ratios should be 0.88:1, 1:1, and 0.52:1. Then fraction ratios for the competing reactions, reactions 12 and 13, can be estimated<sup>24</sup> as

0.47:0.53 for cyclopentane, 0.50:0.50 for cyclohexane, and 0.34:0.66 for cycloheptane. These values show that fractions for reactions 12 and 13 are about 0.5 for both reactions.

Finally, the average carbon atom numbers for the carbonyl compounds produced by the degradation cycle of the type of reactions 10-13 were estimated<sup>25</sup> to be 4.3, 5.2, and 6.5 for C<sub>5</sub>-C<sub>7</sub> cycloalkanes, respectively. Since the carbonyl compound produced by reactions 10-13 has two CHO, carbon atom numbers per C=O stretching are 2.2, 2.6, and 3.2 for C<sub>5</sub>-C<sub>7</sub> cycloalkane, respectively. The normalizations of the carbonyl yield shown in Table II were done by the use of these numbers. The average carbon atom numbers of nitrates are difficult to estimate. The numbers  $1/2(4.3 + 5)$ ,  $1/2(5.2 + 6)$ , and  $1/2(6.5 + 7)$  were used for the normalization in Table II, because nitrates can be produced by reaction 14 subsequent to reaction 10.



Of course the  $\text{OHC}(\text{CH}_2)_n\text{CHO}$  produced in reaction 13 and the  $\text{O}_2\text{NOCH}_2(\text{CH}_2)_n\text{CHO}$  produced in reaction 14 can be decomposed by subsequent reactions (i.e., photolysis and OH reactions). In such a case, the average carbon atom numbers for the carbonyls and nitrates might become smaller and the normalized yields also become smaller, and the sum of each normalized product yield (70, 100, and 74% for C<sub>5</sub>-C<sub>7</sub> cycloalkane, respectively) shown in Table II might be overestimated.

*Acknowledgment.* The authors thank Professor T. Endow, Aoyama Gakuin University, for his suggestion on the synthesis of cycloalkyl nitrates.

(24) Assuming the branching ratios of the type shown in reaction 12,  $f$ , and reaction 13,  $1-f$ , are constant in the degradation cycle of the  $\cdot\text{CH}_2(\text{CH}_2)_n\text{CHO}$  radicals,  $f$  can be given by the relation  $f = P/(1+P)$  where  $P$  is the production ratio of H<sub>2</sub>CO to dicarbonyls. For example, in the case of cyclopentane,  $f = 0.47$  was deduced from  $P = 0.88$ .

(25) The average number of carbon atoms of the carbonyls produced in the type of reactions 10-13 was calculated from the expression

$$n(1-f) + (n-1)f(1-f) + (n-2)f^2(1-f) + \dots + 2f^{n-2}(1-f)/1-f + f(1-f) + f^2(1-f) + \dots + f^{n-2}(1-f)$$

for the C<sub>n</sub> cycloalkane.