# Kinetics and Products of the Reactions of OH Radicals with Cyclohexene, 1-Methyl-1-cyclohexene, *cis*-Cyclooctene, and *cis*-Cyclodecene

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Supporting Information

**ABSTRACT:** Rate constants for the reactions of OH radicals with four  $C_6-C_{10}$  cycloalkenes have been measured at  $297 \pm 2$  K using a relative rate technique. The rate constants (in units of  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) were cyclohexene,  $6.35 \pm 0.12$ ; *cis*-cyclooctene,  $5.16 \pm 0.15$ ; *cis*-cyclodecene,  $4.18 \pm 0.06$ ; and 1-methyl-1-cyclohexene,  $9.81 \pm 0.18$ , where the indicated errors are two least-squares standard deviations and do not include uncertainties in the rate constant for the reference compound 1,3,5-trimethylbenzene. In addition, a rate constant of  $(4.8 \pm 1.3) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was derived for the reaction of OH radicals with 1,6-hexanedial, relative to our measured rate constant for OH + cyclohexene, Analyses of products of the OH + cyclohexene, 1-methyl-1-cyclohexene,



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and *cis*-cyclooctene reactions by direct air sampling atmospheric pressure ionization mass spectrometry and/or by combined gas chromatography—mass spectrometry showed the presence of products attributed to cyclic 1,2-hydroxynitrates and the dicarbonyls 1,6-hexanedial, 6-oxo-heptanal, and 1,8-octanedial, respectively. These dicarbonyl products, which are those formed after decomposition of the intermediate cyclic 1,2-hydroxyalkoxy radicals, were quantified as their dioximes, with molar formation yields of 76  $\pm$  10%, 82  $\pm$  12%, and 84  $\pm$  18% from the cyclohexene, 1-methyl-1-cyclohexene, and *cis*-cyclooctene reactions, respectively. Combined with literature data concerning 1,2-hydroxynitrate formation from OH + alkenes and the estimated fractions of the overall reactions proceeding by H-atom abstraction, 90  $\pm$  12%, 95  $\pm$  13% and 108  $\pm$  20% of the products or reaction pathways from the OH radical-initiated reactions of cyclohexene, 1-methyl-1-cyclohexene, and *cis*-cyclooctene in the presence of NO are accounted for.

# ■ INTRODUCTION

Alkenes and cycloalkenes emitted into the atmosphere from biogenic<sup>1</sup> and anthropogenic<sup>2</sup> sources react in the atmosphere with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub>,<sup>3,4</sup> with the OH radical reaction often being the dominant daytime chemical loss process.<sup>3,4</sup> In the presence of NO, such that the dominant reaction of organic peroxy radicals is with NO, the key intermediates in the OH radical-initiated transformations of alkenes are 1,2-hydroxyalkoxy radicals formed by reactions 1, 2, and 3b.<sup>4</sup>

$$OH + RCH = CHR' \rightarrow RCH(OH)C^{\bullet}HR'$$
(1)

 $RCH(OH)C^{\bullet}HR' + O_{2}(+M)$  $\rightarrow RCH(OH)CH(OO^{\bullet})R'(+M)$ (2)

 $RCH(OH)CH(OO^{\bullet})R' + NO(+M)$  $\rightarrow RCH(OH)CH(ONO_{2})R'(+M)$ (3a)

$$RCH(OH)CH(OO^{\bullet})R' + NO$$
  

$$\rightarrow RCH(OH)CH(O^{\bullet})R' + NO_{2}$$
(3b)

As for other alkoxy radicals, the 1,2-hydroxyalkoxy radicals formed in reaction 3b can decompose by C–C bond scission, isomerize (generally through a 1,5-H shift via a 6-membered ring transition state), and react with O<sub>2</sub>, noting that not all of these reactions may be feasible for a given 1,2-hydroxyalkoxy radical.<sup>5</sup> For the OH radical-initiated reactions of  $\geq$ C<sub>5</sub> acyclic alkenes, decomposition and isomerization of the intermediate 1,2-hydroxyalkoxy radicals are competitive, and both dominate over reaction with O<sub>2</sub> (Table 1).<sup>5,6</sup> For example, for the mix of CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH(OH)CH<sub>2</sub>O<sup>•</sup> and CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH(O<sup>•</sup>)CH<sub>2</sub>OH radical-initiated reaction of 1-octene in the presence of NO, ~42% undergo decomposition

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 $CH_{2}(CH_{2})_{5}CH(O^{\bullet})CH_{2}OH$ 

		$RO^{\bullet}$ reaction rate $(s^{-1})$ due to			
RO•	O <sub>2</sub> reaction	decomposition	isomerization <sup>a</sup>		
linear alkoxy <sup>b</sup>	$4.7 \times 10^{4}$	$\sim 3 \times 10^4$	$\sim 4 \times 10^6 n$		
linear 1,2-hydroxyalkoxy <sup>c</sup>	$4.7 \times 10^{4}$	$\sim 8 \times 10^6$	$\sim 4 \times 10^6 n$		
cyclic alkoxy <sup>d</sup>	$4.7 \times 10^{4}$	$(3.3-25) \times 10^5$	$(1.4-15) \times 10^5$		

<sup>*a*</sup>*n* is the number of isomerization pathways possible (for example, n = 1 in 2-heptoxy, n = 2 in 8-tetradecoxy). <sup>*b*</sup>Reaction rates for a secondary alkoxy radical formed from an *n*-alkane, with isomerization occurring from a CH<sub>2</sub> group bonded to two CH<sub>2</sub> groups.<sup>5</sup> <sup>*c*</sup>Based on data for the reactions of 7-hydroxy-8-tetradecoxy radicals,<sup>6</sup> with the decomposition rate being derived from the product distribution<sup>6</sup> assuming an isomerization rate of  $8 \times 10^6$  s<sup>-1</sup>.<sup>5</sup> <sup>*d*</sup>Data for the reactions of cycloheptoxy, cyclooctoxy, and cyclodecoxy radicals.<sup>7</sup>

with the remainder being assumed to isomerize,<sup>6</sup> as shown below for the  $CH_3(CH_2)_5CH(O^{\bullet})CH_2OH$  radical.

$$CH_3(CH_2)_5CH(O^{\bullet})CH_2OH$$
  
→  $CH_3(CH_2)_5CHO + {}^{\bullet}CH_2OH$  (4)

$$\rightarrow$$
 CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sup>•</sup>HCH<sub>2</sub>CH<sub>2</sub>CH(OH)CH<sub>2</sub>OH (5)

The  $CH_3CH_2CH_2C^{\bullet}HCH_2CH_2CH(OH)CH_2OH$  radical reacts further to ultimately form  $CH_3CH_2CH_2CH(ONO_2)$ - $CH_2CH_2CH(OH)CH_2OH$  and  $CH_3CH_2CH_2CH(OH)$ - $CH_2CH_2C(O)CH_2OH$ .<sup>6</sup>

For alkoxy radicals formed subsequent to H-atom abstraction from *n*-alkanes, at room temperature, isomerization (if feasible) dominates over decomposition and reaction with  $O_2$  (Table 1).<sup>5,8,9</sup> However, we have recently shown that, for the cycloalkoxy radicals formed from cycloheptane, cyclooctane, and cyclodecane, at room temperature decomposition and isomerization are more important than the  $O_2$  reactions (Table 1).<sup>7</sup> The increase in the cycloalkoxy radical decomposition rates over those for the corresponding acyclic alkoxy radicals is expected because of ring-strain in the 7-, 8-, and 10-membered ring structures.<sup>7</sup> For the cyclohexoxy radical, isomerization does not occur,<sup>7,10</sup> and there is no significant increase in decomposition rate compared to that of the corresponding acyclic alkoxy radical (as expected, since there is no ring strain in cyclohexane).<sup>7</sup>

As shown in Table 1, at room temperature decomposition of 1,2-hydroxyalkoxy radicals formed after OH radical addition to acyclic (linear) alkenes is  $\sim 10^2$  faster than decomposition of alkoxy radicals formed from *n*-alkanes.<sup>5</sup> It is therefore expected that the cyclic 1,2-hydroxyalkoxy radicals formed from OH + C3-C10 cycloalkenes will dominantly decompose since ring strain will increase the decomposition rates by approximately an order of magnitude or more based on our results for the C7- $C_{10}$  cycloalkoxy radicals,<sup>7</sup> and isomerization rates will be decreased,<sup>7</sup> with no isomerization expected for the cyclic 1,2hydroxyalkoxy radical formed from cyclohexene. However, to date, there have been very few product studies of the OH radical-initiated reactions of simple cycloalkenes,11-13 with a previous study from this laboratory reporting a  $31 \pm 5\%$  molar formation yield of 6-oxo-heptanal from OH + 1-methyl-1cyclohexene in the presence of NO.12

In this work, we have measured rate constants for the reactions of OH radicals with cyclohexene, 1-methyl-1-cyclohexene, *cis*-cyclooctene, and *cis*-cyclodecene and investigated the products of the OH radical-initiated reactions with cyclohexene, 1-methyl-1-cyclohexene, and *cis*-cyclooctene in the

presence of NO to assess the fate of the intermediate cyclic 1,2-hydroxyalkoxy radicals.

#### **EXPERIMENTAL METHODS**

All experiments were carried out at  $297 \pm 2$  K and in the presence of 735 Torr of purified air. The majority of experiments were carried out in a ~7000 L Teflon chamber equipped with two parallel banks of black lamps for irradiation (chamber #1; note that, in the remainder of this article, if no chamber number is stated, it was chamber #1). A few additional experiments, concerning dark decays of 1,6-hexanedial and 1,8-octanedial, and the behavior of 1,6-hexanedial during OH + cyclohexene reactions, were conducted in a similar second ~7000 L Teflon chamber (chamber #2). OH radicals were generated from the photolysis of CH<sub>3</sub>ONO at wavelengths >300 nm, and NO was included in the reactant mixtures to avoid formation of O<sub>3</sub> and hence of NO<sub>3</sub> radicals. In all cases, the light intensity corresponded to an NO<sub>2</sub> photolysis rate of 0.14 min<sup>-1</sup>.

**Kinetic Study of OH + Cycloalkenes.** Rate constants for the reactions of OH radicals with cyclohexene, 1-methyl-1cyclohexene, *cis*-cyclooctene, and *cis*-cyclodecene were measured using a relative rate method in which the relative disappearance rates of the cycloalkenes and a reference compound (whose rate constant for reaction with OH radicals is reliably known) were measured in the presence of OH radicals.<sup>7</sup>

$$OH + cycloalkene \rightarrow products \tag{6}$$

 $OH + reference compound \rightarrow products$  (7)

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

$$\ln\left(\frac{\left[\text{cycloalkene}\right]_{t_0}}{\left[\text{cycloalkene}\right]_t}\right) = \frac{k_6}{k_7} \ln\left(\frac{\left[\text{reference compound}\right]_{t_0}}{\left[\text{reference compound}\right]_t}\right)$$
(I)

where [cycloalkene]<sub>t<sub>0</sub></sub> and [reference compound]<sub>t<sub>0</sub></sub> are the concentrations of the cycloalkene and reference compound, respectively, at time  $t_0$ , [cycloalkene]<sub>t</sub> and [reference compound]<sub>t</sub> are the corresponding concentrations at time t, and  $k_6$  and  $k_7$  are the rate constants for reactions 6 and 7, respectively. Hence, a plot of  $\ln([cycloalkene]_{t_0}/[cycloalkene]_t)$  against  $\ln([reference compound]_{t_0}/[reference compound]_t)$  should have a slope of  $k_6/k_7$  and zero intercept.

The initial reactant concentrations (in molecules cm<sup>-3</sup>) were CH<sub>3</sub>ONO and NO, ~2.4 × 10<sup>14</sup> each; and cycloalkene and reference compound, ~2.4 × 10<sup>13</sup> each. 1,3,5-Trimethylbenzene was used as the reference compound, and irradiations

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were carried out for up to 8-12 min, resulting in up to 50-73%of the initially present cycloalkene or reference compound being consumed by reaction. The concentrations of the cycloalkenes and reference compound were measured during the experiments by gas chromatography with flame ionization detection (GC-FID). Gas samples of 100 cm<sup>3</sup> 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 at 8 °C min<sup>-1</sup>. During each experiment, the following GC-FID analyses were conducted: at least two replicate analyses prior to reaction, one analysis after each of the three irradiation periods and a replicate analysis after the third (and last) irradiation period. Replicate analyses of the cycloalkenes and 1,3,5-trimethylbenzene showed that the measurement uncertainties were typically <3%.

**Product Analysis by API-MS/MS.**  $CH_3ONO-NO-air$ irradiations of cyclohexene, cyclohexene- $d_{10}$ , and *cis*-cyclooctene were carried out during which the chamber contents were sampled through a 25 mm diameter × 75 cm length Pyrex tube at ~20 L min<sup>-1</sup> directly into the 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.<sup>8,10</sup> Both positive and negative ion modes were used in this work. In positive ion mode, protonated water hydrates  $(H_3O^+(H_2O)_n)$ , and NO<sup>+</sup> ions generated by the corona discharge in the chamber diluent air were responsible for the formation of protonated molecules ( $[M + H]^+$ ), water adduct ions  $[M + H + H_2O]^+$ , protonated homo- and heterodimers,<sup>10</sup> and NO<sup>+</sup> adduct ions, while in negative ion mode,  $O_2^-$ ,  $NO_2^-$ , and  $NO_3^-$  ions were largely responsible for formation of adduct ions.<sup>8</sup>

The initial concentrations of CH<sub>3</sub>ONO, NO, and cycloalkene were  $\sim 2.4 \times 10^{13}$  molecules cm<sup>-3</sup> each, and the reactant mixtures were irradiated for 1 min, resulting in ~10% consumption of the initially present cycloalkene.

Kinetic Studies of 1,6-Hexanedial and 1,8-Octanedial. Two experiments (one in each Teflon chamber) were carried out to investigate the importance of dark decay of 1,6hexanedial and 1,8-octanedial. 1,6-Hexanedial and 1,8-octanedial were generated in situ from irradiation of a CH<sub>2</sub>ONO-NO-cyclohexene-cis-cyclooctene-air mixture for 6 min, followed by monitoring 1,6-hexanedial and 1,8-octanedial in the dark for 5.3 or 3.3 h. A 65  $\mu$ m polydimethylsiloxane/ divinylbenzene solid phase microextraction (SPME) fiber was precoated with O-(2,3,4,5,6,-pentafluorobenzyl)hydroxyl amine (PFBHA) for on-fiber derivatization of carbonyl-containing compounds.9 The coated fiber was then exposed to the chamber contents for 5 min with the chamber mixing fan on, with subsequent thermal desorption onto a 30 m DB-5 or DB-1701 megabore column with GC-FID analysis. GC-MS analyses (see Product Analysis by Gas Chromatography section below) confirmed the identity of the peaks attributed to the dioximes of 1,6-hexanedial and 1,8-octanedial.

Two series of experiments (consisting of 3 experiments in each of the two Teflon chambers) were also carried out to monitor the time-dependence of 1,6-hexanedial during irradiated  $CH_3ONO-NO-cyclohexene-air$  mixtures, in order to assess the reactivity of 1,6-hexanedial toward OH radicals. For the reaction system,

$$OH + 1,6$$
-hexanedial  $\rightarrow$  products (8)

the concentration of 1,6-hexanedial at time t is given by,<sup>14</sup>

$$[1,6-hexanedial]_t = A(e^{-x} - e^{-Bx})$$
(II)

where  $A = \alpha k_6 [\text{cyclohexene}]_{t_0}/(k_8 - k_6)$ ,  $B = k_8/k_6$ , and  $x = \ln([\text{cyclohexene}]_{t_0}/[\text{cyclohexene}]_t)$ ,  $\alpha$  is the formation yield of 1,6-hexanedial from OH + cyclohexene [reaction 6a], and  $k_6$  and  $k_8$  are the rate constants for reactions 6a and 8, respectively. The initial reactant concentrations (molecules cm<sup>-3</sup>) were CH<sub>3</sub>ONO and NO, ~1.2 × 10<sup>14</sup> each; and cyclohexene, (2.23–2.42) × 10<sup>13</sup>. Irradiations were carried out for up to 15 min, resulting in up to 87% of the initially present cyclohexene being consumed by reaction. Cyclohexene was monitored by GC-FID analysis of samples collected onto Tenax solid adsorbent, while 1,6-hexanedial was monitored as its dioximes by GC-FID analysis of PFBHA-coated SPME fibers, as described above.

**Product Analysis by Gas Chromatography.** OH radicalinitiated reactions of cyclohexene, 1-methyl-1-cyclohexene, and *cis*-cyclooctene were carried out to investigate product formation yields. The initial concentrations (molecules cm<sup>-3</sup>) of CH<sub>3</sub>ONO, NO, and cycloalkene were ~1.2 × 10<sup>14</sup>, ~1.2 ×  $10^{14}$ , and (2.28–2.46) × 10<sup>13</sup>, respectively, and 2,5-hexanedione was also included at a concentration of ~2.4 × 10<sup>12</sup> or ~4.8 ×  $10^{12}$  molecules cm<sup>-3</sup> as an internal standard. Irradiations (with a single irradiation period per experiment) were carried out for 1.0–2.5 min (cyclohexene), 0.67–2.0 min (1-methyl-1-cyclohexene), and 1.0–4.0 min (*cis*-cyclooctene), resulting in 7.6– 26.9%, 10.2–24.7%, and 6.6-31.3% reaction of the initially present cyclohexene, 1-methyl-1-cyclohexene, and *cis*-cyclooctene, respectively.

Reactants (including 2,5-hexanedione) and products were collected onto Tenax TA solid adsorbent and analyzed by GC-FID as described above. Samples were also collected, starting immediately after the lights were turned off, for 30 min at 15 L min<sup>-1</sup> using an XAD-coated denuder, further coated with PFBHA prior to sampling to derivatize carbonyls to their oximes, and extracted as described previously.<sup>7</sup> The sampling entrance of the denuder extended into the chamber, thereby eliminating any sampling line upstream of the denuder. The extracts were analyzed by combined gas chromatography-mass spectrometry in positive chemical ionization (PCI GC-MS) mode and by GC-FID, with both analyses using DB-5 columns (60 m for the GC-MS analyses and 30 m for the GC-FID analyses). 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, and methane-PCI gives characteristic protonated molecules  $([M + H]^+)$  and smaller adduct ions at  $[M + 29]^+$ and  $[M + 41]^{+.7}$ 

1,6-Hexanedial, 6-oxo-heptanal, and 1,8-octanedial were quantified as their dioximes from replicate GC-FID analyses of the extracts from the PFBHA-coated denuder samples. 2,5-Hexanedione served as an internal standard and corrections for the differing FID responses of the dioximes of the dicarbonyls and of 2,5-hexanedione were made using the Effective Carbon Numbers of Scanlon and Willis<sup>15</sup> and Nishino et al.<sup>16</sup> Five or six separate experiments, each at a different extent of reaction, were conducted for each cycloalkene studied.

 $OH + cyclohexene \rightarrow \alpha 1,6$ -hexanedial (6a)

Chemicals. The chemicals used and their stated purity levels were cyclohexene (99%), ChemSampCo; cyclohexene-

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 $d_{10}$  (99+% atom D), Isotec, Inc.; *cis*-cyclooctene (95%), *cis*-cyclodecene (95%), 2,5-hexanedione (98+%), 1-methyl-1-cyclohexene (97%), and 1,3,5-trimethylbenzene (98%), Aldrich; *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (99+%), Alfa Aesar; and NO ( $\geq$ 99.0%), Matheson Gas Products. Methyl nitrite was prepared as described by Taylor et al.<sup>17</sup> and stored at 77 K under vacuum.

# RESULTS AND DISCUSSION

**Rate Constants for Reaction with OH Radicals.** The experimental data from CH<sub>3</sub>ONO–NO–cycloalkene–1,3,5-trimethylbenzene–air irradiations are plotted in accordance with eq I in Figure 1, and the rate constant ratios  $k_6/k_7$  obtained



**Figure 1.** Plots of eq I for the reactions of OH radicals with cyclohexene, 1-methyl-1-cyclohexene, *cis*-cyclooctene, and *cis*-cyclodecene, with 1,3,5-trimethylbenzene as the reference compound. The data for *cis*-cyclooctene, cyclohexene, and 1-methyl-1-cyclohexene have been displaced vertically by 0.10, 0.20, and 0.20 units, respectively, for clarity. The data are from GC-FID analyses of samples collected onto Tenax solid adsorbent, and 3 experiments were conducted for each cycloalkene.

from least-squares analyses of these data are given in Table 2. These rate constant ratios are placed on an absolute basis using a rate constant of  $k_7(1,3,5$ -trimethylbenzene) =  $5.67 \times 10^{-11}$  cm<sup>3</sup>molecule<sup>-1</sup> s<sup>-1</sup> at 297 K,<sup>4</sup> and the resulting rate constants  $k_6$  are also given in Table 2. The available literature data for cyclopentene,<sup>18,19</sup> cyclohexene,<sup>18–25</sup> cycloheptene,<sup>18</sup> and 1-methyl-1-cyclohexene<sup>21</sup> are also given in Table 2; our present measurements for *cis*-cyclooctene and *cis*-cyclodecene are the first reported for these two cycloalkenes. As evident from Table 2, our present rate constants for cyclohexene and 1-methyl-1-cyclohexene are in generally good agreement with the available literature data.<sup>18–25</sup> In particular, our present rate constant for cyclohexene measured relative to that for 1,3,5-trimethylbenzene is in excellent agreement with that we previously measured relative to OH + 2-methyl-1,3-butadiene (isoprene).<sup>18</sup>

H-atom abstraction from the  $CH_2$  and  $CH_3$  groups in cyclohexene and 1-methyl-1-cyclohexene is predicted<sup>26,27</sup> to account for 8% and 5% of the overall OH radical reactions with cyclohexene and 1-methyl-1-cyclohexene, respectively. Therefore, the rate constants for OH radical reaction with

cyclohexene and 1-methyl-1-cyclohexene are expected to be similar to those for the acyclic alkenes with the same degree and position of alkyl-substitution,<sup>26,28</sup> i.e., *cis*-2-butene ( $5.67 \times 10^{-11}$  cm<sup>3</sup>molecule<sup>-1</sup> s<sup>-1</sup> at 297 K<sup>4</sup>) and 2-methyl-2-butene ( $8.74 \times 10^{-11}$  cm<sup>3</sup>molecule<sup>-1</sup> s<sup>-1</sup> at 297 K<sup>4</sup>), respectively. Consistent with this expectation, the rate constants obtained here for OH radical addition to the C=C bond in cyclohexene and 1-methyl-1-cyclohexene are only slightly higher (by 4% and 7%, respectively) than those for OH radical addition to the C=C bonds in *cis*-2-butene and 2-methyl-2-butene, respectively.

Our present rate constants for cyclohexene, cis-cyclooctene, and cis-cyclodecene can be combined with our previous rate constants for cyclopentene and cycloheptene<sup>18</sup> to assess the effect of ring size on the reactivity toward OH radicals (Table 2), noting that our present and previous<sup>18</sup> rate constants for cyclohexene agree to within 6% (Table 2). The ring-strain energies in cyclopentene, cyclohexene, cycloheptene, ciscyclooctene, and cis-cyclodecene are 5.8, 1.1, 4.9, 5.5, and 14.8 kcal mol<sup>-1</sup>, respectively.<sup>29</sup> Previous work has shown no significant effect of ring-strain on the rate constants for OH radical addition to cyclic alkenes containing ≤7-membered rings,<sup>18</sup> and this is evident from the similarity of the rate constants for OH radical reaction with cyclopentene and cyclohexene (Table 2). Since the alkyl substituents on the C =C bonds in cyclopentene, cyclohexene, cycloheptene, ciscyclooctene, and *cis*-cyclodecene are all in the *cis*- configuration, one could expect that the rate constants would be essentially independent of ring size, with a slight increase from cyclopentene through cis-cyclodecene due to H-atom abstraction of  $\sim 1.4 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> per additional CH<sub>2</sub> group.<sup>26,27</sup> While the measured rate constants from this and our previous<sup>18</sup> work for cyclopentene, cyclohexene, and cycloheptene are essentially identical, with an average value of 6.8  $\times$  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, those for *cis*-cyclooctene and *cis*cyclodecene are lower by factors of 1.3 and 1.6, respectively. The reason for this decrease in rate constants for the C8- and  $C_{10}$ -cycloalkenes compared to those for the  $C_5$ - $C_7$  cycloalkenes is not obvious, although steric factors could possibly play a role (as has been observed in the reactions of  $O_3$  with certain acyclic and cyclic alkenes<sup>30</sup>).

Product Analyses of the OH Radical-Initiated Reactions by API-MS/MS. CH<sub>3</sub>ONO-NO-air irradiations of cyclohexene, cyclohexene- $d_{10}$ , and *cis*-cyclooctene were carried out with analysis by API-MS and API-MS/MS in both positive and negative ion modes. Representative API-MS spectra are shown in Figure 2 for the cyclohexene reaction, and the ion peak assignments derived from API-MS/MS spectra of selected ion peaks observed in the API-MS spectra are listed in the caption to Figure 2. Analogous API-MS and API-MS/MS spectra were obtained for the cyclohexene- $d_{10}$  and *cis*cyclooctene reactions (see Figures S1 and S2 in Supporting Information). In an experiment with cyclohexene with added water vapor present, the ion peaks at 112, 144, and 258 u (attributed to NO<sup>+</sup> adducts; see caption to Figure 2) and at 227 u were not present, while ion peaks at 113 u ( $[112 + H]^+$ ) and 162 u ( $[161 + H]^+$ ) appeared. The ion peak at 113 u together with its water adduct at 131 u (which was also present in the absence of added water vapor) suggests that the ion peak at 227 u in the absence of added water vapor was  $[114 + 112 + H]^+$ . This is evidence for the presence of a molecular weight 112 product, which could be  $HC(O)CH=CHCH_2CH_2CHO$  (or isomers) arising after H-atom abstraction. There was some evidence for the corresponding H-atom abstraction product

cycloalkene	$k_{6}/k_{7}^{a}$	$10^{11} \times k_6 \; (\mathrm{cm}^3 \; \mathrm{molecule}^{-1} \; \mathrm{s}^{-1})$	reference
cyclopentene		$6.66 \pm 0.24^{b}$	Atkinson et al. <sup>18</sup>
		$5.02 \pm 0.40^{c}$	Rogers <sup>19</sup>
		$5.97 \pm 0.16^{d}$	Rogers <sup>19</sup>
cyclohexene		6.59 <sup>e</sup>	Wu et al. <sup>20</sup>
		$7.56 \pm 1.52^{f}$	Darnall et al. <sup>21</sup>
		6.54 <sup>g</sup>	Cox et al. <sup>22</sup>
		6.75 <sup>g</sup>	Barnes et al. <sup>23</sup>
		$6.45 \pm 0.25^{h}$	Ohta <sup>24</sup>
		$6.70 \pm 0.17^{b}$	Atkinson et al. <sup>18</sup>
		$5.43 \pm 0.24^{c}$	Rogers <sup>19</sup>
		$6.18 \pm 0.81^{i}$	Nielsen et al. <sup>25</sup>
	$1.12 \pm 0.02$	$6.35 \pm 0.12^{j}$	this work
cycloheptene		$7.37 \pm 0.23^{b}$	Atkinson et al. <sup>18</sup>
cis-cyclooctene	$0.910 \pm 0.025$	$5.16 \pm 0.15^{j}$	this work
<i>cis</i> -cyclodecene	$0.738 \pm 0.009$	$4.18 \pm 0.06^{j}$	this work
1-methyl-1-cyclohexene		$9.44 \pm 1.89^{f}$	Darnall et al. <sup>21</sup>
	$1.73 \pm 0.03$	$9.81 \pm 0.18^{j}$	this work

Table 2. Rate Constant Ratios  $k_6/k_7$  and Rate Constants  $k_6$  for the Reactions of OH Radicals with Cycloalkenes at 297  $\pm$  2 K, Together with Literature Data

<sup>*a*</sup>At 297 ± 2 K, relative to k(OH + 1,3,5-trimethylbenzene). The indicated errors are two least-squares standard deviations. The estimated overall uncertainties are the two least-squares standard deviations or ±6%, whichever is larger. <sup>*b*</sup>At 298 ± 2 K. Relative to k(OH + 2-methyl-1,3-butadiene) =  $1.00 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>*c*</sup>At 298 ± 3 K. Relative to k(OH + trans-2-butene) =  $6.40 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>*d*</sup>At 298 ± 3 K. Relative to k(OH + trans-2-butene) =  $6.40 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>*d*</sup>At 298 ± 3 K. Relative to k(OH + cis-2-butene) =  $5.49 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>*d*</sup>At 305 ± 2 K. Relative to k(OH + 2-methylpropene) =  $4.94 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>*d*</sup>At 297 ± 2 K. Relative to k(OH + 1,5-hexadiene) =  $6.20 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>*d*</sup>At 298 ± 2 K. Absolute rate measurement. <sup>*j*</sup>Placed on an absolute basis using a rate constant of  $k_7(OH + 1,3,5$ -trimethylbenzene) =  $5.67 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>*d*</sup> The indicated errors are two least-squares standard deviations and do not take into account the uncertainties associated with the rate constant  $k_7$ .



Figure 2. API-MS spectra of an irradiated CH<sub>3</sub>ONO-NO-cyclohexene-air mixture. The products identified were 1,6-hexanedial (MW 114) and the C<sub>6</sub>-cyclic hydroxynitrate (MW 161). Top: positive ion spectrum. On the basis of positive ion API-MS/MS analyses, the ion peak assignments are 112 u (present in prereaction API-MS spectra and diminished in intensity with the extent of reaction), [cyclohexene  $+ \text{NO}^{+}$ ; 115 u,  $[114 + \text{H}^{+}$ ; 131 u,  $[112 + \text{H} + \text{H}_2\text{O}^{+}]$ ; 144 u,  $[114 + \text{H}_2\text{O}^{+}]$ NO]<sup>+</sup>; 180 u, [161 + H + H<sub>2</sub>O]<sup>+</sup>; 185 u, [114 + 71]<sup>+</sup>; 227 u, [114 + 112 + H]<sup>+</sup>; 229 u, [114 + 114 + H]<sup>+</sup>; 247 u, [114 + 114 + H + H<sub>2</sub>O]<sup>+</sup>; 258 u,  $[114 + 114 + NO]^+$ ; and 276 u,  $[114 + 161 + H]^+$ . Bottom: negative ion spectrum. On the basis of negative ion API-MS/MS analyses, the ion peak assignments are 146 u,  $[114 + O_2]^-$ ; 160 u, [114+ NO<sub>2</sub>]<sup>-</sup>; 174 u, [114 + 60]<sup>-</sup>; 176 u, [114 + NO<sub>3</sub>]<sup>-</sup>; 189 u, [114 + 75]<sup>-</sup>; 193 u, [161 + O<sub>2</sub>]<sup>-</sup>; 207 u, [161 + NO<sub>2</sub>]<sup>-</sup>; 221 u, [161 + 60]<sup>-</sup>; 223 u,  $[161 + NO_3]^-$ ; and 354 u (not shown),  $[161 + 161 + O_2]^-$ . The ion peak at 237 u could not be readily assigned.

from the *cis*-cyclooctene reaction, but no API-MS/MS analysis was conducted on the small ion peak at 283 u (potentially [142 + 140 + H]<sup>+</sup>). The molecular weights of the products observed from the cyclohexene, cyclohexene- $d_{10}$ , and *cis*-cyclooctene reactions were consistent with formation of two major products from each  $C_n$ -cycloalkene: a  $C_n$ -cyclic hydroxynitrate and a  $C_n$ dicarbonyl. These are the products expected after initial OH radical addition to the C=C bond, with the intermediate cyclic 1,2-hydroxyalkyl peroxy radicals reacting via reactions 1 through 3a,b to form the cyclic 1,2-hydroxynitrate or the cyclic 1,2-hydroxyalkoxy radical, followed by decomposition of the cyclic 1,2-hydroxyalkoxy radical (Scheme 1). No evidence was observed in the API-MS analyses for product ion peaks arising from isomerization of the intermediate cyclic 1,2-hydroxyalkoxy radicals (see Scheme 1).

Dark Decays of 1,6-Hexanedial and 1,8-Octanedial and Reactivity of 1,6-Hexanedial toward OH Radicals. The relative concentrations of 1,6-hexanedial and 1,8hexanedial (generated in situ from OH + cyclohexene and *cis*-cyclooctene) were measured by GC-FID analyses of PFBHA-coated SPME fibers exposed to the chamber contents over periods of 5.3 h (chamber #1) and 3.3 h (chamber #2). Least-squares analyses of the experimental data, in the form  $\ln([dicarbonyl]_{t_0}/[dicarbonyl]_t)$  against time, resulted in dark decay rates for 1,6-hexanedial of  $(1.36 \pm 0.25) \times 10^{-5} \text{ s}^{-1}$  in chamber #1 and  $(3.0 \pm 2.7) \times 10^{-6} \text{ s}^{-1}$  in chamber #2, and for 1,8-octanedial of  $(1.46 \pm 0.21) \times 10^{-5} \text{ s}^{-1}$  in chamber #1 and  $(4.2 \pm 3.3) \times 10^{-6} \text{ s}^{-1}$  in chamber #2, where the indicated errors are two least-squares standard deviations.

The 1,6-hexanedial concentrations (in units of GC-FID area counts of the oximes of 1,6-hexanedial) from three irradiated  $CH_3ONO-NO-cyclohexene-air$  mixtures in chamber #1, with three irradiation periods per experiment, are plotted

Scheme 1. Expected Products Arising after OH Radical Addition to Cyclohexene; Products Observed by API-MS and GC-MS Analyses Are Shown in Boxes (See Text)



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against the extent of reaction, defined as  $\ln([cyclohexene]_t/$  $[cyclohexene]_t$ , in Figure 3. The durations of the experiments, from the start of the first irradiation period to the midpoint of the sampling period after the third (and last) irradiation period, were 116-158 min, and the measured 1,6-hexanedial concentrations were corrected for dark decay using the dark decay rate measured in this chamber. As evident from eq II, the dependence of the 1,6-hexanedial concentration with the extent of reaction is determined by A (which affects the scaling of the *Y*-axis) and by  $B = k_8/k_6$ . The value of  $\ln[[cyclohexene]_{t_0}/$  $[cyclohexene]_t$  at which the 1,6-hexanedial concentration is a maximum depends only on the rate constant ratio  $k_8/k_6$  and is given by  $\ln(k_8/k_6)/[(k_8/k_6) - 1] = \ln B/(B - 1)$ .<sup>14</sup> The data in Figure 3 are well fitted with  $k_8/k_6 = 0.7$ , and considering that small corrections had to be made for dark decay of 1,6hexanedial, this derived rate constant ratio is expected to be uncertain to a factor of ~1.3, and hence,  $k_8/k_6 = 0.7 \pm 0.2$ .

An independent series of analogous experiments were carried out in chamber #2, with the GC-FID analyses of the PFBHAcoated SPME fibers using a 30 m DB-1701 column. The 1,6hexanedial concentrations from three irradiated CH<sub>3</sub>ONO– NO–cyclohexene–air mixtures in chamber #2, corrected for the dark decay of 1,6-hexanedial in this chamber (a factor of ~4 lower than that in chamber #1), were well fit by  $k_8/k_6 = 0.8 \pm$ 0.2. Thus, the two independent measurements of the rate constant ratio  $k_8/k_6$  are in good agreement, with an average of  $k_8/k_6 = 0.75 \pm 0.2$ , which, when combined with our measured rate constant  $k_6$  (Table 2), corresponds to  $k_8 = (4.8 \pm 1.3) \times$  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 297  $\pm$  2 K.

Product Analyses of the OH Radical-Initiated Reactions by Gas Chromatography. PCI GC-MS analyses of

extracts of PFBHA-coated denuder samples collected from the OH radical-initiated reactions of cyclohexene, 1-methyl-1cyclohexene, and cis-cyclooctene showed the presence of dioximes (with no mono-oximes) of products of molecular weight 114, 128, and 142, respectively. This is consistent with the API-MS analyses of the cyclohexene and cis-cyclooctene reactions (see above), and these dicarbonyl products are attributed to 1,6-hexanedial from cyclohexene, 6-oxo-heptanal from 1-methyl-1-cyclohexene, and 1,8-octanedial from ciscyclooctene. There was no evidence in any of these reactions for the presence of oximes of the cyclic hydroxycarbonyl formed from reaction of the initially formed cyclic 1,2hydroxyalkoxy radical with O2, nor for those of the dihydroxycarbonyls formed after isomerization of the cyclic 1,2-hydroxyalkoxy radical (shown in Scheme 1 for the cyclohexene reaction). However, in order to obtain upper limits to their yields, authentic standards of these potential products would be needed to determine GC retention times of their oximes.

1,6-Hexanedial, 6-oxo-heptanal, and 1,8-octanedial are not commercially available, and hence, no standards could be used to determine GC retention times or collection and analysis efficiencies. It should be noted that no significant product peaks were observed from GC-FID analyses of samples collected from reacted OH + cyclohexene or OH + *cis*-cyclooctene mixtures onto Tenax solid adsorbent with subsequent thermal desorption, suggesting that 1,6-hexanedial and 1,8-octanedial were not amenable to analysis using that procedure. For samples collected from reacted OH + 1-methyl-1-cyclohexene mixtures, a product peak (attributed to 6-oxo-heptanal) was observed by this sampling and analysis procedure, but replicate



**Figure 3.** Plot of the measured relative concentrations of the dioximes of 1,6-hexanedial, corrected for wall loss (see text), as a function of the extent of reaction, defined as  $\ln([cyclohexene]_{t_0}/[cyclohexene]_t)$ , in three OH + cyclohexene reactions conducted in chamber #1. The differing symbols refer to different experiments. The lines are calculated from the expression [1,6-hexanedial] =  $A\{\exp(-k_6[OH]t)\}$  –  $\exp(-k_8[OH]t)\}$ , where  $k_6[OH]$  is the rate of reaction of cyclohexene and  $k_8[OH]$  is the rate of reaction of OH + 1,6-hexanedial. Cyclohexene was measured by GC-FID analyses of samples collected onto Tenax solid adsorbent, and the dioximes of 1,6-hexanedial were measured by GC-FID analyses of samples collected onto PFBHA-coated SPME fibers. The rate constant ratio  $k_8/k_6 = 0.4$  would result from combination of the rate constant for OH + 1,5-pentanedial reported by Rogers<sup>19</sup> with the rate constant  $k_6$  measured here for OH + cyclohexene (Table 2).

GC-FID analyses showed that the GC peak area was quite variable and corresponded to 6-oxo-heptanal formation yields  $\leq$ 50%. This can be compared to our previous study of the OH + 1-methyl-1-cyclohexene reaction where samples were also collected onto Tenax solid adsorbent with subsequent thermal desorption and GC-FID analysis, with a measured formation yield of 6-oxo-heptanal of 31 ± 5%.<sup>12</sup> Our present analyses suggest that 6-oxo-heptanal is either not efficiently collected onto, and/or thermally desorbed from, Tenax solid adsorbent, or that 6-oxo-heptanal does not efficiently elute from GC columns, and that our previously reported formation yield<sup>12</sup> was erroneously low.

1,6-Hexanedial, 6-oxo-heptanal, and 1,8-octanedial were therefore quantified as their dioximes from GC-FID analyses of extracts of PFBHA-coated denuder samples. Experiments were carried out with 2,5-hexanedione present as an internal standard in the initial reactant mixtures (i.e., before reaction). The rate constant for the reaction of OH radicals with 2,5hexanedione has been measured to be (7.13  $\pm$  0.34)  $\times$  10  $^{-12}$  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> at 298 K,<sup>31</sup> and hence 2,5-hexanedione is less reactive toward OH radicals than the cycloalkenes studied here by factors of 6-14. On the basis of GC-FID analyses of Tenax samples collected before and after reaction, the percentages of 2,5-hexanedione which were consumed by reaction were <6% in all cases, consistent with expectations based on the reactivities of 2,5-hexanedione and the cycloalkenes and the fractions of the cycloalkenes reacted. 2,5-Hexanedione was observed in the PFBHA-coated denuder samples as its dioximes (no mono-oximes were observed). Hence, by ratioing the GC-FID peaks areas of the dioximes of the dicarbonyls to those of 2,5-hexanedione and taking into account the differing FID responses of the dioximes of the dicarbonyls and of 2,5-hexanedione,<sup>15,16</sup> the concentrations of the dicarbonyls in the chamber could be derived. Replicate postreaction GC-FID analyses of the extract of each PFBHA-coated denuder sample were conducted, with excellent reproducibility relative to the internal standard.

The concentrations of the dicarbonyls measured in the chamber after the reaction then need to be corrected for reaction with OH radicals. Rate constants for the reactions of OH radicals with 1,6-hexanedial, 6-oxo-heptanal, and 1,8octanedial have not been directly measured to date, and the only room temperature rate constants available for analogous dialdehydes and keto-aldehyes are for 1,5-pentanedial (2.4  $\times$  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)<sup>19</sup> and pinonaldehyde (3.9 ×  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>).<sup>32</sup> Since H-atom abstraction from –CHO groups is generally the dominant reaction pathways for aldehydes,<sup>4,26,32</sup> 1,5-pentanedial is expected to be more reactive than the keto-aldehyde pinonaldehyde. Rate constants for 1,5pentanedial, 1,6-hexanedial, 6-oxo-heptanal, 1,8-octanedial, and pinonaldehyde, calculated using the Kwok and Atkinson estimation method<sup>26</sup> are  $5.75 \times 10^{-11}$ ,  $5.22 \times 10^{-11}$ ,  $3.15 \times 10^{-11}$ ,  $5.50 \times 10^{-11}$ , and  $2.71 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively, with the calculated rate constant for 1,5pentanedial being a factor of 2.4 higher than the measured value<sup>19</sup> and with the estimated rate constant for pinonaldehyde being a factor of 1.4 lower than the currently recommended rate constant.<sup>32</sup> Therefore, both our estimated rate constants and that measured for pinonaldehyde<sup>32</sup> suggest that the measured rate constant for 1,5-pentanedial<sup>19</sup> may be low.

The time-dependent behavior of 1,6-hexanedial during OH + cyclohexene reactions indicates that  $k_8 = (4.8 \pm 1.3) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, consistent with the estimated<sup>26</sup> rate constant of 5.22 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> but a factor of 2 higher than that of  $2.4 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> reported by Rogers<sup>19</sup> for 1,5-pentanedial (the additional CH<sub>2</sub> group in 1,6hexanedial is estimated to have little effect on the rate constant;<sup>26</sup> see above). Therefore, corrections for reactions of OH radicals with 1,6-hexanedial, 6-oxo-heptanal, and 1,8octanedial with OH radicals were made using our measured rate constants for cyclohexene, 1-methyl-1-cyclohexene, and ciscyclooctene and calculated rate constants<sup>26</sup> of 5.22  $\times$  10<sup>-11</sup>,  $3.15 \times 10^{-11}$ , and  $5.50 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for 1,6hexanedial, 6-oxo-heptanal, and 1,8-octanedial, respectively. The multiplicative correction factors, F, increase with the rate constant ratio k(OH + dicarbonyl)/k(OH + cycloalkene) and with the extent of reaction. Because the extents of reaction were kept low ( $\leq$ 31%), the maximum values of *F* were 1.14 for the cyclohexene reactions, 1.05 for the 1-methyl-1-cyclohexene reactions, and 1.23 for the cis-cyclooctene reactions.

Plots of the amounts of dicarbonyl observed, corrected for reaction with OH radicals, against the amounts of cycloalkene reacted are shown in Figure 4. For all three cycloalkenes, significant negative intercepts are observed, suggesting that a loss of dicarbonyl occurs before efficient collection and derivatization happens. Least-squares analyses (without inclusion of a 0,0 point) leads to the dicarbonyl formation yields given in Table 3. Note that, even if the rate constants for the reactions of OH radicals with 1,6-hexanedial, 6-oxo-heptanal and 1,8-octanedial are a factor of 2 lower than those calculated and used, the multiplicative correction factors *F* would change by <12%, with the largest effect being for *cis*-cyclooctene for which the 1,8-octanedial yield would decrease from  $84 \pm 18\%$ 



**Figure 4.** Plots of the amounts of 1,6-hexanedial, 6-oxo-heptanal, and 1,8-octanedial formed, corrected for reaction with OH radicals (see text), against the amounts of cyclohexene, 1-methyl-1-cyclohexene, and *cis*-cyclooctene, respectively, reacted with OH radicals. The data for 6-oxo-heptanal and 1,6-hexanedial have been displaced vertically by  $1.0 \times 10^{12}$  and  $3.0 \times 10^{12}$  molecules cm<sup>-3</sup>, respectively, for clarity. The least-squares intercepts on the Y-axis are (in units of  $10^{12}$  molecules cm<sup>-3</sup>):  $-0.615 \pm 0.364$  for OH + cyclohexene,  $-0.521 \pm 0.415$  for OH + 1-methyl-1-cyclohexene, and  $-1.15 \pm 0.765$  for OH + *cis*-cycolooctene, where the indicated errors are two least-squares standard deviations. The cycloalkene concentrations were measured by GC-FID analyses of samples collected onto Tenax solid adsorbent, and the dioximes of the dicarbonyls were measured by GC-FID analyses of extracts of PFBHA-coated denuder samples (see text).

to  $75 \pm 15\%$ . The yields obtained directly from the experiment at the greatest extent of reaction for each cycloalkene (i.e., yield = ([dicarbonyl formed], corrected for reaction with OH radicals)/[cycloalkene reacted]) are 69% for cyclohexene, 76% for 1-methyl-1-cyclohexene, and 74% for *cis*-cyclooctene, and these would then be lower limits.

The other products expected are the cyclic 1,2-hydroxynitrates formed from the cyclic 1,2-hydroxyalkyl peroxy radical + NO reaction (Scheme 1) and products arising after H-atom abstraction. As noted above, our API-MS analyses showed the formation of the expected hydroxynitrates, and their formation yields can be estimated using the data of O'Brien et al.<sup>33</sup> for 1,2hydroxynitrate formation from the OH radical-initiated reactions of a series of  $C_2-C_6$  alkenes or through the expression presented by Matsunaga and Ziemann<sup>34</sup> to fit their 1,2-hydroxynitrate formation yields in the aerosol phase from the OH radical-initiated reactions of a series of  $C_8-C_{17}$ alkenes. A linear regression of the 1,2-hydroxynitrate formation yields of O'Brien et al.<sup>33</sup> against carbon number results in yield = (-1.8 + 1.2n)%, and the calculated 1,2-hydroxynitrate yields from the cycloalkenes studied here are listed in Table 3. The expression presented by Matsunaga and Ziemann<sup>34</sup> was based on the equation proposed by Arey et al.<sup>8</sup> for secondary alkyl nitrate formation from a series of  $C_3-C_8$  alkanes, scaled by a factor of 0.455,<sup>34</sup> and the calculated 1,2-hydroxynitrate yields using this approach are also listed in Table 3. The two estimation methods predict reasonably similar hydroxyalkylnitrate formation yields, and an average is used for the calculations below.

The fraction of the overall reaction proceeding by H-atom abstraction can be derived by calculating the rate constant for H-atom abstraction using the Kwok and Atkinson estimation method<sup>26</sup> together with our overall OH radical reaction rate constants, and the resulting percentage of the overall reactions proceeding by H-atom abstraction are also given in Table 3. Assuming that the extent of H-atom abstraction and of 1,2hydroxynitrate formation are each uncertain to  $\pm 50\%$ , then Hatom abstraction, cyclic 1,2-hydroxynitrate formation (after OH radical addition), and cyclic 1,2-hydroxyalkoxy radical decomposition account for 90  $\pm$  12%, 95  $\pm$  13% and 108  $\pm$  20% of the overall reaction pathways for the OH radical-initiated reactions of cyclohexene, 1-methyl-1-cyclohexene, and ciscyclooctene, respectively. Thus, the reaction pathways are accounted for, to within ~20%, and under our experimental conditions where the cyclic 1,2-hydroxyalkoxy radicals were formed from the exothermic  $RO_2^{\bullet}$  + NO reaction, decomposition of these cyclic 1,2-hydroxyalkoxy radicals is the dominant pathway, leading to ring-opened dicarbonyls.

# ASSOCIATED CONTENT

#### Supporting Information

API-MS spectra obtained from the OH + cyclohexene- $d_{10}$  and OH + *cis*-cyclooctene reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

Table 3. Products Observed and Quantified from the OH Radical-Initiated Reactions of Cycloalkenes, Together with Estimated Formation Yields of Cyclic 1,2-Hydroxynitrates and H-Atom Abstraction Products

		molar yield (%)		
cycloalkene	dicarbonyl product	decomposition <sup>a</sup>	cyclic hydroxynitrate	H-atom abstraction <sup>b</sup>
cyclohexene	1,6-hexanedial	$76 \pm 10$	$5.4^c; 6.7^d$	8.1
1-methyl-1-cyclohexene	6-oxo-heptanal	$82 \pm 12$	$6.6^c$ ; $9.1^d$	5.4
<i>cis</i> -cyclooctene	1,8-octanedial	$84 \pm 18$	$7.8^{c}; 9.5^{d}$	15.1

<sup>*a*</sup>This work. Obtained from least-squares analyses of the data plotted in Figure 4. The indicated errors are two least-squares standard deviations of the data in Figure 4, combined with estimated uncertainties in the GC-FID response factors for the cycloalkenes and 2,5-hexanedione of  $\pm$ 5% each. <sup>*b*</sup>Calculated from the estimated H-atom abstraction rate constants<sup>26</sup> and our measured overall OH radical reaction rate constants (Table 2). <sup>*c*</sup>Based on the hydroxyalkyl nitrate yields of O'Brien et al.<sup>33</sup> from the reactions of OH radicals with a series of C<sub>2</sub>-C<sub>6</sub> alkenes at 296  $\pm$  3 K and atmospheric pressure of air, using a linear regression of the hydroxyalkyl nitrate yields<sup>33</sup> versus carbon number *n*, with yield = (-1.8 + 1.2*n*)%. <sup>*d*</sup>Calculated from the expression presented by Matsunaga and Ziemann,<sup>34</sup> for hydroxyalkyl nitrate formation from the OH + alkene addition pathway, which was based on the alkyl nitrate formation yield expression of Arey et al.<sup>8</sup> scaled by a factor of 0.455.<sup>34</sup> The cited yields are calculated for 297 K and 735 Torr pressure.

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## Notes

The authors declare no competing financial interest.

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