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# Kinetic and Mechanistic Studies of the Reactions of Cyclopentylperoxy and Cyclohexylperoxy Radicals with HO<sub>2</sub>

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The kinetics and mechanism of the reactions  $c-C_5H_9O_2 + HO_2 \rightarrow c-C_5H_9OOH + O_2$  (1) and  $c-C_6H_{11}O_2 + HO_2 \rightarrow c-C_6H_{11}OOH + O_2$  (2) have been studied using both the flash photolysis/UV absorption and continuous photolysis/FTIR product analysis techniques. End product analysis experiments at 295 ± 2 K demonstrated that the yield of hydroperoxide was (96 ± 3)% and (99 ± 3)% for reactions 1 and 2, respectively, although systematic errors could add an additional 15% uncertainty. Experiments between 248 and 364 K showed that  $k_1$  and  $k_2$  demonstrated virtually indistinguishable kinetic behavior at all temperatures, with  $k_1/cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> = (2.1 ± 1.3) × 10<sup>-13</sup> exp((1323 ± 185) K/T) and  $k_2/cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> = (2.6 ± 1.2) × 10<sup>-13</sup> exp((1245 ± 124) K/T). Absolute uncertainties on  $k_1$  and  $k_2$ , including experimental scatter and uncertainties in the analysis parameters, are estimated to be 18%. No dependence of  $k_1$  or  $k_2$  on pressure between 200 and 760 Torr was found. The room temperature rate constants for reactions 1 and 2 are significantly greater than those measured for other alkylperoxy radicals to date. The reactions of Cl atoms with cyclopentane, Cl +  $c-C_3H_{10} \rightarrow HCl + c-C_5H_9$  (6) and cyclohexane, Cl +  $c-C_6H_{11} \rightarrow HCl + c-C_6H_{11}$  (8) were measured relative to that with methanol, Cl +  $CH_3OH \rightarrow HCl + CH_2OH$  (4). Neither  $k_6$  nor  $k_8$  varied significantly with temperature over the range 248–364 K, with  $k_6/cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> = (2.3 ± 0.2) × 10<sup>-10</sup> and  $k_8/cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> = (2.4 ± 0.3) × 10<sup>-10</sup>, using  $k_4/cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> = 5.7 × 10<sup>-11</sup>. Errors are 1 $\sigma$  and represent experimental scatter only, unless stated otherwise.

#### Introduction

The importance of peroxy radicals in tropospheric chemistry is well established.<sup>1</sup> However, although a great deal of work has been done on the self-reactions of peroxy radicals,<sup>2</sup> much less information is available on their reactions with HO<sub>2</sub>, which are more significant in the atmosphere.<sup>3</sup> To date, work has been published only for the reactions of  $CH_3O_2$ ,<sup>4,5</sup>  $C_2H_5O_2$ ,<sup>4</sup>  $CH_3C$ -(O)O<sub>2</sub>,<sup>6</sup> HOCH<sub>2</sub>O<sub>2</sub>,<sup>7,8</sup> and HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>,<sup>9,10</sup> with HO<sub>2</sub>. As can be seen from Table I, the existing database is not sufficient to allow structure-reactivity correlations to be established with confidence. For example, although the room temperature rate constants for the methylperoxy and ethylperoxy radicals are very close in value, it is not known if this similarity extends to secondary and tertiary alkylperoxy radicals, or to primary alkylperoxy radicals containing more than two carbon atoms.

We have recently studied the UV spectra, kinetics, and mechanism of the self-reactions of the cyclohexylperoxy<sup>11</sup> and cyclopentylperoxy radicals.<sup>12</sup> In this paper, we present results on the kinetics and mechanism of the reactions of the cyclopentylperoxy and cyclohexylperoxy radicals with the hydroperoxy radical:

$$c-C_5H_9O_2 + HO_2 \rightarrow c-C_5H_9OOH + O_2$$
(1)

$$c-C_6H_{11}O_2 + HO_2 \rightarrow c-C_6H_{11}OOH + O_2$$
 (2)

TABLE I: Comparison of RO<sub>2</sub> + HO<sub>2</sub> Rate Constants

R	k <sub>298 K</sub> <sup>a</sup>	Aª	$E/R^b$	
CH <sub>3</sub> O <sub>2</sub>	4.8	0.33	-800 <sup>c</sup>	
$C_2 H_5 O_2$	5.8	0.65	-650°	
$CH_3C(O)O_2$	13	0.43	-1040 <sup>d</sup>	
HOCH <sub>2</sub> O <sub>2</sub>	12	0.0056	-2300e	
HOCH <sub>2</sub> CH <sub>2</sub> O <sub>2</sub>	10⁄			
c-C <sub>5</sub> H <sub>9</sub> O <sub>2</sub>	18	0.21	-1320 <sup>g</sup>	
$c - C_6 H_{11} O_2$	17	0.26	-1250 <sup>g</sup>	

<sup>*a*</sup> Units of  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>*b*</sup> Units of kelvin. <sup>*c*</sup> Recommendation of ref 4. <sup>*d*</sup> Reference 6. <sup>*e*</sup> References 7 and 8. <sup>*f*</sup> Average of values of refs 9 and 10. <sup>*g*</sup> This work.

These two radicals present several interesting features: the carbon atom at both radical centers is secondary, they are much larger than any peroxy radical whose reaction with  $HO_2$  has been studied to date, and although very similar, they possess different ring structures which may modify their behavior.

#### **Experimental Section**

Two experimental setups were used for the present work: one for the product analysis experiments, the other for the kinetics experiments. Both sets of apparatus have been described in detail previously<sup>13,14</sup> and are consequently only dealt with briefly here. Experimental conditions and procedures were almost identical for the study of both reaction 1 and reaction 2: the two reactions

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will thus be treated in a parallel fashion. For both sets of experiments, peroxy radicals were generated by the photolysis of molecular chlorine in the presence of the appropriate cycloalkane and methanol in oxygen/nitrogen mixtures: $^{4,15-18}$ 

$$Cl_2 + h\nu (\lambda > 280 \text{ nm}) \rightarrow 2Cl$$
 (3)

followed by

$$Cl + CH_3OH \rightarrow HCl + CH_2OH$$
 (4)

$$c_4/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = 5.7 \times 10^{-11}$$

$$CH_2OH + O_2 \rightarrow HCHO + HO_2$$
 (5)

$$k_5$$
/cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> = 9.1 × 10<sup>-12</sup>

and

$$Cl + c - C_5 H_{10} \rightarrow c - C_5 H_9 + HCl$$
 (6)

$$k_6/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = 2.3 \times 10^{-10}$$

$$c-C_5H_9 + O_2 + M \rightarrow c-C_5H_9O_2 + M$$
(7)

 $k_7/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> = 1.7 × 10<sup>-11</sup>

or

$$Cl + c - C_6 H_{12} \rightarrow c - C_6 H_{11} + HCl$$
 (8)

 $k_8$ /cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> = 2.4 × 10<sup>-10</sup>

$$c-C_6H_{11} + O_2 + M \rightarrow c-C_6H_{11}O_2 + M$$
 (9)

 $k_9/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> = 1.4 × 10<sup>-11</sup>

The rate constants above refer to room temperature and the high-pressure limit, where appropriate. The concentrations of the reagents were chosen to ensure rapid and quantitative conversion of chlorine atoms into peroxy radicals.

All product analysis experiments were performed in a 140-L Pyrex reactor surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to initiate experiments, performed at 15 or 700 Torr total pressure and 295  $\pm$  2 K. The loss of cycloalkane and the formation of products were monitored by Fourier transform infrared spectroscopy using an infrared path length of 26.6 m and a spectral resolution of 0.25 cm<sup>-1</sup>; spectra were derived from 32 to 128 co-added interferograms. Products were identified and quantified by fitting reference spectra of the pure compounds, obtained by expanding known volumes of the reference material into the long path length cell, to the observed product spectra using integrated absorption features over the following wavelength ranges (in cm<sup>-1</sup>); cyclopentane, 850-940; cyclopentanone, 1760-1780; cyclohexane, 820-920 and 1420-1500; cyclohexanone, 1710-1760. Reference spectra for cyclopentyl hydroperoxide and cyclohexyl hydroperoxide were unavailable and yields of these products were estimated by comparing the integrated absorption over the region 3575-3625 cm<sup>-1</sup> with that of a calibrated spectrum of ethyl hydroperoxide acquired earlier.13 To check this approach, the absorption features in the region 3575-3625 cm<sup>-1</sup> in calibrated reference spectra of methyl hydroperoxide, ethyl hydroperoxide, and tert-butyl hydroperoxide were compared: the integrated absorptions were the same to within 10%. Potential systematic uncertainties associated with quantitative analyses are estimated to be under 10% for the cycloketones, and under 15% for the hydroperoxides. Initial concentrations of the gas mixtures for the cyclohexane experiments were:  $[c-C_6H_{12}]_0 = 48-77 \text{ mTorr}; [CH_3OH]_0 = 302-517 \text{ mTorr}; [c-C_6H_{12}]_0 = 48-77 \text{ mTorr}; [c-C_6H_{12}]_0 = 48-77 \text{ mTorr}; [c-C_6H_{12}]_0 = 48-77 \text{ mTorr}; [c-C_6H_{12}]_0 = 302-517 \text{ mTorr}; [c-C_6H_{12}]_0 = 48-77 \text{ mTorr}; [c-C_6H_{12}]_0 = 302-517 \text{ mTorr}; [c-C_6H_{12}]_0 = 302-51$  $C_6H_{12}_0/[CH_3OH]_0 = 0.15-0.20; [Cl_2] = 112-307 \text{ mTorr}; [O_2]$ = 15-700 Torr; total pressure = 15 or 700 Torr; alkane consumption range = 3-23%. For the cyclopentane experiments, the conditions were:  $[c-C_5H_{10}]_0 = 149-167 \text{ mTorr}; [CH_3OH]_0 = 800$ mTorr;  $[c-C_5H_{10}]_0/[CH_3OH]_0 = 0.19-0.21$ ;  $[O_2] = 160-700$  Torr; total pressure = 700 Torr; alkane consumption range = 5-25%. All reagents were purchased from commercial vendors at purities of >99% and used without further purification. Experiments were performed using three different oxygen concentrations; 15, 150,

and 700 Torr, with nitrogen used, where appropriate, to bring the total pressure up to 700 Torr.

For kinetic experiments, slowly flowing cycloalkane/Cl<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures were flash photolyzed in a cylindrical, Pyrex, thermostated cell, 70 cm long. The time between flashes was maintained such that the flowing gas mixture was flashed once or twice during its residence time. The concentrations of cycloalkane, methanol, and oxygen were chosen so as to ensure that radical generation was complete within a few microseconds, i.e., on a time scale much shorter than that of their subsequent removal. Synthetic air (AGA Gaz Spéciaux), chlorine (5% in nitrogen, AGA Gaz Spéciaux), cyclopentane (97%, Aldrich), cyclohexane (>99.5%, SDS), and methanol (99.97%, Aldrich) were all used without further purification. Reagent concentrations were, in units of molecules cm<sup>-3</sup>: cycloalkane  $(1-3) \times 10^{16}$ ; methanol  $6 \times 10^{15}$ ; chlorine (2.6-6.6)  $\times$  10<sup>16</sup>; balance air. Initial radical concentrations were in the range  $(0.5-2.0) \times 10^{14}$  molecules cm<sup>-3</sup>. Radicals were monitored by their time-resolved UV absorption from 210 to 300 nm. The resulting decay traces were averaged, typically over 16 shots, and stored on a microcomputer for analysis using numerical integration with nonlinear least-squares fitting.

Unless otherwise stated, errors are  $1\sigma$  and represent experimental uncertainties only.

## Results

**End Product Analysis Experiments.** After the rapid production of the peroxy radicals, as described above, the following reactions can take place:

$$c-C_5H_9O_2 + HO_2 \rightarrow c-C_5H_9OOH + O_2$$
(1)

$$2c - C_5 H_9 O_2 \rightarrow 2c - C_5 H_9 O + O_2$$
(10a)

$$\rightarrow c - C_5 H_9 OH + c - C_5 H_8 O + O_2 \qquad (10b)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{11}$$

or

$$c-C_6H_{11}O_2 + HO_2 \rightarrow c-C_6H_{11}OOH + O_2$$
 (2)

$$2c-C_6H_{11}O_2 \rightarrow 2c-C_6H_{11}O + O_2$$
 (12a)

$$\rightarrow$$
 c-C<sub>6</sub>H<sub>11</sub>OH + c-C<sub>6</sub>H<sub>10</sub>O + O<sub>2</sub> (12b)

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{11}$$

As shown below, the rate constants for reactions 1 and 2 are more than 2 orders of magnitude greater than those for the self-reactions  $(10)^{12}$  and  $(12)^{11}$  at room temperature and by suitable choice of initial conditions it was therefore possible to conduct experiments whereby the alkylperoxy radicals were lost solely by reaction with HO<sub>2</sub>. Experiments were performed with initial concentration ratios,  $[CH_3OH]_0/[c-C_5H_{10}]_0 = 4.8-5.3$ , and  $[CH_3OH]_0/[c-C_6H_{12}]_0 = 5.0-6.7$ . Simulation of the chemistry within the chamber using the ACUCHEM kinetic modeling program<sup>19</sup> and the chemical mechanism given in Table II showed that under such experimental conditions more than 98% of the cycloalkylperoxy radicals react with HO<sub>2</sub> radicals.

Figure 1A,B shows typical spectra taken before (A) and after (B) irradiation of a mixture of 73 mTorr of cyclohexane, 453 mTorr of methanol, and 238 mTorr of chlorine in 700 Torr of oxygen. Figure 1C is the residual spectrum, obtained by subtracting features attributable to formaldehyde, formic acid, and methanol from spectrum 1B. Figures 1D and 1E are reference spectra of 10.36 mTorr of cyclohexanons and 46.2 mTorr of ethyl hydroperoxide, respectively. The loss of cyclohexane is 14.6 mTorr (20% of the initial concentration). The yield of hydroperoxide is 14.2 mTorr; the upper limit for the yield of cyclohexanone is 1.0 mTorr.

By comparing the integrated absorption features in the region  $3575-3625 \text{ cm}^{-1}$  in our product spectrum to that in our reference spectrum for ethyl hydroperoxide, we derive the total yield of hydroperoxide in the system. If alkyl hydroperoxides other than the cycloalkyl hydroperoxides are formed, then our measured yield will represent an upper limit. One potential complication is the

 
 TABLE II: Reaction Mechanism for the Simulation of End Product Analysis Experiments

reaction		rate constant <sup>a</sup>
(3)	$Cl_2 + h\nu \rightarrow 2Cl$	
(6, 8)	$Cl + cycloalkane \rightarrow HCl + R$	$2.4 \times 10^{-10} (C_5),$
		$2.7 \times 10^{-10} (C_6)^b$
(7, 9)	$c-R + O_2 + M \rightarrow c-RO_2 + M$	$1.7 \times 10^{-11}$ (C <sub>5</sub> ),
		$1.4 \times 10^{-11} (C_6)^c$
(4)	$Cl + CH_3OH \rightarrow CH_2OH + HCl$	$5.7 \times 10^{-11} d$
(5)	$CH_2OH + O_2 \rightarrow HCHO + HO_2$	$9.1 \times 10^{-12 d}$
(10, 12)	$c-RO_2 + c-RO_2 \rightarrow products$	$7.0 \times 10^{-14} (C_5),$
		$2.4 \times 10^{-14} (C_6)^e$
(1, 2)	$c-RO_2 + HO_2 \rightarrow products$	$1.8 \times 10^{-11}$ (C <sub>5</sub> ),
		$1.7 \times 10^{-11} (C_6)^{f}$
(11)	$HO_2 + HO_2 \rightarrow products$	$2.8 \times 10^{-12 d}$

<sup>a</sup>Units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup>Values of  $k_6$  and  $k_8$  were measured relative to k(Cl+n-butane) = 2.25 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>15,18</sup> As discussed in the text, there is a growing body of data which suggests this is 25–30% too high. Accordingly, here we use values for  $k_2$  based upon k(Cl+n-butane) = 1.7 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>c</sup>Reference 16. <sup>d</sup>Reference 4. <sup>e</sup>References 12 and 11, respectively. <sup>f</sup>This work, see text.





Figure 1. Infrared spectra taken before (A) and after (B) a 40-s irradiation of a mixture of 73 mTorr of cyclohexane, 453 mTorr of CH<sub>3</sub>OH, and 238 mTorr of Cl<sub>2</sub> in 700 Torr of oxygen. (C) is the residual after subtraction of HCHO, HCOOH, and CH<sub>3</sub>OH features from (B). Spectrum D is a reference spectrum of cyclohexanone and spectrum E is a reference spectrum of ethyl hydroperoxide.

formation of hydroxymethyl hydroperoxide via the reaction of  $HO_2$  radicals with formaldehyde:<sup>7,8</sup>

$$HO_2 + HCHO \leftrightarrow HOCH_2O_2$$
 (13)

$$HOCH_2O_2 + HO_2 \rightarrow HOCH_2OOH + O_2$$
 (14)

To check for this complication, mixtures of 0.4 Torr of chlorine and 0.4 Torr of methanol in 700 Torr of oxygen were irradiated for up to 90 s, a typical photolysis time used in this work. No hydroperoxide formation was observed and formation of hydroxymethyl hydroperoxide should thus be of negligible importance in the present work. The observed product features at  $\approx$ 3600 cm<sup>-1</sup> following the irradiation of cycloalkane/Cl<sub>2</sub>/CH<sub>3</sub>OH/O<sub>2</sub> mixtures are therefore ascribed to the formation of cycloalkyl hydroperoxide.

Figure 2 shows a plot of the observed increase in cycloalkyl hydroperoxide as a function of the loss of cycloalkane. As seen



**Figure 2.** Plot of the observed yield of hydroperoxide versus the loss of cycloalkane following irradiation of  $CH_3OH/Cl_2$  mixtures with:  $c-C_3H_{10}$  in 700 Torr of air (filled circles);  $c-C_5H_{10}$  in 15 Torr of  $O_2 + 685$  Torr of  $N_2$ , (open circles);  $c-C_6H_{12}$  in 700 Torr of  $O_2$ , (filled triangles);  $c-C_6H_{12}$  in 15 Torr of  $O_2 + 685$  Torr of  $N_2$  (open triangles);  $c-C_6H_{12}$  in 15 Torr of  $O_2$  (diamonds). The solid line is a line of unity slope for visual comparison with the data.

TABLE III: Analysis Parameters for Time-Resolved Experiments

	absorption c	cross section <sup>a</sup>	
radical	220 nm	260 nm	ref
HO <sub>2</sub>	$3.7 \times 10^{-18}$	$0.3 \times 10^{-18}$	20
c-C <sub>5</sub> H <sub>9</sub> O <sub>2</sub>	$2.67 \times 10^{-18}$	$4.77 \times 10^{-18}$	12
c-C6H11O2	$2.54 \times 10^{-18}$	$4.56 \times 10^{-18}$	11
ROOH	$0.15 \times 10^{-18}$	$0.03 \times 10^{-18}$	Ь
$H_2O_2$	$0.26 \times 10^{-18}$	$0.05 \times 10^{-18}$	23
	Rate Const	ants	
$k_{11}/\text{cm}^3$ mol	$ecule^{-1} s^{-1} = 3.8 \times$	$10^{-13} \exp(780 \text{ K}/7)$	) <b>+</b>
$1.2 \times 10^{-3}$	$^{3}[M] \exp(1150 \text{ K})$	T) 22	
$k_{10}/\mathrm{cm}^3$ mol	$ecule^{-1} s^{-1} = 4.4 \times$	$10^{-13} \exp(-552 \text{ K})$	$(T)^{12}$
$k_{12}/\mathrm{cm}^3$ mol	$ecule^{-1} s^{-1} = 2.0 \times$	10-13 exp(-487 K/	$(T)^{11}$

<sup>*a*</sup> Units of cm<sup>2</sup> molecule<sup>-1</sup>. <sup>*b*</sup> Assumed equal to the absorption cross sections of CH<sub>3</sub>OOH, which are similar to those of  $H_2O_2$ .<sup>23</sup>

in Figure 2, within the experimental errors, the yield of the hydroperoxide in both systems is independent of the oxygen partial pressure over the range 15-700 Torr. In the cyclohexane system, no effect of total pressure was observed over the range 15-700 Torr.

Linear least-squares fitting of the data shown in Figure 2 gives hydroperoxide yields of  $96 \pm 3\%$  and  $99 \pm 3\%$  for the reaction of cyclohexylperoxy and cyclopentylperoxy radicals with HO<sub>2</sub>, respectively. Quoted errors are  $1\sigma$ . Cyclohexanone and cyclopentanone were not identified as products; an upper limit of 10% was established for their yields.

**Kinetic Experiments.** Reactions 1 and 2 were studied between 249 and 364 K. Most experiments were performed at 760 Torr, but some additional experiments were done at 200 Torr and room temperature. Cyclopentylperoxy and cyclohexylperoxy radicals display very similar UV absorption spectra, typical of alkylperoxy radicals, peaking near 250 nm, where  $\sigma(c-C_5H_9O_2)/cm^2$  molecule<sup>-1</sup> = 5.22 × 10<sup>-18</sup> and  $\sigma(c-C_6H_{11}O_2)/cm^2$  molecule<sup>-1</sup> = 4.95 × 10<sup>-18,11,12</sup> The HO<sub>2</sub> UV spectrum is similarly broad and structureless, but is displaced to shorter wavelengths.<sup>20,21</sup> The differences between the spectra of the cycloalkylperoxy radicals and HO<sub>2</sub> enable the absolute initial concentrations of RO<sub>2</sub> and HO<sub>2</sub> to be determined from pairs of experiments, performed at different wavelengths, but under otherwise identical conditions, as was done in earlier experiments on the CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> reaction.<sup>22</sup>

Values for the cross-reaction rate constants,  $k_1$  and  $k_2$ , were extracted from pairs of experiments that differed only in the analysis wavelength. In general, the wavelengths chosen were 220 nm, where  $\sigma(HO_2) > \sigma(RO_2)$  and 260 nm, where  $\sigma(HO_2) \ll \sigma(RO_2)$ . The 220-nm wavelength was preferred to 210 nm, where the difference in the cross sections of HO<sub>2</sub> and RO<sub>2</sub> is greater,



Figure 3. Typical decay traces and fits,  $c-C_6H_{11}O_2 + HO_2$  system, 364 K. The individual contributions of each significantly absorbing species is shown. (a) Monitoring wavelength 220 nm. (b) Monitoring wavelength 260 nm.  $[c-C_6H_{11}O_2]_{t=0} = 5.54 \times 10^{13}$  molecules cm<sup>-3</sup>,  $[HO_2]_{t=0} = 4.82 \times 10^{13}$  molecules cm<sup>-3</sup>,  $k_2 = 7.63 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

because the agreement among the published values of the absolute  $HO_2$  absorption cross sections at wavelengths of 220 nm and longer is very good.<sup>20,21</sup> The data were analyzed using a nonlinear least-squares optimization program which numerically integrated the reaction system (reactions 1, 10, and 11 or reactions 2, 11, and 12); pairs of decay traces were fitted simultaneously, returning initial concentrations of both radicals plus the cross-reaction rate constant. The rate constants and absorption cross sections used in the analysis are given in Table III.

A typical pair of decay traces and corresponding fits are shown in Figure 3. At each temperature, at least five pairs of experiments were performed, at different initial  $[HO_2]/[RO_2]$  ratios between 1.5 and 0.6. This range of initial concentrations is most appropriate for extracting values of the cross-reaction rate constants.<sup>22</sup> In addition, experiments were also performed with HO<sub>2</sub> alone and RO<sub>2</sub> alone to confirm the total radical density and to check the self-reaction rate constants used in the analysis. No systematic dependence of the values of  $k_1$  or  $k_2$  on the total radical concentration or the initial  $[HO_2]/[RO_2]$  ratio was observed. The

TABLE IV: Rate Constants  $k_1$  and  $k_2$ 

 	$10^{11}k/cm^3$ molecule <sup>-1</sup> s <sup>-1</sup>	
T/K	c-C5H9O2	c-C <sub>6</sub> H <sub>11</sub> O <sub>2</sub>
 249	$3.73 \pm 1.06 (5)^a$	$3.77 \pm 0.76 (5)$
258		$3.25 \pm 0.38(5)$
274	$2.85 \pm 0.49$ (6)	$2.41 \pm 0.70(5)$
300	$1.83 \pm 0.57$ (16)	$1.98 \pm 0.34(7)$
	$2.07 \pm 0.31 (3)^{6}$	$1.68 \pm 0.38 (3)^{b}$
324	$1.31 \pm 0.13$ (5)	$1.17 \pm 0.18$ (5)
348	$1.02 \pm 0.28$ (5)	
364	$0.71 \pm 0.17$ (5)	$0.78 \pm 0.11$ (5)

<sup>a</sup> Errors  $1\sigma$ , including a Student's t; numbers in parentheses are the number of determinations, i.e., pairs of experiments. <sup>b</sup> Total pressure 200 Torr.

results are summarized in Table IV. Within experimental error, both  $k_1$  and  $k_2$  were independent of pressure in the range 200-760 Torr. In addition,  $k_1$  was independent of oxygen partial pressure



**Figure 4.** Arrhenius plots for  $k_1$  and  $k_2$ . The lines represent best weighted fits to  $k = A \exp(B/T)$ . c-C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>: filled squares and solid line; c-C<sub>6</sub>H<sub>11</sub>O<sub>2</sub>: empty squares and dashed line.

#### from 10 to 720 Torr at room temperature.

Weighted Arrhenius fits to the data in Table IV gave

 $k_1/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} =$ (2.1 ± 1.3) × 10<sup>-13</sup> exp((1323 ± 185) K/T)

 $k_2/\mathrm{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> =

$$(2.6 \pm 1.2) \times 10^{-13} \exp((1245 \pm 124) \text{ K}/T)$$

The corresponding plots are shown in Figure 4. Consideration of the covariance between the Arrhenius parameters gives average experimental uncertainties of 6.5% for both rate constants over the experimental temperature range.

As  $k_1$  and  $k_2$  were extracted from a relatively complex, albeit well-defined chemical system, it is essential to quantify their sensitivity to the analysis parameters. Sensitivity parameters were derived as described previously.<sup>22</sup> Artificial decay traces were generated using the kinetic scheme described above, with [HO2],=0 =  $[RO_2]_{t=0}$  = 5 × 10<sup>13</sup> molecules cm<sup>-3</sup> and for a temperature of 300 K. The more important analysis parameters were then varied by  $\pm 10\%$  or  $\pm 20\%$  and the fractional change in the values of  $k(RO_2 + HO_2)$  returned from the data analysis program examined. The sensitivity of  $k(RO_2+HO_2)$  to changes in  $k(RO_2+RO_2)$  was negligible. The pair of decay traces shown in Figure 3 clearly demonstrate this fact: for this pair of experiments, the initial alkylperoxy radical concentration was somewhat greater than that of  $HO_2$  and the apparent residual absorption at the end of each trace is due to the presence of cyclohexylperoxy radicals which remain after all the HO<sub>2</sub> had been removed and which react only very slowly with themselves. Furthermore,  $k(RO_2+HO_2)$  was also very insensitive to  $k(HO_2+HO_2)$ , as this rate constant is approximately a factor of 5 smaller than  $k(RO_2+HO_2)$ , the only important rate constant in the system. Only the values (both relative and absolute) of the cross sections of HO<sub>2</sub> and RO<sub>2</sub> had a significant effect on  $k(RO_2+HO_2)$ . Using average uncertainties of 10% for  $k_{11}/\sigma(\text{HO}_2)$ , 6% for  $k_{10}$  (or  $k_{12})/\sigma(\text{RO}_2)$ , 10% for the relative absorption cross sections of  $HO_2$  and  $RO_2$  and 15% for their absolute cross sections, the additional uncertainty in  $k_1$  and  $k_2$  is 16%. Combining this uncertainty with the experimental scatter results in total estimated absolute uncertainties of 18% in  $k_1$  and  $k_2$ .

As the present analysis extracts values of the initial HO<sub>2</sub> and RO<sub>2</sub> concentrations for each pair of experiments, the ratios  $k_4/k_6$  and  $k_4/k_8$  can be calculated at each temperature, using the known concentrations of methanol and the cycloalkane. The results are summarized in Table V, where a value of  $k_4/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> =  $5.7 \times 10^{-11}$ , independent of temperature, was used.<sup>4</sup> Within experimental error, both  $k_6$  and  $k_8$  are independent of temperature over the range 249–364 K, with  $k_6/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> =  $(2.3 \pm 0.2) \times 10^{-10}$  and  $k_8/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> =  $(2.4 \pm 0.3) \times 10^{-10}$ , respectively, where the errors do not include uncertainties in  $k_4$ .

TABLE V: Rate Constants  $k_6$  and  $k_8$ 

T/K	$k_6^a$	k <sub>8</sub> <sup>a</sup>
249	2.18 • 0.53	$2.81 \pm 0.53$
258		2.71 • 0.17
274	$2.10 \pm 0.39$	$2.57 \pm 0.34$
300	$1.95 \pm 0.53$	$2.38 \pm 0.27$
324	$2.28 \pm 0.06$	$2.44 \pm 0.16$
348	$2.42 \pm 0.13$	
364	$2.45 \pm 0.13$	$2.32 \pm 0.09$
$av^b$	$2.32 \pm 0.24$	2.42 • 0.25

<sup>a</sup> Units  $10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; errors  $1\sigma$ , including a Student's t/ measured relative to a value of  $k_4$ /cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $5.7 \times 10^{-11}$ .<sup>4</sup> <sup>b</sup> Weighted average; errors  $1\sigma$ , including a Student's t and an estimated 10% uncertainty in the relative cross sections of HO<sub>2</sub> and RO<sub>2</sub>.

#### Discussion

As in the present work, all previous temperature-dependent experiments performed on  $RO_2 + HO_2$  reactions have found the rate constant to decrease with increasing temperature: it is generally accepted that these reactions pass by the reversible formation of a tetroxide intermediate which rearranges to give the products. Two reaction channels have been postulated. One involves transfer of a hydrogen atom via a four-membered cyclic intermediate to form an alkyl hydroperoxide and oxygen, and the other involves the formation of a six-membered cyclic transition state to yield a carbonyl compound, water, and oxygen:

$$RO_2 + HO_2 \rightarrow ROOH + O_2$$
 (a)

$$\rightarrow R'R''CO + H_2O + O_2$$
 (b)

The second channel was suggested by Jenkin et al.<sup>24</sup> who observed significant HDO production from the  $CD_3O_2 + HO_2$  reaction, and who reported a branching ratio  $k_b/k\approx 0.4.\,$  As discussed recently, this branching ratio was obtained by detailed modelling of a complex system, and a subsequent reevaluation of their system using the latest rate data suggests the branching ratio  $k_b/k <$  $0.20.^{5,25}$  The product data from the present work shows that the reactions of cyclohexylperoxy and cyclopentylperoxy radicals with hydroperoxy radicals form the hydroperoxide in essentially 100% yield. The importance of any reaction channel leading to cycloketone formation is less than 10%. This observation is consistent with previous determinations of yields of methylhydroperoxide and ethylhydroperoxide close to unity from the reactions of methylperoxy and ethylperoxy radicals with HO<sub>2</sub>.<sup>26,27</sup> In the absence of convincing evidence to the contrary, it seems reasonable that alkylperoxy + HO<sub>2</sub> reactions in computer models of atmospheric chemistry should include the single reaction channel (a), although the possibility of a small contribution from channel (b) cannot be neglected.

As neither  $k_1$  nor  $k_2$  have been measured previously, no direct comparison with literature values is possible. However, as can be seen from Table I, the room temperature values of  $k_1$  and  $k_2$ are greater than the rate constants for other RO<sub>2</sub> + HO<sub>2</sub> reactions measured to date, and are more than a factor of 3 larger than the room temperature rate constants for the reactions of the methylperoxy and ethylperoxy radicals with HO<sub>2</sub>. The reasons for this difference are not obvious but could be due to either the greater size of the cyclic alkylperoxy radicals or a systematic difference in the behavior of primary and secondary alkylperoxy radicals or both. It is clear that further work is needed to resolve this question, which could have important consequences for tropospheric modelling as, in the absence of experimental data other than for the methylperoxy and ethylperoxy radicals, modelers have tended to use low values of  $(3-5) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for generic room temperature RO<sub>2</sub> + HO<sub>2</sub> rate constants.<sup>28,29</sup>

The very close similarity between  $k_1$  and  $k_2$  at all temperatures demonstrates that differences in the two ring structures do not affect the overall kinetic behavior. This is not the case for the peroxy radical self-reactions, as  $k_{10}$  is approximately a factor of 2 greater than  $k_{12}$  over the present temperature range.<sup>11,12</sup> Indeed, the room temperature  $RO_2 + HO_2$  rate constants measured to date (see Table I) vary over less than a factor of 4, whereas the

room temperature rate constants for peroxy radical self-reactions vary over several orders of magnitude.<sup>2</sup> This difference in behavior between the two sets of reactions presumably arises because the alkyl group behaves rather as a spectator in the  $RO_2 + HO_2$ reactions, but participates in the six-membered cyclic Russell<sup>30</sup> intermediate in the RO<sub>2</sub> self-reactions.<sup>14</sup>

Measurements of  $k_6$  and  $k_8$  to date conducted at the Ford Motor  $Co.^{14,18}$  have used relative rate techniques, with *n*-butane as a reference compound, using  $k(Cl+n-butane) = 2.25 \times 10^{-10} \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup> (the only direct measurement of this rate constant).<sup>31</sup> As discussed in detail elsewhere,<sup>15</sup> there is a growing body of data which suggests that this value for k(Cl+n-butane) is 25-30% too high. Accordingly, here we have used values for  $k_6$  and  $k_8$  based upon  $k(Cl+n-butane) = 1.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Our values of  $k_6$  and  $k_8$  are in good agreement with previous room temperature determinations of  $2.4 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>  $(k_5)^{18}$  and  $2.7 \times 10^{-10}$   $(k_6)$ .<sup>17,18</sup> As the present values of  $k_6$  and  $k_8$  are obtained in a rather indirect manner, it is expected that the previous measurements will be more accurate. More importantly, we have shown the  $k_6$  and  $k_8$  are independent of temperature over the range 249-364 K and the good agreement between the present values and the literature values gives us confidence in our radical generation system.

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Registry No. c-C<sub>6</sub>H<sub>11</sub>O<sub>2</sub>, 2143-59-1; c-C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>, 20682-76-2; HO<sub>2</sub>, 3170-83-0; Cl, 22537-15-1; c-C<sub>5</sub>H<sub>10</sub>, 287-92-3; c-C<sub>6</sub>H<sub>11</sub>, 110-82-7; CH.OH, 67-56-1.

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# Gas-Phase Hydrolysis of Trifluoromethyl Carbonyl Halides to Trifluoroacetic Acid

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The structures, energetics and vibrational features of the transition structures for gas-phase hydrolysis of  $CF_3C(O)X$  (where X = H, F, or Cl) compounds are described. The activated complexes are four-membered ring structures which involve the addition of the OH bond from water across the CO bond of  $CF_3C(O)X$ . The calculated activation energies are 54.6, 35.5, and 50.1 kcal mol<sup>-1</sup> for  $CF_3C(O)H$ ,  $CF_3C(O)F$ , and  $CF_3C(O)Cl$ , respectively. Decomposition of the hydrolysis product, CF<sub>3</sub>CX(OH)<sub>2</sub>, into trifluoroacetic acid, CF<sub>3</sub>C(O)OH, has been examined, and activation energy barriers are 75.9, 38.5, and 7.6 kcal mol<sup>-1</sup>, for X = H, F, and Cl, respectively. The present calculations suggest that gas-phase hydrolysis of CF<sub>3</sub>C(O)H is more likely to form stable CF<sub>3</sub>C(O)H<sub>2</sub>, while CF<sub>3</sub>C(O)F and CF<sub>3</sub>C(O)Cl will produce CF<sub>3</sub>C(O)OH and hydrogen halide.

#### Introduction

Presently, there is a major search for alternative halocarbons that are suitable replacements for chlorofluorocarbons. Alternative halocarbon that are being considered are of the type of  $CF_3CX_2H$ , where X = H, F, or Cl. However, little is known about the environmental acceptability of these compounds. Some studies suggest that a major byproduct from the atmospheric degradation of these compounds is trifluoroacetic acid.<sup>1</sup> This compound is of major concern since it is believed that soil bacteria metabolizes trifluoroacetic acid to produce monofluoroacetic acid-a potent mammalian toxin. To understand how to minimize the production of trifluoroacetic acid from alternative halocarbons, it is necessary to establish the route by which it is formed. Major byproducts from degradation of alternative halocarbons such as  $CF_3CX_2H$ are  $CF_3C(O)X$  compounds.<sup>2,3</sup> The removal of these compounds by reaction with OH radials will be slow. Moreover, these compounds only have significant UV absorption thresholds below 330 nm, which suggests that photooxidation in the troposphere is not a major removal process of  $CF_3C(O)X$  compounds. One route for the removal of  $CF_3C(O)X$  compounds in the troposphere could