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The kinetics and mechanism of the self-reaction of cyclopentylperoxy radicals:

$$2 c-C_5 H_9 O_2 \rightarrow 2 c-C_5 H_9 O + O_2 \tag{1a}$$

$$\rightarrow c-C_5H_9OH + c-C_5H_8O + O_2 \tag{1b}$$

have been studied using both time-resolved and end-product-analysis techniques. Determination of the product yields from the photolysis of  $CI_2$ -c- $C_5H_{10}$ - $O_2$ - $N_2$  mixtures using FTIR spectroscopy demonstrates that ring-opening of the cyclopentoxy radical formed in channel (1*a*):

 $c-C_5H_9O + M \rightarrow CH_2(CH_2)_3CHO + M$ (3)

dominates over reaction with oxygen:

$$c-C_5H_9O + O_2 \rightarrow c-C_5H_8O + HO_2$$
<sup>(2)</sup>

under atmospheric conditions. Flash photolysis–UV absorption experiments were used to obtain the UV spectrum of the cyclopentylperoxy radical and the kinetics of reaction (1). The spectrum of  $c-C_5H_9O_2$  is similar to those of other alkylperoxy radicals, with a maximum cross-section of  $(5.22 \pm 0.20) \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> at 250 nm, measured relative to a value of  $4.55 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> for  $CH_3O_2$  at 240 nm. The observed second-order rate constant,  $k_{obs}$   $(-d[c-C_5H_9O_2]/dt = 2k_{obs}[c-C_5H_9O_2]^2)$ , for removal of cyclopentylperoxy radicals was dependent on the oxygen partial pressure. Experiments as a function of temperature from 243 to 373 K gave limiting minimum and maximum values of  $k_{obs}$  at low (<1 Torr) and high (>50 Torr) oxygen partial pressures, respectively:  $k_{min}/cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> =  $(1.3 \pm 0.4) \times 10^{-14} \exp[(188 \pm 83)K/T]$  and  $k_{max}/cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> =  $(2.9 \pm 0.8) \times 10^{-13} \exp[-(555 \pm 77)K/T]$ . At low oxygen partial pressures, the only effective removal channel for cyclopentylperoxy radicals is the molecular channel (1*b*) and  $k_{min}$  can be equated to  $k_{1b}$ . Simulations suggest that  $k_{max}$  represents an upper limit on  $k_1$  and is at most 25% greater. In light of the present results on the cyclopentylperoxy radical, further experiments were performed on the cyclohexylperoxy radical self-reaction:

$$2 c-C_6 H_{11}O_2 \rightarrow 2 c-C_6 H_{11}O + O_2$$
(16a)

$$\rightarrow c - C_6 H_{11} O H + c - C_6 H_{10} O + O_2$$
(16b)

at low oxygen partial pressures, giving  $k_{16b}/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> =  $(1.3 \pm 0.3) \times 10^{-14} \exp[(185 \pm 15)K/T]$  and an estimated  $k_{16}/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> =  $7.7 \times 10^{-14} \exp(-184 K/T)$ . The above errors are  $1\sigma$  and represent experimental uncertainty only.

The importance of alkylperoxy radicals in combustion and atmospheric processes<sup>1</sup> has resulted in extensive studies of their reactions.<sup>2</sup> For the smaller ( $C_1$  and  $C_2$ ) alkylperoxy radicals there now exists a significant body of kinetic and mechanistic data. However, for species containing larger alkyl groups and in particular radicals containing more than four carbon atoms, the chemistry is less well understood. Furthermore, the reactions of secondary alkylperoxy radicals, R'R"CHO<sub>2</sub>, are also relatively poorly characterised. We have recently studied the self-reaction and spectrum of cyclohexylperoxy<sup>3</sup> radicals as part of a programme directed at understanding the gas-phase chemistry of large radicals.4 alkylperoxy The analogous study of cyclopentylperoxy radicals presented here represents an extension of this work, with an aim to investigate the effect of the different ring structures on the behaviour of the peroxy radicals.

The self-reactions of alkylperoxy radicals are believed to

proceed via a tetroxide association complex. Subsequent decomposition of this complex results in both radical and molecular products with the elimination of a molecule of oxygen. Three principal reaction channels have been identified: the formation of alkoxy radicals, disproportionation to give an alcohol and a carbonyl, and the formation of a peroxide. For cyclopentylperoxy radicals, these channels are shown in Fig. 1 as reactions (1a), (1b) and (1c), respectively. The branching ratio for the non-terminating channel (1a), is defined here as  $\alpha$ . The fraction of radicals proceeding via channel (1a) to that proceeding via the molcular channels, (1b) and (1c), is defined as  $\beta$ . Hence  $\beta = \alpha/(1 - \alpha)$ . In previous studies of the self-reactions of alkylperoxy radicals, channel (1c) has usually been shown to be of minor importance;  $\beta$  therefore generally represents the ratio of the rate constants for the individual channels  $k_{1a}/k_{1b}$ . The rate constant for the overall reaction (1),  $k_1$ , is thus simply  $(k_{1a} + k_{1b})$ .

1369

2

$$2 - 0 + 0_2$$
 (1a)

$$O_2$$
  $O_2$   $O_1$   $O_2$   $O_2$ 

Fig. 1 Primary channels for the self-reaction of cyclopentylperoxy radicals

The production of alkoxy radicals via the non-terminating channel (1a) results in secondary chemistry. The cyclopentoxy radical can react with oxygen:

$$c-C_5H_9O + O_2 \rightarrow c-C_5H_8O + HO_2$$
(2)

or reversibly isomerise with ring opening, via  $\beta$ -scission:

$$c-C_5H_9O \rightleftharpoons HC(O)(CH_2)_3CH_2$$
 (3, -3)

Reaction (-3) has been shown to be much slower than the ring-opening step (3) in solution near ambient temperatures, owing to its much smaller A factor;<sup>5</sup> it is not expected to be important here, as the ring-opened radical will be rapidly scavenged under most conditions by molecular oxygen, giving a further peroxy radical,  $R'O_2$ :

$$HC(O)(CH_2)_3CH_2 + O_2 + M \rightarrow HC(O)(CH_2)_3CH_2O_2 + M$$
(4)

Both  $HO_2$  and  $R'O_2$  could then react with themselves and the other peroxy radicals present in the system.

In principle, product analysis can give mechanistic information concerning the relative contributions of different channels to the overall reaction. Coupled with kinetic data, an estimation of the branching ratio and hence the rate constants for the individual reactions involved can be made. This paper presents results from a collaborative study of the self-reaction of cyclopentylperoxy radicals using two techniques. In the first, FTIR spectroscopy has been used to analyse the reaction products; in the second, flash photolysis with UV absorption spectroscopy has been employed to collect kinetic data.

#### Experimental

The FTIR product analysis and flash photolysistime-resolved UV absorption experiments used in this study have both been described in detail previously<sup>6–8</sup> and are not therefore discussed here. Furthermore, conditions for the generation and monitoring of radicals were in both cases nearly identical to those used for the analogous cyclohexylperoxy radical study reported above.<sup>3</sup>

Radicals were generated from the photolysis of molecular chlorine in the presence of cyclopentane and oxygen, according to the reaction scheme (5)-(7) below:

$$hv(\lambda > 280 \text{ nm}) + \text{Cl}_2 \rightarrow 2 \text{ Cl}$$
 (5)

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

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

Both reactions (6) and (7) are fast  $(k_6 = 3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1};^9 k_7 = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1};^{-10})$  and, with the choice of appropriate conditions, result in stoichiometric conversion of chlorine atoms to cyclopentylperoxy radicals practically instantaneously (<10 µs for the flash photolysis study) on the timescale of the self-reaction decay kinetics. All reagents were obtained from commercial vendors

# J. CHEM. SOC. FARADAY TRANS., 1992, VOL. 88

at purities exceeding 99.5% for the gases and 97% for the cyclopentane.

For the FTIR study, the analysis beam pathlength was 26.6 m; spectra were obtained from 32 co-added interferograms. The initial concentration ranges of reactants, expressed as partial pressures, were 75–100 mTorr† cyclopentane, 55 mTorr molecular chlorine and 5–700 Torr oxygen, with nitrogen used to bring the pressure up to 700 Torr. Reference spectra were fitted to product spectra using the following wavelength ranges (in cm<sup>-1</sup>): cyclopentane 850–940; cyclopentanone 1760–1780; cyclopentanol 960–1100 and 3620–3670; glutaric dialdehyde 1720–1770; hydrogen chloride 2700–3000; formaldehyde 1700–1800. All experiments were performed at a total pressure of 700 Torr and at 295  $\pm$  2 K.

For the flash photolysis study, radicals were monitored by time-resolved UV absorption at wavelengths between 210 and 300 nm. Typically, each experiment required the averaging of 8–10 decay traces. Initial concentrations of reactants were, in molecule cm<sup>-3</sup>: cyclopentane (2.9– 4.5) × 10<sup>16</sup>, chlorine (1.2–3.6) × 10<sup>16</sup>, oxygen (0.03– 260) × 10<sup>17</sup>, balance nitrogen, resulting in initial radical concentrations of (0.5–2.5) × 10<sup>14</sup> molecule cm<sup>-3</sup>. The residence time of the reactant gas mixture was such that it was replaced after at least every other flash. Kinetic simulations were produced by numerical integration and fitted to the decay traces using non-linear least-squares analysis. Experiments were performed from 243 to 373 K, with varying oxygen partial pressures, and at total pressures from 200 to 760 Torr at constant oxygen partial pressure.

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

#### Results

# FTIR Product Analysis Study

The products of the self-reaction of cyclopentylperoxy radicals were investigated at  $295 \pm 2$  K by irradiation of  $c-C_5H_{10}-Cl_2-O_2$  mixtures at four different partial pressures of oxygen: 700, 150, 15 and 5 Torr.

Fig. 2(a) shows a typical spectrum acquired before a 2 min irradiation of a mixture of 75.5 mTorr cyclopentane, 55 mTorr chlorine and 150 Torr oxygen, with nitrogen added to bring the total pressure up to 700 Torr. Fig. 2(b) shows the spectrum after irradiation. Comparison of Fig. 2(c) with a reference spectrum of cyclopentanone [Fig. 2(c)] clearly shows that this species is a major product. Fig. 2(d) shows the residual after cyclopentanone features (equivalent to 2.77 mTorr) have been removed from Fig. 2(b). Comparison of Fig. 2(d) with a reference spectrum of glutaric dialdehyde, HC(O)(CH<sub>2</sub>)<sub>3</sub>CHO [Fig. 2(e)] shows this compound is also a product. Finally, the subtraction of the glutaric dialdehyde feature from Fig. 2(d) yields Fig. 2(f). The minor features around 1740, 1760 and 1825 cm<sup>-1</sup> are unidentified.

In addition to cyclopentanone and glutaric dialdehyde, four other products were identified by virtue of their IR features, namely cyclopentanol, carbon dioxide, hydrogen chloride and a hydroperoxide (identified by the ROO—H 3600 cm<sup>-1</sup> feature). The identity of the hydroperoxide is unknown but is presumably c-C<sub>5</sub>H<sub>9</sub>OOH or HC(O)(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>OOH. No significant features specifically attributable to formaldehyde or peroxides were observed. After subtracting IR features attributable to cyclopentane, cyclopentanone, cyclopentanol, glutaric dialdehyde, hydrogen chloride and carbon dioxide, and the 3600 cm<sup>-1</sup> feature

 $<sup>\</sup>dagger 1 \text{ Torr} = (101 \ 325)/760 \text{ Pa}.$ 



**Fig. 2** Infrared spectra taken before (a) and after (b) a 2 min irradiation of a mixture of cyclopentane and  $Cl_2$  in 700 Torr of air. (c) Reference spectrum of cyclopentanone. Subtraction of cyclopentanone features from (b) yields (d). (e) Uncalibrated reference spectrum of glutaric dialdehyde. (f) Residual spectrum after glutaric dialdehyde features have been removed from (d). For clarity, successive spectra have been shifted vertically

ascribed to the hydroperoxide, there remained significant IR features at 925, 995, 1080 and 1350 cm<sup>-1</sup>, and trace features at 1740, 1760 and 1825 cm<sup>-1</sup> [Fig. 2(f)].

The observed yields of cyclopentanone, cyclopentanol and hydroperoxide are plotted as functions of cyclopentane in Fig. 3, 4 and 5, respectively. The results are summarised in Table 1, together with the yield of hydrogen chloride. For the hydroperoxide, reference spectra for the two compounds



Fig. 3 Plot of the observed yields of cyclopentanone vs. loss of cyclopentane following irradiation of  $c-C_5H_{10}-Cl_2$  mixtures in the presence of either 700 ( $\odot$ ), 150 ( $\bigcirc$ ), 15 ( $\bigtriangleup$ ) or 5 ( $\blacktriangle$ ) Torr of oxygen. The solid line represents a linear least-squares fit



Fig. 4 Plot of the observed yield of cyclopentanol vs. loss of cyclopentane following irradiation of  $c-C_5H_{10}-Cl_2$  mixtures in the presenced of either 700 ( $\bigoplus$ ), 150 ( $\bigcirc$ ), 15 ( $\triangle$ ) or 5 ( $\bigstar$ ) Torr of oxygen. The solid line represents a linear least-squares fit



**Fig. 5** Plot of the observed yields of hydroperoxide product vs. loss of cyclopentane following irradiation of  $c-C_5H_{10}-Cl_2$  mixtures in the presence of either 700 ( $\odot$ ), 150 ( $\bigcirc$ ), 15 ( $\triangle$ ) or 5 ( $\blacktriangle$ ) Torr of oxygen. The solid line represents a linear least-squares fit

c-C<sub>5</sub>H<sub>9</sub>OOH and HC(O)(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>OOH were not available, and thus the product was quantified by comparison of the integrated absorption around 3600 cm<sup>-1</sup> with that of a calibrated reference spectrum of C2H5OOH acquired earlier.6 Yields of all products were independent of the partial pressure of oxygen, and the yield of hydrogen chloride was unity under all conditions. With the exception of carbon dioxide, the yields of all products were, within experimental uncertainties, independent of the conversion of cyclopentane (4-25%). This linearity suggests that secondary reactions of Cl atoms with products are not a significant complicating factor in the present work. The yield of carbon dioxide was 5-10% in molar terms or 1-2% in carbon terms, and increased with cyclopentane conversion, suggesting that it is formed as a minor secondary product (probably from the reaction of chlorine atoms with glutaric dialdehyde). The fact that secondary reactions are unimportant, even at fairly high conversions, is not surprising as the rate constant for reaction (6) is very fast: it is unlikely that any of the reaction products react more rapidly with chlorine atoms than cyclopentane.

The yield of glutaric dialdehyde was not quantifiable, owing to the lack of a calibrated reference spectrum. To obtain a reasonable quantity of this low-volatility material in the gas phase for calibration, it was necessary to heat the infrared cell.<sup>11</sup> The partial pressure of the gas in the cell was unknown, thereby precluding quantification. In the present experiments, this feature was also found to decay upon standing in the dark with a lifetime of *ca.* 3-5 min. Concurrently there was evidence for the formation of an aerosol in the chamber. This evidence took the form of a shift in the baseline, which was most pronounced at shorter wavelengths. The maximum shift corresponded to an absorbance change of 0.2 units at  $3700 \text{ cm}^{-1}$ .

### Flash Photolysis-UV Absorption Study

Strong initial absorbances at wavelengths between 210 and 300 nm were generated from flashing the reaction mixtures. This absorbance decayed over a period of *ca.* 1 s and was

Table 1 Product yields from the photolysis of Cl\_2–c-C<sub>5</sub>H<sub>10</sub>–O<sub>2</sub>–N<sub>2</sub> mixtures at 295  $\pm$  2 K and 700 Torr total pressure

product	yield <sup>a</sup>	
c-C <sub>5</sub> H <sub>8</sub> O c-C <sub>5</sub> H <sub>9</sub> OH 'ROOH' CO <sub>2</sub> HCHO HCI	$\begin{array}{c} 0.18 \pm 0.01 \\ 0.16 \pm 0.02 \\ 0.07 \pm 0.02 \\ 0.05 - 0.10^{b} \\ < 0.02 \\ 0.95 \pm 0.03 \end{array}$	

<sup>*a*</sup> Expressed as a molar fraction of the c-C<sub>5</sub>H<sub>10</sub> consumed; errors are  $1\sigma$ . <sup>*b*</sup> Varies with conversion.

J. CHEM. SOC. FARADAY TRANS., 1992, VOL. 88



**Fig. 6** Typical experimental decay trace, second-order fit and residuals, for cyclopentylperoxy radicals in 760 Torr air at 298 K. Monitoring wavelength 250 nm. Initial radical concentration  $2.35 \times 10^{14}$  molecule cm<sup>-3</sup>;  $k_{obs}/cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> =  $6.35 \times 10^{-14}$ ; maximum absorbance 0.0746. The residuals have been expanded by a factor of 2.5 for clarity

attributed to the cyclopentylperoxy radical. A typical experimental trace is given in Fig. 6. The kinetics of removal were well described by a process second-order with respect to cyclopentylperoxy radicals under most conditions.

The spectrum of cyclopentylperoxy radicals was recorded from 210 to 300 nm by measuring the initial absorbance following the photolysis flash. Errors in extrapolation to t = 0 were minimised by using data recorded over a timescale short (20 ms) compared with the total decay time. No systematic dependence of the initial absorbance on O<sub>2</sub> concentration or the residence time of the gas in the reaction cell was noted, given the concentration ranges and conditions stipulated above. The resulting spectrum was calibrated against the well established methylperoxy radical spectrum, using  $\sigma(CH_3O_2)/cm^2$  molecule<sup>-1</sup> = 4.55 × 10<sup>-18</sup> at 240 nm,<sup>12</sup> by replacing cyclopentane with methane  $(1.9 \times 10^{18}$ molecule  $cm^{-3}$ ) under otherwise identical conditions. The cyclopentylperoxy radical spectrum is given in Table 2 and Fig. 7. The spectrum peaks near 250 nm, where  $\sigma/\text{cm}^2$  molecule<sup>-1</sup> =  $(5.22 \pm 0.20) \times 10^{-18}$ . The absolute uncertainties quoted in Table 2 (11% at 250 nm) include an uncertainty of 10% in the methylperoxy radical cross-sections used for calibration.12

Kinetic experiments were performed at temperatures ranging from 243 to 373 K. At each temperature the partial pressure of oxygen was varied from ca. 0.13 to 730 Torr, with nitrogen used to make up the pressure to 760 Torr. At

 Table 2
 UV absorption cross-sections of the cyclopentylperoxy radical

λ/nm	$\sigma/10^{-18} \text{ cm}^2$ molecule <sup>-1</sup> a	number of determinations
210	$1.43 \pm 0.15^{b}$	3
220	$2.67 \pm 0.29$	3
230	$4.02 \pm 0.43$	3
240	$5.02 \pm 0.51$	3
250	$5.22 \pm 0.56$	18
260	$4.77 \pm 0.48$	3
270	3.67 + 0.40	3
280	2.46 + 0.28	3
290	$1.32 \pm 0.14$	3
300	$0.63 \pm 0.086$	3

<sup>a</sup> Calibrated against CH<sub>3</sub>O<sub>2</sub>, using  $\sigma_{240 \text{ nm}}$ (CH<sub>3</sub>O<sub>2</sub>) = 4.55 × 10<sup>-18</sup> cm<sup>2</sup> molecule<sup>-1</sup>. <sup>12</sup> <sup>b</sup> Errors include a Student's-*t* factor and a 10% uncertainty in  $\sigma_{240}$ (CH<sub>3</sub>O<sub>2</sub>)



Fig. 7 UV absorption spectrum of cyclopentylperoxy radicals. The curve represents a cubic spline fitted through the data. The spectrum is calibrated against that of the methylperoxy radical, using  $\sigma(CH_3O_2)/cm^2$  molecule<sup>-1</sup> = 4.55 × 10<sup>-18</sup>.<sup>12</sup>

oxygen partial pressures less than 0.13 Torr, incomplete conversion of the chlorine atoms into peroxy radicals was apparent from a reduction in the initial absorbance. The effect of variation of the total pressure from 200 to 760 Torr was also investigated at ambient temperature, (298 K) with a constant oxygen partial pressure of 145 Torr.

Under most experimental conditions, the kinetics were well described by a second-order kinetic scheme with a slight residual absorption. The residual absorption was always less than 10% of the initial absorption and usually considerably less. In addition, small deviations from this model were observed under certain experimental conditions, notably high temperature and high oxygen partial pressure; this deviation took the form of a slight convex curvature to the decay trace at short decay times. At low temperatures (<273 K) the decay traces reverted to pure second order, without any apparent absorbing product. It is worth noting that these small deviations from pure second-order behaviour could only be detected owing to the extremely high signal-to-noise ratios of our experimental decay traces.

No systematic dependence of the value of  $k_{obs}(-d[c-C_5H_9O_2]/dt = 2k_{obs}[c-C_5H_9O_2]^2)$  on  $Cl_2$  concentration, flash-lamp energy, residence time of the gas in the cell or the monitoring wavelength was noted, given the concentration ranges and conditions stipulated above. In addition,  $k_{obs}$  was unchanged between total pressures of 200 and 760 Torr, at a constant oxygen partial pressure at 298 K.

At all temperatures, the effective second-order rate constant,  $k_{obs}$ , varied somewhat with the oxygen partial pressure: overall,  $k_{obs}$  increased with oxygen partial pressure, reaching a limiting value at both the low and high ends of the oxygen concentration range. Closer investigation showed that  $k_{obs}$  depended on the ratio  $[O_2]/[Cl_2]$ , as shown for temperatures of 273, 298 and 323 K in Fig. 8. It can be seen that  $k_{obs}$  reaches a maximum value,  $k_{max}$ , for values of  $[O_2]/[Cl_2] > 50$  and a minimum value for values of  $[O_2]/[Cl_2] < 1$ . The values of  $k_{obs}$  at all temperatures and oxygen partial pressures are given in Table 3. The average values of  $k_{min}$  and  $k_{max}$  are plotted in Arrhenius form in Fig. 9. Unweighted, logarithmic fits give:

$$k_{\min}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = (1.3 \pm 0.4) \times 10^{-14}$$

 $\times \exp[(188 \pm 83) \text{K}/T]$ 

$$k_{\text{max}}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = (2.9 \pm 0.8) \times 10^{-13} \times \exp[-(555 \pm 77)\text{K}/T]$$



**Fig. 8** Variation in  $k_{obs}$  for the cyclopentylperoxy radical self-reaction with  $[O_2]/[Cl_2]$  at 273 K ( $\blacksquare$ ,  $\theta = 1$ ), 298 K ( $\blacktriangle$ ,  $\theta = 10$ ) and 323 K ( $\blacklozenge$ ,  $\theta = 100$ ).  $\theta$  is a scaling factor, introduced for clarity

As can be seen from Fig. 8 and 9, the fractional increase in  $k_{obs}$  between the maximum and minimum limiting values increases with increasing temperature.

#### Discussion

The UV absorption spectrum of the cyclopentylperoxy radical is of similar form and magnitude to that of the cyclohexylperoxy radical<sup>3</sup> and indeed all other unsubstituted alkylperoxy radicals, demonstrating further that the electron transition is relatively insensitive to the nature of the alkyl group.<sup>13</sup>

Considering the mechanism of the cyclopentylperoxy self-reaction, the end-product analysis confirms the existence



**Fig. 9** Arrhenius plot and fit for  $k_{\min}$  ( $\blacksquare$ ) and  $k_{\max}$  ( $\square$ ) for the cyclopentylperoxy radical self-reaction

of molecular products from channel (1*b*), but provides no conclusive evidence for the formation of the peroxide in channel (1*c*). Some of the small, unidentified FTIR features observed in the product spectra at 925, 995, 1080 and 1350 cm<sup>-1</sup> could be tentatively assigned to ROOR, but the lack of characteristic absorption bands of the peroxidic O—O bond in organic peroxides precludes any definite identification. Channel (1*c*) is clearly not a major contributor to the reaction, an observation consistent with previous studies of peroxy radical self-reactions.<sup>2</sup>

The low yields of cyclopentanone and cyclopentanol and the lack of complete carbon balance in these two products indicate that the non-terminating channel (1a) is important. Furthermore, the very small yield of hydroperoxide, ROOH, shows that the production of HO<sub>2</sub> radicals from the cyclopentoxy radical formed in reaction (1a) is low, and consequently that this species preferentially undergoes ring-opening [reaction (3)] rather than reaction with oxygen [reaction (2)]. In addition, the invariance of the product yields with oxygen partial pressure shows that this is the case at all experimental partial pressures of oxygen, in contrast to the cyclohexylperoxy system<sup>3</sup> where reaction of cyclohexoxy radicals with oxygen dominated at high oxygen partial pressures. The greater instability of the cyclopentoxy radical with respect to ring-opening is attributable to the greater ring strain in the alkyl group.

The ring-opening reaction (3) results in the formation of a substituted alkyl radical  $HC(O)(CH_2)_3CH_2$ , which could then react with oxygen via reaction (4) to yield the primary alkylperoxy radical,  $HC(O)(CH_2)_3CH_2O_2$ . This species could then react with itself or the other radicals present:

$$HC(O)(CH_2)_3CH_2O_2 + c-C_5H_9O_2$$
  

$$\rightarrow HC(O)(CH_2)_3CH_2O + c-C_5H_9O + O_2 \qquad (8a)$$

$$\rightarrow \text{HC}(\text{O})(\text{CH}_2)_3\text{CHO} + \text{c-C}_5\text{H}_9\text{OH} + \text{O}_2 \quad (8b)$$

$$\rightarrow \text{HC}(\text{O})(\text{CH}_2)_3\text{CH}_2\text{OH} + \text{c-C}_5\text{H}_8\text{O} + \text{O}_2 \quad (8c)$$

$$HCO(CH_2)_3CH_2O_2 + HO_2$$

$$\rightarrow$$
 HC(O)(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>OOH + O<sub>2</sub> (9)

 $2 \operatorname{HCO}(\operatorname{CH}_2)_3\operatorname{CH}_2\operatorname{O}_2 \to 2 \operatorname{HC}(\operatorname{O})(\operatorname{CH}_2)_3\operatorname{CH}_2\operatorname{O} + \operatorname{O}_2$ (10*a*)

$$\rightarrow \text{HC}(O)(CH_2)_3CH_2OH + \text{HC}(O)(CH_2)_3CHO + O_2$$
(10b)

to give a variety of products, including the identified glutaric dialdehyde,  $HC(O)(CH_2)_3CHO$ . The formation of the alkoxy radical,  $HC(O)(CH_2)_3CH_2O$ , in reactions (8a) and (10a) would be followed either by its reaction with oxygen:

$$HC(O)(CH_2)_3CH_2O + O_2 \rightarrow HC(O)(CH_2)_3CHO + HO_2$$
(11)

by cleavage of the  $\beta$ -carbon–carbon bond:

$$HC(O)(CH_2)_3CH_2O + M$$

$$\rightarrow \text{HC(O)(CH}_2)_2\text{CH}_2 + \text{HCHO} + M \quad (12)$$

or by isomerisation:<sup>14</sup>

$$HCO(CH_2)_3CH_2O + M$$

$$\rightarrow \text{HC}(\text{O})\text{CH}(\text{CH}_2)_2\text{CH}_2\text{OH} + \text{M}$$
(13*a*)

$$\rightarrow \text{HOCH}_2(\text{CH}_2)_2\text{CH}_2\text{CO} + M \tag{13b}$$

The lack of formaldehyde in the end-product analyses suggests that reaction (12) is of minor importance, however. Hydroperoxy radicals produced in reaction (11) are a possible source of the observed yield of ROOH.

**Table 3** Variation of  $k_{obs}^{a}$  for the cyclopentylperoxy radical self-reaction with oxygen partial pressure

p <sub>O2</sub> /Torr	243 K		256 K		273 K		298 K		323 K		373 K	
	k <sub>obs</sub>	[O <sub>2</sub> ]/[Cl <sub>2</sub> ]	k <sub>obs</sub>	[O <sub>2</sub> ]/[Cl <sub>2</sub> ]	k <sub>obs</sub>	[O <sub>2</sub> ]/[Cl <sub>2</sub> ]	k <sub>obs</sub>	[O <sub>2</sub> ]/[Cl <sub>2</sub> ]	k <sub>obs</sub>	[O <sub>2</sub> ]/[Cl <sub>2</sub> ]	k <sub>obs</sub>	[O <sub>2</sub> ]/[Cl <sub>2</sub> ]
0.13							2.05	0.10	2.18	0.12	3.12	0.14
0.24	2.70	0.26	2.93	0.25	2.78	0.17	2.37	0.19	2.08	0.21	2.84	0.20
0.49	2.73	0.53	3.01	0.51	2.48	0.35	2.18	0.38	1.96	0.44	2.39	0.35
0.98	2.77	1.06	3.07	1.02	2.72	0.71	2.14	0.40	2.34	0.87	2.32	0.70
0.98	_			_			2.74	1.50				
0.98							2.53	0.76				
2.50		_				1.81	3.31	2.03			2.55	1.76
4.90	3.92	4.38	2.81	5.13	4.00	3.54	3.65	4.74	4.03	4.37	3.41	3 51
9.80					_	7.08			5.66	8.74	4.66	7.03
12.10					4.57	8.74			_			
25	4.64	22.30	4.33	26.19	4.81	28.17	6.30	20.28	6.20	23.20	6.65	26.85
49	5.17	43.77	3.90	51.34		55.22	6.04	39.45			8.82	52.63
74	_			_	6.18	83.39	_	_				
98			3.63	102.67			6.36	80.50	7.40	90.94	9.66	105.26
146	4.27	130.43	4.60	116.66	6.94	164.53	6.83	99.39	6.93	135.48	10.40	134.02
243		_	4.46	194.17		_	6.84	165.40	7.94	225.49		
387	<u> </u>						6.76	263.45	_	_		
491			4.28	514.40	6.19	553.31		_	_		_	
581	_	_				_	6.35	395.52		_	-	
736			4.93	771.08	6.91	829.40	6.87	_	7.39	682.97	11.18	622.60
$k_{\min}^{a,b}$	2.73		3.00		2.66		2.19		2.14		2.36	
$k_{\max}^{a,b}$	4.69		4.57		6.56		6.73		7.42		10.91	

<sup>*a*</sup> Units of  $10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>*b*</sup> Averages.

Isomerisation (13a, b) would result in the formation of further alkyl and consequently alkylperoxy radicals, thereby continuing the propagation of the reaction sequence. The products would include a complex mixture of multifunctional carbonyl and alcohol type species which, being of typically low volatility, are, together with glutaric dialdehyde, the likely source of the observed aerosol formation and the low carbon balance. The low yield of carbon dioxide presumably arises from acylperoxy radicals formed either via the isomerisation (13b) or, at the significant conversions used in these experiments, from the reactions of chlorine atoms with aldehydic products of the primary reaction sequence. Aliphatic aldehydes have low UV absorption cross-sections at the monitoring wavelengths used in the flash photolysis experiments and formation of these compounds is not expected to affect our observed absorbance traces.

The ring-opening [reaction (3)] and subsequent production of a second peroxy radical [reaction (4)] can explain the slight distortions, away from pure second order, of the UV absorption decay traces in the flash photolysis experiments under some conditions: these distortions could be successfully modelled by including the production of a second alkylperoxy radical *via* reaction (1), using reasonable rate constants for its subsequent self- and cross-reactions. Note that this absorption was significant only at the highest experimental temperatures (>323 K) and oxygen partial pressures (>150 Torr), and that under most conditions the observed second-order rate constant represented a good fit to the experimental data.

The fall off in the values of  $k_{obs}$  with decreasing partial pressures of oxygen is analogous to the behaviour shown in the cyclohexylperoxy system.<sup>3</sup> In the latter this effect was attributed to the competition between the reaction of cyclohexoxy radical with oxygen (forming HO<sub>2</sub>) and ring-opening, to produce a further alkylperoxy radical. Clearly, from the product analysis, this is not so for the present system, where ring-opening dominates under all conditions. The variation of  $k_{obs}$  with oxygen partial pressure increases with temperature; this suggests that the non-terminating channel (1*a*) is responsible for the effect, as typically alkylperoxy radical self-reactions show a positive temperature dependence of  $\alpha$ .<sup>4,8,15,16</sup> The reaction of the HCO(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub> radical with molecular chlorine provides the most likely explanation for the observed behaviour:

$$HCO(CH_2)_3CH_2 + Cl_2 \rightarrow HCO(CH_2)_3CH_2Cl + Cl$$
 (14)

This reaction produces an alkyl chloride, which would not be expected to interfere in the present experiments, and a chlorine atom, which would immediately regenerate a cyclopentylperoxy radical via reactions (6) and (7). The effect of regenerating the original alkylperoxy radical in this way is two-fold: (i) the observed second-order rate constant diminishes as one of the reaction channels is removed and (ii) the kinetic behaviour reverts to pure second order as the production of peroxy radicals other than cyclopentylperoxy radicals is suppressed. Both effects were observed experimentally. Although the rate constant for reaction (14) is not known, the equivalent reaction of ethyl radicals is fast, with a room-temperature rate constant of  $1.9 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>17</sup> As the rate constants for saturated alkyl radicals with molecular chlorine correlate with the ionization potential of the radical<sup>17,18</sup> and the ionization potentials for straight-chain primary alkyl radicals are similar,<sup>19</sup> it is likely that  $k_{14}$  will be close to  $2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Similarly, although reaction (4) has not been studied, the high-pressure limiting rate constants for the reactions of ethyl, n-propyl and n-butyl radicals with molecular oxygen are around  $5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, <sup>20–22</sup> and so we anticipate  $k_{14}/k_4 \approx 4$ . The experimental results support this estimate: the maximum rate of change of  $k_{obs}$  with  $[O_2]/[Cl_2]$  [which should occur when reactions (4) and (14) are approximately equally important] is found around  $[O_2]/[Cl_2] = 5$ ; the proposed mechanism thus seems reasonable.

Analogously, at the lowest values of  $[O_2]/[Cl_2]$ , it is clear that there will also be competition between the reaction of cyclopentyl radicals with molecular chlorine:

$$c-C_5H_9 + Cl_2 \rightarrow c-C_5H_9Cl + Cl$$
(15)

and that with molecular oxygen [reaction (7)] in the initial radical generation sequence, particularly as secondary alkyl radicals react more quickly with molecular chlorine than primary alkyl radicals.<sup>17</sup> Indeed, a marked increased initial consumption of molecular chlorine was observed at very low oxygen partial pressures. However, the chlorine atom produced in reaction (15) will go on to react with a further cyclopentane molecule and complete conversion of chlorine atoms into cyclopentylperoxy radicals will be achieved within a few rapid cycles of reactions (6) and (15). Furthermore, the conversion of a small fraction of cyclopentane to cyclopentyl chloride will not affect the absorbance–time traces as both compounds have low absorption cross-sections at our monitoring wavelengths.<sup>23</sup>

Reactions (14) and (15) should be unimportant in the product analysis experiments reported here, for which the lowest  $[O_2]/[Cl_2]$  ratios were around 100. Furthermore, attempts to identify  $HCO(CH_2)_3CH_2Cl$  and cyclopentyl chloride by FTIR spectroscopy at lower  $[O_2]/[Cl_2]$  ratios were unsuccessful: there is no universally characteristic R—Cl IR absorption feature and identification must rely on reference samples. Unfortunately, the IR features of cyclopentyl chloride closely match those of cyclopentane, apart from one broad band centred around 1300 cm<sup>-1</sup> and we were not able to quantify the concentration of cyclopentyl chloride in the presence of cyclopentane with any precision;  $HCO(CH_2)_3CH_2Cl$  is not available commercially.

The lower limiting rate constant,  $k_{\min}$ , thus represents the situation where ring-opened alkyl radicals undergo reaction (14) exclusively and cyclopentylperoxy radicals consumed via channel (1a) are rapidly regenerated via reactions (3), (14), (6) and (7). Under such conditions,  $k_{\min}$  can therefore be equated to  $(1 - \alpha)k_1$  (or  $k_{1b}$ ). It is unfortunately not possible to use the present data to extract accurate values for  $\alpha$  or  $k_1$  since, owing to the complex nature of the secondary chemistry, the relationship between  $k_{max}$  and  $k_1$  is not well defined. Rate constants and branching ratios for the reactions of  $HC(O)(CH_2)_3CH_2O_2$  would be required to determine  $\alpha$  and  $k_1$  precisely. This behaviour is different from that found for the cyclohexylperoxy system, where  $k_{max}$  was simply a factor of  $(1 + \alpha)$  greater than the real rate constant.<sup>3</sup> However, it does seem clear that  $\alpha$  increases with temperature, as both  $k_{\rm max}/k_{\rm min}$  and the slight distortions away from pure second-order behaviour also increase with temperature. Fuller simulations, including the chemistry of the  $HC(O)(CH_2)_3CH_2O_2$  radical, were performed in order to evaluate the effect of the secondary chemistry on  $k_{obs}$  at high oxygen partial pressures. Very good fits could be obtained with a wide range of values of  $\alpha$ ,  $k_8$  and  $k_{10}$ ; the optimised value of  $k_1$  changes little from  $k_{max}$ , however. We believe that the values of  $k_{max}$  represent upper limits on  $k_1$  and are probably no more than 25% higher at 373 K, the errors decreasing at lower temperatures where  $\alpha$  is smaller.

# Cyclohexylperoxy Radical Self-reaction: Further Results

In light of the present data, a reinterpretation of our earlier results on the cyclohexylperoxy radical self-reaction:<sup>3</sup>

$$2 c-C_6 H_{11}O_2 \to 2 c-C_6 H_{11}O + O_2$$
 (16a)

$$\rightarrow c - C_6 H_{11} O H + c - C_6 H_{10} O + O_2$$
 (16b)

is necessary. Previously, the decrease of  $k_{obs}$  with decreasing oxygen partial pressure in the cyclohexylperoxy system was solely attributed to the competition between ring-opening followed by reaction with O<sub>2</sub> [reactions (17) and 18)] and

1375

reaction with oxygen [reaction (19)]:

$$c-C_6H_{11}O + M \to HC(O)(CH_2)_4CH_2 + M$$
 (17)

$$\mathrm{HC}(\mathrm{O})(\mathrm{CH}_2)_4\mathrm{CH}_2 + \mathrm{O}_2 + \mathrm{M}$$

$$\rightarrow \text{HC}(\text{O})(\text{CH}_2)_4\text{CH}_2\text{O}_2 + \text{M}$$
(18)

$$c-C_6H_{11}O + O_2 \rightarrow c-C_6H_{10}O + HO_2$$
 (19)

Reaction (17) gives rise to the substituted alkylperoxy radical  $HC(O)(CH_2)_4CH_2O_2$ , which will undoubtedly react more slowly with the parent alkylperoxy radical than will  $HO_2$ . The effect of replacing reaction (19) with reaction (17) would be thus to reduce  $k_{obs}$ . However, given that the methods of radical generation were essentially identical in the two systems (apart from the replacement of cyclopentane with cyclohexane), it is likely that the reduction in  $k_{obs}$  at values of  $[O_2]/[Cl_2]$  below 50 is almost entirely due to the reaction of the ring-opened alkyl radical with molecular chlorine:

$$HOCH_2(CH_2)_4CH_2 + Cl_2$$

$$\rightarrow$$
 HOCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>Cl + Cl (20)

Variation in  $k_{obs}$  with  $[O_2]/[Cl_2]$  at higher values of  $[O_2]/[Cl_2]$  will still be due to competition between reactions (17) and (19), however.

The arguments presented above for estimating the relative importance of reaction (14) are equally valid for reaction (20) and we expect very similar behaviour in both systems;  $k_{\min}$ should thus be equal to  $(1 - \alpha)k_{16}$ . Furthermore, the endproduct-analysis experiments showed that, at least at room temperature, reaction (19) dominates over reaction (17) at high  $[O_2]/[Cl_2]$  and that  $k_{max}$  is equal to  $(1 + \alpha)k_{16}$ ;  $\alpha$  is thus equal to  $(k_{\text{max}} - k_{\text{min}})/(k_{\text{max}} + k_{\text{min}})$ . It should be noted, however, that  $k_{17}$  will increase more rapidly with temperature than  $k_{19}$  and that this equivalence may not hold at temperatures above ambient. As experiments in the cyclohexylperoxy system had not been performed at as low oxygen concentrations as for the cyclopentylperoxy system and a lower limiting value for  $k_{obs}$  had consequently not been observed, additional experiments were performed here at low  $[O_2]/[Cl_2]$ . The results, very similar to those obtained for the cyclopentylperoxy system, are summarised in Table 4. Also shown in the table are calculated values of  $\alpha$ . The roomtemperature value of 0.24 is in reasonable agreement with the more directly determined value of 0.29 derived from the product-analysis studies, supporting the assumption that  $k_{min}$ is equal to  $(1 - \alpha)k_1$ . Furthermore,  $\alpha$  increases systematically with temperature up to 323 K, as anticipated. The drop in  $\alpha$ between 323 and 373 K is caused by a sharp upturn in  $k_{\min}$ which is attributed to problems associated with incomplete conversion of chlorine atoms into peroxy radicals before a limiting value of  $k_{\min}$  was reached at the higher temperature. Fitting to values of  $\beta$  below 373 K and scaling to reproduce  $\alpha = 0.29$  at 296 K, gives:

$$\beta = 1146 \exp[-(2350 \pm 320) \mathrm{K}/T]$$

**Table 4** Values of  $k_{\min}$  and  $k_{\max}$  for the cyclohexylperoxy self-reaction

T/K	$k_{min}^{a}$	k <sub>max</sub> ª	$k_{\rm max}/k_{\rm min}$	α <sup>b</sup>
253	2.80	3.15	1.13	0.06
273	2.46	3.29	1.34	0.14
294	2.39	3.92	1.64	0.24
323	2.37	4.60	1.94	0.32
373	3.67	5.97	1.63	0.24

<sup>a</sup> Units of  $10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup> Calculated using  $\alpha = (k_{max} - k_{min})/(k_{max} + k_{min})$ .



**Fig. 10** Arrhenius plot and fit for  $k_{\max}$  ( $\Box$ ) and  $k_{\min}$  ( $\blacksquare$ , point at 373 K not included in the fit; see text) for the cyclohexylperoxy radical self-reaction

This temperature dependence of  $\beta$  is rather greater than that found for other peroxy radical self-reactions<sup>4</sup> and should be regarded as approximate. Unweighted, logarithmic fits to the values of  $k_{\min}$  and  $k_{\max}$ , apart from the value of  $k_{\min}$  at 373 K, are shown in Fig. 10 and give:

$$k_{\min}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = (1.3 \pm 0.3) \times 10^{-14}$$
  
  $\times \exp[(185 \pm 15)\text{K}/T]$ 

and

$$k_{\text{max}}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = (2.4 \pm 0.4) \times 10^{-13} \times \exp[-(530 \pm 30)\text{K}/T]$$

Note that the expression for  $k_{\min}$  is almost identical to that for the cyclopentylperoxy self-reaction, underlining the close similarity between the behaviour of the two radicals. Using the expression above for  $\beta$  to correct  $k_{\max}$  to  $k_{16}$  by dividing by  $(1 + \alpha)$  at each experimental temperature and refitting to an Arrhenius expression gives a final estimate for  $k_{16}$ :

$$k_{16}/\text{cm}^3$$
 molecule<sup>-1</sup> s<sup>-1</sup> = 7.7 × 10<sup>-14</sup> exp(-184 K/T)

which is very close to that previously estimated<sup>3</sup> using a temperature dependence of  $\beta$  based on the self-reactions of other radicals.

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