# Flash Photolysis Study of the Spectra and Self-reactions of Neopentylperoxy and t-Butylperoxy Radicals

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The self-reaction of neopentylperoxy radicals, neo-C<sub>5</sub>H<sub>11</sub>O<sub>2</sub> (NPTO<sub>2</sub>):

$$NPTO_2 + NPTO_2 \rightarrow 2t - C_4 H_9 C H_2 O + O_2$$
(1a)

$$\rightarrow t-C_4H_9CHO + t-C_4H_9CH_2OH + O_2$$
(1b)

$$\rightarrow t - C_4 H_9 C H_2 O O C H_2 C_4 H_9 - t + O_2$$
(1c)

has been studied from 248 to 373 K and from 50 to 760 Torr total pressure. The neopentylperoxy radicals fromed via channel (1a) react, under most experimental conditions, by unimolecular decomposition:

$$t-C_{a}H_{g}CH_{2}O + M \rightarrow t-C_{a}H_{g} + HCHO + M.$$
<sup>(2)</sup>

The t-butyl radicals so formed are rapidly converted into t-butylperoxy radicals under the conditions employed in this work; these radicals are unreactive on the timescale of the NPTO<sub>2</sub> decay and enable the branching ratio for reaction (1) to be determined *via* their UV absorption. The overall rate constant for reaction (1) displays a strong negative temperature dependence, being well described by  $k_1/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> = 3.02 × 10<sup>-19</sup>(T/298)<sup>9.46</sup> exp(4260/T) over the temperature range studied here. The non-terminating channel (1a) becomes increasingly important with increasing temperature, with  $\beta = (197 \pm 67)\text{exp}[-(1658 \pm 98)/T]$ , where  $\beta$  is the ratio of those radicals which react *via* the non-terminating channel (1a) to those which react *via* the terminating channels (1b) and (1c). By measuring the reduction in the fraction of NPYO<sub>2</sub> radicals converted to t-butylperoxy radicals with increasing oxygen concentration, rate constants for reaction (2) were determined, giving  $E_2/\text{kJ}$  mol<sup>-1</sup> = 42.7 ± 2.1. The UV spectra of NPTO<sub>2</sub> and t-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub> have been determined relative to that of CH<sub>3</sub>O<sub>2</sub>; both are similar in shape and magnitude to those of other alkylperoxy radicals, displaying maxima around 240 nm, with  $\sigma_{240 \text{ nm}}(\text{INPTO}_2)/\text{ cm}^2$  molecule<sup>-1</sup> = (6.2 ± 1.1) × 10<sup>-18</sup> and  $\sigma_{240 \text{ nm}}(\text{t-C}_4\text{H}_9\text{O}_2)/\text{cm}^2$  molecule<sup>-1</sup> = (4.7 ± 0.8) × 10<sup>-18</sup>. The self-reaction of t-butylperoxy radicals:

$$2t-C_4H_9O_2 \rightarrow 2t-C_4H_9O + O_2 \tag{3}$$

was also briefly studied, resulting in  $k_3/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>  $\approx 1.0 \times 10^{-11} \exp(-3894/T)$ . Errors are 1 $\sigma$ .

The importance of alkylperoxy radicals as intermediates in the atmospheric oxidation and low-temperature combustion of hydrocarbons is well established.<sup>1</sup> However, although the reactions of the smaller alkylperoxy radicals have received a considerable amount of interest [see, for example, ref. (2)], very little is known of the gas-phase behaviour of alkylperoxy radicals containing more than four carbon atoms. Despite the fact that the combustion of petrol and diesel fuels must pass *via* such large radicals and their central role in determining autoignition phenomena,<sup>3</sup> no direct studies of their reactivity are available.

The self-reactions of alkylperoxy radicals have proved to be particularly interesting from a theoretical point of view: they often display a weak and sometimes negative temperature dependence of the overall rate constant, which is nevertheless considerably below the collisional limit. At least three product channels have been identified. This behaviour can be rationalised by the formation of an intermediate tetroxide, which can either redissociate or go on to form products. For the general case:  $^{2}RO + O_{2}$  (a)

$$RO_2 + RO_2 \rightleftharpoons RO_4 R \longrightarrow ROH + R'CHO + O_2$$
 (b)

**ROOR** +  $O_2$ . (c)

The fraction of alkylperoxy radicals which react via the nonterminating channel (a), we define as  $\alpha$ . Similarly, we define the ratio of radicals reacting via channel (a) to those which react via the terminating channels (b) and (c) as  $\beta$ . In all cases where channel (c) has been observed, it has been shown to make only a minor contribution and  $\beta$  thus often simply reflects the relative importance of channels (a) and (b). In studies of methylperoxy,<sup>4</sup> ethylperoxy<sup>5</sup> and isopropylperoxy<sup>6</sup> radicals,  $\beta$  has been shown to increase with temperature, and the non-terminating channel (a) is predicted to dominate at cool flame temperatures (T > 600 K). This seemingly general shift in mechanism with temperature underlines the inapplicability of using room-temperature branching ratios for atmospheric and combustion modelling and the necessity of 2928

performing experiments over as wide a range of temperature as possible.

In this paper, we present results on the UV absorption spectrum and self-reaction of neopentylperoxy radicals,  $(CH_3)_3CCH_2O_2$  (NPTO<sub>2</sub>). According to the general mechanism above, this reaction can proceed in three ways:

 $(0.2-27.8) \times 10^{18}$ ; initial radical concentration (4.4-11.9)  $\times 10^{13}$ ; balance nitrogen. No systematic dependence of the experimental results on the concentrations of chlorine and neopentane, the flash-lamp energy, the initial radical concentration, the apparatus used or the time between flashes was noticed. For most experiments, the flash repetition rate

$$2(CH_3)_3CCH_2O + O_2 \tag{1a}$$

$$2NPTO_2 \rightleftharpoons (CH_3)_3 CCH_2 O_4 CH_2 C(CH_3)_3 \rightarrow (CH_3)_3 CCH_2 OH + t - C_4 H_9 CHO + O_2$$
(1b)

$$(CH_3)_3CCH_2OOCH_2C(CH_3)_3 + O_2$$
(1c)

In addition, we present results on the spectrum and self-reaction of the *t*-butylperoxy radical,  $t-C_4H_9O_2$ .

# Experimental

The apparatus used in the present study has been described in detail recently.<sup>4</sup> Two sets of flash photolysis/UV absorption apparatus were used: one covers the temperature range 248–413 K, the other the range 298–800 K. Peroxy radicals are monitored via their time-resolved absorption between 200 and 300 nm, following the flash-lamp photolysis of suitable precursor mixtures. The resulting decay profiles are averaged, typically over 16 shots and stored on a microcomputer for subsequent analysis via numerical integration/non-linear least-squares analysis. Unless otherwise stated, errors are  $1\sigma$ and refer only to experimental uncertainty.

Oxygen (>99.5%), nitrogen (>99.995%), synthetic air, methane (>99.5%) and chlorine (5% in nitrogen), all from l'Air Liquide, and neopentane (>99%, chief impurity n-butane <1%), from Argo International Ltd and Phillips Petroleum Ltd., were all used without further purification.

# **Results and Discussion**

This section is split up as follows: (i) The method of generating the radicals, general form of the decay traces and the UV spectrum of the NPTO<sub>2</sub> radical; (ii) the proposed mechanism of the reaction system; (iii) the UV absorption spectrum of the t-butylperoxy radical; (iv) the rate constant and branching ratio for reaction (1); (v) the unimolecular decomposition of neopentoxy radicals; (vi) the self-reaction of the t-butylperoxy radical.

# (i) Radical Generation and the NPTO<sub>2</sub> Absorption Spectrum

Neopenty peroxy radicals (NPTO<sub>2</sub>) were produced by the flash-lamp photolysis of  $Cl_2/neopentane/O_2/N_2$  mixtures at wavelengths above the Pyrex cut-off:

hv > 280 nm

$$Cl_2 \rightarrow Cl + Cl$$
 (4)

$$Cl + (CH_3)_4C \rightarrow HCl + (CH_3)_3CCH_2$$
 (5)

$$(CH_3)_3CCH_2 + O_2 + M \rightarrow NPTO_2 + M.$$
(6)

Reaction (5) is fast, with  $k_5/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> = 1.1 × 10<sup>-10</sup> at 296 K,<sup>7</sup> and a partial pressure of around 1 Torr<sup>+</sup> of neopentane was sufficient to ensure complete removal of chlorine atoms *via* reaction (5). Oxygen concentrations were always maintained sufficiently high to ensure stoichiometric conversion of neopentyl radicals to NPTO<sub>2</sub>.<sup>8</sup>

Experiments were performed from 248 to 418 K. At room temperature, the total pressure was varied from 50 to 760 Torr; at other temperatures, atmospheric pressure was used. Reagent concentrations were, in units of molecule cm<sup>-3</sup>: neopentane  $(1.3-5.8) \times 10^{16}$ ; chlorine  $(3.2-6.8) \times 10^{16}$ ; oxygen

was such that the entire cell contents were replaced between flashes. At temperatures at and below ambient, the effect of systematically varying the oxygen partial pressure from a few Torr up to 760 Torr was examined.

Experiments gave rise to striking absorption-time profiles: a strong initial absorption, decaying over ca. 50 ms to a residual absorption which was unchanging on the timescale of the initial decay. At temperatures at and below ambient, the lifetime of this residual absorption was longer than the residence time (around 45 s) of the gas mixture in the cell. With increasing temperature, its lifetime shortened, falling to a few seconds at 418 K. In addition, the magnitude of the residual absorption increased with temperature, from around 10% of the initial absorption at 248 K to around 50% at 373 K. Under all conditions, the initial decays were well fitted by second-order kinetics with an absorbing product; typical traces are shown in fig. 1.

The initial absorption, peaking at around 240 nm, is attributed to the NPTO<sub>2</sub> radical. Its spectrum, similar in shape to those of other alkylperoxy radicals, was calibrated against the methylperoxyl spectrum,<sup>9</sup> by replacing neopentane by methane in the photolysis mixtures, under otherwise identical conditions. The two spectra are compared in fig. 2 and table 1. The NPTO<sub>2</sub> spectrum is red-shifted by *ca.* 10 nm with respect to the methylperoxyl spectrum and is somewhat more intense at the peak. Using a 10% uncertainty in our relative cross-section determination and a 15% uncertainty for the absolute values of  $\sigma(CH_3O_2)$ , we estimate an 18% absolute uncertainty for the NPTO<sub>2</sub> cross-sections in table 1. No



Fig. 1. NPTO<sub>2</sub> decay traces at different temperatures, 240 nm, 1 atm, air diluent. The respective contributions of NPTO<sub>2</sub> and t-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub> are shown, together with the fitted total absorption. In each case, the decay was fitted as a second-order decay with an absorbing product [reaction (1), followed rapidly by reactions (2) and (7)]; the optimised parameters were the initial NPTO<sub>2</sub> concentration,  $k_1$  and the fraction of reaction (1) which produces t-C<sub>4</sub>H<sub>9</sub>CH<sub>2</sub>O via channel (1a),  $\alpha$ . (a) 248 K, full timescale 20.48 ms; (b) 288 K, full timescale 51.2 ms; (c) 373 K, full timescale 102.4 ms.

<sup>† 1</sup> Torr  $\approx$  101 325/760 Pa.



Fig. 2. UV absorption spectra of  $CH_3O_2$  ( $\Box$ )<sup>9</sup> and NPTO<sub>2</sub> ( $\blacksquare$ ). The curves represent fourth-order polynomials fitted through the data points.

Table 1. NPTO<sub>2</sub>, t-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> UV absorption spectra

wavelength/nm	$\sigma/10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$			
	NPTO <sub>2</sub>	t-C <sub>4</sub> H <sub>9</sub> O <sub>2</sub>	CH <sub>3</sub> O <sub>2</sub> "	
210	2.1	1.6	2.5	
220	3.6	2.9	3.9	
230	5.3	4.1	4.7	
240	6.2	4.7	4.8	
250	6.0	4.2	4.4	
260	5.6	3.5	3.6	
270	4.1	2.2	2.55	
280	2.6	1.4	1.75	
290	1.7	_		

" Ref. (9).

published data is available on the NPTO<sub>2</sub> spectrum, although Dagaut and Kurylo, using a flash photolysis/ UV absorption apparatus, have recently obtained a spectrum similar to our own in form, but around 15% less intense on average.<sup>10</sup>

# (ii) Mechanism

In this section, we discuss and provide evidence for the proposed mechanism; the details of our results are described in further sections below.

The wavelength dependence of the residual absorption followed that of NPTO<sub>2</sub> closely, but not exactly, the ratio of initial to residual absorption increasing systematically by *ca.* 40% from 210 to 270 nm. Possible molecular products of reaction (1) do not absorb strongly enough in the region 200–280 nm to explain the observed absorptions, suggesting that the residual absorption is due to a second alkylperoxy radical which reacts extremely slowly. A good candidate for such a radical would be the t-butylperoxy radical, which has a rate constant for its self reaction of around  $1 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature.<sup>11,12</sup> Experiments, described in (vi) below, indeed showed that the residual absorption decayed in a sensible second-order manner, with a value of  $k/\sigma$  and a temperature dependence similar to that observed previously.<sup>11,12</sup>

The origin of the t-butylperoxy radicals presumably lies in

the unimolecular decomposition of neopentoxy radicals produced via channel (1a):

$$(CH_3)_3CCH_2O + M \rightarrow t - C_4H_9 + HCHO + M$$
(2)

followed rapidly by reaction with molecular oxygen:

$$t-C_4H_9 + O_2 + M \rightarrow t-C_4H_9O_2 + M$$
 (7)

Reaction (2) will be in competition with the reaction of neopentoxy radicals with molecular oxygen:

$$(CH_3)_3CCH_2O + O_2 \rightarrow t - C_4H_9CHO + HO_2$$
(8)

It is known that the unimolecular decomposition of large alkoxy radicals to form carbonyl compounds and relatively stable alkyl radicals can compete effectively with the corresponding reaction with oxygen under atmospheric conditions.<sup>13</sup> It is shown below that, in the present study, reaction (8) only becomes important at low temperatures and high oxygen concentrations. The isomerisation:

$$(CH_3)_3CCH_2O \rightarrow CH_2(CH_3)_2CCH_2OH$$
 (9)

involves a five-membered cyclic transition state with the breaking of a primary C—H bond and so should be very slow with respect to reactions (2) and (8) at room temperature.<sup>13</sup>

The present system provides a sensitive method for detecting the occurrence of reaction (8): neopentoxy radicals converted into hydroperoxy radicals *via* reaction (8) will not go on to form the quasi-stable t-butylperoxy product, which absorbs strongly. If reaction (8) is important, then the steadystate absorption at the end of the decay traces should diminish with increasing oxygen concentration. The ratio of the residual to initial absorption was reduced by only a few per cent on varying the oxygen concentration from  $1.5 \times 10^{17}$  to  $2.5 \times 10^{19}$  molecule cm<sup>-3</sup> at room temperature, demonstrating that reaction (8) is unimportant under such conditions. However, at lower temperatures, the reduction in the residual absorption with increasing oxygen concentration was more pronounced. This point will be returned to in detail later.

In the presence of  $t-C_4H_9O_2$ , the cross-reaction:

$$NPTO_2 + t-C_4H_9O_2$$
  

$$\rightarrow (CH_3)_3CCH_2O + t-C_4H_9O + O_2 \quad (10a)$$

$$\rightarrow$$
 t-C<sub>4</sub>H<sub>9</sub>CHO + t-C<sub>4</sub>H<sub>9</sub>OH + O<sub>2</sub> (10b)

$$\rightarrow t - C_4 H_9 C H_2 OOC_4 H_9 - t + O_2 \qquad (10c)$$

might be expected to be important. However, at ambient temperature, flashing the reaction mixture several times just before each recorded flash, thus creating significant quasi-stationary concentrations of t-butylperoxy radicals ([t- $C_4H_9O_2$ ]  $\approx$  [NPTO<sub>2</sub>] at t = 0), had no discernible effect on the NPTO<sub>2</sub> kinetics. Thus  $k_1 \geq 10 \ k_{10}$  at 295 K. Parkes<sup>11</sup> observed similar behaviour in molecular modulation experiments involving t-butylperoxy and methylperoxy radicals, where the cross-reaction:

$$CH_3O_2 + t - C_4H_9O_2 \rightarrow CH_3O + t - C_4H_9O + O_2 \qquad (11a)$$

$$\rightarrow \text{HCHO} + \text{t-C}_4\text{H}_9\text{OH} + \text{O}_2 \quad (11b)$$

$$\rightarrow t - C_4 H_9 OOCH_3 + O_2 \qquad (11c)$$

although several orders of magnitude faster than the tbutylperoxy self-reaction:

$$t-C_4H_9O_2 + t-C_4H_9O_2 \rightarrow 2t-C_4H_9O + O_2$$
 (3a)

$$\rightarrow (t - C_4 H_9 O)_2 + O_2 \qquad (3c)$$

[N.B. in this case, channel (b) is not possible], was shown to

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be significantly slower than the methylperoxy self-reaction:

$$CH_{3}O_{2} + CH_{3}O_{2} \rightarrow 2CH_{3}O + O_{2}$$
(12*a*)

$$\rightarrow$$
 CH<sub>3</sub>OH + HCHO + O<sub>2</sub> (12b)

$$\rightarrow CH_3OOCH_3 + O_2 \qquad (12c)$$

Osbourne and Waddington, in an end-product analysis study of the photo-oxidation of azoisobutane, likewise showed that reaction (11) was much slower than reaction (12), in this case by more than two orders of magnitude at room temperature.<sup>14</sup> These results suggest that in the present case, as long as the rate constants for the two self-reactions are separated by several orders of magnitude, then the faster reaction can be studied without interference from the crossreaction. As is discussed below, the rate constant for the self-reaction of t-butylperoxy radicals increases rapidly with temperature and the effect of the cross-reaction did become detectable at temperatures of around 373 K, effectively imposing an upper temperature limit on the present study of reaction (1).

To summarise the results of this section: the self-reaction of NPTO<sub>2</sub> radicals proceeds by at least two channels, one giving rise to neopentoxy radicals, the other(s) giving rise to stable products. The neopentoxy radicals react exclusively by unimolecular decomposition to t-butyl radicals and formaldehyde under typical experimental conditions. The t-butyl radicals so produced form t-butylperoxy radicals by reaction with oxygen; these t-butylperoxy radicals are inert on the timescale of the NPTO<sub>2</sub> decay and give rise to a strong residual absorption. Under these conditions, we can extract both the absolute value of  $k_1$  and the branching ratio for the production of neopentoxy radicals,  $\alpha$ , as is shown below.

# (iii) t-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub> Absorption Spectrum

The stoichiometric conversion of neopentoxy radicals to tbutylperoxy radicals provides a means of measuring the fraction,  $\alpha$ , of NPTO<sub>2</sub> radicals which react via channel (1a), as  $\alpha = [t-C_4H_9O_2]/[NPTO_2]_{t=0}. \text{ Calculation of } [t-C_4H_9O_2]$ requires a knowledge of its absolute absorption spectrum. Parkes,<sup>11</sup> using molecular modulation spectrometry, found a spectrum which was very similar in shape to those of other alkylperoxy radicals. The maximum of this spectrum was considerably lower than those of other alkylperoxy radicals, however, with  $\sigma_{240 \text{ nm}}$  cm<sup>2</sup> molecule<sup>-1</sup> =  $2.2 \times 10^{-18}$ , more than a factor of two weaker than the corresponding maximum cross-section for CH<sub>3</sub>O<sub>2</sub>.<sup>9</sup> However, more extensive but unpublished results by the same group<sup>15</sup> give  $\sigma_{240 \text{ nm}}$  cm<sup>2</sup> molecule<sup>-1</sup> = 4.0 × 10<sup>-18</sup>. In a flash photolysis study of methylperoxy and t-butylperoxy reactions, Anastasi et al. found that the spectra of the two radicals were very alike in form.<sup>12</sup> However, although the two spectra were collected under very similar conditions and showed very similar absorbances, they were not calibrated and it was not possible to determine whether the similarity extended to absolute values.

In view of this lack of information, we have independently determined the t-butylperoxy absorption spectrum using the flash photolysis of molecular chlorine in the presence of tbutylhydroperoxide in an oxygen-free system. The chlorine atoms created in the flash can abstract a hydrogen atom either from the t-butyl or the hydroperoxide group:

$$Cl + t-C_4H_9OOH \rightarrow HCl + t-C_4H_9O_2$$
 (13a)

$$\rightarrow$$
 HCl + CH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>COOH. (13b)

Neither the total rate constant nor the branching ratio for

this reaction are known. Equating  $k_{13b}$  to 3/4  $k_5$  and  $k_{13a}$  to 1/2  $k_{14}$ :<sup>16</sup>

$$Cl + H_2O_2 \rightarrow HCl + HO_2$$
(14)

gives  $\Gamma$  (defined here as  $k_{13a}/k_{13b} \approx 0.0025$  at room temperature. Thus, reaction (13) might be expected to proceed almost exclusively via channel (13b) under our conditions. Indeed, we hoped to use this reaction in the presence of oxygen to generate  $O_2CH_2(CH_3)_3COOH$  ( $\equiv O_2QOOH$ ). In the absence of oxygen, however, the substituted alkyl radicals produced in reaction (13b) will react with the molecular chlorine present, regenerating chlorine atoms:

$$CH_2(CH_3)_2COOH + Cl_2 \rightarrow ClCH_2(CH_3)_2COOH + Cl \quad (15)$$

which will in turn react with the hydroperoxide via reaction (13). Thus, as alkyperoxy radicals are unreactive towards molecular chlorine, at least at room temperature, the chlorine atoms produced in the flash will be stoichiometrically converted to t-butylperoxy radicals by successive cycles of reactions (13) and (15), provided that these two steps are fast enough to prevent radical-radical reactions; the number of cycles required will, of course, depend on  $\Gamma$ . The chlorinated hydroperoxide formed in reaction (15) is not expected to display an absorption spectrum significantly different from the parent hydroperoxide over our experimental wavelength range and no significant baseline shifts are anticipated. The rate constant for reaction (15) has not been measured, but the rate constants for all alkyl radicals measured to date are greater than  $1 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature.<sup>17</sup> Using this value as a lower limit for  $k_{15}$ , then the first-order rate of removal of CH2(CH3)COOH via this reaction would be  $>3 \times 10^4$  s<sup>-1</sup> for typical experimental conditions of 1 Torr Cl<sub>2</sub>. Equating  $k_{13}$  to 3/4  $k_5$ , then  $k_{13}$  [t-C<sub>4</sub>H<sub>9</sub>OOH]  $\approx 5 \times 10^5$  s<sup>-1</sup>, for a typical t-butylhydroperoxide concentration of ca.  $5 \times 10^{15}$  cm<sup>-3</sup>, measured by UV absorption spectroscopy at 210 nm using the absorption coefficient for methylhydroperoxide (the absorption spectra for hydrogen peroxide and methylhydroperoxide<sup>18</sup> are very similar in this region and differences between the spectra of hydroperoxides are expected to be small). Reaction (15) is thus the rate-limiting step in the production of t-butylperoxy radicals.

Scattered light and resulting fluorescence from the flashlamp pulse prevents us from making absorption measurements for approximately the first 250 µs following the flash. In all cases, the production of t-butylperoxy radicals was observed to be complete within the timescale of the flash. The resulting absorption profile was flat on the timescale of several seconds and the relative spectrum was identical to that of the residual absorption in the experiments with NPTO<sub>2</sub>, providing further evidence for the production of tbutylperoxy radicals in the latter system. The t-butylperoxy spectrum was calibrated against that of the methylperoxy radical. No systematic dependence of the t-butylperoxy spectrum on either [t-C<sub>4</sub>H<sub>9</sub>OOH] [(2.5-14.5) × 10<sup>15</sup> molecule cm<sup>-3</sup>] or [Cl<sub>2</sub>] [(2.6-7.6) × 10<sup>16</sup> molecule cm<sup>-3</sup>] was observed, demonstrating that reactions (13) and (15) were sufficiently fast to ensure complete conversion of chlorine atoms into t-butylperoxy radicals.

Our spectrum is compared with previous studies in fig. 3 and with the spectra of methylperoxy radicals and NPTO<sub>2</sub> in table 1. The spectrum peaks at 240 nm, with  $\sigma/$  cm<sup>2</sup> molecule<sup>-1</sup> = 4.7 × 10<sup>-18</sup>, more than a factor of two greater than that quoted by Parkes,<sup>11</sup> but much more in line with the later values of Parkes and Kirsch.<sup>15</sup> In fig. 3, the relative spectrum of Anastasi *et al.*<sup>12</sup> has been normalised to the present cross-section at 240 nm. The three spectra are very similar in form. The t-butylperoxy spectrum is very similar to J. CHEM. SOC. FARADAY TRANS., 1990, VOL. 86



**Fig. 3.** UV absorption spectra of t- $C_4H_9O_2$ . () Present study, flash photolysis of  $Cl_2/t-C_4H_9OOH/N_2$  mixtures; () Anastasi *et al.*,<sup>12</sup> flash photolysis of (t- $C_4H_9$ )<sub>2</sub> $N_2/N_2/O_2$  mixtures, relative spectrum normalised to the present spectrum at 240 nm; (**O**) Parkes,<sup>11</sup> molecular modulation study of (t- $C_4H_9$ )<sub>2</sub> $N_2/O_2/N_2$  mixtures; (**0**) Kirsch and Parkes,<sup>15</sup> molecular modulation study of (t- $C_4H_9$ )<sub>2</sub> $N_2/O_2/N_2$  mixtures. The curves represent fourth-order polynomials fitted through the data points.

that of the methylperoxy radical at wavelengths longer than or equal to 240 nm, but is rather weaker at shorter wavelengths. As for the NPTO<sub>2</sub> spectrum, the absolute uncertainties in our cross-section values are estimated to be 18%.

It is clear from the prompt production of t-butylperoxy radicals that the ratio  $\Gamma$  must be significantly greater than that calculated above, as the cycle of reactions (13) and (15) could only turn a few times during the duration of the flash. We were able to estimate  $\Gamma$  by observing the disappearance of molecular chlorine at 330 nm, where  $\sigma_{Cl_2}/cm^2$  molecule<sup>-1</sup> = 25.6 × 10<sup>-20</sup>.<sup>16</sup> For  $\Gamma$  = 1.0, the amount of molecular chlorine removed is equal to half the number of t-butylperoxy radicals produced. For  $\Gamma < 1.0$ , the ratio of the amount of chlorine removed to t-butylperoxy radicals produced is given by:

$$[Cl_2]_{consumed}/[t-C_4H_9O_2] = 1/(1-\Gamma) - 1/2.$$
 (I

As for the production of t-buylperoxy radicals, the consumption of chlorine was complete within the timescale of the flash. A series of eight experiments gave [Cl<sub>2</sub>]<sub>consumed</sub>/[t- $C_4H_9O_2$ ] = 1.72 ± 0.19, thus  $\Gamma = 0.55 \pm 0.05$ , over a factor of 200 greater than that derived above. The C-H bond energies in t-butylhydroperoxide and neopentane should not be very different, and in any case very little temperature dependence (and hence barrier to reaction) has been observed in the abstraction reactions of chlorine atoms with saturated hydrocarbons with more than one carbon atom,<sup>16</sup> so it might be expected that the rate constant for chlorine atom attack at the C-H bonds in the hydroperoxide would be comparable to that in neopentane. This suggests that the hydroperoxyl group of t-butylhydroperoxide is much more reactive than that in hydrogen peroxide. A comparable observation has been made for ethylhydroperoxide, for which the rate constant for chlorine-atom attack is significantly greater than that for ethane.<sup>19</sup> Similarly, the total rate constant for the reaction of hydroxyl radicals with t-butylhydroperoxide<sup>12</sup> is a factor of 3.4 greater than that for reaction with neopentane<sup>20</sup> and the abstraction of the hydroperoxyl hydrogen atom from methylhydroperoxide by hydroxyl is a factor of four greater than that expected on the basis of the reaction of hydroxyl with hydrogen peroxide at room temperature.<sup>21</sup> All these observations suggest that the O—H bond in alkylhydroperoxides is more reactive than that in hydrogen peroxide, despite the fact that the O—H bond energy is thought to remain constant.<sup>22</sup>

# (iv) The NPTO<sub>2</sub> Self-reaction

The experiments reported below were performed between 248 and 373 K. At higher temperatures, the timescales of the decays of the NPTO<sub>2</sub> radicals and the t-butylperoxy radicals were not sufficiently different to enable the two kinetics to be treated separately. Experiments were performed at higher temperatures, where all the peroxy radicals react on similar timescales, but these experiments did not enable us to extract unambiguously the individual rate constants and we do not report on them here. The decay traces collected at all temperatures were analysed initially as second-order decays with t-butylperoxy as an inert absorbing product. The variation of the apparent values of  $k_1$  and  $\alpha$  with the concentration of oxygen at 298, 273 and 248 K is shown in fig. 4 and 5. Above 273 K, the apparent value of  $k_1$  did not depend on the oxygen concentration and an average of all experiments was taken. At lower temperatures, the apparent value of  $k_1$ increased slightly with [O<sub>2</sub>] and the production of HO<sub>2</sub> via reaction (8) had to be taken into account, as is discussed in the next section. The maximum change in the apparent value of  $k_1$  was of the order of 10%. The branching ratio,  $\alpha$ , varied more strongly with  $[O_2]$  than  $k_1$ , decreasing with increasing [O<sub>2</sub>] owing to the removal of neopentoxy radicals in reaction (8) and the consequent reduction in the t-butylperoxy radical yield. As for  $k_1$ , the effect of changing the oxygen concentration decreased with increasing temperature, being almost insignigicant at 298 K. At 248, 273 and 298 K,  $\alpha$  was obtained by extrapolating the results to zero oxygen concentration, as described in section (v) below. At 373, 333 and 288 K, simple averages were taken, as the experiments were performed in air at 1 atm, † where the correction to zero oxygen concentration was negligible at these temperatures.



**Fig. 4.** Apparent  $k_1$  values from second-order fits, with an absorbing product, to the present data vs.  $[O_2]$  at 298 ( $\Box$ ), 273 ( $\triangle$ ) and 248 K ( $\bigcirc$ ). The lines are simple linear-regression fits to indicate how the apparent value of  $k_1$  increases slightly with  $[O_2]$  at low temperatures.

† 1 atm = 101 325 Pa.





**Fig. 5.**  $1/\alpha$  (=[NPTO<sub>2</sub>]<sub>*t*=0</sub>/[*t*-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub>]<sub>*t*= $\infty$ </sub>) vs. [O<sub>2</sub>] at 298 ([]), 273 ( $\Delta$ ) and 248 K (()). The lines represent linear-regression fits, used to extrapolate to the values of  $\alpha$  at zero oxygen concentration. See text for details and table 3 for the values of  $\alpha$ .

At room temperature, experiments were performed as a function of wavelength from 210 to 270 nm, although poor signal-to-noise ratios at wavelenghs below 230 nm allowed only the branching ratio to be extracted; no systematic dependence of either the total rate constant or the branching ratio on wavelength was noticed, confirming the validity of our relative spectra of the two radicals. At other temperatures, experiments were mostly performed close to the NPTO<sub>2</sub> absorption maximum at 240 nm, although a few experiments were usually performed at other wavelengths; no dependence of the kinetic parameters on wavelength was observed.

The importance of the cross-reaction (10) was checked by rapidly flashing the reaction mixture several times to build up a stationary concentration of t-butylperoxy radicals of the order of  $1 \times 10^{14}$  molecule cm<sup>-3</sup> just before the recorded flash. Below 373 K, no difference in the kinetics between the experiments with and without initial t-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub> was observed. At 373 K, the presence of the initial t-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub> caused a significant (20%) reduction in the apparent value of  $\alpha$ . Including reaction (10) and the subsequent chemistry (see table 2) in the reaction mechanism enabled experiments with and without initial t-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub> to be well-simulated with  $k_{10}$  cm<sup>3</sup>

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Table 2. Reactions and rate constants used in simulations

-			
(1 <i>a</i> )	$NPTO_2 + NPTO_2$	$\rightarrow 2(CH_3)_3CCH_2O + O_2$	a
(1b)		→ products	
(2)	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> O	→ t-C₄H9 + HCHO	b
(7)	$t-C_4H_9+O_2+M$	$\rightarrow$ t-C <sub>4</sub> H <sub>9</sub> O <sub>2</sub> + M	С
(8)	$(CH_3)_3CCH_2O + O_2$	$\rightarrow HO_2 + t-C_4H_9CHO$	d
(10 <i>a</i> )	$NPTO_2 + Bu'O_2$	$\rightarrow$ (CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> O + t-C <sub>4</sub> H <sub>9</sub> O + O <sub>2</sub>	е
(10 <i>b</i> )		→ products	
(11a)	$CH_3O_2 + t-C_4H_9O_2$	$\rightarrow CH_3O + t-C_4H_9O + O_2$	f
(11 <i>b</i> )		→ products	
(3a)	$2t-C_4H_9O_2$	$\rightarrow 2t - C_4 H_9 O + O_2$	g
(3b)		$\rightarrow$ t-C <sub>4</sub> H <sub>9</sub> OOC <sub>4</sub> H <sub>9</sub> -t + O <sub>2</sub>	-
(12 <i>a</i> )	2CH <sub>3</sub> O <sub>2</sub>	$\rightarrow 2CH_{3}O + O_{2}$	h
(12b)		→ products	
(16)	$NPTO_2 + HO_2$	$\rightarrow$ (CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> OOH + O <sub>2</sub>	i
(17)	$t-C_4H_9O_2 + HO_2$	$\rightarrow$ t-C <sub>4</sub> H <sub>9</sub> OOH + O <sub>2</sub>	j
(18)	$t-C_4H_9O + M$	$\rightarrow$ CH <sub>3</sub> COCH <sub>3</sub> + CH <sub>3</sub> + M	k
(19)	$CH_{3} + O_{2} + M$	$\rightarrow CH_3O_2 + M$	l
(20)	$CH_{3}O + O_{2}$	$\rightarrow HO_2 + HCHO$	m
(21)	$CH_{3}O_{2} + HO_{3}$	$\rightarrow CH_{3}OOH + O_{7}$	n
(22)	$HO_{2} + HO_{3}$	$\rightarrow$ H, $O$ , + O,	0

<sup>a</sup> This study. See text and table 3. <sup>b</sup> This study. See text. <sup>c</sup> Assumed to occur rapidly on the timescale of our experiments, ref. (8). <sup>d</sup>  $k_8 = 5.26 \times 10^{-14} \exp(-689/T)$ . Calculated, see text for details. <sup>e</sup> This study.  $k_{10} = (3 \pm 1) \times 10^{-14}$  at 373 K. A branching ratio of  $\alpha = 0.5$  was assumed at this temperature in line with branching ratios for other alkylperoxy radical self-reactions. See text for details. <sup>f</sup>  $k_{11a} = 2.3 \times 10^{-12} \exp(-2558/T)$ ,  $k_{11b} = 1.0 \times 10^{-13} \exp(-2558/T)$ ,  $k_{11b} = 1.0 \times 10^{-13} \exp(-256/T)$ ;  $k_{11a} = 1.0 \times 10^{-13} \exp(-3894/T)$ . Channel (3b) was assumed to be of negligible importance, as found in ref. (14). <sup>b</sup>  $k_{12} = 1.3 \times 10^{-13} \exp(365/T)$ ; ln  $\beta = 3.80 - 1470/T$ , ref. (4). <sup>i</sup>  $k_{16}$  was set to  $10k_1$ . See ref. (29) and text for details. <sup>j</sup>  $k_{17}$  was assumed to be equal to  $k_{21}$ . <sup>k</sup>  $k_{18} = 650 \text{ s}^{-1}$  at 298 K and 1 atm pressure, ref. (35). At higher temperatures,  $k_{18}$  is significantly greater and it was assumed that reaction (18) occur instantaneously on the timescale of our experiments, ref. (16). <sup>m</sup> Rapid with respect to our experimental timescale and other possible reactions of CH<sub>3</sub>O, ref. (16). <sup>n</sup>  $k_{21} = 4.4 \times 10^{-13} \exp(780/T)$ , ref. (9). <sup>c</sup>  $k_{22} = 3.8 \times 10^{-13} \exp(580/T) + 1.2 \times 10^{-33} [M]exp(1150/T)$ , ref. (9). All rate constants are in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, unless otherwise stated.

molecule<sup>-1</sup> s<sup>-1</sup> =  $(3 \pm 1) \times 10^{-14}$  at 373 K. The effect of the inclusion of reaction (10) was to increase the values of  $k_1$  and  $\alpha$  by 13 and 4%, respectively; it is these corrected values which are included in table 3. Thus, at 373 K,  $k_1/k_{10} = 19 \pm 7$ ; at higher temperatures, reaction (10) would be even more important and it was not possible to extract precise values for  $k_1$ .

The present values of  $k_1$  are shown in Arrhenius form in fig. 6. A direct, non-linear, weighted fit<sup>23</sup> to the data gave  $k_1/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> = (1.6 ± 0.6) × 10<sup>-15</sup> exp[(1961 ±

T/K	P/Torr	[O <sub>2</sub> ] <sup><i>a</i></sup>	wavelength/nm	no. expt	k <sub>1</sub> <sup>b</sup>	α
248	760	1.98-27.8	240	28	4.58 ± 0.46	$0.15 \pm 0.01^{\circ}$
273	760	0.53-26.7	220–280	26	$2.11 \pm 0.32$	$0.25 \pm 0.02^{\circ}$
			(210	6	_	$0.43 \pm 0.03$
			220	6	_	$0.41 \pm 0.03$
			230	5	$1.51 \pm 0.18$	$0.38 \pm 0.02$
288	760	5.05	<b>{ 240</b>	10	$1.50 \pm 0.13$	$0.36 \pm 0.04$
			250	21	$1.42 \pm 0.19$	$0.37 \pm 0.03$
			260	11	$1.65 \pm 0.20$	$0.40 \pm 0.08$
			(270	5	$1.60 \pm 0.20$	$0.43 \pm 0.04$
	50-760	0.2-5.05	240	8	$1.29 \pm 0.10$	0.36 ± 0.01
		average at 288 K		72	$1.46 \pm 0.21$	0.38 ± 0.05
298	760	3.23-24.2	240	16	$1.04 \pm 0.09$	$0.40 \pm 0.01^{\circ}$
333	760	4.26	240	10	$0.76 \pm 0.06$	$0.56 \pm 0.02$
373	760	3.80	210-270	10	$0.56 \pm 0.10$	$0.72\pm0.04$

**Table 3.** Experimental values of  $k_1$  and  $\alpha$ 

Errors are  $1\sigma$  and refer only to experimental uncertainty. <sup>*a*</sup> Units of  $10^{18}$  molecule cm<sup>-3</sup>. <sup>*b*</sup> Units of  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>*c*</sup> Extrapolated to  $[O_2] = 0.0$ . See text for details.



**Fig. 6.** Arrhenius plot for  $k_1$ . Error bars refer to experimental scatter. (---) Weighted fit to  $k = A \exp(-E/RT)$ ; (----) weighted fit to  $k = A(T/298)^n \exp(-E/RT)$ , see text for values.

100) K/T, but it is apparent that there is some curvature in the plot and a better representation of the data is given by  $k_1/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> =  $3.02 \times 10^{-19} (T/298)^{9.46} \exp(4260/T)$ ; both fits are shown in fig. 6.

Thus, at room temperature,  $k_1$  is considerably larger than the rate constants for other alkylperoxy radicals, the fastest of which (for  $CH_3O_2$ ) is at least a factor of three slower. The negative temperature dependence is very strong,  $k_1$  decreasing by around a factor of 8 from 248 to 373 K. Marked negative temperature dependences for the rate constant of the self-reaction have also been observed for the halogenated peroxy radicals CH2ClCH2O2, CH2ClO2 and CH<sub>2</sub>FO<sub>2</sub>.<sup>24,25</sup> This strong negative temperature dependence demonstrates clearly that the reaction passes through the reversible formation of an association complex. In each case where a rapid decrease in the self-reaction rate constant with temperature has been observed, the absolute value of the rate constant is rather elevated with respect to that for CH<sub>3</sub>O<sub>2</sub>: the rate constants for the self-reactions of the three halogenated radicals above at room temperature are, in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,  $3.57 \times 10^{-12}$ ,  $3.78 \times 10^{-12}$  and  $3.07 \times 10^{-12}$ , respectively, compared with  $4.3 \times 10^{-13}$  for CH<sub>3</sub>O<sub>2</sub>.<sup>4</sup> Dagaut et al.<sup>24</sup> have suggested that such behaviour is consistent with a strong binding energy in the tetroxide intermediate, leading to a high activation energy for the redissociation and hence a strong negative temperature dependence. With such a mechanism, it is by no means necessary for the rate constant to behave according to the Arrhenius law. The rate constant for the self-reaction of hydroperoxy radicals, shows a similar upward curvature at high temperatures.<sup>26</sup> RRKM calculations on the decomposition of the HOOOOH intermediate predicted a strong upward curvature of the forward rate constant.<sup>27</sup> although in this case there is a possibility of a direct abstraction pathway at high temperature.28

The corresponding values of  $\alpha$  are listed in table 3 and a plot of the non-terminating/terminating branching ratio  $\beta$  [= $\alpha/(1 - \alpha)$ ] is shown in Arrhenius form in fig. 7. A weighted fit gave  $\beta = (197 \pm 67) \exp[-(1658 \pm 98/T)]$ . Over our experimental temperature range,  $\alpha$  passes from 0.15 to 0.72 with increasing temperature, *i.e.* the reaction changes from being essentially a termination reaction to being largely a propagation reaction. Also shown in fig. 7 are Arrhenius



Fig. 7. Arrhenius plot for  $\beta$ , the non-terminating/terminating ratio for several peroxy radical self-reactions,  $\beta = \alpha/(1 - \alpha)$ . (I) NPTO<sub>2</sub>, this study, (----) weighted fit to  $\beta = A \exp(-E/RT)$ ; (-----) CH<sub>3</sub>O<sub>2</sub>;<sup>4</sup>(...)) C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>;<sup>5</sup>(---) i-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>.<sup>6</sup>

plots of  $\beta$  adapted from earlier work on CH<sub>3</sub>O<sub>2</sub>, <sup>4</sup> C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>, <sup>5</sup> and i-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>. <sup>6</sup> In each case, the values of  $\beta$  observed cover the same range over approximately the same range of temperature, despite the fact that the actual rate constants for the self-reactions differ by several orders of magnitude, pointing to a common intermediate for the two pathways.<sup>4</sup>

#### (v) The Unimolecular Decomposition of Neopentoxy Radicals

As discussed above, the values of  $k_1$  and  $\alpha$  were not sensitive to the oxygen concentration under most experimental conditions, indicating that, for the majority of experiments, the unimolecular decomposition of neopentoxy radicals [reaction (2)] was rapid with respect to their reaction with oxygen [reaction (8)]. However, a slight diminution of the t-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub> yield was noticed at high (ca. 1 atm) partial pressures of oxygen at room temperature; this diminution, together with a corresponding slight increase in  $k_1$ , became more pronounced with decreasing temperature.

Hydroperoxy radicals produced via reaction (8) can react either with NPTO<sub>2</sub> or t-butylperoxy radicals:

NPTO<sub>2</sub> + HO<sub>2</sub> 
$$\rightarrow$$
 (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>OOH + O<sub>2</sub> (16)

$$-C_4H_9O_2 + HO_2 \rightarrow t-C_4H_9OOH + O_2.$$
(17)

However, as significant quantities of hydroperoxy radicals are produced only at low temperatures where  $\alpha$  and hence  $[t-C_4H_9O_2]$  are low, reaction (16) will be by far the most important loss process for HO<sub>2</sub>.

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The hydroperoxy radicals produced in reaction (8) would result in a distortion of the observed traces at short wavelengths ( $\lambda < 230$  nm), where the hydroperoxy radical absorption spectrum is stronger than those of NPTO<sub>2</sub> and the t-butylperoxy radicals, if they were produced in significant quantities and were sufficiently long-lived. Such an effect was observed in the self-reaction of methylperoxy radicals at elevated temperatures.<sup>4</sup> However, in the present case, the kinetics of the system was independent of wavelength at all oxygen concentrations, suggesting that reaction (16) is significantly faster than reaction (1).<sup>29</sup> †

<sup>†</sup> Preliminary work in this laboratory indicates that  $k_{16}$  is considerably greater than  $k_1$  at room temperature, where  $k_{16}/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>  $\approx 2.0 \times 10^{-11}$ .

The dependence of our experimental results on the oxygen concentration was analysed as follows. Assuming that all hydroperoxy radicals react with NPTO<sub>2</sub> and that  $k_{16} \ge k_1$ , then the value of  $\alpha$  observed in the second-order fits is related to the real value by:

$$1/\alpha_{obs} = 1/\alpha + (1 + \alpha)k_8[O_2]/(\alpha k_2).$$
 (II)

Full numerical simulations showed that this linear dependence on  $[O_2]$  holds as long as  $k_{17}$  is not much bigger than  $k_{16}$ . At 298, 273 and 248 K,  $\alpha$  was obtained from the intercepts of such plots, as shown in fig. 5. These values of  $\alpha$  were used in a reanalysis of the decay traces, including reactions (16) and (17) in the system. The optimised parameters were the initial concentration,  $k_1$  and the fraction of (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>O radicals which do not react with oxygen,  $\delta [=k_8[O_2]/(k_2 + k_8[O_2])]$ . In each case, the slight dependence of  $k_1$  on  $[O_2]$  was removed; the values shown in table 3 are averages at all oxygen concentrations. Plots of  $1/\delta$  $(=1 + k_8[O_2]/k_2)$  against  $[O_2]$  were sensibly linear (fig. 8); the slopes, equal to  $k_8/k_2$  from the analysis above, are given in table 4. Using our values of  $k_8/k_2$ , the importance of reaction (8) can be gauged: at our lowest temperature and highest oxygen partial pressure (248 K, 1 atm), ca. 40% of neopentoxy radicals react with oxygen. At the same temperature, but with an air bath gas, only 8% of the neopentoxy radicals react in this way; at ambient temperature, this figure is reduced to under 3%, justifying our assumption that unimolecular decomposition was the sole fate for neopentoxy radicals in the experiments at 288 K in 1 atm air.

In order to extract information about the decomposition reaction (2) from our data, we need the rate constant for reaction (8). No published information is available on this reaction. However, Balla et al., 30 from an analysis of the available data for a number of alkoxy radicals, derived  $\log(A/cm^3)$ molecule<sup>-1</sup> s<sup>-1</sup>) =  $-13.58 + \log(n)$  (where n is the number of abstractable hydrogen atoms) and  $E/kJ \text{ mol}^{-1} = 47.9 + 0.30$  $\Delta H_r$  for all alkoxy plus O<sub>2</sub> reactions; the errors in this procedure were estimated to be  $\pm 50\%$ . Using group additivity methods,<sup>31</sup> we estimate the heat of formation of the neopentoxy radical to be  $-94.6 \pm 8.4$  kJ mol<sup>-1</sup>, assuming  $E_d$  $(O-H)/kJ \text{ mol}^{-1} = 435$ . Similarly, we calculate  $-248 \pm 8.4$ kJ mol<sup>-1</sup> for the heat of formation of pivaldehyde. We use this value, rather than the published value of -243 kJ mol<sup>-1</sup>, <sup>32</sup> in the hope of cancelling errors in the group addivity method. Thus,  $k_8/\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> = 5.26 × 10<sup>-14</sup> exp(-689 K/T). Assuming an uncertainty of  $\pm 8.4 \text{ kJ mol}^{-1}$ in our calculation of  $\Delta H_8$ , the estimated errors in log  $k_8$  are  $\pm 0.51$ , including the 50% uncertainty estimated by Balla et al. The calculated values of  $k_8$  and hence  $k_2$  for our experimental temperatures are listed in table 4.

The very limited temperature range for our values of  $k_2$  preclude an Arrhenius fit to the data. Choo and Benson<sup>33</sup> estimate  $\log(A/s^{-1}) = 13.7 \pm 0.3$  for alkoxy radical decompositions giving formaldehyde and an alkyl radical. Using this value, and fitting to our values of  $k_2$ , we obtain  $E_2/kJ$  mol<sup>-1</sup> = 42.7 ± 2.1. Choo and Benson have analysed the available data on alkoxy radical decomposition reactions and conclude that the activation energies for alkoxy radical decompositions giving rise to t-butyl radicals should be rep-

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**Fig. 8.** Plot of  $1/\delta$  (=1 +  $k_8[O_2]/k_2$ ), the inverse of the fraction of neopentoxy radicals which react with  $O_2$  rather than by unimolecular decomposition; ( $\Box$ ) 298 K, ( $\Delta$ ) 273 K, ( $\bigcirc$ ) 248 K. For reasons of clarity, the data and fits for 273 and 248 K have been displaced upwards by 1 and 2 units, respectively. The straight lines represent linear fits with slopes  $k_8/k_2$ . See table 4 for the values of  $k_8/k_2$ .

resented to ca.  $\pm 0.8$  kJ mol<sup>-1</sup> by E/kJ mol<sup>-1</sup> = 30.5 + 0.42  $\Delta H_r$ . We calculate  $\Delta H_2/kJ$  mol<sup>-1</sup> = 34.3  $\pm$  8.6,<sup>31,34</sup> thus  $E_2/kJ$  mol<sup>-1</sup> = 44.8  $\pm$  3.8. This estimate is in excellent agreement with our experimentally derived value, demonstrating that the observed experimental dependence of  $\alpha$  on [O<sub>2</sub>] is entirely consistent with the proposed mechanism.

# (vi) The t-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub> Self-reaction

The self-reaction of t-butylperoxy radicals [reaction (3)] was studied by observing the disappearance of the residual absorption at the end of the NPTO<sub>2</sub> decay. As the tbutylperoxy radical decay was always very slow (over a few seconds at fastest), a large time constant (RC = 22 ms) could be used for the detection electronics. In this way, the fast NPTO<sub>2</sub> kinetics were effectively removed from the decay and single-shot experiments could be performed. At room temperature, the t-butylperoxy decay was too slow to be captured on the digital storage oscilloscope and a chart recorder was used instead. In contrast to the study of reaction (1), reaction (3) could be studied at temperatures where the timescales of the two reactions interact, as long as the first 100 ms, where the two radicals coexisted, are ignored in the analysis. A brief series of experiments was performed at three temperatures: 293, 373 and 423 K. In each case, the radical decay was sensibly second-order. At room temperature, the absorption did not return to the baseline and indeed showed a tendency to increase again after several minutes. Problems with residual absorptions have been noted in previous studies, where it was thought that it might be due to a polyoxide intermediate<sup>11</sup> or a photolysis or reaction product.<sup>12</sup>

**Table 4.** Rate constants for the t- $C_4H_9CH_2O$  decomposition reaction

T/K	$(k_8/k_2)/10^{-21}$ cm <sup>3</sup> molecule <sup>-1</sup>	$k_{\rm g}/10^{-15} {\rm ~cm^3~molecule^{-1}~s^{-1}}$ a.b	$k_2/10^5 \text{ s}^{-1}$ "
248	$22.8 \pm 3.1$	3.24	1.41
273	$21.1 \pm 3.2$	4.16	2.00
298	$5.0 \pm 0.5$	5.25	10.5

<sup>a</sup> Estimated uncertainties in log k are  $\pm 0.51$ .<sup>b</sup> Calculated, see text for details.

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**Table 5.** Rate constants for the t-butylperoxy self-reaction

$compariso (k / \sigma)/cm s^{-1}$	on of room-tempera	ture measurements o	of $k_{obs}$ :
(Robs/0)/em 3	1/1	101.	
6.4	295	11	
6.4	298	12	
5.2	300	15ª	
5.0	293	this study	
T/K	$\begin{array}{c} \text{comparison of } k_{\text{obs}} \\ k_{\text{obs}}/\text{cm}^3 \\ \text{molecule}^{-1} \text{ s}^{-1} \end{array}$	and $k_3^{b}$ values: $k_3/cm^3$ molecule <sup>-1</sup> s <sup>-1</sup>	k <sub>obs</sub> /k <sub>3</sub>
293	$2.4 \times 10^{-17}$	$1.7 \times 10^{-17}$	1.4
373	$5.8 \times 10^{-16}$	$3.1 \times 10^{-16}$	1.9
410	$1.7 \times 10^{-15}$	$80 \times 10^{-16}$	10

<sup>a</sup> Calculated from the Arrhenius expression in ref. (15). <sup>b</sup> Obtained using the full kinetic model: reactions (3) and (11)-(21). See table 2 and text for details.

However, in the present study it was observed that, if the analysis beam was blocked for most of the time, only being allowed to pass through the cell briefly every minute or so to allow the absorption to be measured, then the decay did indeed return to the baseline. This suggests that, in this and the previous studies, the residual absorption can be accounted for by the slow photolysis of the precursor by the analysis beam. At higher temperatures, where the radical decay is much faster, this problem does not arise. Of course, for reactions as slow as this, the existence of heterogeneous effects must be possible, at least at temperatures around ambient, where the radicals would have time to come into contact with the reactor walls on the timescale of their decay. At our highest temperature, however, the timescale of the radical decay is only of the order of a few seconds and diffusion to the reactor walls should not be significant at 1 atm total pressure; the linear Arrhenius plot obtained would then suggest that heterogeneous reactions were not important under our conditions.

The kinetics of reaction (3) have been studied by two groups. Their results, together with those of the present study, are summarised in table 5. The agreement between the observed values of  $(k/\sigma)$  is excellent. An Arrhenius plot of the various values of  $k_{obs}$ , normalised to our values of  $\sigma$ (t-C<sub>4</sub>H<sub>9</sub>O<sub>2</sub>), is shown in fig. 9. A fit to the present values gives  $\log(k_{obs}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -(10.34 \pm 0.17) - (4233 \pm 108)/2.303T$ , rather different from the expression of Kirsch and Parkes,<sup>15</sup> although the actual values of  $k_{obs}$  are in good agreement.

The observation of a second-order decay does not, however, neccessarily mean that a simple second-order reaction is being followed. The t-butoxy radicals produced in reaction (3) do not contain an  $\alpha$ -hydrogen atom and so, unlike neopentoxy, cannot react with oxygen, reacting rapidly by unimolecular decomposition under our conditions to form acetone and methyl radicals:<sup>35</sup>

$$H_{2}-C_{4}H_{9}O + M \rightarrow CH_{3}COCH_{3} + CH_{3} + M.$$
(18)

The methyl radicals thus produced react rapidly with oxygen to form methylperoxy radicals:<sup>16</sup>

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{19}$$

which react in turn, both with t-butylperoxy radicals and with themselves [reactions (11) and (12)]. The methoxy radicals produced in these reactions are converted rapidly, under our conditions of high oxygen concentration, to hydroperoxy radicals.<sup>16</sup>

$$CH_3O + O_2 \rightarrow HO_2 + HCHO$$
 (20)



Fig. 9. Arrhenius plot of the apparent second-order rate constant for the self-reaction of t-butylperoxy radicals: ( $\blacksquare$ ) this study; (\*) ref. (11); ( $\square$ ) ref. (12); (---) ref. 15. The solid line represents an unweighted fit to  $\ln k = \ln A - E/RT$  for the present data.

thus introducing a further species which may react with all the other peroxy radicals present. The t-butoxy radicals produced in reaction (11) reform methylperoxy radicals via reactions (18) and (19) and so reaction (11a) acts as a chain propagating step, converting t-butylperoxy radicals into the more reactive hydroperoxy radicals. A complete list of all the reactions involved is given in table 2. There have been three product analysis studies of reaction (3). Thomas and Calvert,<sup>36</sup> measuring product concentrations by FTIR spectroscopy, proposed a mechanism in which alkoxy radicals played a major role. No account was taken of the important reaction (20). Kirsch and Parkes,<sup>37</sup> using gas chromatographic detection of the products found rather different relative product yields and proposed a mechanism similar to that shown in table 2, in which peroxy radical reactions play a dominant role. Osbourne and Waddington,<sup>14</sup> using gas chromatographic detection, with colorimetric analysis of formaldehyde, found similar product ratios to Kirsch and Parkes and proposed a similar mechanism. However, there are serious discrepancies between the latter two studies. In particular, the absolute rate constants for reaction (11) used by Kirsch and Parkes and derived from the molecular modulation study of Parkes, were incompatible with the product yields of Osbourne and Waddington, who needed to use rate constants more than an order of magnitude lower. In addition, the branching ratios for this reaction obtained from the two latter studies are in serious disagreement. Moreover, Osbourne and Waddington did not observe the di-t-butylperoxide product of reaction (3c), whereas Kirsch and Parkes observed the product with a 14% yield at 298 K, decreasing rapidly with temperature. In the present study, we have preferred the results of the more extensive study of Osbourne and Waddington.

It is clear that the mechanism of t-butylperoxy removal is complex and that a simple measurement of the pseudosecond-order removal rate constant does not constitute a measurement of  $k_3$ . This problem has been discussed by Parkes,<sup>11</sup> who used a steady-state analysis of his reaction scheme to estimate that, at room temperature,  $k_{obs}$  was around a factor of four greater than the true rate constant. We reanalysed the present decay traces using the full scheme in table 2; the results are summarised in table 5. At each temperature, the derived  $k_3$  was significantly less than  $k_{obs}$ .

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The fact that no significant deviation from second-order behaviour was noticed is attributed to the rapidity of subsequent reactions of  $CH_3O_2$  and  $HO_2$  relative to reaction (3), resulting in very low, pseudo-stationary values for their concentrations. An unweighted fit to the present values of  $k_3$ gives  $\log(k_3/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -11.0 - 3894/2.030 \text{ J}^2$ . the values of  $k_3$  obtained depend sensitively on the rate constant and branching ratios for reaction (11), as has already been pointed out.<sup>11</sup> Replacing Osbourne and Waddington's values at room temperature with those of Parkes reduced  $k_3$ by a factor of two. Thus, the present values of  $k_3$  should be considered as rough estimates only. However, it is clear that  $k_3$  displays a positive temperature dependence greater than that for the rate constants for the equivalent reactions of other alkylperoxy radicals, which display weak and sometimes negative temperature dependences. We have previously discussed<sup>4</sup> the possibility that, at least at temperatures around ambient, both channels (a) and (b) for alkylperoxy self-reactions proceed via the six-membered cyclic Russell intermediate. In the case of the t-butylperoxy radical, there is no hydrogen atom  $\alpha$  to the carbon centre and the formation of such an intermediate is not possible; the tetroxide intermediate must thus decompose directly, which could explain the high activation energy for reaction (3).

One interesting aspect of the overall mechanism is its dependence on temperature. At temperatures below ambient, the reactions between alkyperoxy radicals are largely terminating and neopentylperoxy radicals are mostly converted into pivaldehyde and neopentyl alcohol via channel (a) of reaction (1). At cool flame temperatures (ca. 700 K), all these reactions serve largely to convert alkylperoxy radicals into the corresponding alkoxy radicals, which in turn either react with oxygen to form hydroperoxy radicals or decompose to smaller alkyl radicals (and thus alkylperoxy radicals) and carbonyl compounds. Thus, at high temperatures, the larger peroxy radicals are rapidly converted into smaller radicals, notably the methylperoxy and hydroperoxy radicals, underlining the importance of these latter species in combustion kinetics.

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#### References

- R. A. Cox, in Modern Gas Kinetics, ed. M. J. Pilling and I. W. M. Smith (Blackwell Scientific, Oxford, 1987), chap. C1 and C2.
- F. Westley, J. T. Herron and R. J. Cvetanovic, Compilation of 2 Chemical Kinetic Data for Combustion Chemistry, Part I, (NSRDS-NBS 73) (US Govt Printing Office, Washington, 1987).
- R. A. Cox and J. A. Cole, Combust. Flame, 1985, 60, 109.
- P. D. Lightfoot, B. Veyret and R. Lesclaux, J. Phys. Chem., 1990, 4 **94,** 700.
- C. Anastasi, D. J. Waddington and A. Wooley, J. Chem. Soc., 5 Faraday Trans. 1, 1983, 79, 505.

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- L. J. Kirsch, D. A. Parkes, D. J. Waddington and A. Wooley, J. 6 Chem. Soc., Faraday Trans. 1, 1978, 74, 2298.
- 7 R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet., 1985, 17, 33.
- Z. Xi, W-J. Han and K. D. Bayes, J. Phys. Chem., 1988, 92, 3450; 8 D. Wu and K. D. Bayes, Int. J. Chem. Kinet., 1986, 18, 547. P. D. Lightfoot, B. Veyret and R. Lesclaux, J. Phys. Chem., 1990,
- 9 94, 708.
- 10 P. Dagaut and M. J. Kurylo, personal communication.
- D. A. Parkes, 15th International Symposium on Combustion (The Combustion Institute, Pittsburgh, 1975), p. 795.
- 12 C. Anastasi, I. W. M. Smith and D. A. Parkes, J. Chem. Soc., Faraday Trans. 2, 1978, 74, 1693.
- 13 A. C. Baldwin, J. R. Barker, D. M. Golden and D. G. Henry, J. Phys. Chem., 1977, 81, 2483.
- D. A. Osbourne and D. J. Waddington, J. Chem. Soc., Perkin 14 Trans. 2, 1984, 1861.
- D. A. Parkes and L. J. Kirsch, unpublished work referred to in L. J. Kirsch, D. A. Parkes, D. J. Waddington and A. Wooley, J. Chem. Soc. Faraday Trans. 1, 1978, 74, 2293, and also in ref. (12). 15
- W. B. DeMore, M. J. Molina, S. P. Sander, D. M. Golden, R. F. 16 Hampson, M. J. Kurylo, C. J. Howard and A. R. Ravishankara, Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation Number 8., (JPL Publication 87-41, 1987).
- 17 R. S. Timonen and D. Gutman, J. Phys. Chem., 1986, 90, 2987.
- 18 G. L. Vaghjiani and A. R. Ravishankara, J. Geophys. Res., 1989, 94, 3487.
- T. J. Wallington, C. A. Gierczak, J. C. Ball and S. M. Japar, Int. 19 J. Chem. Kinet., 1989, 21, 1077.
- D. L. Baulch, D. G. Bowers, D. G. Malcolm and R. T. Tuckers-20 man, J. Phys. Chem. Ref. Data, 1986, 15, 465.
- G. L. Vaghjiani and A. R. Ravishankara, J. Phys. Chem., 1989, 21 93, 1948.
- 22 P. S. Nangia and S. W. Benson, J. Phys. Chem., 1979, 83, 1138.
- 23 R. J. Cvetanovic, D. L. Singleton and G. Paraskevopoulos, J.
- Phys. Chem., 1979, 83, 50. P. Dagaut, T. J. Wallington and M. J. Kurylo, Chem. Phys. Lett., 24
- 1988, 146, 589. 25 P. Dagaut, T. J. Wallington and M. J. Kurylo, Int. J. Chem.
- Kinet., 1988, 20, 815. P. D. Lightfoot, B. Veyret and R. Lesclaux, Chem. Phys. Lett., 26 1988, 150, 120.
- 27 R. Patrick, J. R. Barker and D. M. Golden, J. Phys. Chem., 1984, 88, 128.
- 28 R. R. Baldwin, C. E. Dean, M. R. Honeyman and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 1986, 82, 89.
- 29 P. D. Lightfoot, P. Roussel and R. Lesclaux, unpublished results. 30 R. J. Balla, H. H. Nelson and J. R. McDonald, Chem. Phys.,
- 1985, 99, 323. 31
- S. W. Benson, Thermochemical Kinetics, (Wiley, Chichester, 2nd edn, 1976).
- 32 F. Westley, J. T. Herron, R. J. Cvetanovic, R. F. Hampson and W. G. Mallard, NIST Chemical Kinetics Database, Version 1.1, 1989.
- 33 K. Y. Choo and S. W. Benson, Int. J. Chem. Kinet., 1981, 13, 833.
- 34 J. A. Seetula, J. J. Russell and D. Gutman, J. Am. Chem. Soc., 1990, in press.
- L. Batt and G. N. Robinson, Int. J. Chem. Kinet., 1987, 18, 391.
- 36 S. S. Thomas and J. G. Calvert, J. Am. Chem. Soc., 1962, 84, 4207
- L. J. Kirsch and D. A. Parkes, J. Chem. Soc., Faraday Trans. 2, 37 1981, 77, 293.

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