Photodecomposition of Iodopentanes in Air: **Product Distributions** from the Self-Reactions of *n*-Pentyl Peroxyl Radicals

GERALD HEIMANN,^{1,3} HEINZ-JÜRGEN BENKELBERG,¹ OLAF BÖGE,² PETER WARNECK¹

¹Max-Planck-Institut für Chemie, 55020 Mainz, Germany

²Institut für Troposphärenforschung, 04303 Leipzig, Germany ³Verein Deutscher Ingenieure, 40239 Düsseldorf, Germany

Received 5 April 2001; accepted 8 October 2001

ABSTRACT: Product distributions from the 254-nm photooxidation of the three iodopentane isomers were explored as a technique for studying the self-reactions of individual pentyl peroxyl radicals (in air at ambient temperature and pressure). Pentanols and the associated carbonyl compounds (pentanal or pentanones) were major products as expected. Other major products resulted from the isomerization of pentan-1-oxyl and pentan-2-oxyl radicals, but their nature could not be identified. Minor products were alcohols and carbonyl compounds arising from the decomposition of pentoxyl radicals. Diols and mixed hydroxycarbonyl compounds from cross-combination reactions were essentially absent, in contrast to expectation. The observed product distributions were evaluated to derive branching ratios for the radicalpreserving pathways of the self-reactions, 0.42 ± 0.17 , 0.46 ± 0.10 , 0.39 ± 0.08 , for pentan-1-yl peroxyl, pentan-2-yl peroxyl, and pentan-3-yl peroxyl, respectively. Rate coefficients derived for the decomposition of the corresponding pentoxyl radicals, relative to their reaction with oxygen, are $(5.1 \pm 0.5) \times 10^{18}$, $(1.0 \pm 0.2) \times 10^{18}$, and $(3.2 \pm 0.3) \times 10^{18}$ molecule cm⁻³, respectively. Rate constants for the isomerization of pentan-1-oxyl and pentan-2-oxyl were estimated from the contributions of isomerization products to the total amounts of products as $(4.0 \pm 1.1) \times 10^5 \text{ s}^{-1}$ and $(1.0 \pm 2.0) \times 10^5 \text{ s}^{-1}$, respectively. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 34: 126–138, 2002

INTRODUCTION

Alkyl peroxyl radicals, RO₂, and alkoxyl radicals, RO, are essential intermediates in the low temperature

© 2001 John Wiley & Sons, Inc.

DOI 10.1002/kin.10031

oxidation of hydrocarbons in general, and of alkanes in particular [1]. In the atmosphere, the oxidation occurs primarily in the gas phase, and that of alkanes is initiated by reaction with OH or NO3 radicals. Mechanisms of alkane oxidation under atmospheric conditions have been extensively reviewed [2-4], and general reaction schemes have been established. Alkyl peroxyl radicals are formed by the addition of O_2 to the site where the OH (or NO₃) radical had removed a hydrogen atom. The predominant fate of RO2 radicals in the atmosphere

Correspondence to: Peter Warneck; e-mail: biogeo@mpchmainz.mpg.de.

Contract grant sponsor: German Federal Ministry for Research and Technology.

is reaction with NO.

$$OH + HR \rightarrow R + H_2O$$
 (I)

$$\mathbf{R} + \mathbf{O}_2 \to \mathbf{RO}_2 \tag{II}$$

$$RO_2 + NO \rightarrow RO + NO_2$$
 (major) (IIIa)

$$\rightarrow$$
 RONO₂ (minor) (IIIb)

This reaction sequence converts most of the alkyl peroxyl radicals to alkoxyl radicals. Under laboratory conditions, in the absence of NO, the RO2 radicals react mainly with each other

$$\begin{aligned} \text{RO}_2 + \text{RO}_2 &\rightarrow 2\text{RO} + \text{O}_2 \end{aligned} \qquad (\text{IVa}) \\ &\rightarrow \text{alcohol} + \text{aldehyde/ketone} + \text{O}_2 \end{aligned}$$

(IVb)

where alkoxyl radicals are again produced in the first channel and stable products in the second [5,6]. Alkoxyl radicals react with oxygen, and they undergo decomposition and isomerization processes.

$$RO + O_2 \rightarrow HO_2 + aldehyde/ketone$$
 (Va)

$$RO \rightarrow R' + aldehyde (decomposition)$$
 (Vb)

$$RO \rightarrow HOR''$$
 (isomerization) (Vc)

Here, R is the parent alkyl radical, R' is an alkyl radical of lower carbon number, and HOR" is a hydroxyalkyl radical resulting from internal hydrogen abstraction by the alkoxyl group. The HOR" radical subsequently attaches O_2 to form a hydroxyperoxyl radical, HOR" O_2 , that undergoes further reactions. Isomerization by internal H-atom abstraction is less well understood than the other processes, but the ring strain involved suggests that isomerization via 1,5 H-atom transfer is structurally and energetically favored over 1,4- or 1,6-H-atom shift [7,8]. Butane is the first member of *n*-alkane homologues allowing 1,5 H-atom shift to take place.

Details of the oxidation mechanisms for C_1-C_4 hydrocarbons are well established [4–6]. The oxidation of higher alkanes involves an increasing number of isomeric RO₂ radicals that can complicate the oxidation pathways. The oxidation of *n*-pentane is already so complex that it has not yet been fully elucidated. Three types of RO₂ radicals are involved: pentan-1-yl peroxyl, pentan-2-yl peroxyl, and pentan-3-yl peroxyl. The latter two are formed with greater probability than the first because the abstraction of a secondary H-atom from an alkane is energetically favored over that of a primary H-atom [4,9]. In this study, we examine the photolysis of iodopentanes in air as a means of generating individual pentylperoxyl radicals. Iodoalkanes excited to the first higher electronic state are well known to undergo predissociation. The major products are an excited iodine atom and the corresponding alkyl radical [10]. In the case of secondary iodoalkanes one observes also the elimination of HI with alkenes as additional products. This process is not expected to complicate the system. The primary aim of our study was to determine from the product distributions the branching ratios of reaction (IV) for the self-reactions of the three pentylperoxyl isomers and to learn more about the products resulting from the decomposition and isomerization processes of the associated pentoxyl radicals.

The reaction mechanisms induced by the selfreactions of individual pentylperoxyl radicals are still complex because additional alkylperoxyl radicals are produced by the decomposition and isomerization processes. Figure 1 shows, as an example, the basic mechanism expected to follow from the self-reaction of pentan-2-yl peroxyl. Pentan-2-one and pentan-2-ol are the stable products from reaction (IV). Decomposition of pentan-2-oxyl yields propylperoxyl and 1,5 H-atom shift yields 4-hydroxypentan-1-yl peroxyl, respectively, as secondary peroxyl radicals. Isomerization ultimately leads to the formation of 1-hydroxypentan-4-one, 4-hydroxypentanal, and 1,4-pentandiol as stable products. Most of these products should be identifiable by gas chromatography. The relative yields are expected to indicate the extent of alkoxyl radical decomposition and isomerization. Thus, another aim of this study was to confirm and quantify the expected decomposition and isomerization products and compare the results with other data [11-13] reported previously.

EXPERIMENTAL

Apparatus and experimental techniques were similar to those described earlier [14,15]. Reactions were carried out in 2-1 spherical glass bulbs. The interior walls were treated with dimethyldichlorosilane followed by heating to 200°C to minimize the surface activity toward polar compounds. Each bulb was fitted with Teflonstoppered shut-off valves, a Teflon-coated silicone rubber septum, and a quartz finger reaching into the center of the bulb, into which a Penray mercury lamp was placed. Special quartz was used to block ozone-forming radiation ($\lambda < 235$ nm), whereas emissions at 254 nm and at longer wavelengths were fully transmitted. Compressed nitrogen served as a coolant of the lamp as well as to flush out ozone formed in the quartz tube. A bulb was filled with a mixture of 0.01–0.1% iodopentane in



Figure 1 Scheme of reactions resulting from the self-reaction of pent-2-yl peroxyl radicals. Reactions following decomposition and 1,5 H-atom shift isomerization of pent-2-oxyl radical were discussed by Atkinson [4], 1,4 H-atom shift, which should be less important, is not included.

synthetic air, usually to a pressure slightly above atmospheric. A thin Teflon tube was pushed through a hole pierced in the rubber septum toward the center of the bulb, the other end was joined to the sampling loop of a gas chromatograph. The inlet tubes were made of quartz-lined stainless steel, and the sampling valve was kept at 160°C. The Penray lamp was activated for about 10 min to stabilize its output before the lit lamp was inserted in the quartz finger. Irradiation times were 30-120 s. Subsequently, a sample was transferred from the reaction vessel to the sampling loop of the gas chromatograph and was injected into the nitrogen carrier gas flow (3 $\text{cm}^3 \text{min}^{-1}$). The products were separated on a capillary column and detected with a flame ionization detector. This procedure was repeated at least three times in order to check the stability and precision of the analysis.

Two columns (50 m long, 0.32 mm i.d.) were mainly used: a CPSil 76 column, coated with dimethylpolysiloxane (0.34 μ m film thickness), and a CP-Wax 52 column, coated with polyethylene glycol (1.2 μ m film thickness). The temperature program in the first case was 30°C isothermal for 3 min, heating to

65°C at a rate of 8°C min⁻¹, further heating to 200°C at a rate of 30°C min⁻¹, and finally constant for 3 min at 200°C. The temperature program used with the CP-WAX 52 column was 40°C isothermal for 2 min, heating to 160°C at a rate of 20°C min⁻¹, constant for 10 min at 160°C, further heating to 210°C at a rate of 30° C min⁻¹, and finally constant for 2 min at 210°C. Although temperature programs were chosen so as to achieve an optimal peak separation, a full separation of all products was not always possible. Products were identified, as far as possible, by comparison of retention times with authentic samples of alcohols, aldehydes, and ketones. Table I provides a reference list of retention times on the CP-WAX 52 column for several compounds that were either expected as products or served as markers for product identification. Peak area calibration of product compounds was performed with authentic samples in air prepared by successive dilution of starting mixtures of known composition.

Two of the iodopentanes, namely 1-iodopentane and 3-iodopentane were commercially available. Both contained unknown but photochemically inactive

Compound	Retention Time (min)	Compound	Retention Time (min)
Acetaldehyde	1.75	Pentanol	7.15
Propanal	2.45	1-Hydroxypropanone	7.88
Butanal	3.35	Glycolaldehyde	8.00
Ethanol	3.90	2-Hydroxy-2-methylpentan-4-one	8.40
Pentanal	4.50	1-Hydroxy-3-methylbutan-2-one	8.40
Pentane-2-one	4.50	1-Hydroxybutan-2-one	8.56
Pentane-3-one	4.50	Methyl glyoxal	9.10
Propanol	5.10	Pentan-2,4-diol	12.3
Pentan-3-ol	5.80	Butan-1,2-diol	12.4
Pentan-2-ol	5.90	1-Hydroxypentan-4-one	13.5
Butanol	6.00	Pentan-1,2-diol	14.8
Pentan-2,4-dione	7.00	Pentan-1,4-diol	18.4

Table IApproximate Retention Times (min) of Several Compounds on the CP-WAX 52 Gas ChromatographicColumn^a

^{*a*}For operating conditions see Experimental section.

impurities. These compounds were used as received. 2-Iodopentane, which was not commercially available, was synthesized following the procedure of Brown and Wheeler [16]. Sodium iodide was reacted with pentan-2-yl methane sulfonate, which was prepared from pentan-2-ol and methane sulfonyl chloride in the presence of pyridine according to Williams and Mosher [17], followed by distillation from the extract. The purity obtained, determined by mass spectrometry, was better than 95%. The main impurity presumably was pent-2-ene resulting from a partial decomposition of the methane sulfonate.

RESULTS

1-Iodopentane

Table II presents a suggested reaction mechanism for the photooxidation of 1-iodopentane. The major products expected are pentanal, pentanol, and mixed 1,4 hydroxycarbonyl compounds. Butanal and butanol are assumed to result from the decomposition of the pentan-1-oxyl radical, which leads to the formation of butyl peroxyl radicals. Acetaldehyde would be a product of the decomposition of the 1-hydroxypentan-4-oxyl radical. Figure 2 shows a chromatogram of irradiated 1-iodopentane obtained with the CP-Wax-52 column. Pentanal, pentanol, and butanal were identified as products. Butanol, which was expected to occur in conjunction with butanal, was hidden underneath an impurity peak, but it showed up weakly on the CPSil 76 column. Figure 3a shows that the yield of pentanal rises linearly with irradiation time and that the ratio of the yields for pentanal and 1-pentanol is constant with time. The average ratio (given by the slope of the straight line in Fig. 3b) is 1.14 ± 0.06 . The yield

of butanol was estimated to be about 33% of that of butanal. The yield of butanal relative to that of pentanol was determined to be 0.102 ± 0.008 . As shown in Fig. 2, a signal at the retention time of 1,4 dihydroxvpentane (18.4 min, compare Table I) was present, but the associated product 1-hydroxypentan-4-one, which should have eluted after about 13.5 min, was absent. If 1-hydroxypentan-4-one is not formed, the identification of the peak at 18.4 min as 1,4 dihydroxypentane will also be in doubt. Partly, this peak may be due to 1-hydroxypentan-4-hydroperoxide rather than the corresponding diol. Two peaks at retention times of about 8.1 and 8.6 min must be isomerization products, but their nature could not be identified. The calibration for mixed hydroxycarbonyl compounds such as 1-hydroxypentan-4-one was used to obtain an estimate



Figure 2 Chromatograms (CP-WAX 52 column) of 1-iodopentane in air at atmospheric pressure before and after irradiation (lower and upper traces). Identified product peaks are accentuated: (1) butanal, (2) pentanal, (3) 1-iodopentane, (4) pentanol, (5) pentan-1,4-diol.

	$C_4H_9CH_2I + h\nu \rightarrow C_4H_9 \dot{C}H_2 + I$	$k_{\rm phot}$
	$\rm I + \rm I + \rm M \rightarrow \rm I_2 + \rm M$	
	$C_4H_9\dot{C}H_2 + O_2 \rightarrow C_4H_9CH_2OO \cdot$	rapid
(1a)	$2C_4H_9CH_2OO \rightarrow 2C_4H_9CH_2O + O_2$	$\alpha k_{ m pp}$
(1b)	$\rightarrow C_4H_9CH_2OH + C_4H_9CHO + O_2$	$(1 - \alpha)k_{\rm pp}$
(2a)	$C_4H_9CH_2O + O_2 \rightarrow C_4H_9CHO + HO_2$	$^{1}k_{O_{2}}$
(2b)	$C_4H_9CH_2O \rightarrow C_3H_7 \dot{C}H_2 + HCHO$	$^{1}k_{\text{dec}}$
(2c)	$C_4H_9CH_2O \rightarrow HOCH_2(CH_2)_2 \dot{C}HCH_3$	$^{1}k_{\rm iso}$
(3)	$C_3H_7CH_2 + O_2 \rightarrow C_3H_7CH_2OO$	rapid
(4)	$HOCH_2(CH_2)_2 \dot{C}HCH_3 + O_2 \rightarrow HOCH_2(CH_2)_2CH(OO)CH_3$	rapid
(5)	$HOCH_2(CH_2)_2CH(OO\cdot)CH_3 + C_4H_9CH_2OO\cdot$	
(5a)	\rightarrow HOCH ₂ (CH ₂) ₂ CH(O·)CH ₃ + C ₄ H ₉ CH ₂ O· + O ₂	fk_{sp}
(5b)	\rightarrow HOCH ₂ (CH ₂) ₂ CH(OH)CH ₃ + C ₄ H ₉ CHO + O ₂	$0.5(1-f)k_{\rm sp}$
(5c)	\rightarrow HOCH ₂ (CH ₂) ₂ COCH ₃ + C ₄ H ₉ CH ₂ OH + O ₂	$0.5(1-f)k_{\rm sp}$
(6a)	$C_{3}H_{7}CH_{2}OO \cdot + C_{4}H_{9}CH_{2}OO \cdot \rightarrow C_{3}H_{7}CH_{2}O \cdot + C_{4}H_{9}CH_{2}O \cdot + O_{2}$	$\frac{1}{2}k_{\rm pp}$
(6b)	\rightarrow C ₃ H ₇ CHO + C ₄ H ₉ CH ₂ OH + O ₂	$\frac{1}{4}k_{pp}$
(6c)	\rightarrow C ₃ H ₇ CH ₂ OH + C ₄ H ₉ CHO + O ₂	$\frac{1}{4}k_{\rm nn}$
(7a)	$2HOCH_2(CH_2)_2CH(OO)CH_3 \rightarrow 2HOCH_2(CH_2)_2CH(O)CH_3 + O_2$	$f k_{ss}^{PP}$
(7b)	\rightarrow HOCH ₂ (CH ₂) ₂ CH(OH)CH ₃ + HOCH ₂ (CH ₂) ₂ COCH ₃ + O ₂	$(1-f)k_{\rm ss}$
(9a)	$HOCH_2(CH_2)_2CH(O)CH_3 + O_2 \rightarrow HOCH_2(CH_2)_2COCH_3 + HO_2$	$^{2}k_{O_{2}}$
(9b)	$HOCH_2(CH_2)_2CH(O \cdot)CH_3 \rightarrow HOCH_2CH_2CH_2 + CH_3CHO$	$^{2}k_{\rm dec}$
(9c)	$HOCH_2(CH_2)_2CH(O)CH_3 \rightarrow OCH_2(CH_2)_2CH(OH)CH_3$	k_{iso}
(10)	$HOCH_2CH_2\dot{C}H_2 + O_2 \rightarrow HOCH_2CH_2CH_2OO \cdot$	rapid
(11)	$\cdot OCH_2(CH_2)_2CH(OH)CH_3 + O_2 \rightarrow OCH(CH_2)_2CH(OH)CH_3 + HO_2$	$^{1}k_{O_{2}}$
(12)	$HOCH_2(CH_2)_2CH(OO\cdot)CH_3 + C_3H_7CH_2OO\cdot$	
(12a)	\rightarrow HOCH ₂ (CH ₂) ₂ CH(O·)CH ₃ + C ₃ H ₇ CH ₂ O· + O ₂	$\frac{1}{2}k_{sp}$
(12b)	\rightarrow HOCH ₂ (CH ₂) ₂ CH(OH)CH ₃ + C ₃ H ₇ CHO + O ₂	$\frac{1}{4}k_{sp}$
(12c)	\rightarrow HOCH ₂ (CH ₂) ₂ COCH ₃ + C ₃ H ₇ CH ₂ OH + O ₂	$\frac{1}{4}k_{sp}$
(13a)	$2C_3H_7CH_2OO \rightarrow 2C_3H_7CH_2O + O_2$	$\frac{1}{2}k_{pp}$
(13b)	\rightarrow C ₃ H ₇ CH ₂ OH + C ₃ H ₇ CHO + O ₂	$\frac{1}{2}k_{pp}$
(14)	$C_3H_7CH_2O + O_2 \rightarrow C_3H_7CHO + HO_2$	${}^{1}k_{O_{2}}^{r_{r}}$
(15)	$HOCH_2CH_2CH_2OO + C_4H_9CH_2OO$	
(15a)	\rightarrow HOCH ₂ CH ₂ CH ₂ O· + C ₄ H ₉ CH ₂ O· + O ₂	$\frac{1}{2}k_{\rm pp}$
(15b)	\rightarrow HOCH ₂ CH ₂ CH ₂ OH + C ₄ H ₉ CHO + O ₂	$\frac{1}{4}k_{pp}$
(15c)	\rightarrow HOCH ₂ CH ₂ CHO + C ₄ H ₉ CH ₂ OH + O ₂	$\frac{1}{4}k_{pp}$
(16)	$HOCH_2CH_2CH_2OO + HOCH_2(CH_2)_2CH(OO)CH_3$	11
(16a)	\rightarrow HOCH ₂ CH ₂ CH ₂ O ₂ + HOCH ₂ (CH ₂) ₂ CH(O ₂)CH ₃ + O ₂	$\frac{1}{2}k_{sp}$
(16b)	\rightarrow HOCH ₂ CH ₂ CH ₂ OH + HOCH ₂ (CH ₂) ₂ COCH ₃ + O ₂	$\frac{1}{4}k_{sp}$
(16c)	\rightarrow HOCH ₂ CH ₂ CHO + HOCH ₂ (CH ₂) ₂ CH(OH)CH ₂ + O ₂	$\frac{1}{4}k_{\rm sp}$
(130)	$HOCH_2CH_2CH_2CH_2 + C_3H_7CH_2OO$	Nsp
(17a)	$\rightarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{O} + \text{C}_2\text{H}_2\text{CH}_2\text{O} + \text{O}_2$	$\frac{1}{2}k_{m}$
(17h)	$\rightarrow HOCH_2CH_2OH_2OH_2OH_2OH_2OH_2OH_2OH_2OH_2OH_2O$	$\frac{1}{4}k$
(170)	$\rightarrow \text{HOCH}_2\text{CH}_2C$	$\frac{1}{4}$
(1/c)	$\rightarrow \text{HOCH}_2\text{CH}_2C$	$\frac{4}{1}$ kpp
(18a)	$2HOCH_2CH_2CH_2OO \rightarrow 2HOCH_2CH_2CH_2O \rightarrow 0$	$\frac{2}{1}$ Kpp
(18b)	$\rightarrow \text{HOCH}_2\text{CH}_2C$	$\frac{2 k_{pp}}{1 k_{p}}$
(17)	$\begin{array}{c} \text{Hoch}_{2}\text{Ch}_{2}C$	kO2
(20a)	$OHCH_{2}(CH_{2})_{2}CH(OO_{1})CH_{2} \perp HO_{2} \rightarrow OHCH_{2}(CH_{2})_{2}CH(OOH)CH_{2} \perp O_{2}$	KHO2
(200)	$C_2H_2CH_2OO_2 + HO_2 \rightarrow C_2H_2CH_2OOH + O_2$	kuo
(200)	$HOCH_2CH_2OO + HO_2 \rightarrow HOCH_2CH_2OOH + O_2$	
(21)	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	ku o
()		···n ₂ O ₂

 Table II
 Reaction Scheme for the Photooxidation of 1-Iodopentane^a

^{*a*}Rate constants used in the calculations: photolysis rate (s⁻¹), *k*phot $\approx 1.3 \times 10^{-3}$; bimolecular rate coefficients (cm³ molecule⁻¹ s⁻¹) $k_{pp} = 2 \times 10^{-13}$, $k_{ss} = 2 \times 10^{-15}$, $k_{sp} = 2 \times 10^{-14}$, ${}^{1}k_{O_2} = 9.5 \times 10^{-15}$, ${}^{2}k_{O_2} = 8 \times 10^{-15}$; Decomposition constants (s⁻¹) ${}^{1}k_{dec} = 4.8 \times 10^4$, ${}^{2}k_{dec} = 1 \times 10^4$, Isomerisation constants (s⁻¹) ${}^{1}k_{iso} = 4.0 \times 10^5$, ${}^{2}k_{iso} = 9 \times 10^6$; branching ratios: $\alpha = 0.42$, f = 0.5–0.8.



Figure 3 Left: Rise of pentanal with time in the irradiation of 1-iodopentane in air at near atmospheric pressure (open points for a mixing ratio of 200 ppm, solid points for a mixing ratio of 0.1% scaled by a factor of five). Right: Yield of pentanol versus that of pentanal (the solid line shows the ratio 0.88 ± 0.05).

of the yields. Acetaldehyde was not observed, so that decomposition of the 1-hydroxypentan-4-oxyl radical, if it were involved, must be unimportant compared to competing reactions.

Table III summarizes relative yields for the observed products. The data can be used to estimate the branching ratio $\alpha = k_{1a}/(k_{1a} + k_{1b})$ for the self-reaction of pentan-1-yl peroxyl radicals (see Table II for the assignment of rate coefficients), and values for the decomposition and isomerization constants for the pentan-1oxyl radical. The first quantity is given by

$$\alpha = \frac{[\text{pentanal}] - [\text{pentanol}] + [\text{other products}]}{[\text{pentanal}] + [\text{pentanol}] + [\text{other products}]}$$
$$= 0.42 \pm 0.17$$

The relatively large statistical uncertainty of the branching ratio is caused mainly by the uncertainty in the yield of the isomerization products. The rate of decomposition of the pentan-1-oxyl radical relative to its reaction with oxygen is given by

$$k_{\text{dec}}/k_{\text{O}_2}[\text{O}_2] = \frac{[\text{butanal}] + [\text{butanol}]}{[\text{pentanal}] - [\text{pentanol}]}$$

= 0.97 ± 0.10

whereas the rate of isomerization of the pentan-1oxyl radical relative to its reaction with oxygen is correspondingly

$$k_{\rm iso}/k_{\rm O_2}[{\rm O_2}] = \frac{[\rm isom.products]}{[\rm pentanal] - [\rm pentanol]}$$

= 8.1 ± 2.2

If, as recommended by Atkinson [4], the rate coefficient for the reaction of pentan-1-oxyl radicals with oxygen is 9.5×10^{-15} cm³ molecule⁻¹ s⁻¹, values for the decomposition and isomerization constants will be $k_{dec} \approx (4.8 \pm 0.5) \times 10^4$ and $k_{iso} \approx (4.0 \pm 1.1) \times 10^5$ s⁻¹, respectively. Here, the uncertainty of k_{O_2} is not included in the error limits.

The FACSIMILE computer program [18] was used to calculate relative product yields resulting from the reaction mechanism presented in Table II. For this purpose, the above values for α , k_{O_2} , k_{dec} , and k_{iso} were employed. Rate coefficients for reactions of the peroxyl radicals involved are largely unavailable. The existing data [5.6] show, however, that rate coefficients for the self-reactions of primary alkyl peroxyl radicals, k_{pp} , are of the order of 10^{-13} cm³ molecule⁻¹ s⁻¹, whereas rate coefficients for the self-reactions of secondary alkylperoxyl radicals, k_{ss} , are of the order of 10^{-15} , cm³ molecule⁻¹ s⁻¹. Rate constants of cross-combination reactions, k_{sp} , have intermediate values approximated by the root over the product of the individual rate coefficients [19]. Accordingly we have used $k_{pp} = 2 \times 10^{-13}$, $k_{ss} = 2 \times 10^{-15}$, and $k_{sp} = 2 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹. Branching ratios

	Relative Yield			
		Calcu	Calculated ^a	
Product	Experimental	Case (a)	Case (b)	
Pentanol	1.0 ± 0.09	1.0	1.0	
Pentanal	1.14 ± 0.06	1.14	1.16	
Butanal	0.102 ± 0.008	0.100	0.104	
Butanol	0.034 ± 0.003	0.033	0.035	
Pentan-1,4-diol	0.080 ± 0.025	0.194	0.077	
1-Hydroxypentan- 4-one	≤0.02	0.195	0.080	
Acetaldehyde	≤0.02	0.008	0.001	
Unidentified products ^c	0.91 ± 0.07	_	_	
4-Hydroxypentanal	nd^b	0.375	0.559	
Propan-1,3-diol	nd	0.002	0.003	
3-Hydroxypropanal	nd	0.006	0.009	
Formaldehyde	nd	0.141	0.151	
Hydroperoxides ^d	nd	0.152	0.214	
Hydroxy-	nd	0.439	0.580	
hydroperoxides ^d				

 Table III
 Photooxidation of 1-lodopentane: Observed

 and Calculated Relative Product Distribution

 $^{a}(a)$ and (b): assuming different values for the branching ratio of hydroxypentylperoxy radical reactions, see Table II and text.

 b nd = not determined.

^cOccurring mainly in the peak at 8.51 min retention time (see Fig. 2).

^d Predominantly pentan-1-hydroperoxide and 1-hydroxypentan-4-hydroperoxide.

for peroxyl radical reactions were largely taken to be 0.5 in favor of the radical-preserving pathway and 0.25 for each alcohol-producing channel in the case of crosscombination reactions. The branching ratios for reactions of the 1-hydroxypentan-4-peroxyl radical with itself and with pentan-1-yl peroxyl radicals was varied between f = 0.5 and f = 0.8. Rate coefficients for reactions of HO₂ with alkyl- and hydroxyalkyl peroxyl radicals were set to 1.5×10^{-11} cm³ molecule⁻¹ s⁻¹ in accordance with recommendations for other such cases [5]. The rate constant for the decomposition channel of the 1-hydroxy-pentan-4-oxyl radical was set to ${}^{2}k_{dec} = 9 \times 10^{3} \text{ s}^{-1}$, similar to the value for the decomposition of the pentan-2-oxyl radical (see further below). The second possible decomposition pathway leading to a CH₃ radical and 4-hydroxybutanal should have a lower probability [8] and was ignored. The rate constant ${}^{2}k_{iso}$ for isomerization of the 1hydroxypentan-4-oxyl radical, leading to the formation of 4-hydroxypentanal, was set to 9×10^6 s⁻¹, following the recommendation of Atkinson [4]. Isomerisation and decomposition of the butoxyl radical was neglected. The results of the calculations are included in Table III for two cases, (a) f = 0.5 and

(b) f = 0.8, to allow comparison with the experimental data. In case (a) 1,4-pentandiol and 1-hydroxypentan-4-one should be produced in amounts sufficient for observation. Since they were not observed, some of the underlying assumptions must be wrong. In case (b), which is based on f = 0.8, the production rate of 1,4-pentandiol and 1-hydroxypentan-4-one is considerably reduced. In both cases, 4-hydroxypentanal is an important product. It is likely that the unidentified peak eluting after 8.6 min is associated with this product, but we were unable to prove or disprove it for the lack of an authentic sample. In both cases, decomposition of the 1-hydroxypentan-4-oxyl radical is less important than its isomerization, which may explain why acetaldehyde was not observed.

2-Iodopentane

Figure 4 shows a chromatogram of the product spectrum obtained following irradiation of 2-iodopentane. While pentan-2-one and pentan-2-ol are significant products as expected, only minute amounts of 1,4diol were formed in contrast to expectation. The corresponding mixed hydroxycarbonyl compounds were entirely absent. A prominent peak in the gas chromatogram eluting after 11.8 min indicated an isomerization product. This product was found to be unstable and nonlinear with irradiation time. Simultaneously, in the range of retention times 8-10 min, a greater number of not fully resolved peaks appeared that grew at the expense of the peak at 11.8 min. The reaction thus produces at least one unstable substance that decomposes toward multiple products. Although none of these product could be identified, an estimate of the total yield was made by summing gas chromatographic peak areas and applying an average response factor. The total yield was



Figure 4 Chromatograms (CP-WAX 52 column) of 2iodopentane in air at atmospheric pressure before and after irradiation (lower and upper traces). Identified product peaks are accentuated: (1) acetaldehyde, (2) propanal, (3) pentan-2-one, (4) propanol, (5) pentan-2-ol, (6) pentan-1,4-diol.

proportional to irradiation time. In evaluating the data, we assumed that the peaks appearing at intermediate retention times are associated with products resulting from the isomerization of pentan-2-oxyl radicals. In the lower range of retention times, acetaldehyde, propanal, and propanol were identified as products. These are expected products arising from decomposition of the pentan-2-oxyl radical. Table IV summarizes the relative product yields. The yield of acetaldehyde is higher than that for the sum of propanal and propanol, indicating an additional source of acetaldehyde in this system.

The data were used to estimate the branching ratio α for the self-reaction of pentan-2-yl peroxyl radicals, and values for the decomposition and isomerization constants for the pentan-2-oxyl radical relative to that with oxygen

decomposition and isomerization of the pentan-2-oxyl radical are $k_{dec} = (8.4 \pm 1.7) \times 10^3 \text{ s}^{-1}$ and $k_{iso} = (9.5 \pm 2.0) \times 10^4 \text{ s}^{-1}$, respectively. Again, the uncertainty of k_{O_2} is not included in the error limits.

Computer calculations for the photooxidation of 2-iodopentane were carried out on the basis of the mechanism shown in Fig. 1. The mechanism is similar in many respects to that of peroxyl radicals resulting from 1-iodopentane, so a detailed list of reactions is not presented. Rate coefficients and branching ratios chosen for the interactions of primary and secondary alkyl- and hydroxyalkyl peroxyl radicals were largely identical to those used for modeling the photooxidation of 1-iodopentane. For the self-reaction of propylperoxyl radicals the known rate constant

$$\alpha = \frac{[\text{pentan-2-one}] - [\text{pentan-2-ol}] + [\text{acetaldehyde}] + [\text{isom.products}]}{[\text{pentan-2-one}] + [\text{pentan-2-ol}] + [\text{acetaldehyde}] + [\text{isom.products}]} = 0.46 \pm 0.10$$

$$k_{\text{dec}}/k_{\text{O}_2}[\text{O}_2] = \frac{[\text{propanal}] + [\text{propanol}]}{[\text{pentan-2-one}] - [\text{pentan-2-ol}]} = 0.20 \pm 0.04$$

$$k_{\text{iso}}/k_{\text{O}_2}[\text{O}_2] = \frac{[\text{propanal}] + [\text{propanol}]}{[\text{pentan-2-one}] - [\text{pentan-2-ol}]} = 2.27 \pm 0.47$$

where the uncertainty indicates again the accumulated statistical uncertainty of the measurements. Assuming $k_{O_2} \approx 8 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ as recommended by Atkinson [4], the rate coefficients for

Table IVPhotooxidation of 2-Iodopentane: Observedand Calculated Relative Product Distribution

	Relative Yield			
		Calculated ^a		
Product	Experimental	Case (a)	Case (b)	
Pentan-2-ol	1.0 ± 0.11	1.0	1.0	
Pentan-2-one	1.47 ± 0.18	1.51	1.49	
Propanal	0.073 ± 0.012	0.073	0.072	
Propanol	0.023 ± 0.004	0.024	0.024	
Pentan-1,4-diol	0.015 ± 0.01	0.27	0.24	
4-Hydroxypentanal	nd	0.28	0.24	
Acetaldehyde	0.16 ± 0.02	0.10	0.16	
Unidentified products	1.07 ± 0.22	_	_	
1-Hydroxypentan- 4-one	≤0.02	0.54	0.46	
Hydroperoxides ^c	nd^b	1.06	0.96	
Hydroxy- hydroperoxides ^c	nd	0.042	0.085	

 $^{a}(a)$ According to the mechanism shown in Fig. 1. (b) Including additional reactions given in the text.

 b nd = not determined.

^cPredominantly pentan-2-hydroperoxide and 4-hydroxypentan-1-hydroperoxide.

 $k_{\rm pp} = 3.9 \times 10^{-13} \,\mathrm{cm^3}\,\mathrm{molecule^{-1}\,s^{-1}}$ and branching ratios [5] were used. The rate coefficient for isomerization of the 4-hydroxypentan-1-oxyl radical was set to ${}^2k_{\rm iso} = 1.5 \times 10^7 \,\mathrm{s^{-1}}$, following the suggestion of Atkinson [4]. The results of the calculations are included in Table IV.

As in the case of 1-iodopentane, the calculations predict diols and mixed hydroxycarbonyl compounds to occur in higher yields than those that were actually observed. It is again possible to reduce the calculated yields by adjusting the branching ratios for the reactions of the 4-hydroxypentan-1-yl peroxyl radical with itself and with pentan-2-yl peroxyl. These results will not be presented in view of our failure to account for the many other products appearing in the chromatograms.

Another problem is the insufficient yield of acetaldehyde resulting from the calculation. If in addition to 1,5 H-atom shift the pentan-2-oxyl radical underwent 1,4 H-atom shift, decomposition of the resulting 2-hydroxypentan-4-oxyl radical would provide a natural route to acetaldehyde formation. Baldwin et al. [7] estimated that the ring strain energy imposed on 1,4 H-shift (involving a five-membered ring) is about 25 kJ mol⁻¹ greater than that on 1,5 H-shift (proceeding via a six-membered ring), which is 2.5 kJ mol⁻¹. By combining the activation energy for internal abstraction of a secondary hydrogen atom given by

Atkinson [4] and the different ring strain energies, one estimates a rate constant of about $1 \times 10^2 \text{ s}^{-1}$ for 1,4 H-atom shift. This is greatly insufficient to generate the excess acetaldehyde observed. Another possible pathway for acetaldehyde formation follows from isomerization of the 4-hydroxypentan-1-oxyl radical. Atkinson [4] assumed that isomerization proceeds only by abstraction of the hydrogen atom located on the carbon skeleton opposite the hydroxyl group, but transfer of the H-atom from the hydroxyl group may also occur, even though it would require a seven-membered intermediate ring structure resulting in an increased ring strain energy. We have explored the following mechanism by means of computer simulation:

The rate coefficients required to generate sufficient amounts of acetaldehyde were ${}^{2}k_{iso} = 1.5 \times 10^{7} \, \text{s}^{-1}$, ${}^{4}k_{iso} = 5 \times 10^{6} \, \text{s}^{-1}$, ${}^{5}k_{iso} = 5 \times 10^{6} \, \text{s}^{-1}$, and ${}^{3}k_{dec} = 4 \times 10^{6} \, \text{s}^{-1}$. The results are shown in the last column in Table IV. They indicate that apart from raising the yield of acetaldehyde the distribution of the other products is not greatly affected. In order for this mechanism to explain the formation of excess aldehyde, it will be necessary that hydrogen abstraction from the OH-group is nearly as rapid as that of the neighboring H-atom. The computer simulation suggests a ratio of 1:3 for the rate coefficients involved.

3-Iodopentane

The 3-pentoxyl radical is not expected to undergo isomerization reactions, and this simplifies the oxidation mechanism. Table V shows the corresponding reaction scheme. The principal products were pentan-3one and pentan-3-ol, in accordance with expectation. Additional products were propanal, acetaldehyde, and small amounts of ethanol. These products result from the decomposition of the pentan-3-oxyl radical. The combined yields of acetaldehyde and ethanol are about equal to that of propanal in accordance with the mechanism. The CPSil 76 column was required for the quantification of pentan-3-ol, because in chromatograms obtained with the CP-Wax-52 column the alcohol was obscured by 3-iodopentane. The product distribution obtained after 90-s irradiation of 3-iodopentane in air at near atmospheric pressure is given in Table VI. A number of experiments were made in which the mixing ratio of oxygen was varied, keeping the total pressure of the oxygen-nitrogen mixture nearly constant

Table V Reaction Scheme for the Photooxidation of 3-Iodopentane^a

	*	
	$C_2H_5CH(I)C_2H_5 + h\nu \rightarrow C_2H_5\dot{C}HC_2H_5 + I$	$k_{\rm phot}$
	$\rm I + \rm I + \rm M \rightarrow \rm I_2 + \rm M$	-
	$C_2H_5\dot{C}HC_2H_5 + O_2 \rightarrow C_2H_5CH(OO)C_2H_5$	rapid
(1a)	$2C_2H_5CH(OO \cdot)C_2H_5 \rightarrow 2C_2H_5CH(O \cdot)C_2H_5 + O_2$	$\alpha k_{ m ss}$
(1b)	\rightarrow C ₂ H ₅ CHOHC ₂ H ₅ + C ₂ H ₅ COC ₂ H ₅ + O ₂	$(1-\alpha)k_{\rm ss}$
(2a)	$C_2H_5CH(O \cdot)C_2H_5 + O_2 \rightarrow C_2H_5COC_2H_5 + HO_2$	8×10^{-15}
(2b)	$C_2H_5CH(O \cdot)C_2H_5 \rightarrow C_2H_5CHO + CH_3\dot{C}H_2$	$k_{ m dec}$
(3)	$CH_3\dot{C}H_2 + O_2 \rightarrow C_2H_5OO \cdot$	rapid
(4a)	$2C_2H_5OO \rightarrow 2C_2H_5O + O_2$	4.35×10^{-14}
(4b)	\rightarrow C ₂ H ₅ OH + C ₂ H ₅ CHO + O ₂	2.45×10^{-14}
(5)	$C_2H_5O + O_2 \rightarrow C_2H_5CHO + HO_2$	9.5×10^{-15}
(6a)	$C_2H_5OO + C_2H_5CH(OO \cdot)C_2H_5 \rightarrow C_2H_5O + C_2H_5CH(O \cdot)C_2H_5 + O_2$	$\frac{1}{2}k_{sp}$
(6b)	\rightarrow C ₂ H ₅ OH + C ₂ H ₅ COC ₂ H ₅ + O ₂	$\frac{1}{4}k_{sp}$
(6c)	\rightarrow CH ₃ CHO + C ₂ H ₅ CH(OH)C ₂ H ₅ + O ₂	$\frac{1}{4}k_{sp}$
(7a)	$C_2H_5CH(OO)C_2H_5 + HO_2 \rightarrow C_2H_5CH(OOH)C_2H_5 + O_2$	1.5×10^{-11}
(7b)	$C_2H_5OO + HO_2 \rightarrow C_2H_5OOH + O_2$	$5.8 imes 10^{-12}$
(7c)	$\cdot \mathrm{HO}_2 + \mathrm{HO}_2 \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2$	$2.5 imes 10^{-12}$

^{*a*} Rate coefficients used in the calculations: $k_{ss} = 1 \times 10^{-15}$, $k_{sp} = (2-8) \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹, $k_{phot} \approx 1 \times 10^{-3}$ s⁻¹.

Table VIExperimentally Observed and CalculatedRelative Product Distributions for the Photooxidation of3-Iodopentane

		Calculated ^b		
Product	Experimental ^a	(a)	(b)	(c)
Pentan-3-ol	1.00 ± 0.03	1.0	1.0	1.0
Pentan-3-one	1.80 ± 0.04	1.80	1.83	1.84
Propanal	0.49 ± 0.02	0.49	0.51	0.51
Ethanal	0.33 ± 0.04	0.36	0.37	0.38
Ethanol	0.10 ± 0.04	0.09	0.11	0.12
Hydroperoxides ^c	nd	1.09	1.10	1.10

^{*a*}About 800 μ mol mol⁻¹ in air at atmospheric pressure; nd = not determined.

^bThe rate constant used for the peroxyl radical cross-combination reaction in cases (a), (b), and (c) were $k_{sp} = 2 \times 10^{-15}$, 8×10^{-15} , and 1.2×10^{-14} cm³ molecule⁻¹ s⁻¹, respectively.

^cPredominantly 3-pentyl-hydroperoxide.

at 103 kPa. Figure 6 shows a plot of ([pentan-3-one] – [pentan-3-ol])/[propanal] as a function of the O₂ concentration. The straight line obtained demonstrates the competition between decomposition of the pentan-3-oxyl radical and its reaction with oxygen. The slope of the line, which should be given by k_{O_2}/k_{dec} , has a value of $(3.15 \pm 0.13) \times 10^{-19}$ cm³ molecule⁻¹.

The branching ratio for the self-reaction of 3pentylperoxyl radicals was obtained from the relative product yields shown in Table VI as

$$\alpha = k_{\rm ssa}/k_{\rm ss}$$

$$= \frac{[\text{pentan-3-one}] - [\text{pentan-3-ol}] + [\text{propanol}]}{[\text{pentan-3-one}] + [\text{pentan-3-ol}] + [\text{propanal}]}$$
$$= 0.39 \pm 0.08$$



Figure 5 Chromatograms (CP-WAX 52 column) of 3iodopentane in air at atmospheric pressure before and after irradiation (lower and upper traces). Identified product peaks are accentuated: (1) acetaldehyde, (2) propanal, (3) ethanol, (4) pentan-3-one, (5) pentan-3-ol is hidden underneath the peak of 3-iodopentane.

The rate of decomposition of the 3-pentoxyl radical relative to its reaction with oxygen is

$$k_{\text{dec}}/k_{\text{O}_2}[\text{O}_2] = \frac{\text{[propanal]}}{\text{[pentan-3-one]} - \text{[pentan-3-ol]}}$$
$$= 0.61 \pm 0.06$$

Assuming again $k_{O_2} = 8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, one obtains $k_{dec} \approx (2.6 \pm 0.2) \times 10^4 \text{ s}^{-1}$. The reciprocal slope of the line in Fig. 6 leads to $k_{dec} \approx (2.5 \pm 0.14) \times 10^4 \text{ s}^{-1}$, which is in good agreement. Again, the uncertainty of k_{O_2} is not included in the error limits.

The branching ratio $\alpha = 0.39$ for pentan-3-yl peroxyl radicals is lower than the values derived for the two other pentylperoxyl radicals. All the products from pentan-3-yl peroxyl radicals were fully quantified, in contrast to the other systems studied, where isomerization products were incompletely characterized and the α values are more uncertain. A possible reason for the apparently low α value might be the occurrence of side reactions of pentan-3-oxyl radicals with iodopentane. The pentan-3-oxyl radical would be more readily affected by such reactions than the corresponding other two species because the absence of isomerization processes reduces the absolute loss rate of the pentan-3oxyl radical and makes it more susceptible to side reactions. However, we found no difference in the product distribution when the mixing ratio of 3-iodopentane in air was raised from 0.1 to 1 mmol mol^{-1} . Accordingly, there is no evidence for the occurrence of side reactions.

As in other cases, computer simulations of the oxidation of 3-iodopentane were carried out. Because pentan-3-yl peroxyl is a secondary radical,



Figure 6 Difference in the yield of 3-pentanone and 3pentanol, relative to the yield of propanal, versus oxygen concentration. The solid point is obtained from the experimental data in Table VI. The straight line demonstrates the competition between decomposition of pentan-3-oxyl and its reaction with oxygen.

the rate coefficient for its self-reaction was assumed to be 1×10^{-15} cm³ molecule⁻¹ s⁻¹. The rate coefficient and branching ratio for the self-reaction of ethylperoxyl radicals are [5] $k_{pp} = 6.8 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, $\alpha = 0.64$. The rate coefficient k_{sp} for the cross-combination reaction between primary ethylperoxyl and secondary pentan-3-yl peroxyl radicals was taken to be an adjustable parameter. The results of the calculations are included in Table VI. The product distribution is best represented with $k_{sp} = (2-8) \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. The calculations further demonstrate that pentan-3-yl hydroperoxide, which cannot be analyzed by gas chromatography, should be formed with a fairly high yield (21%).

DISCUSSION

The results indicate that 254-nm photolysis of 1iodopentane and 3-iodopentane in air predominantly generate pentan-1-yl peroxyl and pentan-3-yl peroxyl radicals, respectively. The photooxidation of 2-iodopentane gave rise to a greater number of unidentified products that may partly have resulted from unknown photodecomposition processes other than clean dissociation to form an iodine atom and pentan-2-yl. If so, this would contrast with 2-iodobutane, where elimination of HI occurs in addition to cleavage of the carbon-iodine bond, but not any other noticeable fragmentation [10]. Hence, we have assumed that the unidentified peaks observed in the case of 2-iodopentane are products resulting from the isomerization of pentan-2-oxyl radicals. Relatively high concentrations of iodopentanes were applied, without any indication that the concentration range was detrimental. In addition to the carbonyl compounds and alcohols resulting from the self-reactions of the three peroxyl radicals studied, products arising from the decomposition pathways of the corresponding alkoxyl radicals could be quantified, and the relative yields were determined. It is disappointing to note that the diols and hydroxycarbonyl compounds predicted to arise from isomerization reactions of the pentan-1-oxyl and pentan-2-oxyl radicals were not observed in the expected amounts. Eberhard et al. [20] have used derivatization with 2,4dinitrophenylhydrazine and liquid chromatography to identify 2-hydroxyhexan-5-one produced in the photolysis of hexan-2-nitrite. Kwok et al. [21] have used atmospheric pressure ionization triple quadrupole mass spectrometry to characterize hydroxycarbonyl compounds derived from the reaction of OH with several *n*-alkanes including *n*-pentane. The presence of NO in both studies ensured that alkylperoxyl radicals were rapidly converted to the corresponding alkoxyl radicals, so that the concentrations of peroxyl radicals were kept low. The experimental conditions of this study did not allow the addition of NO in amounts sufficient to convert all of the peroxyl radicals to alkoxyl radicals. Thus, high concentrations of peroxyl radicals had to be tolerated. In the case of 1-iodopentane, the calculations indicate that 4-hydroxypentanal should be the dominant isomerization product. Although we have observed a signal at a retention time characteristic of this product, no positive identification could be made for the lack of an authentic sample. In contrast to the photooxidation of 1-iodopentane, which is still reasonably well behaved, that of 2-iodopentane has remained largely ambiguous because we were unable to assign a greater number of products at retention times characteristic of mixed hydroxycarbonyl compounds, which appear to arise from the decomposition of an unstable intermediate. Our assumption that these products originate from isomerization of pentan-2-oxyl may be incorrect. In view of this difficulty, only a few exploratory experiments were made with 2-iodopentane. Much more analytical work will be required to enable analysis of these data.

Table VII summarizes our results for the branching ratios of the self-reactions of the three pentylperoxyl radicals studied. The values for pent-1-yl peroxyl and pent-2-yl peroxyl are affected by the extent of isomerization of the corresponding pentoxyl radicals, so that they carry a larger range of uncertainty than the branching ratio for pent-3-yl peroxyl. All three values are rather similar indicating that 40–45% of the reactions enter into the radical propagating channel and 55–60%

Table VII Summary of Branching Ratios for the Self-Reaction of Pentyl Peroxyl Radicals and Approximate Rate

 Coefficients for the Decomposition and Isomerization of Pentoxyl Radicals Relative to Their Reaction with Oxygen

Radical Source	α	$k_{\rm dec}/k_{\rm O_2}$ (10 ¹⁸ molecule cm ⁻³)	$k_{\rm dec}{}^a$ (10 ⁴ s ⁻¹)	$k_{\rm iso}/k_{\rm O_2}$ (10 ¹⁹ molecule cm ⁻³)	$k_{\rm iso}{}^a$ (10 ⁵ s ⁻¹)
1-Iodopentane	0.42 ± 0.17	5.09 ± 0.52	4.8 ± 0.5	4.3 ± 1.2	4.0 ± 1.1
2-Iodopentane	0.46 ± 0.10	1.05 ± 0.21	0.84 ± 0.17	1.2 ± 0.3	1.0 ± 0.2
3-Iodopentane	0.39 ± 0.08	3.20 ± 0.31	2.6 ± 0.3	-	_

^{*a*}Assumptions for pent-1-oxyl $k_{O_2} = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; in the other two cases, $k_{O_2} = 8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $[O_2] = 5.2 \times 10^{18} \text{ molecule} \text{ cm}^{-3}$.

produce alcohols and carbonyl compounds. Similar ratios have been observed for several other alkylperoxyl radicals such as methyl peroxyl 0.35 [5], neo-pentyl peroxyl 0.40 [5], primary 2,3-dimethyl-butyl peroxyl 0.44 [14], propan-2-yl peroxyl 0.39 [14]. In the latter case there exists an alternative value of 0.58 [5].

Table VII includes relative rates for the decomposition and isomerization pathways of pentoxyl radicals. As these data were derived from measurements of the decomposition products, they presumably involve less uncertainties than the isomerization constants. The present result for pentan-2-oxyl, $8.4 \times 10^3 \text{ s}^{-1}$, which is based on an assumed rate coefficient for the reaction of the pentan-2-oxyl radical with oxygen, is in good agreement with that obtained by Dobe et al. [11], who have studied the decomposition of pentan-2-oxyl at elevated temperatures relative to reaction with NO. Their Arrhenius expression extrapolated to 295 K gives $k_{\text{dec}} = 9.4 \times 10^3 \,\text{s}^{-1}$. Atkinson [4] used a revised rate coefficient for the reaction of alkoxyl radicals with NO to obtain a corrected value $9.0 \times 10^3 \text{ s}^{-1}$. Our own value would have been higher, had we used the yield for acetaldehyde rather than the sum of the yields of propanal and propanol. Our value for the decomposition constant of pent-3-oxyl is in excellent agreement with that of Atkinson et al. [12] who found $k_{\rm dec}/k_{\rm O_2} = 3.3 \times 10^{18} \,\mathrm{molecule}\,\mathrm{cm}^{-3}$ using a different method of analysis. It is of interest to note that the decomposition constant for pentan-3-oxyl is higher than that of pentan-2-oxyl, by a factor of about three, although the heat of decomposition is essentially the same in both cases. The surprisingly high rate of decomposition of pentan-1-oxyl disagrees with the estimate of Atkinson [8] for the release of formaldehyde from the hydrocarbon chain, $k_{dec} = 24 \text{ s}^{-1}$. As we did not analyze for formaldehyde, we had to assume that the source of butanal is the butyl radical formed in the decomposition of the pentan-1-oxyl radical. This assumption may be wrong. Our sample of 1-iodopentane also contained unidentified impurities, which may have provided a source of butanal.

In view of the inadequate product characterization, it will be clear that the results for the isomerization pathways included in Table VII carry large uncertainties, especially since we assumed that the unidentified products resulted predominantly from isomerization. Atkinson [4,8] has estimated rate coefficients of 1,5 hydrogen shift isomerization, using revised Arrhenius parameters compared to those originally given by Baldwin et al. [7] The derived values (at 298 K) for pent-2-oxyl and pent-1-oxyl are $2.0 \times 10^5 \text{ s}^{-1}$ and $1.6 \times 10^6 \text{ s}^{-1}$, respectively. In the first case the value obtained here, $1.0 \times 10^5 \text{ s}^{-1}$, is in reasonable agreement with prediction, but still lower than the value obtained by Atkinson et

al. [12], $k_{\rm iso}/k_{\rm O_2} = 3.1 \times 10^{19}$ molecule cm⁻³, which leads to $k_{\rm iso} \approx 2.5 \times 10^5 \,{\rm s}^{-1}$. The value reported by Dobe et al. [11], $k_{\rm iso} \approx 5 \times 10^3 \,{\rm s}^{-1}$, is much too low. In the case of 1-iodopentane, where only two significant isomerization products appeared in our chromatograms, the isomerization constant obtained should be more reliable. however, the value obtained here, $k_{\rm iso} \approx 4 \times 10^5 \,{\rm s}^{-1}$, is significantly smaller than that calculated. Hein et al. [13] have produced pentan-1oxyl radicals by laser photolysis of 1-bromo-pentane at reduced pressure, but they were only able to show that $k_{\rm iso} \geq 1 \times 10^5 \,{\rm s}^{-1}$.

In summary, it has been shown that the photolysis of iodopentanes provides a useful technique for generating individual pentylperoxyl isomers. The observed product distributions were evaluated to determine the branching ratios for the radical-preserving pathways in the self-reactions of the individual pentylperoxyl radicals. Diols and mixed hydroxycarbonyl compounds that should be formed by cross-combination reactions of hydroxyalkyl peroxyl radicals produced from pentan-1-oxyl and pentan-2-oxyl radicals after isomerization were essentially absent, in contrast to expectation. Although the chromatograms indicated isomerization products, we were unable to identify any of them under the conditions of our experiments. On the other hand, the decomposition products of pentan-2-oxyl and pentan-3-oxyl radicals could be quantified and the decomposition constants were determined.

BIBLIOGRAPHY

- Alfassi, Z. B. (Ed.). Peroxyl Radicals; Wiley: Chichester, UK, 1997.
- Carter, W. P. L.; Atkinson, R. J Atmos Chem 1985, 3, 377–405.
- 3. Atkinson, R. Atmos Environ 1990, 24A, 1–41.
- 4. Atkinson, R. J Phys Chem Ref Data 1997, 26, 215-290.
- Lightfoot, P. D.; Cox, R. A.; Crowley, J. N.; Destriau, M.; Hayman, G. D.; Jenkin, M. E.; Moortgat, G. K.; Zabel, F. Atmos Environ 1992, 26A, 1805–1964.
- Wallington, T. J.; Dagaut, P.; Kurylo, M. J Chem Rev 1992, 92, 667–710.
- Baldwin, A. C.; Barker, J. R.; Golden, D. M.; Hendry, D. G. J Phys Chem 1977, 81, 2483–2492.
- 8. Atkinson, R. Int J Chem Kinet 1997, 29, 99–111.
- Kwok, E. S. C.; Atkinson, R. Atmos Environ 1995, 29, 1685–1696.
- Ross, P. L.; Johnston, M. V. J Phys Chem 1995, 99, 4078–4085.
- 11. Dobe, S.; Berces, T.; Marta, F. Int J Chem Kinet 1986, 18, 329–344.
- Atkinson, R.; Kwok, E. S. C.; Arey, J.; Aschmann, S. Faraday Discuss 1995, 100, 23–37.

- 13. Hein, H.; Hoffmann, A.; Zellner, R. Phys Chem Chem Phys 1999, 1, 3743–3752.
- Heimann, G.; Warneck, P. J Phys Chem 1992, 96, 8403– 8409.
- Benkelberg, H.-J.; Böge, O.; Seuwen, R.; Warneck, P. Phys Chem Chem Phys 2000, 2, 4029–4039.
- 16. Brown, H. C.; Wheeler, O. H. J Am Chem Soc 1956, 78, 2199–2202.
- 17. Williams, H. R.; Mosher, H. S. J Am Chem Soc 1954, 76, 2987–2990.
- Curtis, A. R.; Sweetenham, W. P. FACSIMILE/CHECKMAT Users Manual; Aere-R-12805; Her Majesty's Stationary Office: London, 1988.
- Madronich, S.; Calvert, J. G. J Geophys Res 1990, 95, 5697–5715.
- Eberhard, J.; Müller, C.; Stocker, D. W.; Kerr, J. A. Environ Sci Technol 1995, 29, 232– 241.
- 21. Kwok, E. S.; Arey, J.; Atkinson, R. J Phys Chem 1996, 100, 214–219.