Reactions of Alkylperoxyl Radicals in Solution

Part 2.—A Kinetic and Product Study of Self-reactions of 2-Propylperoxyl Radicals between 253 and 323 K

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The self-reactions of 2-propylperoxyl radicals have been studied between 253 and 323 K in decane solution. The ratio of the major products, propanone and propan-2-ol, as a function of temperature is in good agreement with the behaviour of other secondary peroxyl radicals in solution. The roles played by the solvent are considered by comparison with previous studies of this radical in the gas phase. It is concluded that the increase in ketone production relative to the alcohol as the temperature is lowered is best explained by the inclusion of the bimolecular reaction of the peroxyl radical producing propanone and hydrogen peroxide. It is suggested that this reaction has Arrhenius parameters of $A \approx 10^6$ dm³ mol⁻¹ s⁻¹ and $E_a \approx 5$ kJ mol⁻¹.

In the previous paper the results of a detailed kinetic study of the self-reactions of 2-propylperoxyl radicals in solution were presented.¹ The concentrations of peroxyl radicals, formed by the photolysis of *trans*-2,2'-azopropane in several solvents in the presence of oxygen, were monitored with time by e.s.r. It was shown that the removal of peroxyl radicals is essentially a second-order process overall:

$$2Me_2CHO_2 \xrightarrow{k_{obs}} products.$$

This does not imply that a single second-order reaction is occurring. Similar work in the gas phase^{2, 3} suggests that secondary peroxyl radicals react together by at least two mechanisms in competition with each other, either producing molecular products directly (a terminating reaction),

$$2Me_{2}CHO_{2} \rightarrow 2Me_{2}C = O + Me_{2}CHOH + O_{2}$$
(1)

or by producing 2-propoxyl radicals (a propagating reaction),

$$2Me_{2}CHO_{2}^{*} \rightarrow 2Me_{2}CHO^{*} + O_{2}$$
⁽²⁾

Since direct spectroscopic evidence of the kinetic behaviour of 2-propylperoxyl radicals cannot, by itself, distinguish between the two processes, a detailed study of the stable products formed by the reactions has also been undertaken. It is then possible to find the relative importance of these reactions on changing reaction conditions.

Experimental

The Reaction Cell

The central part of the cell was a glass cylinder, A (i.d. 16 mm, length 24 mm) (fig. 1). To the side was joined a 2 mm bore capillary tube, the outside of which was roughened



Fig. 1. The reaction cell. A, Reaction vessel; B, septum cap; C, greaseless tap; D, optical window; E, water jacket.

to allow a brass sleeve with a screw thread on the outside to be attached with epoxy resin. A silicone rubber septum, held against the end of this tube by a cap, B, allowed samples to be withdrawn for analysis using a 25×10^{-3} cm³ gas-tight syringe (SGE). Across the other axis of the cell were attached two 2 mm bore capillary greaseless taps (J. Young), C, leading to greaseless balls by which the cell could be attached to the vacuum line (constructed with greaseless Pyrex Rotaflo taps). At one end of the cell, a flat Pyrex window, D, was affixed with epoxy resin. The other end was tapered to reduce the surface area of the cell not covered by an outside jacket, E, (through which liquids at constant temperature were pumped). The tapering also improved the ability of the cell to withstand stresses caused by temperature changes.

The system allowed the reactant solutions to be degassed thoroughly, measured amounts of added gases to be dissolved and for the cell to be filled completely prior to photolysis. The absence of a gas head-space proved necessary to prevent the escape of volatile products from the solution.

The addition of low concentrations of oxygen was most reliably achieved by premixing the gas well with helium in a bulb on the vacuum line.

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J. E. Bennett et al.

Prior to and during irradation the mixture inside the cell was stirred using a small magnetic follower. After irradation and sampling were completed, the septum cap of the cell was removed and the temperature of the reaction mixture checked with a thermocouple.

Analysis

The analysis of the major reactants and products was performed by g.c. 2,3-Dimethylbutane, propanone, propan-2-ol, *trans*- and *cis*-2,2'-azopropane, di-2-propyl peroxide and 2-hydroperoxypropane were determined on a column (1.75 m length, 4 mm i.d.) of Gas Chrom Q-20% (w/w) dinonyl phthalate, programmed between 313 and 368 K, using a flame-ionization detector. Propane and propene were determined on a column (1.75 m length, 4 mm i.d.) of silica gel (80-100 mesh) at 413 K, also by f.i.d. Oxygen and nitrogen were determined on a column (2.3 m length, 4 mm i.d.) of 5A molecular sieve (60-85 mesh) at 323 K, using a thermal conductivity detector; a pre-column of silica gel was used to absorb the relatively large amounts of solvent added on each injection.⁴

The identities of all the products were checked by g.c.-m.s. (Kratos MS 30). The mass spectrum obtained from the peak assigned to 2-hydroperoxypropane corresponded to that obtained by Cairns⁵ (with the largest peaks having m/z = 43, 45, 58).

Attempts to determine hydrogen peroxide spectrophotometrically were made using the coloured complexes formed with titanium(IV)⁶ and with titanium(IV) and xylenol orange together.^{7, 8} However, the former method proved not to be sensitive enough and the latter proved to be unreliable.

Preparation of Reagents

trans-2,2'-Azopropane was prepared from isopropylamine by a method due to Stowell⁹ and was purified by preparative g.c. [Gas Chrom Q-20% (w/w) di(2-ethylhexyl)sebacate]. 2-Hydroperoxypropane was prepared via 2-propyl methanesulphonate¹⁰ and was stored as an ethereal solution. Di-2-propyl peroxide was also prepared from 2-propylmethanesulphonate¹¹ and was purified by preparative g.c. [Gas Chrom Q-20% (w/w) di(2-ethylhexyl)sebacate]. Its purity was checked by ¹H and ¹³C n.m.r.

The other materials were available commercially and their purities were checked by g.c.

Results

Photolysis of trans-2,2'-Azopropane in Absence of Oxygen

Formation of Products

The principal products of the photolysis of *trans*-2,2'-azopropane in decane between 253 and 323 K are propane, propene, 2,3-dimethylbutane, *cis*-2,2'-azopropane and a branched isomer of decane, possibly (from g.c.-m.s. evidence) 3,4-dimethyloctane.

Products, over the first 10% of reaction, are formed at a constant rate (table 1). The concentration of *cis*-2,2'-azopropane eventually reaches an equilibrium with the *trans* isomer (fig. 2).

Effect of Temperature

The position of the equilibrium between *trans*- and *cis*-2,2'-azopropane does not appear to be affected greatly by temperature (table 2), but the rates of formation of hydrocarbons increase with temperature (table 1). The branched hydrocarbon was not determined quantitatively, but its chromatogram peak area increases in the proportion to that of propene.

ble 1. Des des de Grans de sub-statuets à 6 de seu - 2.27

decane at 298 K (initial conc 2.7×10	entration $()^{-2}$ mol dm	of trans- of tran 1 ⁻³)	2,2 -e s-2,2	'-azo	opropane	ne,
		•			•	

		104	concentra	tion/mol dm ⁻³
T/K	time/s	propane	propene	2,3-dimethylbutane
253	3600	12.1	10.3	6.0
	7200	22.1	18.3	11.8
	9600	34.1	29.2	17.8
278	3300	18.7	16.4	12.5
	4200	23.2	20.6	15.3
	4800	28.7	25.3	17.4
	5400	34.1	26.5	18.7
323	600	4.7	2.7	2.3
	1200	12.0	7.0	5.7
	2400	22.7	13.4	10.4
	3000	27.4	16.2	12.5
	3600	30.6	18.4	14.4

Table 2. The ratio of stationary concentrations of *cis*- and *trans*-2,2'-azopropane found during the photolysis of *trans*-2,2'azopropane in decane (initial concentration of *trans*-2,2'-azopropane, 2.7×10^{-2} mol dm⁻³)

100 × [cis-2,2'-azopropane] /[trans-2,2'-azopropane]
7.01 ± 0.30
8.15 ± 0.37
8.25 ± 0.30
8.41 ± 0.41



Fig. 2. The ratio of concentrations of *cis*- and *trans*-2,2'-azopropane as a function of photolysis time in oxygenated (□) and oxygen-free (∇) solutions of decane at 298 K.

T/K time 7/K /s propal 253 1800 6.2 253 3600 13.0 278 3600 32.5 278 1800 7.5 3600 13.0 9.1 375 2400 9.1 3600 15.3 9.1 3600 15.3 9.1 3600 15.3 9.1 3600 15.3 9.1 3600 21.7 9.1 5400 21.7 5.400 21.7 5.400 21.7	ane propene 2.2 5.8 0.0 12.5 5.31.9 18.1 31.9 2.2 7.3	2,3-dimethyl- butane 4.3 8.5 11.8 20.7 5.4 7.0	propanone 1.3 5.9 8.2 8.2 4.2	propan-2-ol 0.2 0.8 1.2 1.6 1.6 1.6	di-2-propyl peroxide trace 0.1 0.2 trace 0.3	2-hydroperoxy- propane 0.4 0.8 0.9 1.8	[propanone] /[propan-2-ol] 4.48±1.55
253 1800 6.2 3600 13.0 5.1 5400 13.0 3.5 5400 3.5 9600 3.2.5 278 1800 7.5 9.1 3600 18.0 7.5 9.1 3600 18.0 7.5 9.1 3600 18.0 16.3 9.1 3600 14.9 9.1 3600 14.9 5400 21.7 5400 22.1	2. 2. 2. 2. 2. 3. 1. 2. 3. 2. 3. 2. 3. 2. 3. 2. 3. 3. 2. 3. 3. 2. 3. 3. 3. 3. 3. 3. 3. 3. 3. 3. 3. 3. 3.	4.3 8.5 20.7 5.4 20.7	1.3 5.9 8.2 8.2	0.2 1.2 1.6 1.6 1.6 1.6 1.6 1.6 1.6 1.6 1.6 1.6	trace trace 0.1 0.2 0.3	0.4 0.8 1.8	4.48 ±1.55
3600 13.0 5400 18.8 5400 18.8 9600 32.5 7.5 2400 9.1 3600 15.3 3600 14.9 5400 21.7 5400 21.7		8.5 11.8 5.4 7.0	2.2 8.2 8.2 8.2	0.8 1.2 1.6 1.6 1.8	trace 0.1 trace 0.3	0.8	4.48±1.55
5400 18.8 9600 32.5 9600 32.5 278 1800 7.5 2400 9.1 3600 3600 15.3 3600 14.9 5400 21.7 5400 21.7 5400 21.7 5400 21.7	.5 31.9 .5 31.9 .1 9.2	11.8 20.7 5.4	6.2 8.2 2.8 2 4 2 2 8 2 4 2 8	1.2 2.6 1.8	0.1 0.2 0.3 0.3	0.9	CC.1 H 0+.+
9600 32.5 278 1800 7.5 2400 9.1 3600 15.3 3600 14.9 5400 21.7 5400 22.1	.5 31.9 .5 7.3 .1 9.2	20.7 5.4 7.0	8.2 8.2 7.8	2.6 1.6 1.8	0.2 trace 0.3	1.8	
278 1800 7.5 2400 9.1 3600 15.3 3600 14.9 5400 21.7 5400 21.7 5400 21.7	.5 7.3 .1 9.2	5.4 7.0	2.8 4.2	1.6 1.8	trace 0.3		
2400 9.1 3600 15.3 3600 14.9 5400 21.7 5400 22.1	.1 9.2	7.0	4.2	1.8	0.3	-	
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5400 21.7 5400 22.1	.9 14.6	10.7	6.1		:		10.0 - 00.1
5400 22.1	.7 21.4	16.3	9.2	5.0	0.4	1	
	.1 21.6	16.0		:	:	/	
298 1800 6.6	.6 6.4	5.2	3.2	2.1	0.2	[
2700 11.2	.2 10.4	8.5	5.2	2.6	0.2		1 50-10-31
4200 17.5	.5 16.4	12.9	7.4	6.0	0.4		10.01 00.1
4800 19.4	.4 19.6	14.9	9.0	5.6	0.2		
323 1200 5.2	.2 5.0	4.4	2.7	2.5	0.1		
1800 7.7	.7 7.4	6.0	4.6	4.5		:	1 11 ± 0.00
3600	:	13.1	10.4	9.2	0.3	trace [1111 T 0.00
4200 17.4	.4 17.2	14.4	12.2	9.8	0.4	trace	

J. E. Bennett et al.

^a (\cdots) Not determined; (--) not detected.

Table	4.	Products	from	the p	ohoto-	oxidati	on of	trans-2,2'-azoj	propane	in	decane	with
varied	ini	tial oxyger	conce	entratio	on at	298 K	(initial	concentration	of tran.	s-2,2	'-azopro	pane,
					2.1	7×10^{-2}	mol dn	n ⁻³)				-

initial	produ	products as percentages of 2-propyl radicals generated							
concentration /10 ⁻³ mol dm ⁻³	propane+ propene	2,3-dimethyl- butane	propanone	propan-2-ol	di-2-propyl peroxide				
6.86	41	34	12	9					
4.90	42	36	11	8	1				
3.92	41	34	11	9	3				
2.94	39	32	14	9	1				
1.96	43	36	11	9					
0.98	39	31	12	8	2				
0.49	52	35	8	7	4				



Fig. 3. Products from the photo-oxidation of *trans*-2,2'-azopropane in decane at 298 K. Initial concentrations: *trans*-2,2'-azopropane, 2.7 × 10⁻² mol dm⁻³; oxygen, 4.9 × 10⁻⁴ mol dm⁻³.
▽, 2,2,dimethylbutane; □, propane; △, propene; ■, propanone; ◇, propan-2-ol; ○, di-2-propyl peroxide; ●, 2-hydroperoxypropane.

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Table 5. Products from the photo-oxidation of *trans*-2,2'-azopropane in decane (initial concentrations: *trans*-2,2'-azopropane, 2.7×10^{-2} mol dm⁻³; oxygen, 6.9×10^{-4} mol dm⁻³)

				con	centration/10-	⁻⁴ mol dm ⁻³		
T/K	time /s	propane	propene	2,3-dimethyl- butane	propanone	propan-2-ol	di-2-propyl peroxide	2-hydroperoxy- propane
253	2700	9.4	9.1	6.3	2.1	0.4	trace	6.0
	5400	19.3	18.7	12.3	4.7	1.1	trace	1.9
	7200	24.8	23.7	15.4	7.1	2.2	0.5	1.0
	9600	31.4	30.0	19.6	6.0	2.0	0.7	0.9
278	1800	7.5	7.3	5.4	2.8	1.6	trace	1
	3000	11.9	11.8	8.2	4.4	2.6	0.1	ł
	3600	15.8	15.1	10.5	4.8	2.7	0.2	
	4800	21.8	19.7	14.7	4.7	2.8	1.1	
	6000	28.4	25.4	17.5	4.5	2.7	1.4	1
298	600	2.3	2.0	1.7	1.1	0.8	trace	ł
	1800	7.0	7.0	5.6	3.6	2.9	0.2	
	2700	11.3	10.4	8.0	4.2	3.4	0.4	1
	3600	18.7	15.8	11.8	3.5	3.0	1.1	
	4800	26.3	20.2	15.2	3.8	2.5	2.1	Name
323	720	2.9	2.8	2.3	1.4	1.2	trace	
	1200	5.4	4.9	4.3	2.1	2.5	0.3	-
	1800	11.8	8.5	6.6	2.9	2.7	0.6	
	2400	16.4	11.4	8.9	2.1	2.6	0.8	
	3600	24.7	16.3	12.3	2.4	2.7	1.1	

J. E. Bennett et al.



Fig. 4. Products from the photo-oxidation of *trans*-2,2'-azopropane in decane at 253 K. Initial concentrations: *trans*-2,2'-azopropane, 2.7×10^{-2} mol dm⁻³; oxygen, 6.9×10^{-4} mol dm⁻³. Symbols as for fig. 3.

Photolysis of trans-2,2'-Azopropane in Oxygenated Solution

Formation of Products

With oxygen dissolved in the solution, propane, propene and 2,3-dimethylbutane remain the major products from the photodecomposition of the azo compound. In addition, propanone, propan-2-ol and small quantities of di-2-propyl peroxide are also produced, but 2-hydroperoxypropane was not observed at ambient temperatures. The rates of formation of products are linear over the period of the time studied (table 3). Hydrogen peroxide was also identified as a product, but quantitative analysis was not reliably achieved, using either method described in the experimental section. The method yielding a complex with titanium(IV) proved to be too insensitive, in part as a result of absorption at 410 nm by the *cis*-2,2'-azopropane, whilst the method involving the hydrogen peroxide-titanium(IV)-xylenol orange complex was potentially sensitive enough and confirmed the presence of hydrogen peroxide, but proved to be irreproducible.

The rate at which isomerisation of *trans*-2,2'-azopropane to the *cis* form occurs and the final isomer ratio, are both independent of the concentration of oxygen (fig. 2).

Variation of the Initial Oxygen Concentration

A series of experiments was performed in which the concentration of oxygen in solution was varied (table 4). No significant effect was observed in the yields of propanone and propan-2-ol except at the lowest concentrations of oxygen used.

J. E. Bennett et al.

Two series of experiments were performed in which solutions containing comparatively low initial oxygen concentrations were photolysed at 298 K. In both cases, when the oxygen in solution was depleted, the growth of propanone and propan-2-ol concentrations stopped, whilst the rate of formation of the hydrocarbons, particularly propane, increased. The concentration of di-2-propyl peroxide increased significantly around and after the time at which the oxygen apparently became depleted. Fig. 3 gives data for one of these sets of experiments.

Experiments were also performed at 253, 278 and 323 K (tables 3 and 5, fig. 4). As at 298 K, there is a change in the rates of formation of various products when the oxygen was depleted. Small amounts of 2-hydroperoxypropane were observed at 253 and 323 K.

Discussion

Photo-isomerisation of trans-2,2'-Azopropane

2,2'-Azopropane was used as the radical precursor in all the product studies since it is a 'clean' source of 2-propyl radicals, can be prepared with high purity and also because it was used in the corresponding gas-phase studies.² Preparation of the azo compound leads to the formation of the *trans* isomer, but irradiation at 360 nm results in isomerisation and a stationary concentration of the *cis* isomer is reached (fig. 2). The position of equilibrium is unchanged as the temperature is decreased until 253 K (near the solvent freezing point) is reached (table 2). Steel and coworkers¹² found very little *cis* isomer was produced when photolysing *trans*-2,2'azopropane in methanol with benzene or phenylethanone, but that naphthalene could act as a triplet sensitiser resulting in a ratio of [*cis*]/[*trans*] of 0.67, but, on the other hand¹³ found that the photolysis of *trans*azomethane in deuterium oxide, methanol, ethanol and ethoxyethane yielded a [*cis*]:[*trans*] ratio of 0.1 ± 0.01 , invariant with temperature. The [*cis*]:[*trans*] ratio for the photolysis of azoethane in decane over the temperature range 255–323 K is 0.05.¹⁴

The mechanism for photo-isomerisation is not fully understood. At its simplest it can be represented as:

$$A \xrightarrow{nv} A^*$$
$$A^* \rightarrow 2R^{\cdot} + N_2$$
$$A^* + M \rightarrow A^{\ddagger} + M$$
$$A^{\ddagger} \rightarrow cis - A$$
$$A^{\ddagger} \rightarrow trans - A.$$

L.,

The evidence for the two isomers resulting from a common excited state, A^{\ddagger} , is that the sum of Φ (trans \rightarrow cis) and Φ (cis \rightarrow trans) is near to unity,¹² whilst the independence of the photostationary state on temperature indicates that there are no energy barriers between A^{\ddagger} and the ground states of the two isomers. On the basis of molecular orbital calculations¹⁵ it is suggested that A^{\ddagger} is the first excited singlet (S₁) state ¹(n, π^*) which touches the ground (S₀) state energy surface when the angle of rotation about the nitrogen-nitrogen bond is 90° and hence rapid internal conversion to both cis and trans ground states could occur with no energy barriers.¹⁶ A* is presumably in the same electronic state as A^{\ddagger} , but is vibrationally excited.

Products of	Self-reaction	of	2-Propyl	lperoxyl	l Rad	ical	s
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radicals in solution								
T/K	solvent	$k_{\rm d}/k_{\rm e}$	ref.					
253	decane	1.57 ± 0.09	this work					
273	dodecane	1.32	21					
278	decane	1.36 ± 0.05	this work					
298	decane	1.28 ± 0.04	this work					
303	decalin	1.20	22					
	dodecane	1.12	21					
323	decane	1.22 ± 0.06	this work					
	dodecane	1.13	21					

 Table 6. The ratio of the rate constants for the disproportionation and combination of 2-propyl radicals in solution

Self-reactions of 2-Propyl Radicals

Apart from isomerisation to produce the *cis* isomer, photolysis of *trans*-2,2'-azopropane results in decomposition and subsequent formation of propane, propene and 2,3-dimethylbutane (table 1):

L

$$2\text{Me}_{2}\text{CH} \stackrel{\mu_{q}}{\to} \text{C}_{3}\text{H}_{8} + \text{MeCH} = \text{CH}_{2}$$
(3)

$$2Me_2CH \xrightarrow{\kappa_c} Me_2CHCHMe_2.$$
(4)

Reaction (3), disproportionation, produces equal quantities of propane and propene and the excess propane observed is due to abstraction of hydrogen by the 2-propyl radicals, the solvent molecules, SH, being the most abundant substrate:

$$Me_2CH' + SH \to C_3H_8 + S'.$$
(5)

Assuming that reactions (3) and (4) are the only routes to propene and 2,3dimethylbutane, respectively, the ratio of yields of these hydrocarbons is equivalent to the ratio k_d/k_c at any given time. The gas-phase ratio k_d/k_c is well established, 0.60 ± 0.02 at ambient temperature.¹⁷⁻²⁰ The value of 1.28 ± 0.04 obtained in this liquid-phase study, although considerably higher than the corresponding gas-phase ratio, is consistent with the other available data for the 2-propyl radical in solution (table 6).

The difference between the ratio k_d/k_e as observed between the gas and liquid phases is not confined to the 2-propyl radical. Although primary alkyl radicals give very similar ratios of k_d/k_e in the gas phase and in non-polar solvents, secondary and tertiary alkyl radicals show a marked preference for disproportionation when moving from the gas phase to solution, but the extent varies from solvent to solvent.^{2, 3, 17-26}

The dependence of the disproportionation/combination ratio of alkyl radicals upon temperature and phase has in the past been interpreted both in terms of a difference in Arrhenius parameters for the two processes^{27–29} and as a function of the internal pressure of the medium.^{24, 30} Recently, Fischer has argued that the relative rates of the selfreactions of alkyl radicals are attributable to the viscosity of the solvent.^{21, 31, 32}

Under normal conditions the radicals are able to rotate freely in the gas phase, whilst in solution the surrounding molecules will hinder such motion more in some directions than others. Consideration of the three-dimensional structure of the radicals reveals that their ability to adopt suitable configurations to undergo combination will be more seriously impaired than those for disproportionation, particularly in the case of tertiary radicals and hence the ratio will increase from its gas-phase value. The moderate temperature and hence viscosity dependence of the ratio k_d/k_e for the 2-propyl radical

(table 6), compared with the large effect demonstrated by the t-butyl radical³¹ and with the negligible effect observed for the ethyl radical,^{24, 31} is consistent with this model.

Photolysis of trans-2,2'-Azopropane in Oxygenated Solution

One significant difference between the reactions following photolysis of *trans*-2,2'azopropane in presence of oxygen in the gas and liquid phases, is the production of hydrocarbons in the latter system. In the gas phase 2-propyl radicals, formed in the initiation reaction, react very rapidly with oxygen:

$$Me_2CH' + O_2 \rightarrow Me_2CHO_2'$$
 (6)

In contrast, substantial quantities of propane, propene and 2,3-dimethylbutane are produced even though the overall oxygen concentrations were similar in the two phases. This difference is attributable to the high concentration of solvent molecules, creating localised high concentrations of the alkyl radicals.

The significant oxygenated products observed in the liquid-phase photo-oxidation of 2,2'-azopropane are propanone, propan-2-ol, di-2-propyl peroxide, hydrogen peroxide and, at some temperatures, 2-hydroperoxypropane.

However, the distribution of these products is different from that reported in the gas phase.^{2, 33} For example, varying the concentration of oxygen in the gas phase has a marked effect on the yields of propan-2-ol and 2-hydroperoxypropane, while the propanone yield remains unaffected. In contrast, in solution there is no significant trend in the ratio of yields of propanone to propan-2-ol and no 2-hydroperoxypropane was detected at ambient temperature even at the highest oxygen concentrations.

Only at the lowest initial oxygen concentration used is there any appreciable change in the distribution of oxygenated products.

In the gas phase, it has been shown that 2-propylperoxyl radicals undergo two self-reactions:

$$2Me_{2}CHO_{2} \rightarrow Me_{2}C = O + Me_{2}CHOH + O_{2}$$
(1)

$$2Me_{2}CHO_{2}^{*} \rightarrow 2Me_{2}CHO^{*} + O_{2}.$$
⁽²⁾

It is the fate of the 2-propoxyl radicals that affects the gas-phase product distribution.^{2, 33} Reaction with oxygen yields propanone and hydroperoxyl radicals:

$$Me_{a}CHO' + O_{a} \rightarrow Me_{a}C = O + HO_{a}.$$
 (7)

The hydroperoxyl radicals terminate by reaction with 2-propylperoxyl radicals:

$$Me_{2}CHO_{2}^{*} + HO_{2}^{*} \rightarrow Me_{2}CHO_{2}H + O_{2}.$$
(8)

If, however, the concentration of oxygen is not high, other reactions of the 2-propoxyl radicals become kinetically viable:

$$Me_2CHO_2 + Me_2CHO^{\dagger} \rightarrow Me_2C = O + Me_2CHO_2H$$
 (9)

$$Me_2CHO_2H + Me_2CHO' \rightarrow Me_2CHO_2' + Me_2CHOH.$$
 (10)

Thus, whilst propanone and 2-hydroperoxypropane are the exclusive products from the reactions of the 2-propoxyl radicals at high oxygen concentrations, reactions (9) and (10) become significant as the oxygen concentration is lowered and propan-2-ol is a more abundant product than 2-hydroperoxypropane. The yield of propanone remains invariant as it is produced by both routes.

In solution the reactions of 2-propoxyl radicals are considerably influenced by the presence of the solvent, SH, which will be susceptible to hydrogen abstraction by alkoxyl radicals:

$$Me_2CHO' + SH \rightarrow Me_2CHOH + S'$$
. (11)

Direct data for the 2-propoxyl radical reacting with hydrocarbons are not available in either gas or liquid phases, but using the data of Wong³⁴ for the reaction of t-butoxyl radicals with cyclopentane in the liquid phase, the Arrhenius parameters for abstraction from decane (with sixteen secondary hydrogen atoms) are $A = 2.0 \times 10^{10}$ dm³ mol⁻¹ s⁻¹ and E = 25.5 kJ mol⁻¹. The reaction of oxygen with 2-propoxyl radicals has recently been measured directly in the gas phase,³⁵ giving values of $E_7 = 1.63$ kJ mol⁻¹ and $A = 9.1 \times 10^6$ dm³ mol⁻¹ s⁻¹. Thus it appears that reaction (7) is about an order of magnitude faster than reaction (11) at 298 K. However, there is a much larger difference in the concentration of the reactants, the concentration of the decane being 5.13 mol dm⁻³, whilst that of oxygen was always lower than 7×10^{-3} mol dm⁻³. Therefore, the fate of the vast majority of 2-propoxyl radicals will be reaction with the solvent to yield propan-2-ol. This explains the constancy of the product distribution as the oxygen concentration in solution is varied. However, it does not explain why the yields of propanone are larger than those of propan-2-ol.

Just as the decomposition of the azo compound in the liquid phase can lead to geminate pairs of alkyl radicals, so the decomposition of the tetroxide will lead to geminate pairs of alkoxyl radicals in close proximity to an oxygen molecule:

$$Me_2CHO_4CHMe_2 \rightarrow [Me_2CHO' + O_2 + Me_2CHO'].$$
 (12)

Thus the self-reactions of the 2-propoxyl radicals will be enhanced compared to the gas phase where they have been shown to be insignificant,^{2, 3} explaining the formation of di-2-propyl peroxide in solution (table 3). It is also plausible that the reaction between one of the 2-propoxyl radicals and the oxygen molecule would be similarly enhanced:

$$[Me_2CHO' + O_2 + Me_2CHO'] \rightarrow [Me_2C = O + HO_2' + Me_2CHO']$$
(13)

and a further molecule of propanone produced by subsequent reaction:

$$[\operatorname{Me}_{2}\operatorname{CHO}' + \operatorname{HO}_{2}'] \to \operatorname{Me}_{2}\operatorname{C} = \operatorname{O} + \operatorname{H}_{2}\operatorname{O}_{2}.$$
(14)

The fate of hydroperoxyl radicals which move without reaction into the bulk of the solvent also requires consideration. Data from gas-phase studies³⁶ indicate that abstraction reactions of this species will be very slow in the range 253–323 K so its reactions are likely to be with other radical species, such as 2-propylperoxyl radicals which are the most abundant. Other reactions present themselves. One is the formation of the hydroperoxide and oxygen which appears to be highly favourable in gas-phase studies:², ³, ³³, ³⁷, ³⁸

$$Me_2CHO_2^{\prime} + HO_2^{\prime} \rightarrow Me_2CHO_2H + O_2.$$
 (8)

Alternatively, the ketone, water and oxygen are formed by intramolecular hydrogen transfer (similar to the Russell mechanism):^{3, 39}

$$Me_{2}CHO_{2}^{2} + HO_{2}^{2} \longrightarrow Me_{2}C_{H}^{O} \longrightarrow H_{H}^{O} Me_{H}^{O} + (15)$$

While reaction (8) would be expected to have the higher A-factor, reaction (15) is likely to require a lower activation energy and would, therefore, become increasingly favoured as the temperature is lowered. The absence of measurable quantities of 2hydroperoxypropane at ambient temperature is probably a result both of the low numbers of hydroperoxyl radicals available to participate in reaction (8) and of the consumption of the hydroperoxide by reaction (10) or similar processes.

Such a model therefore accounts for the invariance of the oxygenated product distribution with the oxygen concentration in solution. The only noticeable exception is the increased rate of formation of di-2-propyl peroxide around the point of oxygen

depletion. This is likely to be due to the occurrence of the crossed-termination reaction with an alkyl radical [eqn (16)] in the absence of sufficiently high concentrations of 2-propylperoxyl radicals to make their self-reaction viable.

$$Me_2CHO_2^{\bullet} + Me_2CH^{\bullet} \rightarrow Me_2CHO_2CHMe_2.$$
 (16)

The temperature dependence of the product distribution and particularly the ratio of ketone to alcohol is explained less satisfactorily by the mechanism as it stands. The suggested source of the excess propanone over propan-2-ol has been the geminate reaction of 2-propoxyl with oxygen following decomposition of the dialkyl tetroxide. The effectiveness with which these reactive species are obliged to react together rather than diffusing apart is, therefore, governed by the solvent viscosity which, in turn, is related to the temperature. Thus at 253 K the solvent decane is relatively viscous and the alkoxyl radicals cannot easily diffuse apart and are consequently oxidised to propanone, resulting in a relatively high ratio of ketone to alcohol. At 323 K the alkoxyl radicals can escape from the cage much more readily and then abstract a hydrogen atom to form propan-2-ol, leading to a product ratio close to unity. Whilst solvent viscosity can be used to explain the variation in product distribution over the present limited temperature range, it is not adequate when considering lower temperatures.

The increase in ratio of propanone to propan-2-ol (table 4) as the temperature is lowered is in good agreement with the behaviour of several other secondary peroxyl radicals.^{40, 41} It is found that production of the carbonyl compound is increasingly preferred over the alcohol until at *ca*. 173 K over 90% of the alkylperoxyl radicals are leading to the formation of the carbonyl compound. However, the gas-phase data for the separated reactions of the peroxyl radicals² suggest that for the 2-propylperoxyl radical at 173 K, $k_1/k_2 = 11.3$, implying that over 90% of the 2-propylperoxyl radicals should react by the Russell mechanism [reaction (1)] and hence give a [propanone]/[propan-2-ol] ratio close to unity. This discrepancy between the results obtained in the gas-phase studies (as extrapolated to low temperatures) and in solution presents a dilemma: either the rate of reaction (2), producing the alkoxyl radicals, is significantly enhanced in solution or an additional route to the formation of ketone must be operating at these temperatures.

As reactions (1) and (2) are believed to proceed via the same intermediate, the dialkyl tetroxide, then solvent effects are unlikely to change their relative rates significantly on moving from the gas to liquid phase, though the absolute rates may be higher in solution.^{42–44} Thus it appears that the discrepancy may be caused by the occurrence of an additional reaction, which has a low pre-exponential factor and activation energy and so becomes dominant at lower temperatures. Bennett and Summers⁴⁰ have tentatively proposed a mechanism which involves the direct decomposition of the dialkyl tetroxide thus:

$$2RR'CHO_{2} \longrightarrow RR'C \longrightarrow RR'C = 0 + H_{2}O_{2}.$$
(17)

The steric requirements for such a reaction to occur would result in a low pre-exponential factor. As the mechanism is unusual it is difficult to estimate the expected magnitude of an activation energy although such a process does represent a more exothermic pathway than the Russell mechanism [reaction (1)].

If it is assumed that for the self-reactions of 2-propylperoxyl radicals in solution,

$$k_{\rm obs} = k_1 + k_2 + k_{17}$$

then approximate Arrhenius parameters can be calculated for reaction (17) using values of k_{obs} from our direct kinetic studies¹ and k_1 and k_2 calculated from the Arrhenius parameters obtained from the gas-phase studies,² giving:

$$\log(k_{17}/\mathrm{dm^3 \, mol^{-1} \, s^{-1}}) = 6.0 \pm 0.4 - [(4800 \pm 1600)/\mathrm{kJ \, mol^{-1}}]/2.303 RT.$$

The small pre-exponential factor is not without precedence. Ingold and coworkers observed similar Arrhenius parameters for the self-reaction of various dialkyl nitroxides in solution.^{45, 46} This process has similarities to the mechanism under consideration here. Both reactions involve an initial equilibrium between the reactant radicals and the dimer. In both cases an α -hydrogen atom is then transferred from a carbon atom to an oxygen atom *via* a five-membered cyclic transition state together with the breaking of an oxygen-oxygen bond. Thus the similarities in Arrhenius parameters between reaction (17) and the self-reaction of dialkyl nitroxide radicals are plausible.

Using this treatment it is possible to calculate maximum and minimum values for the ratio of ketone/alcohol, depending on whether the 2-propoxyl radicals are oxidized to propanone or abstract hydrogen to form propan-2-ol, respectively. The experimental values of the ratio found in this work and for similar secondary peroxyl radicals^{40, 41} lie between the calculated limits over the whole temperature range for which data are available.

Reaction (17) has also been considered to be significant by von Sonntag and coworkers.⁴⁷⁻⁴⁹ Studying the reactions of various peroxyl radicals generated by the pulse radiolysis of oxygenated solutions of organic compounds in water, they have found in all cases an excess of ketone to alcohol and their reaction mechanisms for explaining the product distributions include the direct conversion of peroxyl radicals to the corresponding ketone and hydrogen peroxide.

At the higher temperatures used in the gas-phase work the rate of reaction (17) will be small compared to those of reactions (1) and (2) and consequently it will not contribute significantly to the product yields, as found experimentally.^{2, 33} Interestingly, in the case of ethylperoxyl radicals a small excess of ethanal over ethanol has been observed³ and this could be the result of the participation of reaction (17).

Thus we believe that the reactions of alkylperoxyl radicals are intrinsically the same in the gas and liquid phases. In the latter, however, the presence of a large concentration of solvent molecules can influence the products formed in a number of ways. First, the creation of localised high concentrations of reactive species can dramatically affect the observed product distribution compared with the homogeneous gas-phase system. Secondly, the solvent represents a very abundant potential reactant. Although the reaction of the peroxyl radicals with the solvent,

$$RR'CHO_2 + SH \rightarrow RR'CHO_2H + S'$$
(18)

was too slow to be of consequence in the present work, this reaction becomes important at slightly higher temperatures.⁵⁰ The corresponding abstraction reaction of the alkoxyl radicals [reaction (11)] does occur and largely explains why the system is not dependent upon the oxygen concentration in this work. Thirdly, the presence of the solvent can affect the absolute and, for processes of different order, the relative rates of reaction compared with gas phase, although it has not been possible to assess the importance of this role in the present studies.

Finally, assuming the conclusions about the relationship between the reactions in the two phases as summarised above are correct, then the source of the excess of ketone produced at sub-ambient temperatures in solution still needs to be explained. Inclusion of the extra reaction first proposed by Bennett and Summers⁴⁰ seems the most satisfactory hypothesis, although the present work adds supportive evidence rather than proving its existence.

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