A Kinetic Study of the Reactions of 2-Propyl Radicals in the Liquid Phase in the Presence and Absence of Oxygen

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ABSTRACT

2-Propyl radicals have been generated from the photolysis of solutions of 2,2-azopropane and 2,4-dimethyl-3-pentanone in decane in a glass and a metal cell. The time course of their reactions in the presence and absence of oxygen has been monitored between 323 and 373 K.

The primary process involves the formation of solvent-caged radical pairs, two 2-propyl radicals and a 2-propyl and a 2-methylpropanoyl radical from the azo and ketone precursors, respectively. Subsequently these radicals are partitioned between cage escape and dimerization and disproportionation within the cage. In oxygenated solution the free 2-propyl radicals are effectively trapped as 2-propylperoxyl radicals. However, oxygen does not react with the solvent-caged radicals. This leads to a major difference in the hydrocarbon products from the two precursors. 2,2'-Azopropane gives propane, propene, and 2,3-dimethylbutane from the start of the reaction whereas the ketone only gives propene. Following the depletion of oxygen, or in the absence of oxygen, both precursors behave analogously and give all three hydrocarbons.

The 2-propylperoxyl radicals undergo self-reaction and hydrogen abstraction from the solvent to give 2-propanol, propanone, and 2-propyl hydroperoxide and, under conditions of low oxygen concentration, by reaction with 2-propyl radicals they give 2.2'-dipropylperoxide.

Although the two cells lead to different overall rates of reaction, the relative rates and product distributions are unaffected by the cell design. A unified mechanism is described and the known and best estimates of rate constants for the individual steps are used to simulate the time dependence of the product yields from the photolysis of both precursors. © 1996 John Wiley & Sons, Inc.

Received May 4, 1995; accepted October 10, 1995 International Journal of Chemical Kinetics, Vol. 28, 201-215 (1996) © 1996 John Wiley & Sons, Inc. CCC 0538-8066/96/030201-15

INTRODUCTION

In order to elucidate the key reactions, and their rate parameters in the autoxidation of newly developing oils and lubricants, we need data for the reactions of substituted alkylperoxyl radicals. Unfortunately, the relevant rate constants and reactions of the radicals formed in these processes are generally not well characterized. As a consequence the development of a computer model to describe these systems suffers from large uncertainties.

We are therefore first obtaining data for reactions of simpler alkylperoxyl radicals and modeling these systems by kinetic simulation. Studies include the reactions of ethylperoxyl [1], 2-propylperoxyl [2], and t-butylperoxyl [3] radicals. The results can then be used to determine how temperature, solvent, and structure affects the reactions of these radicals, which, in turn, will provide information for the more complex systems, for example in the autoxidation of esters.

In earlier articles, we describe studies of the reactions of 2-propyl and 2-propylperoxyl radicals generated by photolysis of 2,2'-azopropane in oxygenated and oxygen-free decane [2]. We have extended the study in two ways. First, we have examined the effect the material, used to make the reaction cells, has on the reaction. The cells were constructed from pyrex and steel. Secondly, we are now able to study the reaction at higher temperatures by using 2,4dimethyl-3-pentanone as the precursor for 2-propyl and 2-propylperoxyl radicals. To check that the new reaction cells gave comparable results to those obtained earlier [2], we have also studied the photolysis and photo-oxidation of 2,2'-azopropane at 323 and 348 K, within and just beyond the range of the initial work.

EXPERIMENTAL

Materials

All the materials were commercially available and used without purification unless stated. Decane was purified by column chromatography and 2,4-dimethyl-3-pentanone by vacuum distillation 33-35 °C (at 25 mmHg). 2,2'-Azopropane was prepared from 2-propylamine by the method of Stowell [4].

Analysis

The reactant and all the products, except for 2-propyl hydroperoxide, were analyzed using two gas chro-

matographs (Pye Unican GCD and PU4500) equipped with flame ionization detectors. A column packed with 20% (w/w) dinonylphthalate on Gas Chrom Q was used for the analysis of 2,3-dimethylbutane and the oxygenated products and silica gel for the analysis of the hydrocarbons. 2-Propyl hydroperoxide was quantified in solution using the horseradish peroxidase method of Frew et al. [5].

Apparatus

The photolysis apparatus and procedures have been reported previously [3]. Two reaction cells were used, one made of pyrex and the other of steel. The windows were pyrex.

RESULTS

Photolysis of 2, 2'-Azopropane and 2,4-Dimethyl-3-Pentanone in Decane

The photolysis of decane solutions of 2, 2'-azopropane at 323 and 348 K and of 2,4-dimethyl-3pentanone between 323 and 373 K were studied (Table I). In all the experiments, the only products detected were propane, propene, and 2,3dimethylbutane, all of which show a linear rate of growth over the first part of reaction. On increasing the temperature, for both systems, the rate of formation of propane relative to that of both propene and 2,3-dimethylbutane increases and there is a small decrease in the rate of formation of propene relative to 2,3-dimethylbutane. The results from the azo compound are compared in Table II with those obtained earlier for the photolysis of 2, 2'-azopropane by Bennett et al. [2].

Photo-Oxidation of 2, 2'-Azopropane and 2,4-Dimethyl-3-Pentanone in Decane

The photolyses of oxygen-saturated decane solutions of 2, 2'-azopropane in a metal cell at 323 and 348 K (Table III) and of the ketone in a metal cell between 323 and 373 K and in a glass cell at 348 K (Table IV) were studied. The photo-oxidation of the ketone leads, in the early stages, to the formation of propanone, 2-propanol, 2-propyl hydroperoxide, and propene. The rates of production of propanone and propanol during this period are large but as the reaction proceeds, they decrease to a point where their concentrations then remain approximately constant. However, at higher temperatures, the concentration of propanone actually decreases before finally level-

Table 1. Photolysis of 2, 2'-azopropane (AZO) and 2,4-dimethyl-3-pentanone (KET) in Decane in a Metal Cell. Initial Concentrations of AZO and KET, 2.7×10^{-2} mol dm⁻³. (Pr_{TOT} Refers to the Total Concentration of Isopropyl Radicals that Form Products)

			Concentration 10 ⁴ / mol dm ⁻³				
Reactant	Temp/K	Photolysis Time/s	C ₃ H ₈	C ₃ H ₆	C ₆ H ₁₄	PR _{TOT}	
		1800	6.6	3.4	2.6	15.2	
AZO	323	3600	12.1	6.5	5.3	29.2	
		5400	20.0	10.3	8.3	46.9	
		1800	7.2	3.2	2.4	15.2	
AZO	348	3600	13.9	7.1	5.7	32.4	
		5400	22.5	9.9	8.9	50.2	
		900	5.0	2.2	0.8	8.8	
	323	1800	12.5	5.1	2.8	23.2	
KET		2700	17.0	7.0	2.3	28.6	
		3600	22.3	9.5	4.3	40.4	
		7200	55.5	20.0	10.0	95.5	
		1800	9.9	2.6	0.3	13.1	
KET	348	3600	21.2	4.9	1.0	28.1	
		5400	29.4	7.1	1.6	39.7	
		900	7.9	0.7	0.2	9.0	
		1800	16.7	1.1	0.4	18.6	
KET	373	2700	23.8	1.9	0.7	27.1	
		5400	44.8	4.0	1.2	51.2	

ing off. The concentration of propanone, in the initial phase of the reaction, is always greater than that of 2-propanol but this is reversed when the final concentrations are reached. The concentration of 2-propyl hydroperoxide also reaches a maximum value during the first phase of reaction and then decreases to zero. The only hydrocarbon product that forms during this initial phase is propene. However, coincident with the disappearance of 2-propyl hydroperoxide and the leveling off of 2-propanol and propanone formation, the production of the other hydrocarbons begins. All hydrocarbon concentrations then increase approximately linearly with time. Although the absolute rates of formation of products are different in the two cells, the relative rates of formation are more-orless the same, with the maximum concentrations of propanone, 2-propanol, and 2-propyl hydroperoxide being in good agreement.

The maximum concentration of both propanone and 2-propanol and the time taken to reach this concentration decrease with increasing temperature, with the final ratio of 2-propanol to propanone also showing a marked increase. The maximum concentration of 2-propyl hydroperoxide is markedly lower at the highest temperature. The rate of growth of propene and 2,3-dimethylbutane also decrease with increasing temperature while for propane, an increase is observed.

Although the same products, propane, 2,3dimethylbutane, 2-propanol, propanone, and 2-propyl hydroperoxide are found in the photo-oxidation of the azo compound, there is one significant difference in

<i>T</i> / <i>K</i>	Cell	[Propane]/[Propene]	[Propene]/[2,3-Dimethylbutane]	Ref.
253	Glass	1.18 ± 0.03	1.63 ± 0.08	[3]
278	Glass	1.17 ± 0.05	1.38 ± 0.07	[3]
323	Glass	1.70 ± 0.04	1.25 ± 0.04	[3]
323	Metal	1.91 ± 0.05	1.26 ± 0.04	This work
348	Metal	2.16 ± 0.10	1.23 ± 0.10	This work

Table II Photolysis of 2, 2'-azopropane in Decane. Initial Concentration of 2, 2'-azopropane, 2.7×10^{-2} mol dm⁻³

Table III Photo-Oxidation of 2, 2'-azopropane (AZO) in Decane in a Metal Cell. Initial Concentration of AZO, 2.7×10^{-2} mol dm⁻³. Pr_{HC}, Pr_{OX}, and Pr_{TOT} refer to the Concentrations of 2-propyl Radicals which Form Hydrocarbon, Oxygenated, and Total Products.

					Concentra	ation 10	4/mol d	m ⁻³			
Oxygen Conc $10^3/\text{mol dm}^{-3}$	T/K	Photolysis Time / s	(CH ₃) ₂ CO	C ₃ H ₇ OH	C ₃ H ₈	C ₃ H ₆	C ₆ H ₁₄	C ₃ H ₇ OOH	Pr _{HC}	Prox	Pr _{TOT}
		1020	1.6	1.6	2.2	2.0	1.5	0.4	7.2	3.6	10.8
		1800	2.9	1.8	3.3	3.2	3.0	0.5	12.5	5.2	17.7
5.6	323	2700	3.5	3.0	5.6	5.0	4.3	0.7	19.2	7.2	26.4
		3780	4.8	4.0	7.4	6.9	6.1	0.9	26.5	9.7	36.2
		6000	6.2	4.4	10.3	10.0	7.5	1.1	35.3	11.7	47.0
		900	1.3	1.1	1.8	1.7	1.2		5.9	2.4	8.3
		1800	2.3	2.2	4.0	3.4	2.5	0.7	12.4	5.2	17.6
		2700	3.3	3.0	5.2	4.8	3.8	1.0	17.6	7.3	24.9
4.8	348	3600	4.1	4.0	7.1	6.6	4.8	2.0	23.3	10.1	33.4
		4500	5.4	4.6	8.4	7.6	6.0	1.8	28.0	11.8	39.8
		5400	6.4	6.0	9.8	9.2	7.2	2.2	33.4	14.6	48.0
		7200	8.6	7.8	13.2	12.3	9.8	3.2	45.1	19.6	64.7

Table IV Photo-Oxidation of 2,4-dimethyl-3-pentanone (KET) in Decane in Metal (M) and Glass (G) Cells. Initial Concentrations of KET, 2.7×10^{-2} mol dm⁻³. Pr_{HC}, Pr_{OX}, and Pr_{TOT} Refer to the Concentrations of 2-propyl Radicals which Form Hydrocarbon, Oxygenated, and Total Products

					Conc	entrati	on 104/	mol dm ⁻	3			
Oxygen Conc 10^3 /mol dm ⁻³	T/K	Photolysis Time / s	(CH ₃) ₂ CO	C ₁ H ₇ OH	C ₁ H ₈	C3H6	CeHia	PrOOH	PrOOPr	Ргис	Prox	Prtot
		000	3.5	3.0	01	13	0.1	0.7	0	1.6	7 2	2 2 2
		1800	5.5	J.0 7.6	0.1	1.5	0.1	1.4	0	1.0	15.2	171
		2700	14.2	1/ 0	27	2.2	0.1	0.3	07	74	10.Z	37.0
56	323(M)	3600	10.2	14.9	10.7	6.4	21	0.5	0.2	213	25.8	17.0
010	020(11)	4500	10.2	14.2	10.7	5.8	2.1	0	0.7	21.5	26.5	47.1
		5400	12.8	130	15.4	83	4.7	0	11	32 1	28.9	61.0
		7200	13.5	13.9	25.6	11.2	4.3	0	1.5	45.4	30.4	75.8
		900	1.2	0.8	0.02	0.1	0	0.6	0	0.1	2.6	2.7
4.8		1800	7.1	5.9	0.1	1.2	0	1.4	0	1.3	14.4	15.7
		1800	7.6	6.1	0.1	1.3	0	-	0	1.4	-	~
	348(M)	2700	11.5	6.4	0.2	1.8	0.03	1.6	0.03	2.0	19.5	21.5
		3600	9.5	9.3	10.6	4.0	0.3	0.1	0.7	15.2	20.3	35.5
		5400	8.7	10.4	21.4	5.9	0.6	0	1.3	28.5	21.7	50.2
		7200	10.6	15.5	42.6	8.1	1.0	0	2.2	52.7	30.5	83.2
		900	2.2	1.2	0.03	0.2	0	0.4	0	0.23	3.8	4.0
		1800	5.0	3.1	0.1	0.5	0	0.9	0	0.6	9.0	9.6
10	248(0)	2700	7.0	4.1	0.1	0.9	0	1.1	0	1.0	12.2	13.2
4.8	340(G)	3600	8.0	6.5	3.8	1.8	0.1	0	0.06	5.8	14.6	20.4
		5400	10.4	10.3	8.2	3.3	0.2	0	0.3	11.9	21.3	33.2
		7200	8.6	10.4	12.4	4.4	0.3	0	0.6	17.4	20.2	37.6
		900	4.2	1.7	0.1	0.4	0	0.2	0	0.5	6.1	6.6
		1800	6.1	2.8	2.6	0.9	0	0.4	0	3.5	9.3	12.8
		1800	9.0	4.4	2.1	0.9	0	0.4	0	3.0	13.8	16.8
4.3	373(M)	2700	9.5	6.6	5.1	1.8	0.1	0.1	0	7.1	16.2	23.3
		3600	7.4	6.3	12.2	2.1	0.1	0	0.16	14.5	14.0	28.5
		4500	4.8	6.0	25.0	3.1	0.2	0	0.51	28.5	11.8	40.3
		6000	4.5	6.0	32.6	3.8	0.5	0	0.86	37.4	12.2	49.6

Table V Photo-Oxidation of 2, 2'-azopropane in a Decane Solution Saturated with Oxygen. Yields of 2-propanol and Propanone. Initial Concentration of 2, 2'-azopropane, 2.7×10^{-2} mol dm⁻³

T/K	Cell	Yield of propanone compared to that of 2-propanol	Ref.
253	Glass	4.48 ± 1.55	[3]
278	Glass	1.89 ± 0.31	[3]
298	Glass	1.59 ± 0.31	[3]
323	Glass	1.11 ± 0.09	[3]
323	Metal	1.27 ± 0.34	This work
348	Metal	1.10 ± 0.08	This work

behavior between the azo and ketone systems: for the former all these products exhibit approximately linear growth over the whole extent of reaction studied (ca 15%). The results are compared with those obtained earlier in Tables V and VI.

On increasing the temperature the rate of formation of propanone relative to that of 2-propanol shows a slight decrease, whilst that of 2-propyl hydroperoxide increases relative to both 2-propanol and propanone. A small increase is also observed in the rate of production of 2,3-dimethylbutane relative to propene, whilst the growth of both these products is found to decrease relative to propane.

DISCUSSION

Initiation Reactions

In the photo-oxidation of 2,4-dimethyl-3-pentanone, hydrocarbons, except for propene, are only found when the oxygen concentration has been depleted. In contrast, for the azo precursor all the hydrocarbon products are formed along with oxygenated compounds from the start of the photo-oxidation. This has been observed previously [3,6] and has been attributed to the ketone yielding a triplet pair of alkyl and an acyl radicals in the cage (Reaction A):

$$\begin{array}{c} O \\ \parallel \\ R - C - R \end{array} \xrightarrow{h\nu} [RCO R] \end{array}$$
 (A)

Their lifetimes ensure that most of the radicals emerge from the cage and that the acyl radical decomposes. On the other hand, the azo compound photolyses to form a singlet pair of alkyl radicals (Reaction B), the majority of which react within the solvent cage to form hydrocarbons by dimerization or disproportionation:

$$\mathbf{R} - \mathbf{N} = \mathbf{N} - \mathbf{R} \xrightarrow{h\nu} [\mathbf{R} \mathbf{N}_2 \mathbf{R}] \qquad (\mathbf{B})$$

For the purpose of computer simulation, the primary processes in the photolyses of both precursors can be treated as two one-step reactions which yield either a pair caged or free radicals. For the azo compound, these are caged and free 2-propyl radicals, Q and Me₂CH, respectively (Reactions 1 and 2, Scheme I). Whereas for the ketone, the equivalent species are the caged and free alkyl and acyl radicals, Q and QCO and Me₂CH and Me₂CHCO, respectively (Reactions 3 and 4, Scheme I). The simulation program for Scheme I distinguishes between Me₂CH and QCO.

Rate constants $(k_1 + k_2)$ and $(k_3 + k_4)$ were calculated using experimental product yield and reaction time data (Tables III and IV). Although the products from Q and Me₂CH, and QCO and Me₂CHCO in this model are the same, it is important to determine the ratios of $k_1 : k_2$ and $k_3 : k_4$ as the amount of Me₂CH controls the observed excess of propane over propene and the value of the rate constant k_{11} is needed to simulate the product concentrations. However, as noted in another article [3], using just data from the photolysis experiments, it is impossible to calculate

Table VI Photo-Oxidation of 2, 2'-azopropane in a Decane Solution Saturated with Oxygen. Yields of Products. Initial Concentration of 2, 2'-azopropane, 2.7×10^{-2} mol dm⁻³. Products as Percentages of 2-propyl Radicals Generated

T/K	Cell	Propane + Propene	2,3-Dimethylbutane	Propanone	2-Propanol	2-Propyl hydroperoxide	Ref.
298	Glass	41	34	12	9	a	[3]
323	Metal	40	32	16	11	3	This work
323	Glass	41	34	13	11	a	[3]
348	Metal	41	30	14	12	5	This work

^aOnly trace determined.

this ratio; it is necessary to use the results from the photo-oxidation experiments.

The fate of the caged radicals are self-reactions resulting in either disproportionation (Reactions 6 and 7) or combination (Reaction 5) and the reverse of Reaction 3. It is assumed for the simulation of these systems that caged radicals do not react with the solvent or oxygen.

Initiation

Me ₂ CHN ₂ CHMe ₂	hυ →	$Q + Q + N_2$	(1)
Me ₂ CHN ₂ CHMe ₂	hu 	Me ₂ CH + Me ₂ CH + N ₂	(2)
Me ₂ CHCOCHMe ₂	<u>μ</u> υ	Q + QCO	(3)
Me ₂ CHCOCHMe ₂	hυ →	Me ₂ CH + Me ₂ CHCO	(4)

Cage reactions

$Q + Q \longrightarrow C_6 H_{14}$

Q + Q	 C_3H_8	+	C ₃ H ₆	(6)
Q + QCO	 C₃H ₆	+	Me _z CHCHO	(7)

Reactions outside the cage

Me	2CHC	20		Me₂CH	+	СО	(8)
Me	2CH	+ Me₂CH		C ₆ H ₁₄			(9)
Me	₂CH	+ Me₂CH	>	C_3H_8	+	C ₃ H ₆	(10)
Me	2CH	+ SH	>	C_3H_8	+	S	(11)
S	+	S		nonradic	al p	roducts	(12)
s	+	Me ₂ CH		C ₃ H ₆	+	SH	(13)
S	+	Me _z CH		C_3H_8	÷	S(-H)	(14)
s	+	Me₂CH		C13H28			(15)

(Q and QCO represent caged Me₂CH and Me₂CHCO radicals; SH is decane, S(-H) is decene and S represents a decyl radical).

Scheme I Reactions used to model the photolysis of 2, 2'-azopropane and 2,4-dimethyl-3-pentanone.

Photolysis of 2, 2'-Azopropane and 2,4-Dimethyl-3-Pentanone: Other Reactions

Following the primary process to generate radicals from the ketone, the free 2-methylpropanoyl radical undergoes rapid decarbonylation (Reaction 8). The temperature dependence of the decarbonylation of the 2-methylpropanoyl radical was studied by Lipscher and Fischer [7] who obtained an A-factor of 10^{14} s⁻¹ and an activation energy of 54.5 kJ mol⁻¹. These values were used in this work.

Free 2-propyl radicals can undergo self-reactions (Reactions 9 and 10) and, in addition, they can abstract hydrogen atoms from the solvent (SH) (Reaction 11). On increasing the temperature, reaction 11 becomes relatively more important and the yield of propane increases. The resulting solvent radicals (S) have numerous possible competing self-combination and disproportionation reactions, but to simplify the model these are collected into one general reaction which yields nonradical products (Reaction 12). Three cross-reactions with the 2-propyl radicals are also possible (Reactions 13-15).

Although the precise values of k_5 and k_6 are not needed, their ratio is. The relative rate of rotation of the radicals within the solvent cage is fast compared to self-reaction and the ratio of disproportionation to combination can thus be assumed to be the same for a caged radical pair as for a free radical encounter pair. Therefore, the rate constants assigned to Reactions 5 and 6 are the same as those for the analogous reactions of Me₂CH. Many studies have been performed on the self-reaction of 2-propyl radicals [7-10]. In this work, the data obtained by Lipscher and Fischer for the self-termination of 2propyl radicals (ie., $2k_9 + 2k_{10}$) determined using a number of solvents over the relevant temperature range, were employed [7]. However, their values for the ratio of k_9 and k_{10} , which ranged from 1.14 at 298 K to 1.05 at 353 K, disagree with those found by Salmon [8] (1.6 to 1.2 from 248 to 348 K) and by Sheldon and Kochi [9] (1.22 at 303 K). Those of Salmon are compatible with this work and thus the following Arrhenius parameters were used:

$$log(A_9/dm^3 mol^{-1} s^{-1}) = 10.4;$$

$$E_9 = 4.7 \text{ kJ mol}^{-1}$$

$$log(A_{10}/dm^3 mol^{-1} s^{-1}) = 10.4;$$

$$E_{10} = 4.3 \text{ kJ mol}^{-1}$$

The Arrhenius parameters used for the selfreaction of the decyl radicals were the same as those used in simulations of the corresponding *t*-butyl system [3]. The overall rate constants for the cross-reactions between 2-propyl and decyl radicals were estimated as lying between the rate constants for the two self-reactions, and the ratio of disproportionation to combination was calculated using the ratio for the 2-propyl radicals.

Values for the rates of the abstraction of hydrogen by 2-propyl radicals from decane are not available. As a first approximation, the value used for the corresponding reaction with *t*-butyl was employed, and then increased by approximately a third, to give a good fit between simulated and experimental results. This approximation was based on the reported similarity of their reactivity in other reactions [11].

The rate constants used are listed in Table VII and the simulated results compared with the experimental results. Examples are shown in Figures 1, 2, and 3. At both temperatures for both processes the simulated results are very close to the experimental product yields, the only real difference being the predicted rate of formation of propene is slightly higher than the observed rate at 323 K when the ketone was used.

The majority of rate constants was acquired from the literature, thus demonstrating the compatibility of this work with earlier studies. Particularly encouraging was the similarity between the values of k_{11} needed to achieve a good fit for the two precursors, 0.75 and 0.80 dm³ mol⁻¹ s⁻¹ at 323 K and 1.8 and 1.5 dm³ mol⁻¹ s⁻¹ at 348 K. These results give Arrhenius parameters of log(A₁₁/dm³ mol⁻¹ s⁻¹) of ca. 5.5 and E₁₁ of ca. 28 kJ mol⁻¹, similar to the values for the corresponding reaction with *t*-butyl [3], obtained in the same way. These values compare well with the experimentally determined values for the reaction of *t*-butyl radicals with 2-propanol, log(A/dm³ mol⁻¹ s⁻¹) = 6.0 and E = 30 kJ mol⁻¹ [12].

Overall, one set of rate constants were used to model the photolysis of the two precursors.

Photo-Oxidation of 2, 2'-Azopropane

The simulation of the experiments on the photooxidation of 2, 2'-azopropane in decane were based on the model produced for the photolysis of this azo compound (Scheme I). Complete oxygen depletion was not allowed to occur, simplifying the model as no free alkyl radical reactions need to be considered except those with oxygen (Scheme II).

The free 2-propyl radicals in an oxygen-saturated solution react rapidly to form 2-propylperoxyl radicals Me_2CHO_2 (Reaction 16). This reaction provides a means of distinguishing the caged radicals,

	Temperature/K					
Reaction No.	323	348	373			
1ª	1.7×10^{-5}	1.6×10^{-5}				
2ª	6.0×10^{-6}	6.9 × 10 ⁻⁶	_			
3ª	4.1×10^{-6}	1.2×10^{-6}	1.4×10^{-6}			
4 ^a	3.0×10^{-6}	1.9×10^{-5}	2.3×10^{-5}			
5	4.5×10^{9}	5.0×10^{9}	_			
6	5.4×10^{9}	5.9×10^{9}	_			
7	1.0×10^{10}	1.0×10^{10}	1.0×10^{10}			
8	1.5×10^{5}	4.7×10^{5}	2.3×10^{6}			
9	4.5×10^{9}	5.0×10^{9}	5.7×10^{9}			
10	5.4×10^{9}	5.9×10^{9}	6.7×10^{9}			
11 ^b	0.75	1.8	_			
11°	0.60	1.5	3.0			
12	6.9×10^{9}	9.0×10^{9}	1.1×10^{10}			
13	2.7×10^{9}	2.9×10^{9}	3.4×10^{9}			
14	2.7×10^{9}	2.9×10^{9}	3.4×10^{9}			
15	4.5×10^{9}	5.0×10^{9}	5.7×10^{9}			

Table VII Rate Constants Used in the Simulations of the Photolyses of 2, 2'-azopropane and 2,4-dimethyl-3-pentanone in Decane

Units for rate constants are $dm^3 mol^{-1} s^{-1}$, except ^a, where units are s^{-1} .

^bFor the photolysis of 2, 2'-azopropane.

^cFor the photolysis of 2,4-dimethyl-3-pentanone.

which form hydrocarbon products, from "free" radicals which form oxygenates. The values of k_1 and k_2 can be calculated from the total product concentrations of hydrocarbons and oxygenates (Table III). Consequently the ratio of cage reaction to cage escape can be calculated for use in the oxygen-free model.

Although no literature values exist for the rates of reaction of 2-propyl radicals with oxygen in hydrocarbon solvents, Maillard et al. [13] studied the analogous reaction of t-butyl and obtained a rate constant of 4.9×10^9 dm³ mol⁻¹ s⁻¹ at 298 K and Marchaj et al. [14] measured rate constants of 3.8×10^9 and 3.2×10^9 dm³ mol⁻¹ s⁻¹, respectively, for the reactions of 2-propyl and t-butyl with oxygen in aqueous solution at 298 K. Although the latter values are lower than those measured by Maillard et al., the similarity is encouraging and the rate constant due to Maillard et al. for t-butyl was used in this work.

The 2-propylperoxyl radical has a choice of selfreactions, termination (Reaction 17) and propagation (Reaction 18). Bennett [15] using u.v. spectroscopy to measure the concentration of peroxyl radicals, found Arrhenius parameters for the overall self-reaction of $A = 5 \times 10^9$ dm³ mol⁻¹ s⁻¹ and E = 20 kJ mol⁻¹. Other studies of the self-reactions of 2-propylperoxyl radicals [2,8,16] have been below 323 K where the



Figure 1 Photolysis of 2, 2'-azopropane in decane in a metal cell. Comparison of experimental and simulated data at 348 K. Azo compound, 2.7×10^{-2} mol dm⁻³. (Δ), 2,3-dimethylbutane; (\Box), propane; and (\bigcirc), propene.

contribution from the propagation reaction is assumed to be negligible and thus the overall rate constant is effectively that of reaction 17.

The self-reactions of a range of alkylperoxyl radicals have been well studied in the gas phase and are reviewed by Wallington et al. [17] and Lightfoot et al. [18]. Rate constants of $2k_t = 1.3 \times 10^6$ [19] and 1.6×10^{6} [20] dm³ mol⁻¹ s⁻¹ at 293 K were obtained for the overall self-reaction of 2-propylperoxyl radicals in the gas phase which compare well with the value of 1.6×10^6 dm³ mol⁻¹ s⁻¹ in the liquid phase obtained by Bennett [15]. Using detailed product studies as well as following the radical concentration by u.v. spectroscopy, a ratio of k_{18} : k_{17} increasing from 1.8 at 323 K to 2.8 at 373 K has been determined [21]. These values appear to be too high for the self-reaction in the liquid phase because a value of 1.8 would lead to a yield of 2-propanol much greater than that of propanone which clearly does not happen. One possible reason for this discrepancy is the solvent cage effect. In the gas phase, the two 2-propoxyl radicals formed in the self-reaction will quickly separate and react as discrete entities. In contrast in the liquid phase, the two 2-propoxyl radicals will be held together within a solvent cage thus increasing the chance of disproportionation oc-



Figure 2 Photolysis of 2,4-dimethyl-3-pentanone in decane in a metal cell. Comparison of experimental and simulated data at 348 K. Ketone, 2.7×10^{-2} mol dm⁻³. (\triangle), 2,3-dimethylbutane; (\Box), propane; and (O), propene.

curring to yield propanone and 2-propanol, the same products as form in Reaction 17. (This is discussed in more detail below). Thus the ratio of k_{18} : k_{17} may be the same in the two phases but, because of the solvent cage effect, the ratio in the liquid phase is distorted. Therefore, in the absence of any literature value for this ratio in the liquid phase, that used for the secondary solvent peroxyl radicals SO₂ in another study has been adopted [3].

The Arrhenius parameters used for reactions 17 and 18 were $\log(A/dm^3 mol^{-1} s^{-1}) = 8.1$ and 12.2 and E = 9.0 and 38.0 kJ mol⁻¹, respectively. In turn these compare with values obtained for the gas-phase reactions of 7.4, 9.1, 12.0, and 21.3, respectively [21].

The self-reaction of 2-propylperoxyl radicals to yield 2. 2'-dipropylperoxide and oxygen was found to be of negligible importance and excluded from the reaction scheme.

In addition to self-reaction, the 2-propylperoxyl radical can also abstract hydrogen from the solvent (Reaction 19). Bennett [15] calculated a rate constant of 6 to $12 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction of this

radical with dodecane at 396 K to form the hydroperoxide. The rate constants used in this work have been calculated from those of Bennett's and assuming an activation energy of ca 70 kJ mol⁻¹ [22]. However, in turn, the hydroperoxide reacts with alkyl radicals (reactions 46, 47) as the reaction proceeds, particularly as oxygen is depleted. These reactions increase in importance on raising the temperature.

The 2-propoxyl radical produced in the selfreaction of 2-propylperoxyl radicals can react with oxygen or solvent [22]. Balla et al. [23] measured a rate constant of 4.9×10^6 dm³ mol⁻¹ s⁻¹ for the reaction of 2-propoxyl radicals with oxygen in the gas phase at 323 K. Literature data do not exist for the abstraction of hydrogen from hydrocarbon substrates by this alkoxyl radical, but a rate constant of 2.5×10^6 dm³ mol⁻¹s⁻¹ was used similar to that used in the study on the *t*-butylperoxyl system [3]. A rate law was deduced, based on earlier work [24–26], and it was found that with solvent in vast excess over oxygen, the reaction between alkoxyl radical and oxygen could be safely ignored in the simulation.

The decyl radical, S, produced in Reactions 19 and 20 reacts rapidly with oxygen under these conditions



Figure 3 Photolysis of 2,4-dimethyl-3-pentanone in decane in a metal cell. Comparison of experimental and simulated data at 373 K. Ketone, 2.7×10^{-2} mol dm⁻³. (\triangle), 2,3-dimethylbutane; (\Box), propane; and (\bigcirc), propene.

$Me_2CH + O_2$		Me ₂ CHO ₂	(16)
$Me_2CHO_2 + Me_2CHO_2$		$Me_2CO + Me_2CHOH + O_2$	(17)
$Me_2CHO_2 + Me_2CHO_2$	>	$Me_2CHO + Me_2CHO + O_2$	(18)
Me ₂ CHO ₂ + SH		$Me_2CHO_2H + S$	(19)
Me ₂ CHO + SH	,	Me2CHOH + S	(20)
S + O ₂	>	SO 2	(21)
$SO_2 + SO_2$		S(-H)=O + SOH + O ₂	(22)
$SO_2 + SO_2$,	SO + SO + O ₂	(23)
SO ₂ + SH		SO₂H + S	(24)
SO + SH		SOH + S	(25)
$SO_2 + Me_2CHO_2$		$S(-H)=O + Me_2CHOH + O_2$	(26)
$SO_2 + Me_2CHO_2$,	$SOH + Me_2CO + O_2$	(27)
$SO_2 + Me_2CHO_2$,	SO + $Me_2CHO + O_2$	(28)
$Me_2CHCO + O_2$		Me ₂ CHCO ₃	(29)
Me ₂ CHCO ₃ + Me ₂ CHCO ₃	>	$Me_2CHCO_2 + O_2$	(30)
$Me_2CHCO_3 + SO_2$	>	$S(-H)=O + Me_2CHCO_2H + O_2$	(31)
Me ₂ CHCO ₃ + Me ₂ CHO ₂	>	$Me_2CHCO_2H + Me_2CO + O_2$	(32)
$Me_2CHCO_3 + SO_2$	-	$Me_2CHCO_2 + SO + O_2$	(33)
Me ₂ CHCO ₃ + Me ₂ CHO ₂	,	$Me_2CHCO_2 + Me_2CHO + O_2$	(34)
Me ₂ CHCO ₃ + SH		Me ₂ CHCO ₃ H + S	(35)
Me ₂ CHCO ₂	;	$Me_2CH + CO_2$	(36)
Me2CHCHO	hu ———	Me ₂ CH + HCO	(37)
HCO + O₂		HO ₂ + CO	(38)
$HO_2 + HO_2$		$H_2O_2 + O_2$	(39)
$HO_2 + Me_2CHO_2$	>	$Me_2CHO_2H + O_2$	(40)
HO ₂ + SO ₂	>	$SO_2H + O_2$	(41)
$HO_2 + Me_2CHCO_3$	>	$Me_2CHCO_3 H + O_2$	(42)
HO ₂ + SH		$H_2O_2 + S$	(43)
$Me_2CH + Me_2CHO_2H$	>	C_3H_8 + Me_2CHO_2	(44)
S + Me ₂ CHO ₂ H		$SH + Me_2CHO_2$	(45)
Me ₂ CH + SO ₂ H		$C_3H_8 + SO_2$	(46)
S + SO₂H		SH + SO ₂	(47)
$Me_2CH + Me_2CHO_2$		Me ₂ CHO ₂ CHMe ₂	(48)
Me ₂ CH + SO ₂		SO ₂ CHMe ₂	(49)
S + Me ₂ CHO ₂		SO ₂ CHMe ₂	(50)
$S + SO_2$;	SO₂S	(51)

(S represents decyl)

Scheme II Additional reactions used to model the photo-oxidation of 2, 2'-azopropane and 2,4-dimethyl-3-pentanone.

Reaction No.	Temperature/K		
	323	348	373
la	1.7×10^{-5}	1.6×10^{-5}	_
2ª	6.4×10^{-6}	6.9×10^{-6}	_
3 ^{a,b}	3.0×10^{-6}	2.4×10^{-6}	1.4×10^{-6}
3 ^{a,c}	_	8.6×10^{-7}	-
4 ^{a,b}	3.9×10^{-5}	3.0×10^{-5}	2.2×10^{-6}
4 ^{a,c}	_	1.4×10^{-5}	-
5	4.5×10^{9}	5.0×10^{9}	-
6	5.4×10^{9}	5.9×10^{9}	-
7	1.0×10^{10}	1.0×10^{10}	1.0×10^{10}
8ª	1.6×10^{5}	5.0×10^{5}	2.0×10^{6}
16	5.2×10^{9}	5.4×10^{9}	5.6×10^{9}
17	3.5×10^{6}	4.9×10^{6}	5.8×10^{6}
18	3.5×10^{5}	1.1×10^{6}	2.8×10^{6}
19	1.7×10^{-3}	1.2×10^{-2}	7.4×10^{-2}
20	2.5×10^{6}	3.9×10^{6}	5.6×10^{6}
21	5.2×10^{9}	5.4×10^{9}	$5.6 \times 10^{\circ}$
22	4.7×10^{6}	5.5×10^{6}	5.8×10^{6}
23	4.7×10^{5}	1.4×10^{6}	3.9×10^{6}
24	1.7×10^{-3}	1.2×10^{-2}	7.4×10^{-2}
25	2.5×10^{6}	3.9×10^{6}	5.6×10^{6}
26	1.5×10^{6}	2.0×10^{6}	3.3×10^{6}
27	1.5×10^{6}	2.0×10^{6}	3.3×10^{6}
28	3.5×10^{5}	1.0×10^{6}	2.7×10^{6}
29	5.2×10^{9}	5.4×10^{9}	5.6×10^{9}
30	1.4×10^{7}	1.9×10^{7}	2.5×10^{7}
31	1.6×10^{7}	1.9×10^{7}	2.4×10^{7}
32	1.4×10^{6}	1.8×10^{6}	2.2×10^{6}
33	1.6×10^{6}	4.0×10^{6}	6.8×10^{6}
34	1.4×10^{6}	3.4×10^{6}	6.0×10^{6}
35	1.7×10^{-3}	1.2×10^{-2}	7.4×10^{-2}
36 ^a	1.1×10^{10}	1.1×10^{10}	1.1×10^{10}
37 ^{a,b}	3.5×10^{-6}	2.4×10^{-6}	2.2×10^{-6}
37 ^{a.c}	_	1.3×10^{-6}	_
38	5.2×10^{9}	5.4×10^{9}	5.6×10^{9}
39	1.5×10^{9}	1.7×10^{9}	1.9×10^{9}
40	1.5×10^{8}	2.0×10^{8}	2.6×10^{8}
41	1.7×10^{8}	2.2×10^{8}	2.7×10^{8}
42	2.9×10^{8}	3.6×10^{8}	4.4×10^{8}
43	6.8×10^{-3}	3.6×10^{-2}	0.19
44	73	143	300
45	73	143	300
46	73	143	300
47	73	143	300
48	5.2×10^{9}	5.4×10^{9}	5.6×10^{9}
49	5.2×10^{9}	5.4×10^{9}	5.6×10^{9}

Table VIII Rate Constants Used in the Simulations of the Photo-Oxidation of 2, 2'-azopropane and 2,4-dimethyl-3-pentanone in Decane

Table VIII.	(Continued)
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Reaction No.	Temperature/K		
	323	348	373
51	5.2×10^{9}	5.4×10^{9}	5.6×10^{9}

Units for rate constants are $dm^3 mol^{-1} s^{-1}$, except ^a, where units are s^{-1} .

^bMetal cell.

^cGlass cells.

Reactions 9-15 are listed in Table IV.

to form a decylperoxyl radical SO₂ (Reaction 21). Similar rate parameters for reactions 22-25, to those used in our study of *t*-butyl radicals have been employed here [3]. Because both peroxyl radicals in this system are secondary, there are three cross-reactions (Reactions 26-28). Literature values do not exist for their rate parameters and the cross-combination rule was used. The termination reactions were given the same rate constants, the difference in energy between the two transition states being assumed to be negligible. The value used for the ratio of nontermination to the termination reactions was assumed to be the same as for the two self-reactions.

The rate constants used in the simulations of this system are listed in Table VIII and simulated product concentrations compared with the experimental values in Figures 4 and 5. The correlation between the two sets of results is not as close as that obtained with photolysis experiments at 323 K, the rate of production of all the oxygenated products appears to be decreasing at long reaction times with a corresponding increase in that of the hydrocarbon products but this is not seen int the model. Further, because of the significant differences in Arrhenius parameters for reactions 17 and 18 discussed above, the ratio of yields of propanone to 2-propanol will increase, according to the model, from 1.0 at low temperatures to >1.0 at higher temperatures, and indeed this increase in the ratio does occur in the gas phase [21]. In the liquid phase however, there is an unexpectedly large amount of "excess" propanone at low temperatures. This excess of ketone over alcohol was noted by Bennett and Summers [27] for the selfreactions of various secondary alkylperoxyl radicals. They proposed that the alkylperoxyl radicals were able to terminate by another concerted mechanism (Reaction C) in addition to the Russell mechanism. There is another plausible pathway. As was discussed

$$2 \operatorname{Me_2CHO_2} \longrightarrow \begin{bmatrix} \operatorname{Me} & \operatorname{O_O} & \operatorname{H} & \operatorname{Me} \\ \operatorname{Me} & \operatorname{H} & \operatorname{O_O} & \operatorname{Me} \end{bmatrix} \longrightarrow$$
$$2 \operatorname{Me_2C} = \operatorname{O} + \operatorname{H_2O_2}$$
(C)

earlier, the ratio of termination to propagation selfreactions of 2-propylperoxyl radicals appears to be much higher in the liquid phase than in the gas phase. The difference may be due to a solvent cage effect in which 2-propoxyl radicals, formed by reaction 18, undergo disproportionation whilst still in the solvent cage [9]. These 2-propoxyl radicals are produced from the decomposition of the tetroxide intermediate which also yields a molecule of oxygen (Reaction D):

$$Me_2CHOOOOCHMe_2 \longrightarrow$$

$$[Me_2CHO O_2 OCHMe_2]$$
(D)

Since the oxygen is contained within the same solvent cage as the two 2-propoxyl radicals, oxidation of 2-propoxyl radical within the solvent cage could be a kinetically viable process (Reaction E):

$$[Me_2CHO O_2 Me_2CHO] \longrightarrow$$

$$[Me_2C=O HO_2 Me_2CHO] \qquad (E)$$

However, for this reaction to result in an excess of ketone the other 2-propoxyl radical must also form propanone rather than diffuse out of the solvent cage and abstract a hydrogen atom to yield 2-propanol. This can be achieved by reaction with the hydroperoxyl radical still within the solvent cage (Reaction F):

$$[Me_2C=O HO_2 Me_2CHO] \longrightarrow 2Me_2C=O + H_2O_2$$
(F)



Figure 4 Photo-oxidation of 2, 2'-azopropane in a metal cell. Comparison of experimental and simulated data at 323 K. Azo compound, 2.7×10^{-2} mol dm⁻³ and oxygen, 5.6 × 10⁻³ mol dm⁻³. (\triangle), 2,3-dimethylbutane; (\blacktriangle), 2-propanol: (\Box), propane; (\bigcirc), propane; (\diamondsuit), propanone; and (\bigcirc). 2-propyl hydroperoxide.

There are no direct kinetic data to compare the rate of reaction (F) with that of reaction (G):

$$[Me_2C=O HO_2 Me_2CHO] \longrightarrow Me_2C=O + Me_2CHOH+O_2$$
(G)

However, by using enthalpies of formation of the reactants and products, reaction (F) can be shown to be the more favorable route by some 117 kJ mol⁻¹, although it is not known how important this reaction is compared to cage escape which would result in free 2-propoxyl and hydroperoxyl radicals. In contrast to 2-propoxyl radicals, hydrogen abstraction reactions for hydroperoxyl radicals will be unimportant and therefore reaction with other radical species predominates, for example by reaction 42.

The reaction between alkoxyl radicals and solvent will increase in importance as the temperature is increased, leading to higher yields of propanol.

The remainder of the products all give a good fit to the simulation with some relatively minor problems (Figs. 4 and 5). For example, the small experimentally observed difference between the concentrations of propane and propene is not seen in the simulated results. Secondly, although the overall fit for the simulated results at 348 K for the photo-oxidation of the azo compound is good, the ratio of propanone to 2-propanol again differs between the two sets of results. The simulated results predict an excess of 2-propanol over propanone which was not observed experimentally.

Photo-Oxidation of 2,4-Dimethyl-3-Pentanone in Decane

The mechanism used was based on that described for the photolysis of the ketone (Scheme I) and that for the photo-oxidation of 2, 2'-azopropane (Scheme II). However, the initial photochemical steps of the photolysis of 2,4-dimethyl-3-pentanone lead to the formation of the free 2-methylpropanoyl radical. In oxygen-free solvent, this radical decarbonylates (Reaction 8) but in oxygen-saturated solvent, competition arises from the reaction with oxygen to yield a 2-methylpropanoylperoxyl radical (Reaction 29), the rate of which is assumed to be



Figure 5 Photo-oxidation of 2, 2'-azopropane in a metal cell. Comparison of experimental and simulated data at 348 K. Azo compound, 2.7×10^{-2} mol dm⁻³ and oxygen, 4.8×10^{-3} mol dm⁻³. (Δ), 2,3-dimethylbutane; (\blacktriangle), 2-propanol; (\Box), propane; (\bigcirc), propane; (\diamondsuit), propanone; and (\bullet), 2-propyl hydroperoxide.

diffusion-controlled. The 2-methylpropanoylperoxyl radical behaves in the same way as the other peroxyl radicals already discussed and for the self-reaction (Reaction 30) the rate parameters for the *t*-butyl analogue, 2,2-dimethylpropanoylperoxyl, were used in this work [3]. The 2-methylpropanoylperoxyl radical also undergoes cross-reactions with both 2-propylperoxyl and decylperoxyl radicals, and because these two radical are secondary, both termination and propagation reactions are likely (Reactions 31–34). The values for the rate constants of these reactions were calculated using the cross-combination rule.

The 2-methylpropanoylperoxyl radical can also abstract hydrogen from the solvent (Reaction 35). Again no literature value exists for the rate constant and the value for the corresponding reaction of the 2,2-dimethylpropanoylperoxyl radical was used [3]. A rate constant of $1.1 \times 10^{10} \text{ s}^{-1}$ at 293 K for the decarboxylation of 2-methylpropanoyloxyl radical (Reaction 36) has been determined [28]. It was assumed that no other reaction of this radical competes with decarboxylation.

2-Methylpropanal was not detected amongst the products and it was assumed, as found previously for 2,2-dimethylpropanal, that it is rapidly photolyzed yielding 2-propyl and formyl radicals (Reaction 37). Reactions 38-51 were introduced to account for the subsequent reactions of these species.

As the oxygen dissolved within the solvent is depleted during photolysis, other reactions become important. These include the reactions of alkyl radicals already discussed in the oxygen-free models (Reactions 9-15). Furthermore, the decrease to zero of the concentration of 2-propyl hydroperoxide subsequent to oxygen depletion is attributed to the abstraction of hydrogen by either of the two alkyl radicals, 2-propyl, and decyl (Reactions 44 and 45). The reactions of decyl hydroperoxide were also included (Reactions 46 and 47), using rate constants for analogous reactions in the t-butyl system [3]. A further consequence of the oxygen depletion, is the large reduction in the concentration of peroxyl radicals. However, there is also a resultant increase in the concentration of alkyl radicals and thus there is the possibility of cross-reactions which result in the formation of a dialkylperoxide. The rates of these cross-reactions were assumed to be diffusion-controlled,

The rate constants used in the final model are listed in Tables VII and VIII and examples of the comparison between the model and experimental results are given in Figure 6. The results shown in Figure 6 are particularly pleasing as the model accounts well for the product distribution for the reaction in presence of oxygen, as the oxygen depletes, and after it has



Figure 6 Photo-oxidation of 2,4-dimethyl-3-pentanone in a metal cell. Comparison of experimental and simulated data at 323 K. Ketone, 2.7×10^{-2} mol dm⁻³ and oxygen, 5.6×10^{-3} mol dm⁻³. (\triangle), 2,3-dimethylbutane; O, 2,2'-dipropylperoxide; (\Box), propane; (\blacktriangle), 2-propanol; (\diamondsuit), propanone; (\bigcirc), propene; and (\bigcirc), 2-propyl hydroperoxide.

been consumed. Nevertheless, the predicted time for depletion at both 323 and at 348 K is slightly greater than that observed. Further, the model predicts that the concentrations of propanone and 2-propanol are similar and this does not occur early in the reaction. However, it is encouraging that there are good fits for two sets of experiments performed in the metal and glass cells. This is an excellent test as only the rate constants for the two photolysis steps are different, which is to be expected, and small changes, within experimental error had to be made to reaction 11 (Table VII).

CONCLUSION

A mechanism is presented to account for the reactions of 2-propyl and 2-propylperoxyl radicals in a hydrocarbon solvent, using two different precursors, 2, 2'-azopropane and 2,4-dimethyl-3-pentanone. The time-dependent product distributions from both precursors, under varying conditions, have been effectively modeled by computer simulation, and tested by changing the conditions to include reactions in

CONCLUSION

A mechanism is presented to account for the reactions of 2-propyl and 2-propylperoxyl radicals in a hydrocarbon solvent, using two different precursors, 2, 2'-azopropane and 2,4-dimethyl-3-pentanone. The time-dependent product distributions from both precursors, under varying conditions, have been effectively modeled by computer simulation, and tested by changing the conditions to include reactions in two different reactors, over a wide temperature range and in the presence and absence of oxygen.

The key to understanding these processes has been to distinguish between the reactions of the germinate pair of radicals formed by photolysis within a solvent cage and those that occur in the bulk of solution. This has been achieved with oxygen-saturated solutions by assuming that radicals that escape the solvent cage are all trapped by oxygen whereas those that remain inside the solvent cage are not. This interpretation also accounts for the difference in the product distributions of gas and solution phase photo-oxidations since the former do not involve a solvent cage.

In some of the reactions, in particular those at higher temperatures where the concentrations of oxygen in decane are lower, near, or complete consumption of oxygen occurs during reaction. The kinetic model accommodates this and accounts for the marked change in product distribution, an increase in hydrocarbons at the expense of oxygen-containing products. Other more subtle product changes that occur when the oxygen is consumed including a decrease in the yield of 2-propyl hydroperoxide and an increase in 2, 2'-dipropylperoxide, are also predicted by the model as a result of the increase in the concentration of alkyl radicals in the anaerobic solutions.

The solution not only influences the reactions through the cage reactions described above but also through its reactions with the 2-propyl, 2propylperoxyl, and 2-propoxyl radicals. This work together with that on the *t*-butyl analogues is the first part of a wider current study towards understanding the reactions of more complex oxygenated radicals, such as those derived from the esters used as synthetic lubricating oils.

We thank John Pragnell and Dr. Andrew Markson, of Castrol International, for helpful discussions, and their company for generous financial support throughout this study.

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