nitrogen in the coal will react with the alkylating agent. N-alkylation often is a much faster process than O-alkylation. The N-alkylation which occurs in coal is primarily unprotonated coal nitrogen going to form an *N*-alkylammonium halide by the coal's reaction with the corresponding alkyl halide. An example would be pyridine going to form *N*-methylpyridinium iodide when reacted with iodomethane. Illinois coal consumed 3.50 mmol of iodomethane/g of dry coal in the presence of a quaternary ammonium hydroxide. Only 2.85 mmol was hydroxyl and the remainder 0.65 mmol was N. Since Illinois no. 6 coal has 1.23% N, there are 0.88 mmol of nitrogen/g of coal. Apparently about three-fourths of them were alkylated. However, within the limits of the experimental error and given the rather small value of the nitrogen level in this coal, all of the nitrogen should be considered alkylatable.

During the routine drying procedure, the coal derivative is put into a vacuum oven and heated to 110 °C overnight. This treatment decomposes the *N*-methylammonium iodide salts which had formed during the methylation step. Only the O-methylated functionality survived this treatment (see Figures 1–3).

Procedure. In a 200-mL round-bottom flask the following were added: (1) 2-naphthol (0.6272 g, 4.35 mmol), (2) Illinois no. 6 coal (1.2947 g, 3.55 mmol of OH plus 1.09 mmol of nitrogen), (3) THF (50.0 mL, freshly distilled), and (4) tetra-*n*-butylammonium hydroxide (1.00 M aqueous, 10.00 mmol). After 30 min of mixing at ambient temperature under a static atmosphere of nitrogen, iodomethane-d_3 (0.7687 g, 5.31 mmol) was added. Two hours later, 20 mL of 1 M HCl was used to quench the reaction. The next day, the reaction mixture was filtered and the solid product was transferred to a Soxhlet thimble and exhaustively washed with methanol for 48 h. The methanol extract (50 mL) was combined with the original filtrate, and then ether (50 mL) was added to effect a phase separation. This solution was carefully concentrated by evaporating off most of the ether and some of the methanol at 30 °C under partial vacuum. At this point the internal standard 1-heptanol (0.3413 g, 2.94 mmol) was added, and the solution was analyzed by gas chromatography for 2-naphthol (1.82 mmol) and the methylated d_3 derivative (2.48 mmol).

The solid coal derivative was transferred from the Soxhlet thimble to the vacuum oven where it was dried at 110 °C overnight. The compositional analysis revealed the following: % moisture 0.05; % C, 66.96; % H, 4.44, % D, 0.80. The empirical formula of this partially alkylated coal is $C_{100.0}H_{79.6}D_{7.2}$. Since 7.2 D per 100 carbons were found, then 2.4 CD_3 must be present per 100 carbons. Thus, just less than half of the available O–H sites in the coal reacted while slighlty more than half of the 2-naphthol was O-methylated. These findings confirmed the GC results.

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Liquid-Phase Autoxidation of Organic Compounds at Elevated Temperatures. 2. Kinetics and Mechanisms of the Formation of Cleavage Products in *n*-Hexadecane Autoxidation

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Abstract: The cleavage products from the autoxidation of liquid *n*-hexadecane in a stirred flow reactor at 160 and 180 °C and 100–110 kPa of oxygen gas pressure have been determined. In the range of 0.1–2.3 mol % conversions the cleavage products are alkanoic acids, methyl ketones, 1-oxo- and/or 1-oxyalkanes, H_2O_2, CO_2, and CO. Measurable quantities of esters and γ-lactones first appear at higher conversions. These results together with those obtained from studies of the thermal decomposition of primary autoxidation products are consistent with two independent modes of cleavage product formation. The first process accounts for the formation of methyl ketones and 50–60 percent of the acids. It involves a first-order molecular decomposition of di- and trifunctional C_{16} autoxidation products which contain α,γ-hydroperoxy ketone structures. The rate constants for the decomposition (in s^{-1}) obey the Arrhenius equation in the temperature range of 120–180 °C with log A equal to 12.3 and $\Delta E^{\ddagger}$ equal to 30 kcal/mol. The second cleavage sequence accounts for the formation of the remaining acids and other cleavage products. This sequence involves reactions of alkoxy radicals formed from initiation reactions and from nonterminating decomposition of dialkyl tetroxide intermediates. Combining these results with those reported in earlier work, the reactivity ratios per hydrogen atom for intra- and intermolecular hydrogen atom transfer reactions of chain-carrying peroxy radicals have been determined for the *n*-hexadecane system at 120 to 180 °C. From these reactivity ratios and the number of hydrogen atoms available for each process, the relative contributions of α,γ-cleavage processes in the liquid-phase autoxidation of *n*-alkanes as a function of the number of methylene groups per molecule have been estimated.

Present knowledge of the kinetics and mechanism of cleavage product formation in the oxidation of *n*-alkanes is limited to the *n*-butane system. Mill et al.[1] showed that the cleavage products from the initiated oxidation of liquid and gaseous *n*-butane at 125 °C could be accounted for by the reactions of alkoxy radicals formed in nonterminating bimolecular reactions of chain-carrying peroxy radicals. However, in the extension of their studies to *n*-pentane and *n*-octane[2] product complexity and incomplete product recovery precluded kinetic analyses of cleavage processes.

This study reports the results of an investigation of the formation of cleavage products in *n*-hexadecane autoxidation by using the stirred flow reactor technique. The technique was previously used in the study of the formation of C_{16} primary oxidation products in *n*-hexadecane autoxidation.[3] This led to the discovery of

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[†] Deceased Feb 4, 1981.

(1) T. Mill, F. Mayo, H. Richardson, K. Irwin, and D. L. Allara, *J. Am. Chem. Soc.*, **94**, 6802 (1972).

(2) D. E. Van Sickle, T. Mill, F. R. Mayo, H. Richardson, and C. W. Gould, *J. Org. Chem.*, **38**, 4435 (1973).

(3) R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, *J. Am. Chem. Soc.*, **101**, 7574 (1979).

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Table I. Analyses of Cleavage Alkanoic Acids and Methyl Ketones in Oxidized *n*-Hexadecane from Run 151 ($[\text{-OOH}]_R = 631 \times 10^{-4}$ M; $[\text{-COOH}] = 154 \times 10^{-4}$ M)[a]

	10^4 [X], M						
	alkanoic acids[b]						
		method 2					
		oxy fraction		fractions 8–10[d]		methyl[c] ketones	
cleavage products	method I GLC	GLC	HPLC	GLC	HPLC	GLC	HPLC
C_4	8.5						5.9
C_5	8.1	7.3		9.3			6.7 (2)^2
C_6	7.9	8.3		9.4			8.2 (0)^2
C_7	8.0	8.7		9.7			9.1
C_8	8.6	9.4		10.1			8.9 (1)^2
C_9	8.3			10.0			
C_{10}	8.0	9.3	12.0		12.0	7.3	45.1 (6)^2
C_{11}	7.5	8.4	10.7[g]		9.4[g]	7.3	
C_{12}	5.8	7.2	8.7[g]		12.8[g]	(8.5)	
C_{13}	4.4		5.4		6.0	6.3	
C_{14}			1.2		1.5	4.9	
C_{15}			~0.3		~0.5	2.3	
C_{16}			~1.0[g]		~1.8[g]		
[R'COOH][e]	91	100 ± 3		115[h]			
$[CH_3COR']$[f]						91	90

[a] The uncertainties of measured values are indicated in parentheses. The values listed are averages obtained by independent analyses; their number is given by a number superscript. For example, 8.9 (1)^2 denotes that two measured values lay in the range 8.9 ± 0.1. [b] Determined as *p*-bromophenacyl esters. [c] Determined as $[CH_3CH(OH)R']_A$ by using GLC and directly using high-pressure LC. [d] Fractions 8–10 were obtained from liquid–solid chromatographic separation on silica gel. The reported results represent the sum from separate analyses of each fraction. [e] Reference 6. Yields of products which could not be determined due to the interferences were estimated from the results of alternate analyses. [f] Reference 9. [g] Values reported might be overestimated due to slight interferences of other components with high-pressure LC peaks of analyzed products. [h] The combined total acid titer for fractions 8–10 was 139×10^{-4} M and for all acid product containing fractions (8–13) 168×10^{-4} M.

intramolecular hydrogen atom abstraction reactions which are important in the oxidation of all *n*-alkanes larger than *n*-butane.

Experimental Section

The reaction techniques, some of the analytical procedures, and many materials used in this study were described in the previous paper of this series.[3] General experimental methods, materials used, and methods for identification and determination of cleavage products are described in the supplementary material.[12] Typical results obtained from the analyses of two major groups of cleavage products, alkanoic acids and methyl ketones, are presented in Table I.

Thermal Decomposition of C_{16} Oxidation Products. The decomposition experiments were carried out in the batch reactor described previously.[3] The 40-mL samples of *n*-hexadecane were first oxidized to obtain a desired total hydroperoxide concentration in the oxidate at 120, 160, or 180 °C.[13] At that point 21–55 mg of antioxidant, 2,6-di-*tert*-butyl-4-methylphenol, was added without interruption of the oxygen flow. Samples of reaction mixture were then withdrawn from the reactor as a function of time. They were immediately quenched at an ice-bath temperature and analyzed as described above and in the first paper of this series.[3] Typical results from these experiments are presented in Table II.

Results and Discussion

General Data. Table III gives the results from analyses of the cleavage products formed in the initial stages of the autoxidation of *n*-hexadecane in the stirred flow reactor at 160 and 180 °C. The yields of all cleavage products increase with hydrocarbon conversion; the ratio of the yields of total acid products, [–COOH], to monofunctional C_{16} products, $[ROH]_A$,[8] increases from ca. 0.18 at $[ROH]_A$ equal to 20×10^{-4} M to 0.38 at $[ROH]_A$ equal to 400×10^{-4} M. At both temperatures the major carbon cleavage products are methyl ketones, CH_3COR', and alkanoic acids. Other cleavage products are H_2O_2, 1-oxo- and/or 1-oxy-substituted alkanes ($R'CHO + R'CH_2O$–), CO_2, and CO.

Despite considerable efforts (cf. supplementary material),[12] our knowledge of the types and the yields of the individual acid products is not complete. By the extraction method the ratios of the sum of the yields of individual alkanoic acids, [R'COOH], to total acids is found to be ca. 0.6. This ratio represents a minimum value since careful liquid–solid separation on silica gel of a sample from run 151 gave a ratio equal to 0.7. The residual

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(4) No condensable cleavage *n*-alkanes or *n*-alkenes were detected in oxidates by GLC analysis of hydrocarbon fractions obtained from oxy fraction concentration on silica gel.[3]

(5) H. D. Durst, M. Milano, E. J. Kikta, S. A. Connelly, and E. Grushka, *Anal. Chem.*, 47, 1797 (1975).

(6) The total yields of alkanoic acids, [R'COOH], were calculated as a sum of yields of C_1–C_{16} alkanoic acids. The yields of C_1–C_3 alkanoic acids were estimated from the yields of C_{13}–C_{15} methyl ketones by assuming that they originate from the decomposition of the same α,γ-hydroperoxyhexadecanone isomers (vide infra).

(7) M. Zinbo, R. K. Jensen, and S. Korcek, *Anal. Lett.*, **10**, 119 (1977).

(8) The designation of the reducing reagents used in this work is the same as that used in the first paper of this series,[3] i.e., $NaBH_4$ (A), $LiAlH_4$ (B), and triphenylphosphine (C). The subscripts in concentration terms correspond to this designation.

(9) The total yields of methyl ketones were estimated from the yields of individual methyl ketones, which were determined as 2-alkanols in the $NaBH_4$-reduced samples, by using the expression

$$[CH_3COR'] = {}^{10}\!/_3([2\text{-}C_{10}H_{21}OH]_A + [2\text{-}C_{11}H_{23}OH]_A + [2\text{-}C_{12}H_{25}OH]_A) + [2\text{-}C_{13}H_{27}OH]_A + [2\text{-}C_{14}H_{29}OH]_A + [2\text{-}C_{15}H_{31}OH]_A$$

This expression was derived by assuming that methyl ketones are formed by cleavage of isomeric α,γ-hydroperoxyhexadecanones (vide infra) and that the yields of isomers which originate from the same hexadecylperoxy radical isomer are the same.

(10) The total yields of 1-oxo- and/or 1-oxy-substituted alkanes were calculated by using the expression

$$[R'CH{=}O] + [R'CH_2O\text{-}] = 2([1\text{-}C_8H_{17}OH]_A + \ldots + [1\text{-}C_{13}H_{27}OH]_A) + [1\text{-}C_{14}H_{29}OH]_A$$

This expression was derived by assuming that the major components in this group of cleavage products originate from alkyl radicals formed on cleavage of hexadecyloxy radicals (vide infra). An alternate assumption that both the cleavage aldehydes and alkyl radicals contributed equally to the yields of these products gives only slightly lower total yields, e.g., for run 151 (see Table I) it was lower by 2%. The yields $[1\text{-}C_{14}H_{29}OH]_A$ were assumed to be equal to $[1\text{-}C_{13}H_{27}OH]_A$ in all these calculations.

(11) B. D. Boss, R. N. Hazlett, and R. L. Shepard, *Anal. Chem.*, **45**, 2388 (1973).

(12) See paragraph at the end of paper regarding supplementary material.

(13) In the 180 °C batch reactor experiments an increase of temperature during the oxidation period was observed due to the exothermicity of the reaction and insufficient heat transfer with the constant temperature bath. In order to reach 180 °C at the desired conversion, we started the oxidation at a lower temperature (120–140 °C).

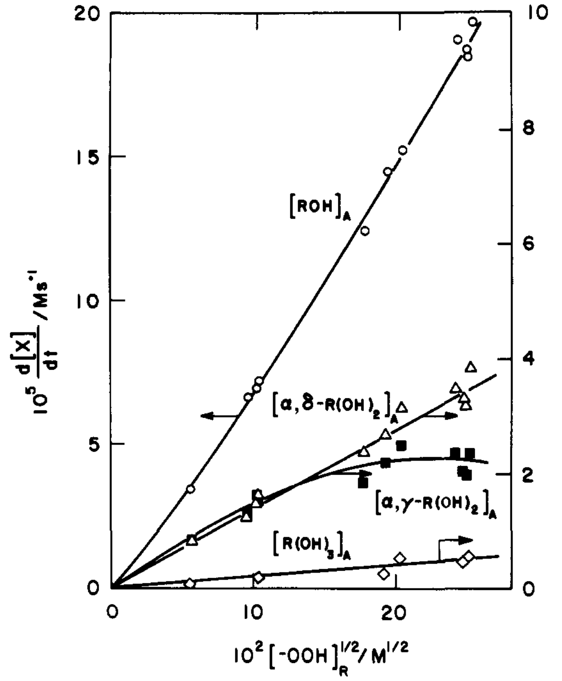


Figure 2. The instantaneous rates of formation of mono-, di-, and trifunctional oxidation products vs. $[-OOH]_R^{1/2}$ at 180 °C.

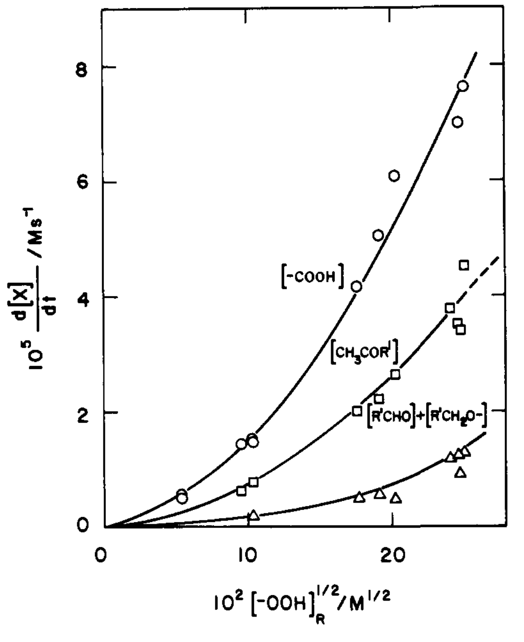
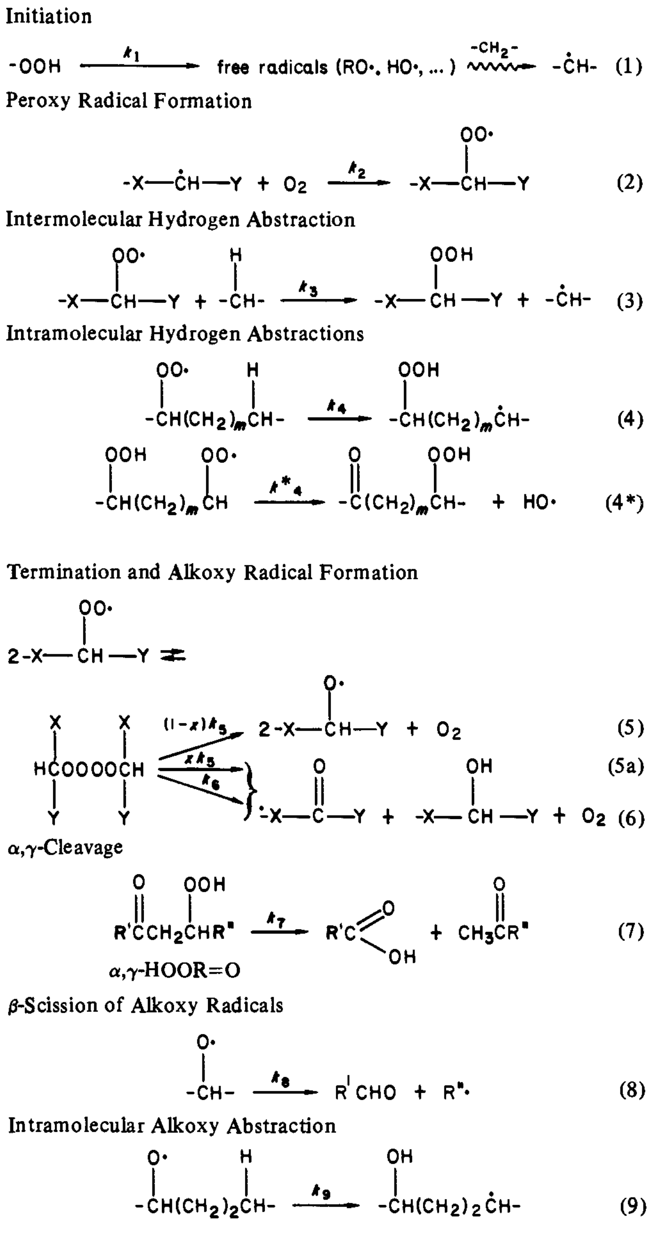


Figure 3. The instantaneous rates of formation of various cleavage products vs. $[-OOH]_R^{1/2}$ at 180 °C.

acid products are probably substituted acids. Although the presence of 4-oxo- or 4-oxy-substituted acids was established by a silica gel separation—LiAlH$_4$ reduction procedure quantitative estimates of their concentrations were not possible.

In Table IV are the yields of cleavage products formed at higher conversions. These data are not amenable to detailed analyses,[14] however, they show that the products obtained under these conditions are similar to those reported for hydrocarbon autoxidation by earlier workers[2,15,16] and that esters and γ-lactones are formed

Scheme I



at appreciable levels only at longer reaction times.

Rates of Product Formation. Plots of instantaneous rates of formation of mono-, di-, and trifunctional primary oxidation products[17] vs. the square root of the total hydroperoxide titer, $[-OOH]_R^{1/2}$, at 180 °C based on the results of our previous study[3] are shown in Figure 2. Similar plots were obtained at 120 and 160 °C. In these plots, $[ROH]_A$ represents hexadecyl hydroperoxides, ROOH, $[R(OH)_2]_A$ represents the sum of hexadecane dihydroperoxides, $R(OOH)_2$, and hydroperoxyhexadecanones or equivalent structures,[18] HOOR=O, and $[R(OH)_3]_A$ represents

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[14] At these higher conversions the temperature in the stirred flow reactor exceeded 180 °C due to the exothermic nature of the reactions. At a bath temperature of 180 °C the measured reaction temperature was found to be 180 ± 0.4 °C for residence times up to 210 s. At a residence time of 347 s the temperature within the reactor increased to 187.5 ± 0.3 °C.[3]

[15] J. H. Adams, *J. Polymn. Sci., Part B*, **8**, 1077 (1970).

[16] B. D. Boss and R. N. Hazlett, *Can. J. Chem.*, **47**, 4175 (1969).

[17] In the stirred flow reactor experiments, the instantaneous rate of formation of any intermediate or reaction product is given by the expression

$$\frac{d[X]}{dt} = \frac{[X]_\tau - [X]_0}{\tau}$$

where $[X]_\tau$ is the concentration of the substance in the reactor or in the effluent from the reactor under steady-state conditions at the residence time τ and $[X]_0$ is the concentration of this substance in the entering liquid.

[18] In our earlier work[3] it was suggested that these species could be a mixture of α,γ-hydroperoxy ketones, α,α,γ-trihydroperoxides, and/or α-hydroperoxy α,γ-cyclic peroxides which upon triphenylphosphine reduction give α,γ-hydroxy ketones and upon NaBH$_4$ reduction α,γ-$R(OH)_2$. More recent results[19] lead us to favor α,γ-hydroperoxy ketones as the major components in the mixture.

Table II. Analysis of Samples from a Thermal Decomposition Experiment at 180 °C

time after addition of inhibitor, s	10^4[X], M						
	$[\text{-OOH}]_R$	$[\text{ROH}]_A$	$[\alpha,\gamma\text{-R(OOH)}_2]^a$	$[\alpha,\gamma\text{-HOOR=O}]^b$	$[\alpha,\delta\text{-R(OOH)}_2]^a$	$[\alpha,\delta\text{-HOOR=O}]^b$	$[\text{CH}_3\text{CO(CH}_2)_{11}\text{CH}_3]^c$
20	422	286	7.3	18.4	21.7	26.6	1.6
50	414	293	7.4	15.4	22.4	25.2	2.0
100	403	281	7.3	10.8	22.8	25.4	2.3
150	394	277	8.0	7.3	24.2	24.7	2.6

[a] Determined as $[\text{R(OH)}_2]_C$.[20] [b] $[\text{HOOR=O}] = [\text{R(OH)}_2]_A - [\text{R(OH)}_2]_C$.[20] [c] Determined as $[\text{CH}_3\text{CH(OH)(CH}_2)_{11}\text{CH}_3]_A$.

Table III. Analysis of Cleavage Products from the Autoxidation of *n*-Hexadecane in the Stirred Flow Reactor at 160 and 180 °C and 100–110 kPa[a]

residence time, s	run no.	10^4[X], M									% conversion[i]
		$[\text{-OOH}]_R{}^c$	$[\text{ROH}]_A{}^d$	$[\text{CH}_3\text{COR'}]^e$	[–COOH]	$[\text{R'COOH}]^g$	$([\text{R'CHO}] + [\text{R'CH}_2\text{O–}])^h$	$[\text{H}_2\text{O}_2]^c$	[CO]	$[\text{CO}_2]$	
160 °C											
206	61	43 (1)^2	19.4	0.9				1.8			
208	42	41 (4)^3	21.9	0.8	3.2			2.6			0.1
410	43	122 (1)^2	68.2	6.8	15.1			7			0.4
430	65	126	74.8	9.4	17.7		2.7	11			0.4
814	44	428	256	47.1	83.9		12.1				1.4
180 °C											
43	34	33 (1)^2	14.5 (1)^2	1.6	2.4 (1)^2			2.6			0.1
43	58	31			2.2			2.6			
78	150	93	51.4	4.8	11.3 (2)^2	5.9		6	0.08	0.97	0.3
84	33	108 (3)^3	60.5	6.5	12.5		1.6	7			0.3
84	57	109			12.8 (3)^2			7			
148	149	314	184	29.7	61.8 (2)^2	33.0	7.2	25	0.75	6.46	1.0
152	142	367 (2)^2	221	33.5, 46^f	76.8 (22)^3	51.5	8.7	20			1.3
154	108	414 (1)^2	235	40.7	93.8 (8)^3		7.9	25			1.4
202	151	631	400	91, 90^f	154	88.5	26.4	58	2.46	17.7	2.3
204	59	615	379	69.3	143 (1)^2		18.9	29			2.2
207	55	579 (6)^6	390	78.4			24.3				
210	32	609 (3)^3	395	73.9	147 (2)^2		26.2	27			2.3
234	109	1260	926	193, 196 (26)$^{2\,f}$	531 (2)^2		85.2	163			5.6

[a] Initial concentrations of *n*-hexadecane at 160 and 180 °C were 2.98 and 2.91 M. [b] The uncertainties of measured values are indicated in parentheses. The values listed are averages obtained by independent analyses; their number is given by a number superscript. For example, 76.8 (22)^3 denotes that three measured values lay in the range 76.8 ± 2.2. [c] By iodometric titration. See ref 3. [d] References 3 and 8. [e] Determined as $[\text{CH}_3\text{CH(OH)R'}]_A$ by using GLC.[9] [f] Determined directly by using high-pressure LC. [g] Reference 6. [h] Reference 10. [i] Conversion (%) = $100\{(1 + a + b' + c)[\text{ROH}]_A + ([\text{-COOH}] - [\text{CH}_3\text{COR'}] + [\text{R'CHO}] + [\text{R'CH}_2\text{O–}])/2\}/[\text{RH}]_0$ where *a*, *b'*, and *c* are molar ratios of di- and trifunctional to monofunctional products reported previously (*a* and *c*)[3] and in this work (*b'*).

Table IV. Analysis of Cleavage Products from the Autoxidation of *n*-Hexadecane in the Stirred Flow Reactor—High Conversion Data[a]

residence time, s	run no.	10^4[X], M								% minimum conversion
		$[\text{-OOH}]_R{}^b$	$[\text{ROH}]_A{}^c$	[–COOH]	$[\text{CH}_3\text{COR'}]$	$[\text{R'CHO}] + [\text{R'CH}_2\text{O–}]$	$[\text{H}_2\text{O}_2]^b$	[–COOR]	$[\text{–}\overline{\text{CH(CH}_2)_2\text{CO}}]$	
210	32	609 (3)^3	395 (1)^2	147 (2)^2	73.9	26.2	27	6	<1	2.3^e
400	35	1844	1600 (13)^2	983	344	323	273	624	82	10
800	36	1553	2111	2232	~332	~420	763	1192	307	16

[a] See ref 14. The temperature in the constant-temperature bath was 180 °C. Oxygen gas pressure was 100–110 kPa. Initial concentration of *n*-hexadecane was 2.91 M. [b] By iodometric titration. See ref 3. [c] References 3 and 8. [d] Minimum conversion (%) = $100\{[\text{ROH}]_A + [\text{–COOR}] + ([\text{–COOH}] + [\text{R'CHO}] + [\text{R'CHO}_2\text{O–}] + [\text{–}\overline{\text{CH(CH}_2)_2\text{CO}}])/2\}/[\text{RH}]_0$. [e] Calculated as in footnote *i* in Table III.

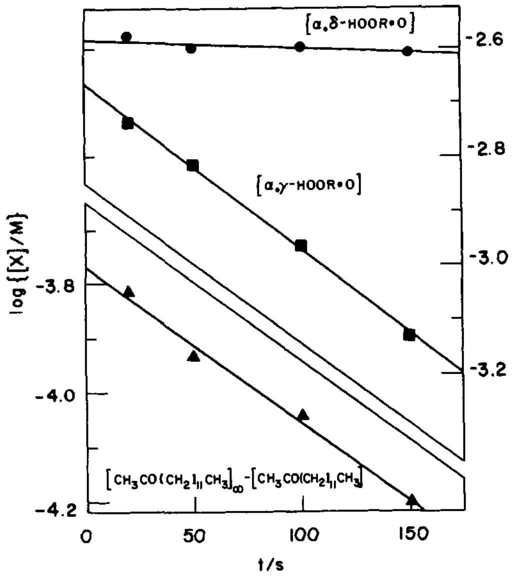

Figure 4. Thermal decomposition of difunctional HOOR=O and formation of 2-tetradecanone in the batch reactor at 180 °C.

hexadecane trihydroperoxides and dihydroperoxyhexadecanones in the unreduced oxidates.[20] For all these species, except those containing α,γ-HOOR=O structures, the instantaneous rates of their formation are linear functions of $[-OOH]_R^{1/2}$ at low conversions.[3] α,γ-HOOR=O, however, exhibits decreasing rates of formation with increasing $[-OOH]_R^{1/2}$. The curve for $[\alpha,\gamma\text{-R(OH)}_2]_A$ in Figure 2 which includes α,γ-HOOR=O reflects this trend. Plots of instantaneous rates of formation of cleavage products presented in Figure 3 show a higher order of dependence on hydroperoxide concentration.

Reaction Scheme. A reaction scheme which describes the formation of both primary and cleavage products and which satisfactorily accounts for the results reported in the earlier[3] and present papers of this series includes the reactions in Scheme I, where -X- is $-CH_2-$, $-C(OOH)H(CH_2)_m-$, $-C(OOH)H(CH_2)_mC(OOH)H(CH_2)_m-$, and $-C(OOH)HCH_2C(OOH)H-$, and -Y is $-CH_2-$ or -H, and *m* is equal to 1 or 2.

Included in the scheme are two independent modes of cleavage product formation. The first is a new process, reaction 7, which involes a rapid molecular decomposition of di- and trifunctional C_{16} products containing α,γ-hydroperoxy ketone or equivalent structures.[18] This process leads to the formation of alkanoic acids and methyl ketones. The additional acids and other cleavage products arise from reactions of alkoxy radicals (reactions 8 and 9).

Decomposition of Difunctional α,γ-HOOR=O Products. The thermal stabilities of the primary autoxidation products of *n*-hexadecane have been determined by using a novel experimental technique. This technique involves the addition of an antioxidant to an autoxidizing hydrocarbon without interruption of oxygen flow. Upon the addition the steady-state concentrations of peroxy radical species decrease many orders of magnitude. The formation of primary products is inhibited, as are self-reactions of peroxy radicals and product decomposition reactions induced by radical species.[21]

In Figure 4 are semilogarithmic plots of the concentrations of α,γ- and α,δ-HOOR=O vs. the time *after* the addition of the antioxidant, 2,6-di-*tert*-butyl-4-methylphenol. In contrast to α,δ-HOOR=O and other primary products (cf. Table II), the difunctional α,γ-HOOR=O undergo significant decay during the time period of the experiment. Similar results were obtained from experiments at 160 °C and from cumyl peroxide-initiated experiments at 120 °C. In all cases the decay rates of difunctional α,γ-HOOR=O showed first-order dependence on their concentrations. The values of the first-order rate constant, k_7, obtained from these studies are 0.045 (±0.003) × 10^{-3} s^{-1} at 120 °C, 1.6 (±0.1) × 10^{-3} s^{-1} at 160 °C, and 7.1 (±0.6) × 10^{-3} s^{-1} at 180 °C.

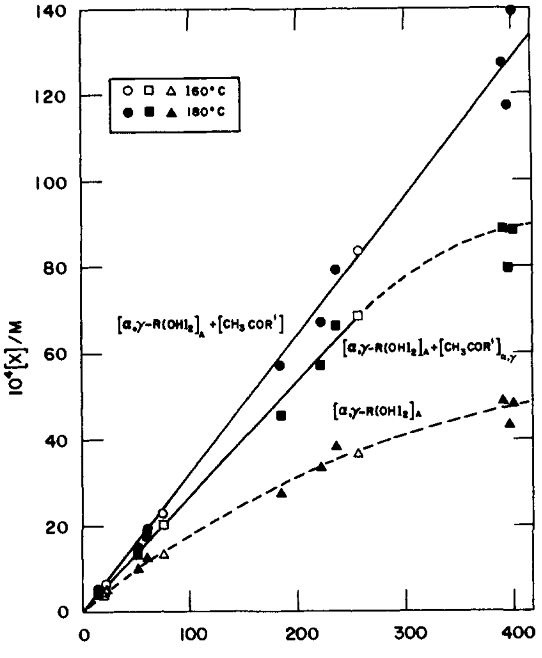

Figure 5. The yields of α,γ-hexadecanediols and methyl ketones vs. the corresponding yields of monfunctional C_{16} products in the sodium borohydride reduced oxidates obtained by the autoxidation of *n*-hexadecane at 160 and 180 °C.

As α,γ-HOOR=O decays, the formation of methyl ketone products is observed. This is illustrated in Figure 4 by a semilogarithmic plot of $\{[CH_3CO(CH_2)_{11}CH_3]_\infty - [CH_3CO(CH_2)_{11}CH_3]\}$ vs. time.[22] This product is a representative methyl ketone which could be accurately determined due to its low volatility. At all temperatures it was found that 2-tetradecanone was formed by a first-order process with rate constants equal to k_7 (see Figure 4).

In the first paper of this series[3] the ratios of the yields of difunctional α,γ-HOOR=O to monofunctional C_{16} products were found to decrease with increasing conversion at 160 and 180 °C (see Figure 5). We shall now show that this decrease is due to the occurrence of reaction 7.

Yields of Methyl Ketones from α,γ-HOOR=O. The yields of methyl ketones from the decomposition of difunctional α,γ-HOOR=O in the stirred flow reactor experiments are calculated from expression I, where $[\alpha,\gamma\text{-HOOR=O}]_\tau$ is the concentration

$$([CH_3COR']_{\alpha,\gamma})_\tau = k_7\tau[\alpha,\gamma\text{-HOOR=O}]_\tau \qquad (I)$$

of difunctional α,γ-HOOR=O at the residence time τ.[17] From the plot in Figure 5 we see that at 160 and 180 °C

$$[\alpha,\gamma\text{-R(OH)}_2]_A + [CH_3COR']_{\alpha,\gamma} = b[ROH]_A \qquad (II)$$

where *b* is equal to 0.27 at concentrations of monofunctional C_{16} products equal to or less than 250 × 10^{-4} M. At higher conversions there appear to be additional processes such as radical-induced decomposition reactions which consume α,γ-HOOR=O species in the stirred flow reactor. The more stable α,δ-HOOR=O show slight decreases at higher conversions.[3] The observation of linear

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[19] E. J. Hamilton, Jr., S. Korcek, L. R. Mahoney, and M. Zinbo, *Int. J. Chem. Kinet.*, 12, 577 (1980).

[20] On the basis of results of our earlier work[3] at sufficiently long chain length and low conversions,[8] $[ROH]_A$ = ROOH, $[R(OH)_2]_A$ = $[R(OOH)_2]$ + [HOOR=O], and $[R(OH)_2]_C$ = $[R(OOH)_2]$.

[21] Note that this method is *not* equivalent to interrupting the availability of oxygen to the system. If oxygen is removed, carbon radical species are continuously formed and may induce product decomposition.

[22] $[CH_3CO(CH_2)_{11}CH_3]_\infty$ = $[CH_3CO(CH_2)_{11}CH_3]_t$ + [α,γ-HOOR=O]/12, where *t* designates the time when the first sample of reaction mixture was withdrawn (20 s).

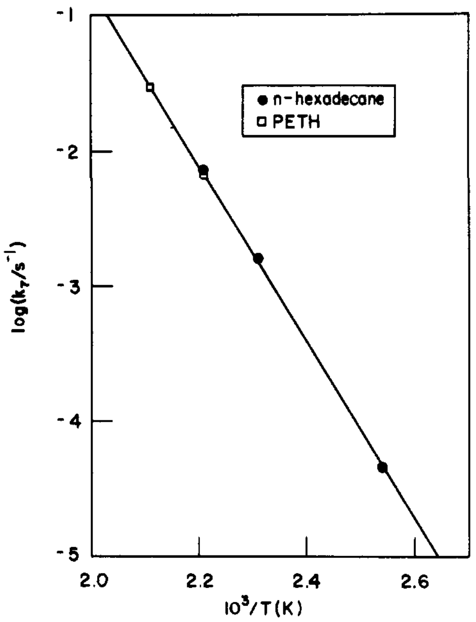


Figure 6. Arrhenius plot of k_7 for *n*-hexadecane and pentaerythrityl tetraheptanoate (PETH).

relationship II is thus consistent with the view that difunctional α,γ-HOOR=O species are primary products of the autoxidation of *n*-hexadecane.

In Figure 5 is also a plot of

$$[\alpha,\gamma\text{-}R(OH)_2]_A + [CH_3COR'] = b'[ROH]_A \qquad (III)$$

from which b' is equal to 0.32. This slope is 0.05 larger than b, suggesting that there are additional sources of methyl ketones. A reasonable class of precursors for the excess methyl ketones, $[CH_3COR']-[CH_3COR']_{\alpha,\gamma}$, is trisubstituted C_{16} products which contain α,γ-hydroperoxy ketone structures. Such products arise from intramolecular abstraction reactions of both α,γ- and α,δ-hydroperoxyhexadecylperoxy radicals. Utilizing reactivity ratio data (vide infra), we calculated the ratio of the yields of such trifunctional products to monofunctional C_{16} products to be 0.04 at 180 °C.[12] This value is in reasonable agreement with the difference between the values b and b'.

Mechanism of α,γ-Cleavage Reaction. An Arrhenius plot of the experimental values of k_7 for the *n*-hexadecane system is shown in Figure 6. From the data

$$\log k_7\ (s^{-1}) = 12.3\ (\pm 0.3) - \frac{29\,700 \pm 600\ (\text{cal mol}^{-1})}{2.3RT} \qquad (IV)$$

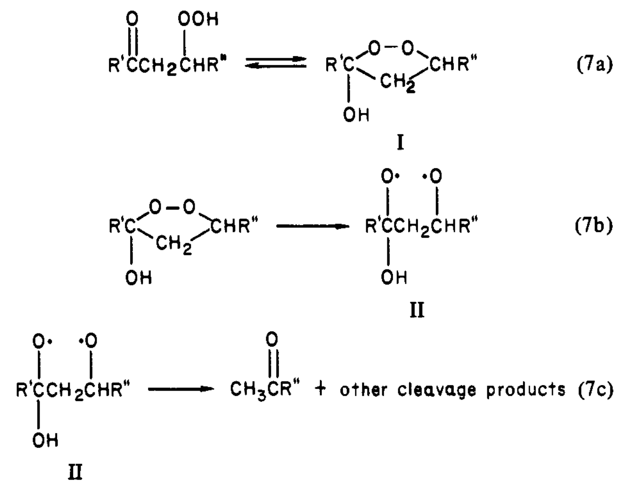
Included in the plot are values of k_7 obtained from a recent study of the autoxidation of pentaerythrityl tetraheptanoate at 180 and 200 °C.[19] The values from the ester system are within experimental uncertainties identical with those observed or extrapolated from *n*-hexadecane autoxidation.

The observed activation parameters are consistent with the mechanism in Scheme II in which a rate-controlling step is the homolytic decomposition of cyclic peroxide species (reaction 7b). The cyclization reaction 7a should be rapid; it is an intramolecular process which is exothermic by ca. 7.0 kcal/mol.[23]

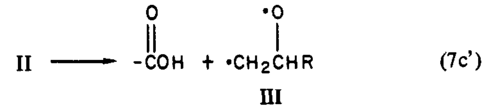
Reaction 7c may proceed by a number of different routes. An internal hydrogen atom transfer of II would yield water and β-diketone products. This reaction does *not* appear to be important in our case since β-diketones *do not* accumulate during the autoxidation and results from batch and stirred flow reactor experiments show that added 5,7-hexadecanedione was *not* consumed during autoxidation.

Initiation processes such as the loss of hydroxy radical from II and/or hydrogen abstraction by the oxy radicals of II are not of major importance. This is based upon the results of studies which show that the contribution of II to the total rate of free radical initiation must be very small.[19,24]

Scheme II



Reaction 7c is then best represented as a direct decomposition

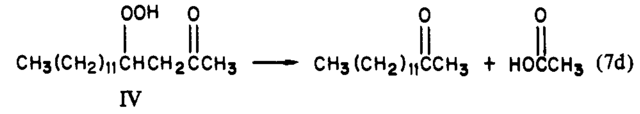


$$\mathrm{II} \longrightarrow -\overset{\overset{\displaystyle O}{\|}}{C}OH + \cdot CH_2\overset{\overset{\displaystyle \cdot O}{|}}{C}HR \qquad (7c')$$

III

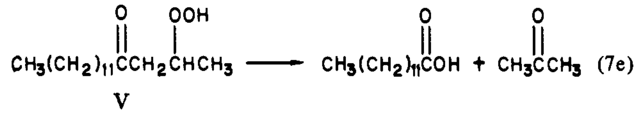
of II to yield acid and methyl ketone either via a concerted process or via the intermediate III. The diradical III then isomerizes to methyl ketone.

Within the limitation of our present individual product analyses this mechanism satisfactorily describes the stoichiometry for the overall reaction. Consider the decomposition of the 2,4 isomeric species IV and V.



$$CH_3(CH_2)_{11}\overset{\overset{\displaystyle OOH}{|}}{C}HCH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \longrightarrow CH_3(CH_2)_{11}\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + HO\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \qquad (7d)$$

IV



$$CH_3(CH_2)_{11}\overset{\overset{\displaystyle O}{\|}}{C}CH_2\overset{\overset{\displaystyle OOH}{|}}{C}HCH_3 \longrightarrow CH_3(CH_2)_{11}\overset{\overset{\displaystyle O}{\|}}{C}OH + CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \qquad (7e)$$

V

From the reactivity ratio data (vide infra), we calculate that species IV and V should be formed in approximately equal amounts.[12,25] Thus $CH_3(CH_2)_{11}COCH_3$ and $CH_3(CH_2)_{11}COOH$ should be also formed in reactions 7d and 7e in approximately equal amounts. From Table II we see that for run 151 at 180 °C the yield of $CH_3(CH_2)_{11}COCH_3$ was 4.9×10^{-4} M and that of $CH_3(CH_2)_{11}COOH$ was $(4.4\text{–}6.0) \times 10^{-4}$ M. A slightly higher yield of the acid is anticipated since it may be formed by the independent cleavage processes described in the following section.

Excess Acid and Other Cleavage Products. If α,γ-cleavage produces methyl ketones and acid products in equal amounts, then reaction 7 accounts for only 50–60 percent of the total acids in the initial stages of the autoxidation of *n*-hexadecane at 160 and 180 °C. In this section it will be shown that the excess acid and other cleavage products are likely to be derived from reactions of alkoxy radicals.

Figure 7 shows plots of the kinetic chain lengths for the formation of various cleavage products, $[X]_\tau/(R_i)_\tau\tau$, vs. $([ROH]_A)_\tau$

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[23] Calculated from the group method of Benson. Cf. S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

[24] R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, in preparation (parts 3 and 4 of this series).

[25] If the isomeric 2,4-hydroperoxyhexadecylperoxy radicals equilibrate by an intramolecular hydrogen transfer reaction, the ratio of yields of IV and V is equal to 1. A ratio of 1.6 is obtained by assuming that the equilibrium reaction does not occur.

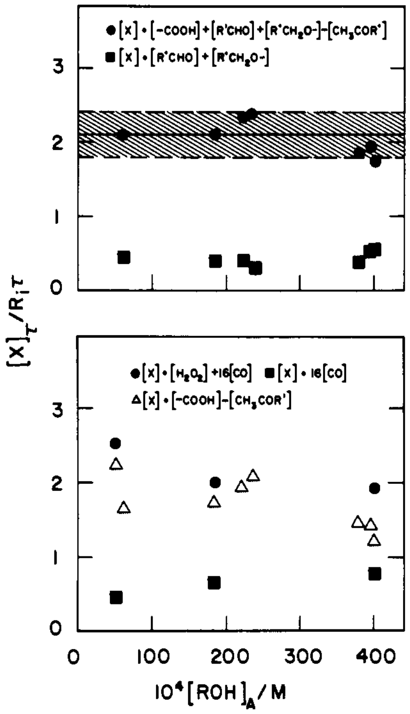


Figure 7. The kinetic chain length for the formation of various cleavage products vs. $(ROH)_A$.

at 180 °C where $(R_i)_\tau$ is the rate of free radical formation at residence time τ.[26] Over a wide range of conversions the kinetic chain lengths for formation of the sum of excess acids and 1-oxo- and/or 1-oxy-substituted alkanes, ([–COOH] – [CH_3COR'] + [R'CHO] + [$R'CH_2O$–]), are equal to 2.1 ± 0.3. A similar value is obtained from the limited data at 160 °C. This suggests that these cleavage products are formed via radical species generated in initiation and/or termination processes. Alkoxy radicals are common to both processes.

In an autoxidizing hydrocarbon alkoxy radicals are formed in the homolysis of hydroperoxide products

$$ROOH \rightarrow RO\cdot + \cdot OH \tag{1a}$$

and via nonterminating decomposition of tetroxide (reaction 5).[1,27] The kinetic chain lengths for formation of alkoxy radicals are then given by eq V, where $(1 - x)$ is that fraction of alkoxy radicals which survive termination reaction and diffuse from the solvent cage.

$$\frac{[RO\cdot]_\tau}{(R_i)_\tau\tau} = 0.5 + \frac{(1 - x)k_5}{k_6 + xk_5} \tag{V}$$

Utilizing values of k_5/k_6 estimated from the data of Mill et al.[1] for the *sec*-butylperoxy system, we calculated the *maximum* kinetic chain length for alkoxy radical formation, i.e., for the case when x equals zero, to be 1.6 and 2.0 at 160 and 180 °C, respectively. Although the kinetic chain length for cleavage product formation depends upon the subsequent reactions of alkoxy radicals, its maximum value would be 2 times the value for alkoxy radicals. Thus the experimental value of 2.1 ± 0.3 at 180 °C is fully consistent with the maximum value calculated from eq V.

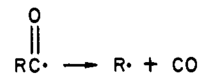
Conventional reaction pathways for secondary alkoxy radicals include β-scission (reaction 8) followed by free radical chain oxidation of aldehydes to acids

$$R'CHO + {}^1/_2O_2 \xrightarrow{XO_T} R'COOH \tag{10}$$

and electrocyclic processes such as

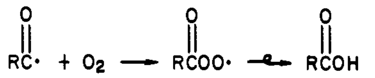
$$R'CHO + HOOCH_2R'' \rightarrow R'COOH + H_2 + R''CHO \tag{11}$$

Reaction 10 is likely to be important in the formation of the excess acids. The ratio of the rate of formation of carbon monoxide from the decomposition of acyl radicals


(12)

$$R\overset{\overset{O}{\|}}{C}\cdot \longrightarrow R\cdot + CO \tag{12}$$

to the rate of oxygen addition and conversion to acids


(13)

$$R\overset{\overset{O}{\|}}{C}\cdot + O_2 \longrightarrow R\overset{\overset{O}{\|}}{C}OO\cdot \xrightarrow{e} R\overset{\overset{O}{\|}}{C}OH \tag{13}$$

have recently been determined from a stirred flow reactor study of the autoxidation of dilute solutions of dodecanal in *n*-hexadecane.[29,30] At 180 °C and 100 kPa of oxygen gas pressure,

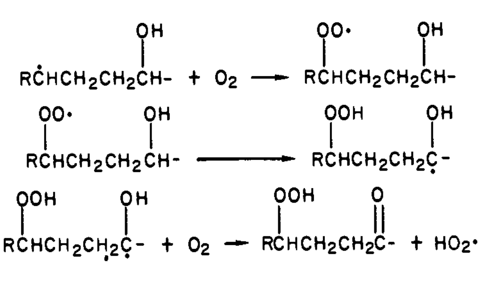
$$\frac{([RCOOH]_\tau)_{13}}{\tau} \bigg/ \frac{[CO]_\tau}{\tau} = 16 \tag{VI}$$

On the reasonable assumption that the relative rates of reactions 12 and 13 are insensitive to the structures of *n*-acyl radicals formed in *n*-hexadecane, we utilize equation VI to calculate the kinetic chain lengths for acid formed via reaction 13 from $[CO]_\tau/\tau$. The results in Figure 7 show that 30–40 percent of the excess acids could be formed from the chain oxidation of aldehydes.

On the basis of the low yields of hexadecanoic acid, the bimolecular reaction (11) is not an important source of acids in the initial stages of the *n*-hexadecane autoxidation. At higher conversions it may become important: Brown and Fish[31] reported the evolution of hydrogen in the autoxidation of 2-methylhexadecane under conditions of high conversion and in an autoxidation in which 0.3 M decanal was initially added.

A reaction sequence which satisfactorily accounts for the excess acid and hydrogen peroxide formation in the *n*-hexadecane system is now proposed. The sequence also explains in part the virtual absence of excess acids and hydrogen peroxide in the autoxidation of pentaerythrityl tetraheptanoate.[19]

On the basis of the work of Walling and Padwa,[32] the α,δ-intramolecular abstraction reactions of alkoxy radicals (reaction 9) would be much more rapid than intermolecular hydrogen abstractions. Thus, reaction 9 could be competitive with the β-scission reaction for secondary oxy radicals and the dominate process for primary oxy radicals.[33] It would be followed by


(14)
(15)
(16)

$$R\dot{C}HCH_2CH_2\overset{\overset{OH}{|}}{C}H\text{-} + O_2 \longrightarrow R\overset{\overset{OO\cdot}{|}}{C}HCH_2CH_2\overset{\overset{OH}{|}}{C}H\text{-} \tag{14}$$

$$R\overset{\overset{OO\cdot}{|}}{C}HCH_2CH_2\overset{\overset{OH}{|}}{C}H\text{-} \longrightarrow R\overset{\overset{OOH}{|}}{C}HCH_2CH_2\overset{\overset{OH}{|}}{\underset{\bullet}{C}}\text{-} \tag{15}$$

$$R\overset{\overset{OOH}{|}}{C}HCH_2CH_2\overset{\overset{OH}{|}}{\underset{\bullet}{C}}\text{-} + O_2 \longrightarrow R\overset{\overset{OOH}{|}}{C}HCH_2CH_2\overset{\overset{O}{\|}}{C}\text{-} + HO_2\cdot \tag{16}$$

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[26] The values of $(R_i)_\tau$ were determined from the lengths of the inhibition periods caused by the addition of phenolic antioxidants to autoxidizing hydrocarbon[18,22] and from the rates of consumption of antioxidants.[22] The absolute values of $(R_i)_\tau$ are proportional to n, the stoichiometric factor for peroxy radical reactions with the phenolic antioxidant. In the present case n is assumed to be equal to 4.0 for 4,4'-methylenebis(2,6-di-*tert*-butylphenol). A different value for n has no effect on the arguments presented in this section.

(27) The alternate mechanism of peroxy radical termination proposed by Benson[28] also leads to the formation of alkoxy radical intermediates.

(28) S. W. Benson and P. S. Nangia, *Acc. Chem. Res.*, **12**, 223 (1979).

(29) R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, Abstracts, 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1977, No. PHYS 11.

(30) R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, in preparation (part 5 of this series).

(31) D. M. Brown and A. Fish, *Proc. R. Soc. London, Ser. A*, **308**, 547 (1969).

(32) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1597 (1963), and earlier reference cited therein.

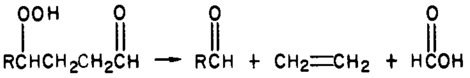
(33) The sequence is less important in pentaerythrityl tetraheptanoate due to the limited number of abstractible δ hydrogens in the oxy radicals formed in its autoxidation.

Table V. Reactivity Ratios for Intra- and Intermolecular Hydrogen Abstraction Reactions of Hexadecylperoxy and Hydroperoxyhexadecylperoxy Radicals[a]

	temp, °C		
ratio/M	120	160	180
$(k_{4\text{-}\alpha,\gamma}/\mathrm{H\ atom})/(k_3/\mathrm{H\ atom})$	5.8	7.6	7.5
$(k_{4\text{-}\alpha,\delta}/\mathrm{H\ atom})/(k_3/\mathrm{H\ atom})$	5.6	5.9	6.7
$(k^*_{4\text{-}\alpha,\gamma}/\mathrm{H\ atom})/(k_3/\mathrm{H\ atom})$	3.0×10^2	3.8×10^2	3.3×10^2
$(k^*_{4\text{-}\alpha,\delta}/\mathrm{H\ atom})/(k_3/\mathrm{H\ atom})$	1.0×10^2	1.1×10^2	0.9×10^2

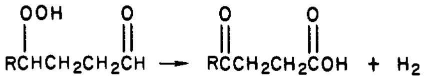
[a] Reference 12.

Acid formation from 4-hydroperoxyaldehyde products from reaction 16 then occurs via a process analogous to reaction 7

 (17)

$$\mathrm{R\overset{OOH}{C}HCH_2CH_2\overset{O}{C}H \longrightarrow R\overset{O}{C}H + CH_2{=}CH_2 + H\overset{O}{C}OH} \quad (17)$$

and/or intramolecular versions of reaction 11

 (18)

$$\mathrm{R\overset{OOH}{C}HCH_2CH_2\overset{O}{C}H \longrightarrow R\overset{O}{C}CH_2CH_2\overset{O}{C}OH + H_2} \quad (18)$$

Little or no changes in the concentrations of α,δ-HOOR=O were observed in the inhibited batch reactor experiments. Thus secondary oxy radicals undergo only the β-scission (reaction 8), or the rates of formation of α,δ-HOOR=O via reactions 9 and 14–16 are equal to the rates of decomposition of α,δ-HOOR=O by processes such as (17).

If reactions 9, 10, and 14–18 are the sole contributors to excess acid formation, the kinetic chain length for excess acid formation must be equal to or less than the values of $\{(16[\mathrm{CO}]_T/(R_i)_T\tau) + ([\mathrm{H_2O_2}]_T/(R_i)_T\tau)\}$. The data in Figure 7 are consistent with that requirement.

The origin of CO_2 formation is not known. It is noteworthy that the value of the kinetic chain length for its formation is constant, equal to 0.34, over a wide range of conversions. An examination of the literature revealed that an identical value was observed in the di-*tert*-butyl peroxide-initiated oxidation of *n*-octane at 125 °C.[2]

Reactivity Ratios for Intra- and Intermolecular Abstraction Reactions. For convenience of discussion, the reactivity ratios for intra- and intermolecular hydrogen atom abstraction reactions of hexadecylperoxy and hydroperoxyhexadecylperoxy radicals have been calculated. The method of their calculation from product ratios *a–e* reported above and in our earlier paper[3] is based on the results of the kinetic analysis which is described in detail in the supplementary material.[12] The values of the reactivity ratios obtained as a function of reaction temperature are summarized in Table V.

Scope of α,γ-Cleavage in *n*-Alkane Autoxidation. In this section we consider the factors which influence the contribution of the new cleavage process (reaction 7) in the autoxidation of *n*-alkanes.

Since the yields of α,γ-HOOR=O structures from the oxidation of *n*-butane will be low,[34] the amount of its cleavage by reaction 7 will be negligible. However for all *n*-alkanes higher than C_4 the yields of α,γ-HOOR=O will be significant. In earlier work[3] it was shown that the reactivity ratios from *n*-hexadecane autoxidation at 120 °C were applicable to the liquid-phase oxidation of *n*-pentane at 125 °C. From the reactivity ratios in Table V we now calculate the ratios of yields in which α,γ-HOOR=O and monohydroperoxide products are formed for a series of liquid *n*-alkanes.[12] At 120 °C the ratios of $[\alpha,\gamma\text{-HOOR}{=}\mathrm{O}]_\mathrm{f}/[\mathrm{ROOH}]_\mathrm{f}$ are equal to 0.16 for *n*-pentane, 0.21 for *n*-octane, 0.19 for *n*-hexadecane, and 0.18–0.12 for C_nH_{2n+2} where *n* is greater than 16. Due to the low-temperature coefficients for the reactivity ratios the ratios of $[\alpha,\gamma\text{-HOOR}{=}\mathrm{O}]_\mathrm{f}/[\mathrm{ROOH}]_\mathrm{f}$ are relatively insensitive to temperature. For *n*-hexadecane this ratio increases to 0.26 at 180 °C.

Steric effects in the reacting hydrocarbon can decrease the value of k_3/H atom and result in higher yields of intramolecular products. These effects have been noted in the oxidation of a branched alkane[35] and in the autoxidation of pentaerythrityl tetraheptanoate.[19] Lower yields of intramolecular products will occur in systems where intermolecular hydrogen abstraction reactions efficiently compete with reactions 4 and 4* for monoperoxy radicals. Thus the yields of α,γ-HOOR=O products from *n*-alkyl-substituted aromatic hydrocarbons will be very low due to the high reactivity of benzylic hydrogens in reaction 3.

In most earlier studies the yields of methyl ketones were not reported since the multitude of products formed at high hydrocarbon conversions precluded their determination. However, we have found two exceptions. In their study of 2-methylhexadecane at 155 °C Brown and Fish[31] reported that the sum of the yields of methyl ketones and aldehydes are slightly lower than the yields of acid products. Cheng et al.[36] noted the presence of unidentified products which had chemical shifts of 43.7 and 208.0 ppm in their ^{13}C NMR study of oxidized polyethylene. These shifts correspond within experimental error to those which would be observed from scission methyl ketone products.[37]

Acknowledgment. The authors wish to acknowledge L. A. Scheich, R. L. Reineck, and C. N. Montreuil for their assistance in performing some of the analyses, Dr. E. J. Hamilton, Jr., for his contributions in the development of the method for determination of total acid products, and Ms. S. Tsang for assistance rendered during final preparation of this paper.

Supplementary Material Available: General experimental methods and materials, identification and determination of cleavage products (identification of cleavage products, determination of total acid products, determination of individual alkanoic acid products (extraction method and silica gel separation method), determination of 4-oxo- and/or 4-oxy-substituted alkanoic acids, GLC determination of cleavage products, liquid chromatographic analysis of methyl ketones, evaporative loss of cleavage products, determination of esters and γ-lactones, and determination of CO and CO_2) (including Figure 1), calculation of the reactivity ratios for intra- and intermolecular abstraction reactions, Table VI, number of hydrogens available for inter- and intramolecular abstractions in *n*-hexadecane and *n*-alkanes, and calculation of the ratios of the yields in which oxidation products are formed (the ratio of the yields in which products containing α,γ-HOOR=O structures and monofunctional products are formed; the ratio of the yields in which trifunctional products containing α,γ-HOOR=O structures and monfunctional products are formed; the ratio of the yields in which IV and V are formed) (18 pages). Ordering information is given on any current masthead page.

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(34) Only occasional hydroxy or alkoxy radical abstractions of primary hydrogens could lead to 1,3-disubstituted primary products.

(35) T. Mill and G. Montorsi, *Int. J. Chem. Kinet.*, **5**, 119 (1973).

(36) H. N. Cheng, F. C. Schilling, and F. A. Bovey, *Macromolecules*, **9**, 363 (1976).

(37) F. A. Bovey, Bell Laboratories, personal communication, 1977.

(38) There are typographical errors in eq VI and VII in ref 3. The correct form of these eq should be

$$[\alpha,\delta\text{-R(OH)}_2]_\mathrm{C} = d[\text{R-MONO}]_\mathrm{C} \qquad \text{(VI)}$$

$$[\alpha,\gamma\text{-R(OH)}_2]_\mathrm{C} = e[\text{R-MONO}]_\mathrm{C} \qquad \text{(VII)}$$