Liquid-Phase Autoxidation of Organic Compounds at Elevated Temperatures. 1. The Stirred Flow Reactor Technique and Analysis of Primary Products from *n*-Hexadecane Autoxidation at 120–180 °C[1]

R. K. Jensen, S. Korcek, L. R. Mahoney,* and M. Zinbo

Contribution from the Research Staff, Ford Motor Company, Dearborn, Michigan 48121. *Received April 30, 1979*

Abstract: The design and utilization of a stirred-flow reactor for kinetic and mechanistic studies of the liquid-phase autoxidation of organic compounds are described. Utilizing a variety of selective reduction, separation, and analytical procedures the primary C_{16} products derived from the initial stages of the autoxidation of *n*-hexadecane with molecular oxygen at 120, 160, and 180 °C have been quantitatively determined. These products include isomeric monohydroperoxides, II, isomeric α,γ- and α,δ-dihydroperoxides, IV, two groups of isomeric α,γ- and α,δ-substituted species which consist of mixtures of hydroperoxy ketones, VI, α,α,γ- and α,α,δ-trihydroperoxides, VIII, and/or α-hydroperoxy-α,γ- and α-hydroperoxy-α,δ-cyclic peroxides, IX, and a further group of trisubstituted products with isolated functional groups. With the exception of the group of α,γ-substituted species VI, VIII, and/or IX at 160 and 180 °C, the ratios of the concentrations of these products to the concentrations of monohydroperoxides are constant at a given temperature in the range of conversions studied. These ratios at 180 °C (120 °C) are equal to 0.054 (0.044) for α,γ-substituted IV, 0.095 (0.076) for α,δ-substituted IV, 0.103 (0.087) for the groups of α,δ-substituted species VI, VIII, and/or IX, and 0.025 (0.017) for trisubstituted products with isolated functional groups. For the group of α,γ-substituted species VI, VIII, and/or IX, the ratio of their concentrations to that of monohydroperoxides is equal to 0.18 at 120 °C. At 160 and 180 °C the ratio decreases with increasing conversion. As will be shown in a later paper of this series, these species are unstable and undergo rapid conversion to secondary products, methyl ketones and carboxylic acids. A reaction scheme consistent with the analytical results is proposed. The scheme consists of a series of consecutive, competitive intra- and intermolecular hydrogen abstraction reactions by hexadecylperoxy radical species. A high percentage of the abstraction reactions from *n*-hexadecane occur via hydroxyl radicals which are produced concurrently with and/or subsequently to the formation of species VI, VIII, and/or IX. Chain initiation occurs via homolytic decomposition of hydroperoxide species and termination by bimolecular reaction of the chain carrying peroxy radicals. Comparison of the experimentally determined hydroperoxide concentrations with those calculated from the concentrations of the reduced products suggests that greater than 90% of the hydroperoxide products are accounted for in the present study. A discussion of the importance of intramolecular hydrogen atom abstraction by peroxy radicals in both the liquid- and gas-phase autoxidations of *n*-alkanes is presented. It is concluded that the failure of earlier workers to observe the products of such reactions in the liquid-phase systems was due to the limitations of their analytical techniques and to the extended reaction times during which the conversion of VI, VIII, and/or IX species to secondary products occurred. The striking similarities of the results of the present study and gas-phase studies at elevated temperatures with regard to the initial distribution of α,γ- and α,δ-substituted products and their subsequent reactions are also discussed.

Much of our present knowledge of the kinetics and mechanism of the reactions occurring in the liquid-phase autoxidation of hydrocarbons has been obtained from the results of studies carried out in the temperature range of 30–100 °C. Under these conditions, the principal products of autoxidation are hydroperoxides:

$$RH + O_2 \rightarrow ROOH$$

These compounds are relatively stable at low temperatures and may be isolated in high yields at moderate conversions. It has been well established that the autoxidation occurs via free radical chain reactions[2] and rate constants of a fundamental nature for these reactions have been determined using a variety of experimental methods.[3] The accumulation of such kinetic data leads to the establishment of relationships which permit the prediction of the oxidation behavior of many hydrocarbon systems at these low temperatures.[4]

As the temperature of hydrocarbon autoxidation is increased above 100 °C the yields of hydroperoxides decrease even at low conversions and very complex mixtures of ketones, alcohols, acids, and esters are obtained as products.[5,6] These secondary products arise from thermal decomposition reactions of primary hydroperoxide products and from a variety of other, less well defined processes. Limited kinetic data for these reactions are available only at temperatures up to 125 °C.[7,8]

Although there have been a number of studies[9,10] of product formation in the autoxidation of organic liquids at still higher temperatures as a function of extended reaction times, kinetic data comparable to that obtained from low-temperature studies may not be extracted from such work. This is not only due to the complexity of the reactions occurring at elevated temperatures, but is also due to the limitations of the conventional experimental techniques employed in such studies. The occurrence of branching reactions leads to autocatalysis at low conversions and increases the oxidation rate to a point where it is difficult to maintain oxygen saturation in the liquid. Consequently the rates of reactions become controlled by the rate of oxygen mass transfer and kinetic interpretations of the results of such experiments become meaningless.

Over 30 years ago Denbigh[11] showed that the instantaneous rate of a chemical reaction occurring in a fluid can be determined by balancing the reaction rate against the rate of flow of the fluid, thus maintaining steady-state conditions. To achieve these conditions, reactants are introduced at a constant flow rate, μ, into a reactor of fixed volume, V, in which there is thorough stirring; a homogeneous, partially reacted mixture is removed at essentially the same flow rate. Such a system ultimately reaches a steady state in which all concentrations of reactants, intermediates, and final products remain unchanged. Under these conditions, the rate of consumption or formation of any *reactant*, *intermediate*, or *reaction product* in the reactor is then given by the expression

$$\frac{d(X)}{dt} = \frac{\mu}{V}((X)_\tau - (X)_0) = \frac{(X)_\tau - (X)_0}{\tau} \qquad (I)$$

where $(X)_\tau$ is the concentration of the substance in the reactor

0002-7863/79/1501-7574$01.00/0

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. The validity of the equation for any reactant, intermediate, or product is not impaired by the occurrence of complex, competing, or consecutive reactions. Thus for kinetic studies of such reactions this method is clearly superior to the usual measurement of quantities reacted or formed in finite time intervals.[12,13]

Based upon these considerations our laboratory has developed a microstirred-flow reactor for kinetic and mechanistic study of the complex reactions occurring in the autoxidation of organic liquids at elevated temperatures.[14] Over the past several years this reactor has been utilized for a systematic investigation of the autoxidation of pure *n*-hexadecane in the temperature range of 120–180 °C. This paper, the first of a series, describes the design and operation of the reactor and the identification and quantitative analyses of the multitude of primary C_{16} products formed in the initial stages of the autoxidation as a function of temperature and reaction time.

Experimental Section

General. IR, UV, and ^1H NMR spectra were recorded with a Perkin-Elmer Model 457 spectrometer, a Cary Model 14 spectrometer, and a JEOL Model JNM-MH-100 spectrometer, respectively.

Electron impact mass spectra were obtained using a Varian MAT 311 with an Incos Data Systems (Data General Computer). Positive and negative chemical ionization (isobutane) mass spectra were obtained using a modified Finnigan 3200 quadrupole mass spectrometer.

Gas chromatograms were recorded with F&M Model 810 and Hewlett-Packard 5730A gas chromatographs operating in the flame ionization mode, using all glass column systems and equipped with an Autolab System IV computing integrator and a Norcon Model RS-1 GC identifier.

A Waters Associates differential refractometer Model R-403 was used as a detector for preparative liquid-solid chromatography.

Materials. *n*-Hexadecane (99+%) from Aldrich Chemical Co. (selected batches only) was passed through silica gel to remove major polar impurities. The final purification over alumina was carried out directly in the reaction system under the inert atmosphere immediately before reaction as described below. *n*-Hexadecane used for reaction contained less than 0.3% of hydrocarbon impurities; no oxygen-containing impurities were detected by GLC after silica gel concentration (see below).

Oxygen was Matheson UHP (minimum purity 99.99%); argon was Matheson grade (minimum purity 99.9995%).

Silica gel used for elution chromatography and material purifications was Davison Grade 12 (28–200 mesh) purified by oxidizing organic impurities with hydrogen peroxide and by multiple washings with water and methanol and then activated at 250 °C for 16 h. The 74–149-μm (100–200 mesh) fraction of this silica gel was used for preparative liquid-solid chromatography.

Alumina was Alcoa Type F-20 (80–200 mesh) obtained from Matheson Coleman and Bell and activated at 400 °C for 16 h.

Triphenylphosphine obtained from Pfaltz and Bauer, Inc., was purified by column chromatography on alumina followed by recrystallization from ethanol. Sodium borohydride, lithium aluminum hydride, and sodium periodate were obtained from J. T. Baker Chemical Co.

The derivatizing kit of *n*-butylboronic acid was obtained from Applied Science Laboratories, Inc.

Samples of 1-hexadecyl hydroperoxide,[15] 2-hexadecyl hydroperoxide,[15] and peroxyhexadecanoic acid[16] were prepared by the reported methods. A sample of 1-hexadecanol was obtained from Matheson Coleman and Bell, 2-, 5-, and 7-hexadecanols, 5- and 7-hexadecanones, and 1,2-alkanediols (C_{15}–C_{18}) from Aldrich Chemical Co., 3- and 6-hexadecanones from K & K Laboratories, Inc., and hexadecanal (sodium bisulfite) and hexadecanoic acid from Pfaltz and Bauer, Inc. Samples of 2,4- and 5,7-hexadecanediones were prepared by acylation of 2-tetradecanone with ethyl acetate and 2-undecanone with methyl pentanoate, respectively, by means of sodium amide.[17] Samples of 2,5- and 3,6-hexadecanediones were prepared by the method of Stetter and Kuhlmann.[18] Samples of 3-hexadecanol, 6-hexadecanol, 2,4-, 2,5-, 3,6-, and 5,7-hexadecanediols were prepared from the corresponding ketones by sodium borohydride reduction. A sample of 2-methyl-5-*n*-undecyltetrahydrofuran was prepared as a major byproduct in an attempted synthesis of the bis(methanesulfonate) derivative of 2,5-hexadecanediol.[19] All these compounds, as well as many others reported separately in our paper on development of the GLC analytical technique,[20] were used throughout this work as standards. Their purity was determined by GLC.

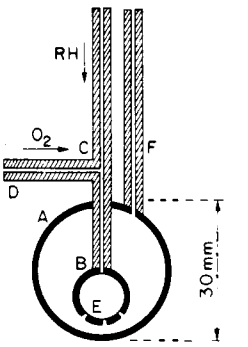


Figure 1. Stirred flow microreactor. Refer to the text for detailed description.

Solvents and analytical reagents used were ACS reagent grade chemicals. *n*-Hexane was passed through silica gel. 2-Propanol was distilled from $NaBH_4$/NaOH or CaH and ethyl ether from $LiAlH_4$ prior to use.

Stirred-Flow Microreactor. The design of the microreactor was suggested by that employed by Mulcahy and Williams[21] in their studies of the gas-phase decomposition of di-*tert*-butyl peroxide. This design results in a rapid, very efficient, oxygen–substrate intermixing and thus minimizes oxygen mass transfer effects previously experienced in hydrocarbon autoxidation experiments at elevated temperatures. The microreactor (Figure 1) consists of two Pyrex glass spheres: a larger outside sphere (A) and a smaller, eccentrically located, and perforated inside sphere (B). A liquid hydrocarbon is delivered to a T joint (C) immediately above the reactor and mixed with a stream of oxygen introduced at the second arm (D). The oxygen–hydrocarbon mixture is injected into sphere A from sphere B through the perforations. The perforations (E) located symmetrically in the base of the inside sphere (seven holes, 0.5 mm diameter) ensure very efficient "ideal mixing" of the oxygen, hydrocarbon, and reaction products in the reactor. The outlet from the reactor (F) is located at the top of the outside sphere.

Flow Scheme and Procedure. The stirred flow reactor system, schematically shown in Figure 2, consists of a microreactor (1), constant-temperature bath (11), hydrocarbon purification and supply (2–6), gas supply (7–10), and reaction mixture collection (12–14) subsystems.

The prepurified hydrocarbon was deoxygenated at about 50 °C by flushing with argon in the heated reservoir (2), then transferred onto the chromatographic column (3), passed through alumina, and stored in the reservoir (4) at room temperature. All these steps were carried out under an atmosphere of dry, oxygen-free argon. The purified hydrocarbon from the reservoir (4), preheated to the reaction temperature in the system of Pyrex glass heat exchangers (5), was injected into the reactor (1) using the syringe pumps (6) (Chromatronix Cheminert Metering Pumps CMP-3 and CMP-3V). The hydrocarbon flow rate was varied by means of various pump gear combinations in order to obtain liquid residence times in the range from 10 to 10^4 s. The stream of oxygen, preheated to the reaction temperature by a series of heat exchangers (7), entered the reactor at a constant flow rate which was measured with flow meters (8) and adjusted at the desired level (up to 8.5 mL s^{-1} at standard conditions) with metering valves (9). The back pressure in the reaction system was monitored by pressure gauges (10). The reaction cell and all heat exchangers were in the constant-temperature bath (11) (Lauda WB-20D; temperature control was ±0.01 to ±0.05 °C in the temperature range 25–300 °C). The reaction mixture continuously flowed out of the reactor through the reactor outlet arm (12) made from capillary tubing (1-mm i.d.). The residence time of the liquid in the outlet arm was very short because the gas to liquid volume flow rate ratio used was very high (50–400).

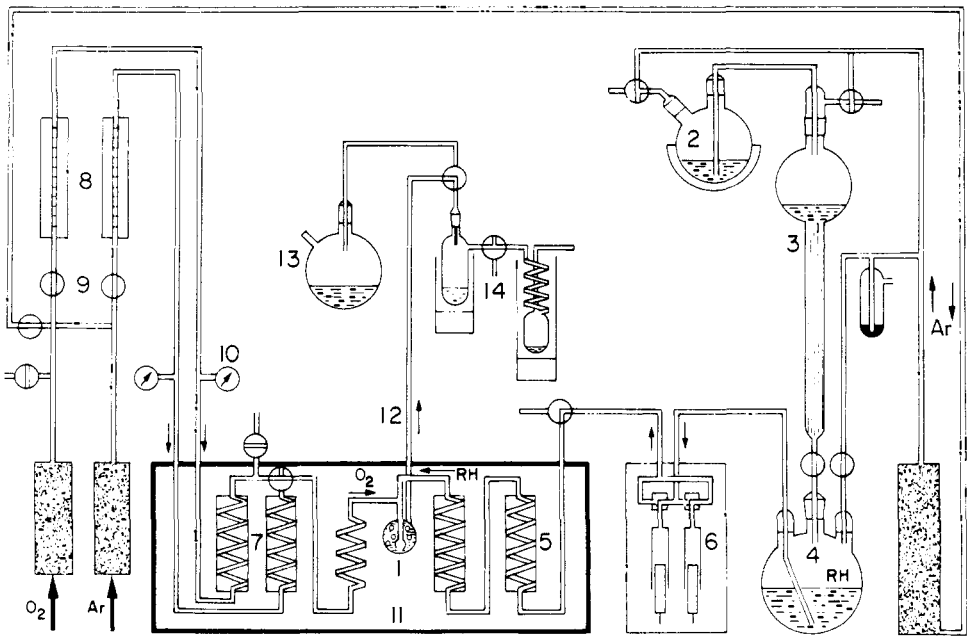


Figure 2. Stirred flow reactor system. Refer to the text for detailed description.

After selecting the desired reaction conditions, the reaction system was allowed to reach steady state. It has been shown[12] that this is attained within 0.1% when $\mu t/V$ (eq I) is equal to 8. During this period the reaction mixture was collected in the waste reservoir (13). After steady-state conditions were attained, the reaction mixture stream was diverted into the collection system. There the reaction was discontinued by thermal quenching to −78 °C (acetone-dry ice bath). The samples of reaction mixture were stored for subsequent analysis at temperatures lower than 0 °C. The chemical composition of samples stored under these conditions did not change with a storage time in excess of 2 years.

The reaction temperature in the microreactor was measured in separate experiments where a chromel-alumel thermocouple made from fine gauge wire (0.003 in. diameter) covered with Teflon was inserted into the reactor through the reactor outlet arm (12). 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 due to exothermic secondary reactions.

Determination of Liquid Residence Time, τ. The instantaneous rates of formation and disappearance of chemical species are calculated from eq I using the concentrations of the species in the liquid reaction mixture and the liquid residence time, τ, determined under a given set of experimental conditions. The values of τ are calculated from the volumetric flow rates of the liquid hydrocarbon and from the effective reactor volume (the volume of the liquid in the reactor), V. Owing to the heterogeneous nature of the reaction mixture, the effective volume varies slightly with reaction conditions. For a given hydrocarbon it was found to be a function of both oxygen and hydrocarbon flow rates. Accordingly, the volume V was separately determined for each experiment. This determination was accomplished by weighing the remaining liquid in the reactor after the flows of hydrocarbon and oxygen gas were simultaneously interrupted. This weight and a separate determination of the liquid density then yielded the value of V. At the experimental conditions utilized in this work the effective reactor volume varied from 7.8 to 8.5 mL.

Effects of Mixing and Oxygen Mass Transfer. The efficiency of mixing and oxygen mass transfer are usually assessed in oxidation studies from the constancy of conversion obtained at different oxygen flow rates with other reaction conditions being constant. This is not possible in our reaction system since, as noted above, a change in the flow rate of oxygen brings also a change in the effective reaction volume and consequently a change in the residence time and conversion. Fortunately, we have observed a relatively simple empirical relationship, which may be predicted from fundamental mechanistic considerations (vide infra), between the instantaneous rates of formation of hydroperoxides, $d(\text{-OOH})_R/dt$, and their concentration, $(\text{-OOH})_R$. In Figure 3 is a plot of $d(\text{-OOH})_R/dt$ vs. $(\text{-OOH})_R^{1/2}$ obtained at 180 °C for residence times up to 230 s. Examination of the plot reveals that there is an approximate linear relation between these quantities when the oxygen flow rate exceeds ca. 1.7 mL s^{-1}. In all of the experiments reported in the present work, unless otherwise noted, the oxygen flow rate was maintained at much higher levels, namely, at 9.1 (8.7) mL s^{-1} at 180 °C (160 °C).

Batch Reactor. The batch reactor design resembles that of the stirred flow reactor in that it consists of two eccentric Pyrex glass spheres. The hydrocarbon (40 mL) was introduced under the flow of argon into the larger outside sphere (55-mm i.d.) and mixed using argon flow during the heating period followed by oxygen during the oxidation period. Both of these gases were introduced into the reactor through perforations (seven holes, 0.5-mm diameter) in a smaller inside sphere (20-mm o.d.) at a flow rate of 13.8 mL s^{-1} at 180 °C. The batch reactor was used with the same gas supply system and constant-temperature bath as those utilized for the stirred-flow reactor (Figure 2). Samples of the reaction mixture at various reaction times were withdrawn using a set of Pasteur disposable pipets and were air quenched to room temperature.

Determination of Total Yields of Peroxide Products. The total yields of hydroperoxide groups, $(\text{-OOH})_R$, peroxides, (-OO-), and hydrogen peroxide, (HOOH), were estimated utilizing the iodometric procedures of Mair and Graupner (methods I and III)[22] in combination with water extraction of hydrogen peroxide.[23] The procedure for method I was modified in the following manner. A solution of 10% glacial acetic acid in 2-propanol (25 mL) was first degassed and saturated with solid carbon dioxide. Potassium iodide (0.3 g) and an aliquot of the oxidized *n*-hexadecane (0.1-1.0 mL) were then added into this solution. The mixture was heated under a carbon dioxide atmosphere using an oil bath at 105-120 °C, refluxed for 7 min, cooled to room temperature again under a carbon dioxide atmosphere, and then titrated with sodium thiosulfate (0.01 M).

Selective Reductions. Sodium borohydride (A),[9] lithium aluminum hydride (B),[9] and triphenylphosphine (C)[24] were utilized to selectively reduce autoxidation products in the reaction mixture (oxidate). All these reagents reduce hydroperoxides to corresponding alcohols. The reagents A and B also reduce ketones and aldehydes and reagent B also reduces carboxylic acids and esters. The use of these selective reducing agents and analysis of corresponding alcohols produced on these reductions allowed identification and determination of parent oxidation products in the oxidate.

The reduction of oxidate (5-15 mL) with A was carried out in methanol (15 mL). The reducing agent (800 mg) was slowly added into the oxidate at room temperature and the mixture was stirred overnight. The excess of A was then destroyed with water (25 mL). An aliquot of the hydrocarbon layer was used for the oxy fraction concentration (see below). If the workup procedure was modified by varying the amounts of A, water, and methanol, significant amounts

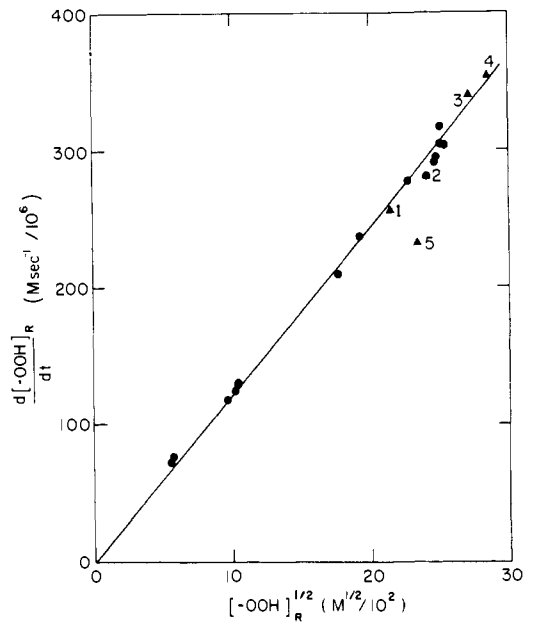


Figure 3. The instantaneous rate of formation of hydroperoxides vs. $[\text{-OOH}]_R^{1/2}$ in the *n*-hexadecane autoxidation at 180 °C and partial pressure of oxygen 100-110 kPa. The triangular points were obtained at *n*-hexadecane flow rate 3.9×10^{-2} mL s^{-1}; the points 1-5 correspond to oxygen flow rates (residence times) of 13.8 (185), 9.1 (207), 6.6 (217), 3.3 (230), and 1.7 (237) mL s^{-1} (s), respectively. The circular points were obtained at an oxygen flow rate of 9.1 mL s^{-1} and at variable *n*-hexadecane flow rates (variable liquid residence times). All flow rates are given at reaction conditions.

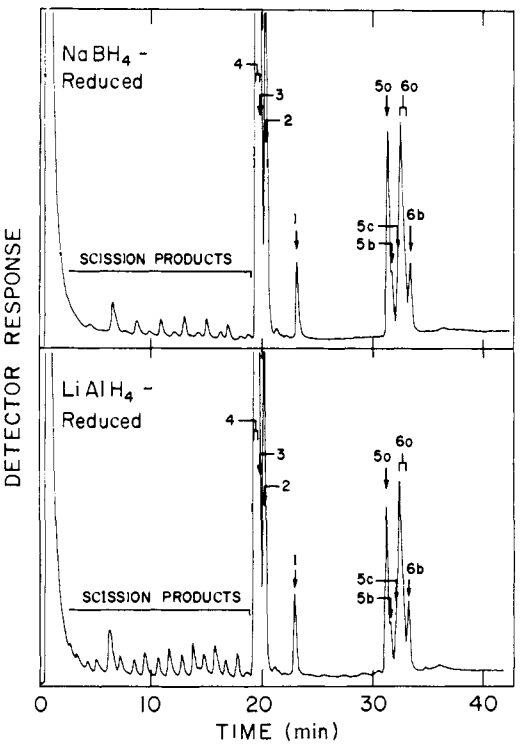


Figure 4. Chromatograms of the oxy fractions from the sodium borohydride and lithium aluminum hydride reduced oxidates obtained by the autoxidation of *n*-hexadecane at 180 °C and residence time 155 s (run 142).

of hexadecanols and hexadecanediols were not recovered.[25]

The reduction of oxidate (5-15 mL) with B was carried out in anhydrous ether (100 mL) which had been distilled from B just prior to use. The reducing agent, ca. 200 mg, was slowly added into the ether solution containing oxidate at room temperature and the mixture was stirred overnight. The excess of B was destroyed by slowly adding sodium sulfate decahydrate and stirring for 4 h. The ether solution was decanted and the solid residue was washed with additional ether. The ether solution and washings were combined, the ether was evaporated in a rotary evaporator, and an aliquot of the reduced oxidate was then used for the oxy fraction concentration.

The reagent C was added in threefold excess (the amount being determined from iodometric titration) into the weighed amount of the oxidate (1.5-4 g) and stirred at room temperature for 2 h. An aliquot of the oxidate reduced with C was transferred to the column for oxy fraction concentration.

Enrichment of Oxy Fractions. In order to carry out a GLC determination of oxidation products in the unreduced and reduced oxidate a sample-concentrating step was required. The oxidates were separated into a hydrocarbon fraction and an oxy fraction by elution chromatography on silica gel.[26,27] The column (1 × 27 cm) was slurry packed in hexane. A gravity flow of 5-7 mL/min was used. The sample size was 1.5-10 g depending on concentration of oxygenated compounds in the oxidate. Approximately 98% of the unreacted *n*-hexadecane was eluted with 200 mL of hexane and the oxy fraction was eluted with 150 mL of methanol. Both eluents were evaporated in a rotary evaporator, the residues were dissolved in a known amount of acetone (5 mL), and the sample aliquots were analyzed by GLC. No oxygenated compounds were detected in the hydrocarbon fraction and in a residue from an additional elution with acetone (100 mL). Small amounts of unreacted *n*-hexadecane, ca. 2% of total, were found in the oxy fraction.

Reduction Efficiency and Recovery. The reduction efficiency and recovery of reduced oxygenated compounds in the workup procedure (reduction with A) and in silica gel enrichment were determined using standard solutions of 3-hexadecanone (29.4 and 50.7×10^{-4} M), 3,6-hexadecanedione (18.1×10^{-4} M), and 5,7-hexadecanedione (16.6×10^{-4} M) in *n*-hexadecane. The recoveries were found to be in all cases equal to 95 ± 2%.

Derivatization of Reduced, Concentrated Oxy Fractions. Trimethylsilylated samples for GLC analysis were prepared by vacuum drying of the acetone oxy fraction solution aliquots (0.5-2.0 mL) and by subsequent treatment of the residues (2-10 mg) with 200 μL of bis(trimethylsilyl)acetamide, 100 μL of trimethylchlorosilane, and 200 μL of pyridine which had been dried over molecular sieves 5A (Linde).[28]

Gas Chromatographic Analyses. Reaction products obtained from reduction, extraction, and separation procedures described above were analyzed by GLC on a 6 ft × 4 mm glass column using 3% Silar-10C or 3% OV-1 (100-120 mesh Gas Chrom Q) packing materials obtained from Applied Science Laboratories, Inc. The details of GLC analyses were described previously.[20] The GLC analyses of oxy fractions from runs 32-98 were done with the F & M 810 gas chromatograph using 3% Silar-10C packings, lot no. SP-1336, 1351, and 1556 (GLC analysis I). With these packings, good separation of 4-8-hexadecanols and 3-hexadecanol was obtained. In later stages of our work (runs 99 and above), the new packing materials, lot no. 1804 and 2080, did not give satisfactory separation of the above components. However, the use of these new packings and also of recycled old packings with the Hewlett-Packard 5730A gas chromatograph resulted in much superior separation of hexadecanediols (GLC analysis II). Therefore, the GLC analyses of the samples 32-98 were repeated also under the conditions of GLC analysis II.

C_{16} Product Identification and Analysis. Typical chromatograms of oxy fractions obtained from hydride reduced oxidates by the silica gel concentrations are shown in Figure 4. We see that in the region of the C_{16} reaction products these chromatograms are practically identical. This indicates that the reduced C_{16} oxidation products and their yields were the same when either of the two reducing agents were used. The peaks 1-4 were identified as 1-hexadecanol (1), 2-hexadecanol (2), 3-hexadecanol (3), and 4-8-hexadecanols (4) by comparison of their retention times with known standards and by an ancillary gas chromatography-EI and CI mass spectrometry.

To identify peaks 5a, 5b, 5c, 6a, and 6b, a preparative liquid-solid chromatographic separation on silica gel[51] of these components was carried out utilizing an oxy fraction from an oxidate (run 47) which had been reduced with lithium aluminum hydride. The successive fractions eluted from the column were analyzed by gas chromatography. The analyses revealed that 1-8 isomeric hexadecanols were eluted first (elution volume up to 100 mL) and the unknown components 5a, 5b, 5c, 6a, and 6b were concentrated in subsequent fractions.

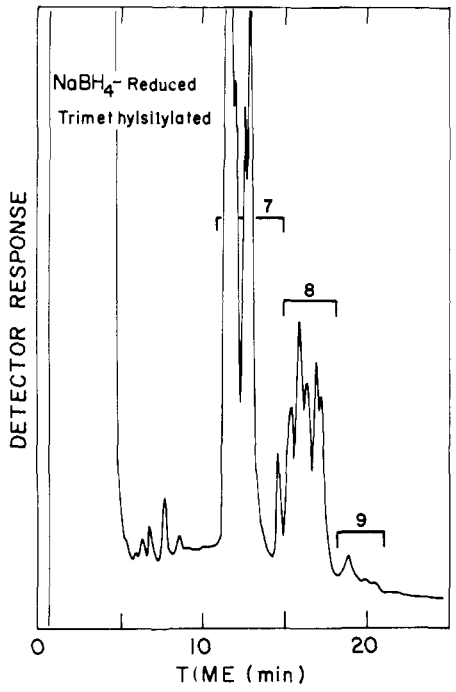


Figure 5. Chromatogram of the trimethylsilylated oxy fraction from the sodium borohydride reduced oxidate obtained by the autoxidation of *n*-hexadecane at 180 °C and residence time 155 s (run 142).

Fraction I, elution volume 100–140 mL, consisted of a mixture of 25% C_9-C_{16} *n*-alcohols and 75% peak 5a and 5b components. Fraction II, elution volume 200–240 mL, contained mainly peak 5c and 6a components with the relative concentrations of component 5c significantly enhanced. Fraction III, elution volume 240–380 mL, contained only the peak 6a component and fraction IV, elution volume 380–540 mL, mainly the peak 6b component. GLC analysis of the trimethylsilylated reduced oxy fraction originally used for the separation and fractions I–IV revealed that peaks 5a + 5b and 6a contained at least five compounds each, suggesting mixtures of isomeric products, and peak 6b only one major compound. All components contained in fractions I–IV exhibited very similar chemical ionization mass spectra with *m/e* values in order of decreasing intensity 259 ($m + 1$), 241 ($m + 1 - 18$), 223 ($m + 1 - 36$), 257 ($m - 1$), and 239 ($m - 1 - 18$), corresponding to the molecular weight of hexadecanediols, 258.

To determine the relative positions of the two hydroxyl groups in these hexadecanediols, fractions I–IV were subjected to periodate oxidation[30,51] and alkylboronation[31,51] reactions. The former was used to identify α,β-diols, the latter to identify α,γ- and α,δ-diols.[32] None of the fraction I–IV subjected to periodate oxidation yielded aldehyde products and all of the fractions on alkylboronation produced *n*-butylboronic derivatives. These results suggest that none of these fractions contains α,β-hexadecanediols and all of them are composed either of α,γ- or α,δ-hexadecanediols.

A final assignment of the structure of the components 5a, 5b, 5c, 6a, and 6b was made by independent syntheses of various model compounds. GLC retention times for 5,7-, 2,4-, 3,6-, and 2,5-hexadecanediols were identical with those obtained for 5a, 5c, 6a, and 6b, respectively. Therefore, we conclude that the group 5 compounds are isomeric α,γ-hexadecanediols and group 6 isomeric α,δ-hexadecanediols, with 5c being 2,4-hexadecanediol and 6b 2,5-hexadecanediol.

In Figure 5 is shown a chromatogram of an oxy fraction obtained from an oxidate reduced with sodium borohydride and derivatized by trimethylsilylation. The series of peaks labeled 7 and 8 are identical with those of silylated derivatives of standard isomeric hexadecanols and hexadecanediols, respectively. The third group of peaks, 9, is tentatively assigned to trimethylsilylated derivatives of isomeric hexadecanetriols.

The total concentrations of isomeric hexadecanols and hexadecanediols, $(ROH)_A$ and $(R(OH)_2)_A$, were determined by a summation of the concentrations of corresponding individual components determined by GLC of oxy fractions obtained from oxidates reduced with sodium borohydride. A further validation of these values was made

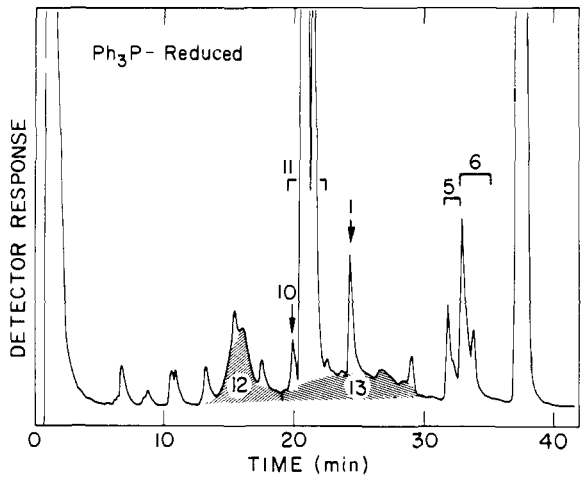


Figure 6. Chromatogram of the oxy fraction from the triphenylphosphine-reduced oxidate obtained by the autoxidation of *n*-hexadecane at 180 °C and residence time 155 s (run 142).

using the GLC data on selected oxy fractions obtained from oxidates reduced with lithium aluminum hydride and trimethylsilylated oxy fractions obtained from oxidates reduced with sodium borohydride. In the case of reduction with lithium aluminum hydride the analytical values for hexadecanols were ca. 6% and for hexadecanediols ca. 8% lower than those obtained for the same oxidate reduced with sodium borohydride. The source of a better recovery of oxidation products with sodium borohydride is in the simpler workup procedure used after reduction of oxidate with sodium borohydride. In the second case, the analysis of trimethylsilylated oxy fractions, the analytical results obtained were within ±5% of those from direct analysis of oxy fractions obtained from oxidates reduced with sodium borohydride. The yields of hexadecanetriols, $(R(OH)_3)_A$, were estimated by GLC of trimethylsilylated oxy fractions obtained from oxidates after reduction with sodium borohydride.

A gas chromatogram of an oxy fraction obtained from an oxidate reduced with triphenylphosphine (C) is shown in Figure 6. The peaks 1, 10, and 11 were identified as 1-hexadecanol, 4-8-hexadecanones, and a mixture of 2-8-hexadecanols, 2-3-hexadecanones, and hexadecanal, respectively. These identifications were accomplished by comparison of GLC residence times of analyzed components with those obtained for known standard compounds and by ancillary gas chromatographic-EI and CI mass spectromeric analyses. The peaks 5abc and 6ab were identified as α,γ- and α,δ-hexadecanediols using the methods already described.

TLC Analysis. TLC was employed throughout the work for monitoring the degree of autoxidation, the reduction, separation, and extraction steps of analytical procedure, synthesis of peroxidic compounds and their purification, and for semiquantitative determination of hydrogen peroxide.[51]

Results and Discussion

The identification and quantitative analyses of the multitude of primary C_{16} reaction products formed during the autoxidation of *n*-hexadecane required a relatively complex analytical scheme (Figure 7). The scheme included chemical analyses for determination of hydroperoxides, peroxides, and hydrogen peroxide, as well as a variety of other techniques for analyses and identification of individual oxidation products. These techniques included selective reductions, derivatizations, oxy fraction enrichments, and separations followed by gas chromatography and ancillary electron impact (EI) and chemical ionization (CI) mass spectrometry. The results of these analyses and the general mechanistic implications of the findings are discussed in the following sections.

C_{16} Products Derived from Hydride Reductions. We will first discuss the results of the analyses of oxidates reduced with sodium borohydride (A) or lithium aluminum hydride (B). With A it is anticipated that hydroperoxides, peroxides, ketones, and aldehydes will be reduced to the corresponding al-

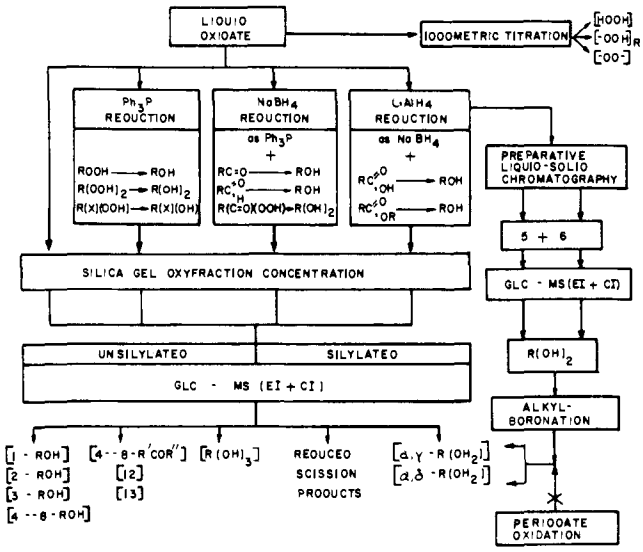


Figure 7. Analysis and identification of C_{16} reaction products from the autoxidation of *n*-hexadecane.

cohols, while B, in addition to the above, will reduce acids and esters to alcohols. The good agreement in the analyses of C_{16} products from the two hydride reductions (see Experimental Section) suggests that negligible amounts of C_{16} products are in the form of esters or acids in the oxidates.

The results of the analyses of individual reaction products and total yields of isomeric hexadecanols, hexadecanediols, and hexadecanetriols, obtained from sodium borohydride reductions, are summarized in Table I.

In Figure 8 are plotted the yields of α,γ- and α,δ-hexadecanediols[33] obtained from sodium borohydride reductions vs. the yields of monosubstituted reaction products obtained at the same residence times at 180 °C. Examination of these plots reveals that a linear relationship was obtained for α,δ-diols (excluding the highest conversion data), i.e.

$$(\alpha,\delta\text{-R(OH)}_2)_A = a(\text{ROH})_A = a(\text{R-MONO})_A \quad \text{(II)}$$

Analogous results were obtained from experiments at 120 and 160 °C. The values of *a* derived from these plots are summarized in Table II.

For α,γ-substituted products a linear relationship between the yields of α,γ-hexadecanediols and yields of monosubstituted products, i.e.

$$(\alpha,\gamma\text{-R(OH)}_2)_A = b(\text{ROH})_A = b(\text{R-MONO})_A \quad \text{(III)}$$

was observed only at 120 °C. At this temperature, two points obtained from the stirred flow reactor experiments and a single point from the cumyl peroxide initiated batch reactor experiment gave a straight line which passes through the origin and gives a value of *b* equal to 0.18. At 160 and 180 °C the yields of α,γ-hexadecanediols relative to yields of monosubstituted products decreased with conversion; this decrease was at 160 °C slight, at 180 °C very strong.

A linear relationship was also observed between the yields of hexadecanetriols and monosubstituted products at 160 and 180 °C:

$$(\text{R(OH)}_3)_A = c(\text{ROH})_A = c(\text{R-MONO})_A \quad \text{(IV)}$$

The values of *c* are also given in Table II.

C_{16} Products Derived from Triphenylphosphine Reductions. With this reducing agent it is anticipated that monohydroperoxides and α,γ- and α,δ-dihydroperoxides will be cleanly reduced to the corresponding alcohols and diols.[24] Any α,α-substituted dihydroperoxides will be converted to carbonyl functions and the resulting carbonyl groups will not be further

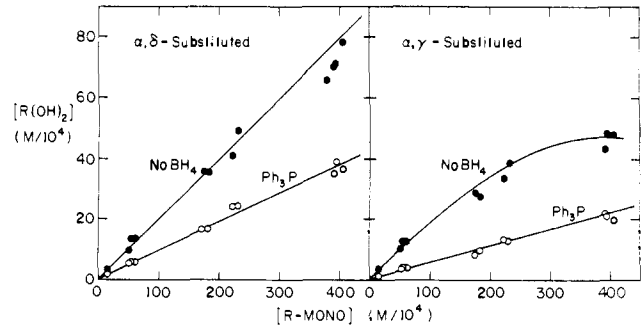


Figure 8. The yields of α,γ- and α,δ-hexadecanediols vs. the corresponding yields of monofunctional products in the sodium borohydride and triphenylphosphine reduced oxidates obtained by the autoxidation of *n*-hexadecane at 180 °C.

reduced by this reagent.

The results derived from the quantitative analysis of oxidates reduced with triphenylphosphine (cf. Table I) revealed that the concentrations of monosubstituted reaction products determined by a summation of concentrations of 1-8-hexadecanols, 2-8-hexadecanones, and hexadecanal, $(\text{R-MONO})_C$, are equal to those obtained with oxidates reduced with sodium borohydride, $(\text{ROH})_A$, i.e.

$$(\text{R-MONO})_C \approx (\text{ROH})_A = (\text{R-MONO})_A \quad \text{(V)}$$

Based upon results obtained from triphenylphosphine reductions, the contribution of hexadecanones to the yields of hexadecanols from sodium borohydride reductions (cf. the yields of 4-8-hexadecanones, $(\text{4-8-R'COR''})_C$, and 4-8-hexadecanols, $(\text{4-8-ROH})_A$, in Table I) in initial stages of oxidation is very small. It does, however, increase with conversion. For example, in the samples obtained at 180 °C at a residence time of 43 s this contribution is ca. 1% and at 210 it is about 4%.

The contribution of hexadecanols present in the autoxidized *n*-hexadecane to the amount of hexadecanols obtained from sodium borohydride reductions was assessed from GLC analyses of a number of *unreduced* trimethylsilylated oxy fraction samples. Under the GLC conditions reported in the present work trimethylsilylated hexadecane hydroperoxides are stable[20,34] and GLC peaks for the derivatized hexadecanols may be clearly distinguished. Although extensive background corrections were involved in their estimation, the results showed that the concentrations of 4-8-hexadecanols are at most slightly higher, ca. 50%, than the concentrations of 4-8-hexadecanones in the original oxidate.

From these results it has been concluded that in the initial stages of oxidation the isomeric hexadecanols obtained on the reduction of oxidates with sodium borohydride and with triphenylphosphine originate almost exclusively from the isomeric monohydroperoxides of *n*-hexadecane, II. With increasing conversion the yields of hexadecanols and hexadecanones formed in the original sample during the autoxidation increase. For example, at 180 °C and residence time of 210 s the yields of these products may represent as much as 10% of total monofunctional products.

In contrast to monosubstituted reaction products, the yields of α,γ- and α,δ-hexadecanediols[33] obtained from the triphenylphosphine reductions were significantly lower than those obtained from the sodium borohydride reductions. In Figure 8 are also included plots of the yields of diols from the triphenylphosphine reductions vs. the yields of monosubstituted reaction products obtained at the same residence times at 180 °C. Linear relationships were obtained for both α,γ- and α,δ-hexadecanediols at all temperatures studied, i.e.

$$(\alpha,\gamma\text{-R(OH)}_2)_C = d(\text{R-MONO})_C \quad \text{(VI)}$$

Table I. Analysis of C_{16} Reaction Products and Hydroperoxide Concentrations for the Autoxidation of *n*-Hexadecane at 120, 160, and 180 °C and 100-110 kPa[a]

residence time τ, s	run no.	GLC procedure[b]	sodium borohydride reduced: monofunctional (1-ROH)$_A$[c] (1)[i]	(2-ROH)$_A$ (2)	(3-ROH)$_A$ (3)	(4-8-ROH)$_A$ (4)	(3-8-ROH)$_A$ (3 + 4)	(ROH)$_A$[d] (1-4)	difunctional (R-DI/A)$_A$[e] (5a + 5b)	(R-DI/B)$_A$[f] (5c + 6a)	(2,5-R(OH)$_2$)$_A$ (6b)	(R(OH)$_2$)$_A$[g] (5abc + 6ab)	trifunctional (R(OH)$_3$)$_A^{TMS}$ (9)
							10^4(X), M[k]—120 °C						
2153	98	I	(0.15)[l]	0.99	0.67	3.29	3.96	5.10				(1.8)[m]	
		II	0.14	0.93			3.59	4.66	0.73	0.85	0.16	1.74	
4112	122	I	(0.56)[l]	3.58			15.5	19.7					0.32
		II	0.50(1)[2]	3.22(5)[2]			14.0(2)[2]	17.7(2)[2]	2.49(14)[2]	2.9(2)[2]	0.69	6.08(7)[2]	
3000[q]	BR67	II						49.5	7.4	8.4	1.9	17.7	
							160 °C						
88	60	I		0.99	0.82	2.32	3.14	4.13				(1.6)[m]	
		II	0.14	0.75			2.61	3.50	0.66	1.07	0.16	1.89	
206	61	I	(0.54(8)[2])[l]	5.06(17)[2]	4.05(9)[2]	13.8(2)[2]	17.8(3)[2]	23.5(2)[2]				(7.0)[m]	0.25
		II	0.84	3.90			14.6	19.4	3.09	3.17	0.59	6.85	
208	42	I	(0.61(2)[2])[l]	3.88(14)[2]	3.11(4)[2]	11.7(2)[2]	14.8(2)[2]	19.3(1)[2]				(7.4)[m]	
		II	0.95	4.47			16.5	21.9	4.36	2.92	0.62	7.90	
410	43	I	(2.71)[l]	14.5	10.2	40.8	51.0	68.2				(26)[m]	
430	65	I	(2.84)[l]	14.8	11.2	44.7	55.9	73.6				(26)[m]	1.3
		II	3.13	15.2			56.5	74.8	11.2	12.4	1.87	25.5	
797	66	I	(9.82)[l]	56.0	44.7	159	204	270				(81)[m]	5.5
814	44	I											
		II	11.1	52.3			193	256	30.4	41.7	9.8	81.9	
							180 °C						
43	34	I	(0.55(4)[3])[l]	3.08(11)[3]	2.45(24)[3]	8.46(61)[3]	10.9(8)[3]	14.5(11)[3]				(7.6-(6)[2])[m]	0.26
		II	0.66(2)[2]	2.99(3)[2]			10.8(1)[2]	14.5(1)[2]	3.00(8)[2]	3.10(6)[2]	0.91(11)[2]	7.02(14)[2]	
43	58	I											
78	150	II	2.40	10.6			38.4	51.4	8.36	9.19	2.09	19.6	
84	33	I	(1.94(3)[2])[l]	11.5(6)[3]	9.61(30)[3]	32.9(18)[3]	42.5(5)[3]	56.0(25)[3]				(21.1)[m]	1.5
		II	2.79	12.3			45.4	60.5	10.6	12.6	3.04	26.3	
84	47	I	(2.24)[l]	12.0	9.69	34.1	43.8	58.1				(23.4)[m]	
		II	2.70	11.2			44.2	58.1	11.0	12.0	2.51	25.5	
84	57	I											
148	149	II	8.29	37.2			138	184	22.8	31.6	8.25	62.6	
152	142	II	8.88	44.5			167	221	27.8	37.8	8.51	74.2	3.9
154	108	II	10.6	49.2			175	235	32.1	46.0	9.30	87.4	8.1
202	151	II	17.5	78.8			304	400	40.1	68.3	17.8	126	10.5
204	59	I	(13.0)[l]	77.9	60.9	228	289	379				(104(5)[2])[m]	
		II	16.2	74.6			289	379	34.0	57.8	14.6	106	
207	56	I											
207	55	I	(11.3)[l]	79.1	65.2	225	290	381				(105)[m]	
		II	16.1	75.6			299	390	40.4	62.6	16.6	120	
210	32	I	(13.6(9)[3])[l]	76.7(24)[3]	65.4(7)[3]	232(3)[3]	298(3)[3]	387(8)[3]				(108)[m]	9.9
		II	15.8(0)[2]	78.2(9)[2]			301(1)[2]	395(1)[2]	36.0(8)[2]	62.2(17)[2]	15.0(9)[2]	113(1)[2]	
234	109	II	32.0	180			714	926	53.5	152	46.2	252	

residence time, s	run no.	GLC procedure[b]	triphenylphosphine reduced: monofunctional (4-8-R′COR″)$_C$ (10)	(R-MONO)$_C$[n] (1 + 10 + 11)	difunctional (R-DI/A)$_C$[e] (5a + 5b)	(R-DI/B)$_C$[f] (5c + 6a)	(2,5-R(OH)$_2$)$_C$ (6b)	(12)	(13[n])	hydroperoxide titration (-OOH)$_R$[t]
				10^4(X), M[k]—120 °C						
2153	98	I	0.027	5.67						7.3
		II			0.23	0.37	0.20	0.28	(0.8)	
4112	122	I	0.21	19.3						25.6
		II			0.69	1.22	0.33	2.2	(1.6)	
3000[q]	BR67	II	1.4	53.6	1.8	3.3	1.0			77
					160 °C					
88	60	I		4.05						7.5(5)[2]
		II			0.21	0.66[o]		0.68	(0.4)	
206	61	I	0.097	24.7						43(1)[2]
		II			1.45	3.12[o]		2.3	(3.9)	
208	42	I	0.084	19.0						41(4)[3]
		II			0.95	1.44	0.43	1.2	(1.7)	
410	43	I	0.53	69.8	3.00[p]	5.15[p]	1.53[p]	4.4[p]	(7.8)	122(1)[2]
430	65	I	0.62	74.3						126
		II			2.80	4.58	1.11	6.5	(4.6)	
797	66	I		281	10.6[p]	17.2[p]	5.18[p]	23[p]	(16)	460
814	44	I	3.77	235						428
		II			10.0	17.2	4.46	18	(24)	
					180 °C					
43	34	I	0.068(14)[3]	14.6(8)[2]						33(1)[2]
		II			0.95	1.58	0.37	1.8	(3.2)	
43	58	I		14.7						31
78	150	II	0.46	51.9	2.73	4.60	1.28	7.7	(10)	93
84	33	I	0.49(3)[2]	55.4(6)[2]						108(3)[3]
		II			3.20	5.00	1.21	4.7		
84	47	I	0.54(2)[2]	59.9						104
		II								
84	57	I	0.48	57.8						109
148	149	II	2.91	184	7.93	14.2	4.03	24	(26)	314
152	142	II	3.56	223	9.2	16.7	4.50	24	(26)	367(2)[2]
154	108	II	4.58	232	10.6	20.4	5.96	22.7		414(1)[2]
202	151	II	9.8	407	16.3	30.8	8.89	42	(46)	631
204	59	I	8.4(7)[3]	385(14)[3]						615
		II								
207	56	I	9.5(10)[2]	408(4)[2]						645(4)[2]

Table I (*Continued*)

207	55	I	9.0	395						579(6)[6]
		II			17.5	31.3	10.9	17		
210	32	I	9.1	392						609(3)[3]
		II			15.6	28.5	9.3	29	(31)	
234	109	II	58.9	903						1260

[a] Initial concentrations of *n*-hexadecane at 120, 160, and 180 °C were 3.11, 2.98, and 2.91 M, respectively. [b] For GLC conditions and column packing used in GLC procedures I and II refer to the text in Experimental Section. [c] The subscript letter in concentration terms designates the reducing agent utilized. [d] $(ROH)_A = (1\text{-}8\text{-}ROH)_A$. [e] $(R\text{-}DI/A) = (3,5\text{-}7,9\text{-}R(OH)_2) = (\alpha,\gamma\text{-}R(OH)_2) - (2,4\text{-}R(OH)_2)$. [f] $(R\text{-}DI/B) = (2,4\text{-}R(OH)_2) + (3,6\text{-}7,10\text{-}R(OH)_2) = (2,4\text{-}R(OH)_2) + (\alpha,\delta\text{-}R(OH)_2) - (2,5\text{-}R(OH)_2)$. [g] $(R(OH)_2) = (\alpha,\gamma\text{-}R(OH)_2) + (\alpha,\delta\text{-}R(OH)_2)$. [h] $(R\text{-}MONO)_C = (1\text{-}8\text{-}ROH)_C + (2\text{-}8\text{-}R'COR'')_C + (R'CHO)_C$. [i] By iodometric titration. [j] The number designations in concentration terms correspond to the peak designation used in Figures 5, 6, and 8. [k] 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, $11.5(6)^3$ denotes that three measured values lay in the range 11.5 ± 0.6. [l] The concentrations of 1-hexadecanol, $(1\text{-}ROH)_A$, obtained by the GLC procedure I are approximate due to the low sensitivity and peak tailing. [m] The concentrations of hexadecanediols, $(R(OH)_2)_A$, obtained by the GLC procedure I are approximate due to the peak tailing and significant background corrections involved in their extraction. [n] The concentrations of the peak **13** components are approximate due to an interference from C_{16} monofunctional products and uncertainties in background corrections. [o] Values include also (6b), i.e., they are equal to (5c + 6a + 6b). [p] Values obtained using GLC procedure II. [q] Batch reactor experiment; cumyl peroxide, CP, initiated; $(CP)_0 = 48.6 \times 10^{-4}$ M. [r] In Me_4Si.

Table II. Summary of Molar Ratios of Di- and Trifunctional to Monofunctional Products[a]

	$NaBH_4$			Ph_3P	
temp, °C	$(\alpha,\delta\text{-}R(OH)_2)$ eq II, *a*	$(\alpha,\gamma\text{-}R(OH)_2)$ eq III, *b*	$(R(OH)_3)$ eq IV, *c*	$(\alpha,\delta\text{-}R(OH)_2)$ eq VI, *d*	$(\alpha,\gamma\text{-}R(OH)_2)$ eq VII, *e*
120	0.163	0.18	0.017[b]	0.076	0.044
160	0.176		0.020	0.077	0.048
180	0.198[c]		0.025	0.095	0.054[c]

[a] Least square. [b] A single point value. [c] For the range up to (R-MONO) equal to 250×10^{-4} M.

$$(\alpha,\delta\text{-}R(OH)_2)_C = e(R\text{-}MONO)_C \qquad (VII)$$

The values *d* and *e* derived from these plots are included in Table II.

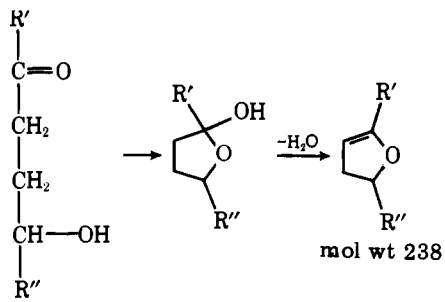
Considering the known reduction behavior of triphenylphosphine[24] and the results of the material balances based upon hydroperoxide titrations, vide infra, we identify the precursors to the triphenylphosphine-derived diols in initial stages of oxidation mainly as α,γ- and α,δ-dihydroperoxides, IV.

Thus, the differences in the yields of diols obtained from the hydride and triphenylphosphine reductions, $(R(OH)_2)_A - (R(OH)_2)_C$, must originate from other α,γ- and α,δ-substituted species. The following observations suggest that these α,γ- and α,δ-substituted species are converted by the triphenylphosphine reduction to the corresponding isomeric hydroxy ketones. In the samples reduced with triphenylphosphine, in addition to C_{16} monosubstituted and hexadecanediol products, two wide groups of products, peaks designated 12 and 13, were observed (Figure 6). The results of GLC–EI and CI mass spectrometric studies revealed that *both* of these groups contain components of molecular weight 238 and 240, with the first one being predominant.

It was found that sums of the yields of 12 and of the α,δ-diols from triphenylphosphine reductions are approximately equal to the yields of α,δ-diols obtained from the sodium borohydride reductions, i.e.

$$(\alpha,\delta\text{-}R(OH)_2)_C + (12)_C = (\alpha,\delta\text{-}R(OH)_2)_A \qquad (VIII)$$

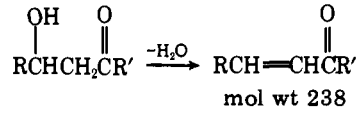
In addition, the GLC retention time of a sample of a C_{16} cyclic ether, 2-methyl-5-*n*-undecyltetrahydrofuran, was found to be within the range of residence times of the group 12 components. These findings are consistent with the view that the group 12 components are isomeric C_{16} dihydrofurans formed from γ-hydroxy ketone compounds via the well-established cyclization and dehydration reaction sequence[35] of reaction 1.



(1)

This view finds further support from the results of a series of experiments in which the triphenylphosphine reductions were carried out under more forcing conditions and in one case in the presence of sulfuric acid, a dehydrating agent.[51]

Analogously, the group 13 components which exhibit a wide range of GLC retention times starting in the area of C_{16} monofunctional products and ending in the area anticipated for C_{16} hydroxy ketones are likely to be the isomeric unsaturated ketones from the in situ dehydration of β-hydroxy ketones[36] under conditions of GLC analysis, i.e., reaction 2. Although

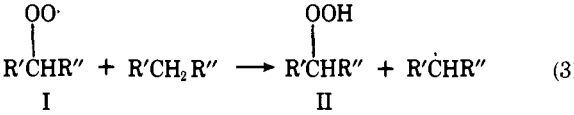


(2)

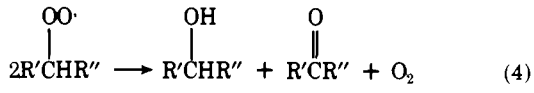
a material balance similar to that shown in eq VIII cannot be obtained for these species owing to the large interference from other products, the results derived from experiments to be reported in a later paper of this series[37] are consistent with the view that group 13 is formed exclusively from such α,γ-substituted species.

The original form of α,γ- and α,δ-substituted species which convert in the triphenylphosphine reduction to β- or γ-hydroxy ketones and sodium borohydride reduction to α,γ- and α,δ-hexadecanediols, respectively, is not well defined. These reduction products are, however, most likely derived from β- and γ-hydroperoxy ketones, VI, and/or from α,α,γ- and α,α,δ-substituted trihydroperoxy, VIII, or cyclic hydroperoxyperoxy, IX, intermediates.

Reaction Scheme for C_{16} Product Formation. A general reaction scheme for the formation of the C_{16} products in *n*-hexadecane autoxidation based upon the results derived from the various reduction methods and hydroperoxide titrations, vide infra, will now be presented. This reaction scheme forms the basis for the kinetic analyses to be presented in a later paper.[38] The isomeric hexadecyl hydroperoxides, II, are formed via the intermolecular abstraction reactions of isomeric hexadecylperoxy radicals, I (reaction 3). The small amounts of hexadecanones and hexadecanols found in oxidates are then formed primarily via bimolecular termination reactions of

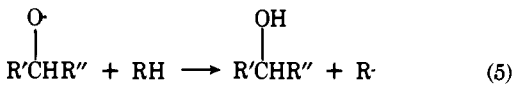


(3)



(4)

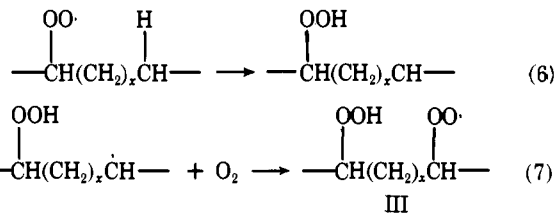
peroxy radicals[39] (reaction 4). In later work[38] we shall, in fact, make use of this data for an estimate of the rate of free-radical termination in our *n*-hexadecane system. The results of those estimates are consistent with the view that kinetic chain lengths in the initial stages of the autoxidation of *n*-hexadecane are very long, e.g., equal to 60 (17) in 43 (210) s experiments at 180 °C. The small excess yields of hexadecanols, relative to hexadecanones, then arise from abstraction reactions of in-



(5)

termediate alkoxy radicals formed in the homolysis of the corresponding hydroperoxides (reaction 5).

The C_{16} dihydroperoxide products, IV, are then formed in the initial stages of autoxidation by the following reaction sequence including an intramolecular hydrogen abstraction reaction of the isomeric hexadecylperoxy radicals, reaction 6,

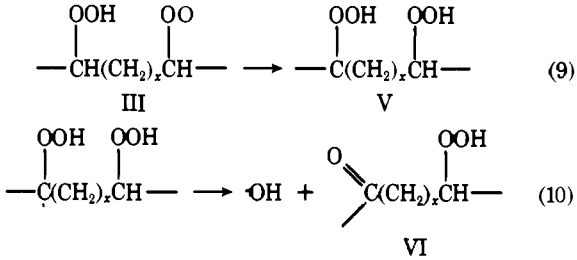


(6) (7) (8)

III IV

followed by a formation of hydroperoxyhexadecylperoxy radicals, III, reaction 7, and by an intermolecular hydrogen abstraction reaction, reaction 8, where x is equal to 1 or 2.

Simultaneously, the intermediate III may undergo the



(9) (10)

III V VI

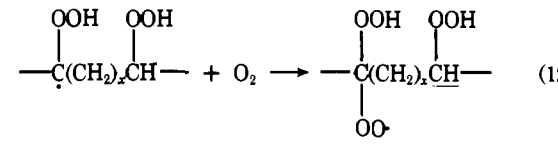
highly favored reaction sequences[49] 9 and 10 followed by the rapid nonselective abstraction reaction 11.

$$HO\cdot + R'CH_2R'' \rightarrow HOH + R'CHR'' \quad (11a)$$

$$HO\cdot + CH_3R''' \rightarrow HOH + CH_2R''' \quad (11b)$$

Based upon estimate of rates of free-radical initiation and termination in the *n*-hexadecane autoxidation[38] species VI must arise primarily from reaction 10. Further, the observed, lower than expected ratios of the yields of 2-hexadecanol to 1-hexadecanol at all temperatures suggest that a high percentage of hydrogen abstractions from hexadecane molecules occur via hydroxyl radicals, reaction 11, and/or via radicals of *low* selectivity compared to organic peroxy radicals. A more detailed analysis and discussion of the isomeric distribution of the monofunctional C_{16} products will be presented in a later work.[38]

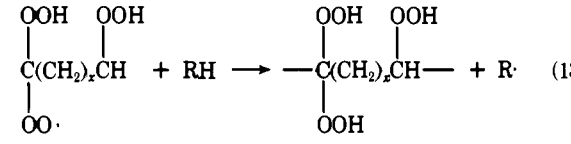
Alternatively, intermediate V may add oxygen (reaction 12) and lead to a further intramolecular abstraction and to a se-



(12)

VII

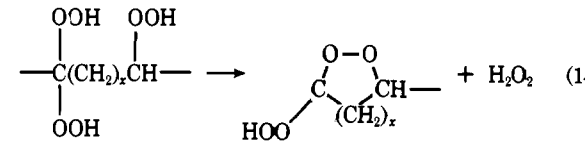
quence analogous to reactions 9 and 10, and/or undergo intermolecular abstraction (reaction 13) followed by loss of



(13)

VIII

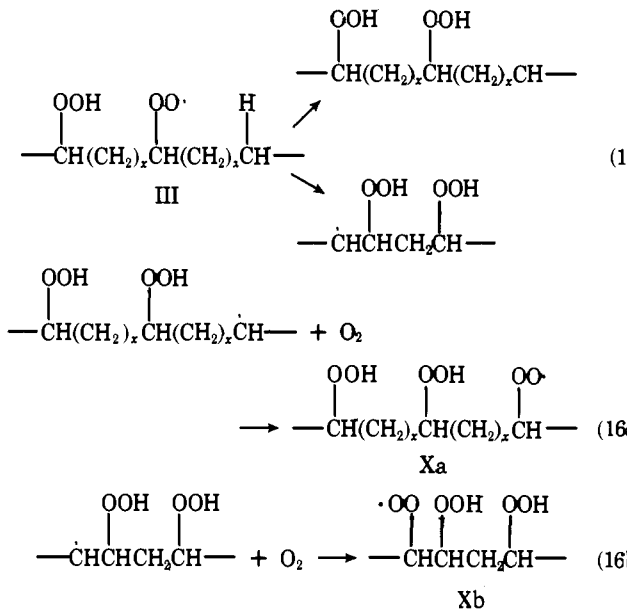
hydrogen peroxide to yield cyclic peroxide species, IX (reaction 14).



(14)

IX

In addition to reactions 8 and 9, the intermediate hydroperoxyhexadecylperoxy radicals, III, may undergo intramolecular hydrogen abstraction reactions similar to reaction 6 followed by a reaction with oxygen (reactions 15 and 16).



(15) (16a) (16b)

III Xa Xb

The dihydroperoxyhexadecylperoxy radicals X then lead to a formation of trifunctional reaction products analogous to IV, IX, and VI and in the latter case also to a concurrent formation of hydroxy radicals.

It is anticipated that substituted hexadecyl ketones and hexadecanols would be formed by termination reactions of the peroxy radicals III, VII, and X analogous to reaction 4 and by abstraction reactions of intermediate alkoxy radicals from homolytic decomposition of hydroperoxides IV, VI, VIII, IX, and those formed from X analogous to reaction 5. The relative yields of these products should parallel those observed in the monofunctional products, i.e., ca. 1 (4)% of their parent hydroperoxide products in the 43 (210) s experiments at 180 °C.

The proposed reaction scheme is strongly supported by the linear relationships observed between the yields of diols or triols derived on sodium borohydride or triphenylphosphine reductions and the yields of monofunctional products (eq II, III, IV, and VI–VII) since the formation of all these products is de-

pendent upon reactions which are first order in parent peroxy radicals. The relative decrease of the yields of α,γ-substituted species VI, VIII, and/or IX with conversion at increased temperatures (see above) can then be accounted for if these species under these conditions are undergoing conversions to other products in the time scale of the autoxidation. As we shall see in the results of analyses of scission products[37] this appears to be the case. Indeed, these α,γ-substituted species are very important precursors of scission methyl ketones and carboxylic acids.

Hydroperoxide Material Balance. Material balances are assessed by a comparison of the original yields of peroxidic products with the yields of products obtained upon analyses of the sample after chemical reduction by a variety of techniques.

The calculation of hydroperoxide contributions based upon the yields of hexadecanols derived from sodium borohydride reductions and hexadecanols and hexadecanediols from triphenylphosphine reductions can be made in a straightforward manner. However, based upon our present knowledge, unambiguous assignments of hydroperoxide contributions from the additional hexadecanediols derived from sodium borohydride reductions cannot be made. Accordingly, we have made material balance calculations based upon two extreme cases. In the first case it is assumed that all of these species are trihydroperoxides, VIII, while in the second case it is assumed that they are hydroperoxy ketones, VI.[40] After corrections for initiation, scission, and termination products,[41] which are extremely small at low conversions and increase to approximately 8% at the highest conversions, the results presented in Figure 9 for 180 °C are obtained. Similar results were obtained at 120 and 160 °C.

Comparison of the data points generated for these two limiting cases with the theoretical line for a quantitative material balance reveals that the assumption that all species are trihydroperoxides cannot be correct since this would imply that the yields of these products obtained upon reduction are greater than theory. In contrast, the assumption that these species are hydroperoxy ketones is consistent with theory if the isolated yields of these products are ca. 90% of theory. This value of the yield is somewhat lower than we have observed in control experiments, cf. Experimental Section, and thus it is possible that we have a mixture of VIII and VI in the original products. Alternatively, these species may be in the form of cyclic hydroperoxy peroxides, IX. Data points generated on this assumption agree, perhaps fortuitously, with the theoretical line. In any case, this treatment reveals that material balances exceed 90% of theory and virtually require that the primary products found in the initial stages of autoxidation are mono-, di-, and polyhydroperoxide species.

Intramolecular Reactions. For some time it has been recognized that α,γ intramolecular abstraction of tertiary hydrogen by peroxy radicals dominates the liquid-phase oxidation of branched hydrocarbons; high yields of difunctional oxygenated products had been reported by a number of investigators.[42-45] In contrast, in the liquid-phase oxidation of *n*-alkanes difunctional oxygenated products had been isolated in only very low yields.[8] In his review of hydrocarbon oxidation kinetics Benson[46] emphasized that these results were inconsistent with those predicted from the generally accepted values of activation parameters for peroxy radical reactions. In view of our findings it is now appropriate to reexamine the earlier liquid-phase work on *n*-alkane systems.

Brown and Fish[9] in their study of the high-temperature autoxidation of 2-methylhexadecane pointed out that C_{17} compounds having two or more functional groups are unlikely to be eluted from the gas chromatographic column under the conditions employed in their analyses. Probably for the same reason Boss and Hazlett[10] failed to report the formation of

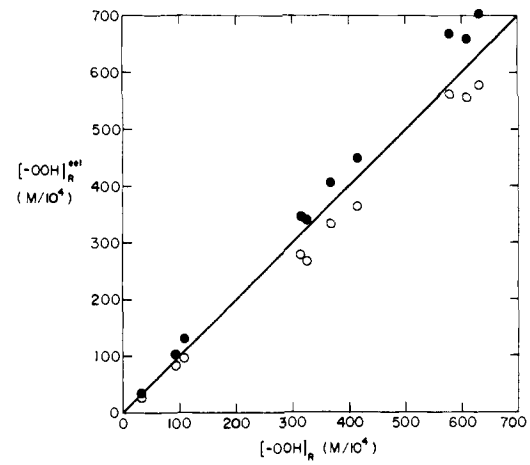


Figure 9. Hydroperoxide material balance at 180 °C obtained assuming that $(R(OH)_2)_A - (R(OH)_2)_C$ represents trihydroperoxides, ●, or hydroperoxy ketones, ○.

difunctional products from the autoxidation of *n*-dodecane at 200 °C in the presence of air.

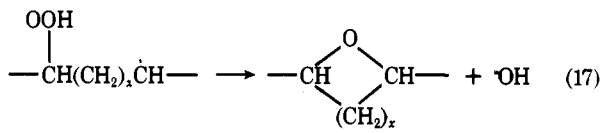
Van Sickle et al.[8] (in further discussion denoted as VS) estimated that in the di-*tert*-butyl peroxide initiated liquid-phase oxidations of *n*-pentane at 100 °C and *n*-octane at 100 and 125 °C difunctional species are produced with maximum yields of only 10% based upon consumed oxygen and the ratio $(k_{intra}/\text{H-atom})/(k_{inter}/\text{H-atom})$ for *n*-pentane equals ca. 1.0. However, as they noted, analyses of reduced products accounted for only 70–80% of the pentanols and 50% of the octanols expected from hydroperoxide titrations and considerable quantities of unspecified acids and of other secondary products were formed during the time periods of their experiments.

From the results reported in this work, the values of $(k_{intra}^{\alpha,\gamma\text{-sec}}/\text{H-atom})/(k_{inter}/\text{H-atom})$ and $(k_{intra}^{\alpha,\gamma\text{-tert}}/\text{H-atom})/(k_{inter}/\text{H-atom})$ at 120 °C are equal to 4.8 and 270 M.[47] We shall now show that the observation of low yields of difunctional products by VS in the *n*-pentane system is likely due to the conversion of metastable α,γ-substituted species to secondary products during the extended time periods of most of their experiments and that their estimate of $(k_{intra}/\text{H-atom})/k_{inter}/\text{H-atom})$ is too low. A reexamination of the results of analyses of reduced samples reported by VS reveals that the ratio of 2,4-pentanediol to pentanols was 0.13 for a 200-min experiment (a result not discussed by VS). The ratio decreased to 0.022 for a 1444-min experiment. Assuming that in their 200-min experiment the 2,4-pentanediol represents the sum of initial 2,4-substituted metastable species and 2,4-dihydroperoxypentane and that in their 1444-min experiment *only* 2,4-dihydroperoxypentane survives to give upon reduction 2,4-pentanediol, values of $(k_{intra}^{\alpha,\gamma\text{-sec}}/\text{H-atom})/(k_{inter}/\text{H-atom})$ and $(k_{intra}^{\alpha,\gamma\text{-tert}}/\text{H-atom})/k_{inter}/\text{H-atom})$ equal to 4.4 and 264 M are obtained.[50] These values are in striking agreement with those observed in the present work at 120 °C.

We now consider some additional observations reported by VS. In the *n*-pentane system the reactivity ratio for secondary to primary hydrogen abstractions, determined from the ratio of 2- and 3-pentanols to 1-pentanol in a reduced sample, was 11. As they noted, this low value suggests the occurrence of hydrogen atom abstraction by radicals *less* selective than secondary peroxy radicals. In the presence of high concentrations of *tert*-butyl hydroperoxide, added to completely suppress intramolecular abstractions, the above reactivity ratio was equal to 38. This higher value is fully consistent with the reactivity ratio reported earlier[7] for hydrogen abstractions by secondary peroxy radicals in the *n*-butane system. Taken together, these results suggest that the reaction sequence 9–10

proposed in the present work, i.e., the formation of hydroxy radicals concurrent with and/or subsequent to the second, highly favored intramolecular abstraction, is of importance in the *n*-pentane systems. Such hydroxy radical producing reactions would then be common to *all* *n*-alkane oxidations of systems larger than *n*-butane.

The distribution of difunctional products reported in recent studies of hydrocarbon oxidation in the gas phase at 400–500 °C is in complete accord with the results obtained in the present study of *n*-hexadecane autoxidation in the liquid phase. At low conversions in the *n*-pentane–H_2–O_2 system at 480 °C[48] 2,4-dimethyloxetane and 3-ethyloxetane, formed via α,γ-abstraction reactions of monoperoxy radicals, are found to represent 38% of the oxygenated products and 2-methyltetrahydrofuran formed via α,δ abstraction to represent 43% of the oxygenated products. These products arise from the cyclization reaction 17. When x is equal to 2, the cyclization rate



(17)

is much faster than oxygen addition. However, when x is equal to 1, the rates of cyclization and oxygen addition are comparable and the yields of scission products increase with increasing oxygen concentration at the expense of the oxetane products. These results suggest the occurrence in the gas phase of a reaction sequence similar to that suggested in the present liquid-phase study, namely, reactions 6, 7, 9, and 10 followed by scission reaction of VI.

Acknowledgments. The authors wish to acknowledge Dr. W. O. Siegl for the synthesis of 5,7-hexadecanedione, Dr. T. M. Harvey, T. J. Prater, and R. Marano for mass spectrometric analyses of reduced oxidates, Dr. E. J. Hamilton, Jr., for a suggestion to measure the temperature changes in the stirred-flow reactor and for the design of the thermocouple system to make these measurements, and L. Toth for skillful construction of the stirred-flow reactor.

Supplementary Material Available: Experimental procedures for preparative liquid–solid chromatography, periodate oxidation, alkylboronation, and TLC analysis; results (Table III) and discussion of triphenylphosphine reductions of an oxidate under forcing conditions (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Presented in part at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, Abstracts, No. PETR 54, PHYS 17, 18.
(2) Cf. J. A. Howard in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, 1973, Chapter 12.
(3) Cf. K. U. Ingold in ref 2, Vol. I, Chapter 2.
(4) S. Korcek, J. H. B. Chenier, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **50**, 2285 (1972).
(5) A. W. Dawkins, *Eur. Chem. News, Normal Paraffins Suppl.*, 49 (Dec 2, 1966).
(6) F. R. Mayo, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, **19**, No. 4, 627 (1974).
(7) T. Mill, F. Mayo, H. Richardson, K. Irwin, and D. L. Allara, *J. Am. Chem. Soc.*, **94**, 6802 (1972).
(8) D. E. Van Sickle, T. Mill, F. R. Mayo, H. Richardson, and C. W. Gould, *J. Org. Chem.*, **38**, 4435 (1973).
(9) D. M. Brown and A. Fish, *Proc. R. Soc. London, Ser. A*, **308**, 547 (1969).
(10) (a) B. D. Boss and R. N. Hazlett, *Can. J. Chem.*, **47**, 4175 (1969); (b) *Ind. Eng. Chem., Prod. Res. Dev.*, **14**, 135 (1975).
(11) (a) K. G. Denbigh, *Trans. Faraday Soc.*, **40**, 352 (1944); (b) B. Stead, F. M. Page, and K. G. Denbigh, *Discuss. Faraday Soc.*, **2**, 263 (1947); (c) K. G. Denbigh, M. Hicks, and F. M. Page, *Trans. Faraday Soc.*, **44**, 479 (1948).
(12) H. H. Young, Jr., and L. P. Hammett, *J. Am. Chem. Soc.*, **72**, 280 (1950).
(13) I. P. Skibida, Z. K. Maizus, and N. M. Emanuel, *Russ. Chem. Rev.* (*Engl. Transl.*) **38**, 1 (1969).
(14) L. R. Mahoney, S. Korcek, R. K. Jensen, and M. Zinbo, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, **21**, No. 4, 852 (1976).
(15) S. Wawzonek, P. D. Klimstra, and R. E. Kallio, *J. Org. Chem.*, **25**, 621 (1960).
(16) W. E. Parker, C. Ricciuti, C. L. Ogg, and D. Swern, *J. Am. Chem. Soc.*, **77**, 4037 (1955).
(17) J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944).
(18) H. Stetter and H. Kuhlmann, *Tetrahedron Lett.*, 4505 (1974).
(19) P. M. Jacobs and A. H. Soloway, *J. Org. Chem.*, **39**, 3427 (1974).
(20) M. Zinbo, R. K. Jensen, and S. Korcek, *Anal. Lett.*, **10**, 119 (1977).
(21) M. F. R. Mulcahy and D. J. Williams, *Aust. J. Chem.*, **14**, 534 (1961).
(22) R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36**, 194 (1964).
(23) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **45**, 785 (1967).
(24) L. Horner and W. Jurgeleit, *Justus Liebigs Ann. Chem.*, **591**, 138 (1955).
(25) M. Zinbo, R. K. Jensen, and S. Korcek, *Anal. Lett.*, in preparation.
(26) R. A. Brown, M. I. Kay, J. M. Kelliher, and W. A. Dietz, *Anal. Chem.*, **39**, 1805 (1967).
(27) B. D. Boss, R. N. Hazlett, and R. L. Shepard, *Anal. Chem.*, **45**, 2388 (1973).
(28) M. Zinbo and W. R. Sherman, *J. Am. Chem. Soc.*, **92**, 2105 (1970).
(29) K. Maruyama, K. Onone, and R. Goto, *J. Chem. Soc. Jpn.*, **77**, 1496 (1956).
(30) G. King, *J. Chem. Soc.*, 1826 (1938).
(31) "Alkylboronates of Bifunctional Compounds", *Gas-Chromatogr. Newsl.*, **17**, No. 2, 1 (1976).
(32) The reactivity of α,γ-diols was confirmed in our laboratory using standard compounds.
(33) The yields of α,γ- and α,δ-hexadecanediols, (α,γ-$R(OH)_2$) and (α,δ-$R(OH)_2$), respectively, were estimated from values of (5a + 5b), (5c + 6a), and (6b) (cf. Table I) assuming that (5c) = 1/5 (5a + 5b), i.e., α,γ-hexadecanediol isomers are formed in equal yields.
(34) R. R. Hiatt, *Can. J. Chem.*, **42**, 985 (1964).
(35) Cf. T. S. Stevens in "Chemistry of Carbon Compounds", Vol. IVA, E. H. Rodd, Ed., Elsevier, Amsterdam, 1957, Chapter 3, p 159.
(36) Cf. A. W. Johnson, C. E. Dalgliesh, W. E. Harvey, and C. Buchanan in ref 35, Vol. IA, Chapter 11, p 711.
(37) R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, in preparation (part 2 of this series).
(38) R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, in preparation (part 3 of this series).
(39) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).
(40) First case:

$$(-OOH)_R^{esl} = (ROH)_A + 2(R(OH)_2)_C + 3((R(OH)_2)_A - (R(OH)_2)_C) + 3(R(OH)_3)_A - Z$$

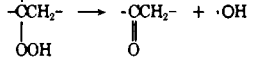
Second case:

$$(-OOH)_R^{esl} = (ROH)_A + 2(R(OH)_2)_C + (R(OH)_2)_A - (R(OH)_2)_C + 3(R(OH)_3)_A - Z$$

where Z is a correction term defined in ref 41.
(41) The correction, Z, for the contribution of termination and initiation products to the yields of alcohols on sodium borohydride reductions and for the contribution of scission primary hydroperoxides, $(R'OOH)_{sci}$, to hydroperoxide titer were based on our data described and discussed in forthcoming papers[37,38] and estimated using the equation

$$Z \simeq 3(4\text{-}8\text{-}R'COR'')_C \frac{(XOH)_A - 2(X'COX'') + (R'OOH)_{sci} + (CH_3COR')}{(4\text{-}8\text{-}ROH)_A - 2.5(4\text{-}8\text{-}R'COR'')_C} - (2R'OOH)_{sci}$$

where $(XOH)_A$ represents a sum of yields of hydroperoxides corresponding to parent terminating peroxy radicals.
(42) F. F. Rust, *J. Am. Chem. Soc.*, **79**, 4000 (1957).
(43) R. R. Arndt, J. B. Barbour, E. J. Engels, D. H. S. Horn, and D. A. Sutton, *J. Chem. Soc.*, 3258 (1959).
(44) D. E. VanSickle, *J. Org. Chem.*, **37**, 145 (1972).
(45) T. Mill and G. Montorsi, *Int. J. Chem. Kinet.*, **5**, 119 (1973).
(46) S. W. Benson, "The Mechanisms of Pyrolysis, Oxidation, and Burning of Organic Materials", *Natl. Bur. Stand. (U.S.), Spec. Publ.*, **No. 357**, 121 (1972).
(47) The value of $(k_{inlra}^{\alpha,\gamma\text{-sec}}/\text{H-atom})/(k_{inler}/\text{H-atom})$ and $(k_{inlra}^{\alpha,\gamma\text{-tert}}/\text{H-atom})/(k_{inler}/\text{H-atom})$ at 120 °C were obtained from the results of a kinetic analysis to be reported in a later paper of this series.[38]
(48) R. R. Baldwin, J. P. Bennett, and R. W. Walker, in "Sixteenth Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, Pa., 1976, p 1041.
(49) The reaction i is exothermic by 44 kcal. Accordingly, it could be sufficiently



(i)

rapid to compete with oxygen addition.
(50) The ratios of total 2,4-disubstituted and of 2,4-dihydroperoxide products to monofunctional products were calculated from the expressions

$$\frac{(\alpha,\gamma\text{-HOOROOH})}{(\text{ROOH})} + \frac{(\alpha,\gamma\text{-HOOR=O})}{(\text{ROOH})} = \frac{n}{m(\text{RH})} \frac{k_{inlra}^{\alpha,\gamma\text{-sec}}/\text{H-atom}}{k_{inler}/\text{H-atom}}$$

and

$$\frac{(\alpha,\gamma\text{-HOOROOH})}{(\text{ROOH})} = \frac{n}{m(\text{RH})} \frac{k_{inlra}^{\alpha,\gamma\text{-sec}}/\text{H-atom}}{k_{inler}/\text{H-atom}} \times \frac{1}{1 + \frac{p}{m(\text{RH})} \frac{k_{inlra}^{\alpha,\gamma\text{-tert}}/\text{H-atom}}{k_{inler}/\text{H-atom}}}$$

where m, n, and p refer to number of possible CH bonds available for intermolecular and intramolecular abstractions (n for reaction 6, p for reaction 11) per peroxy radical. For *n*-pentane $m = 6$, $n = 1.33$, and $p = 1$.
(51) See paragraph at end of paper regarding supplementary material.