Autoxidation of Nonane and Decane: A Product Study

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The autoxidation of nonane and decane has been shown to occur in three stages. The initial stage leads to alkyl hydroperoxide formation and in the second stage the hydroperoxide decomposes to produce alcohols and ketones as major products. These studies support the proposal that hydroperoxide decomposition in the second stage occurs by a radical-induced decomposition. In the third stage the products are oxidised in competition with the alkane. Under the conditions of the autoxidation, the alkanes produce γ-lactones as the major ester components and carboxylic acids are formed in the latter stages of the autoxidation. Decan-2-one is shown to be the precursor of heptan-1-ol and octanal.

The autoxidation of hydrocarbons has been extensively studied and reviewed.[1–6] However, not many product studies at significant conversion have been undertaken and extrapolation from either different reaction conditions or different substrates cannot readily be made. Autoxidation studies are also highly susceptible to traces of metallic species and impurities in the reactants. Whilst our study was in progress, Jensen, Korcek and Zinbo[7] reported on their extensive study of hexadecane oxidation in a stirred-flow microreactor.

The autoxidation of decane at its boiling point requires no initiator since it was found that the reaction was identical with a reaction which was initiated by isooctane (Fig. 1). Cooxidation of organic compounds provides an alternative initiation process[8] and we have found that isooctane effectively initiates the autoxidation of nonane.[9] Hydroperoxides, determined titrimetrically, showed a steady build-up for the first hour, then slowly decreased for the next 2 h and thereafter remained almost constant. Aliquots were withdrawn at intervals and analysed (capillary column GLC) prior to and after treatment with triphenylphosphine. Triphenylphosphine is an established reagent[10] for the reduction of hydroperoxides to alcohols. From a study with a standard solution 2-decyl hydroperoxide in decane it was found that under our GLC conditions it gave decan-2-one (47%) and decan-2-ol (10%). After treatment with triphenylphosphine, the standard solution gave decan-2-ol (90%). Hence the isomeric decanols determined by GLC analysis in the autoxidation reaction aliquot prior to triphenylphosphine treatment are mainly due to their production in the reaction mixture, whereas the decanols in the sample after triphenylphosphine treatment are due to the decanols plus decyl hydroperoxides produced in the reaction. The opposite holds for the isomeric decanones since decyl hydroperoxides produce significant but not quantitative amounts of decanones during GLC analysis. The concentration of decanones produced in the reaction mixture were thus obtained by GLC analysis of the triphenylphosphine-reduced aliquots. When more 2-decyl hydroperoxide than the maximum amount of decyl hydroperoxides produced in the reaction was added to decane prior to its autoxidation (Fig. 2), it was found that the alkyl hydroperoxide concentration decreased until it reached the same steady-state concentration as that found in the previous experiment.

The effect of intermittent amounts of oxygen was determined by successively passing oxygen and nitrogen into boiling decane (Fig. 3). Oxygen leads to the rapid formation of hydroperoxides as well as isomeric decanols and decanones. When nitrogen was bubbled through the solution, the hydroperoxides decreased and this led to an increase in the decanols and, to a smaller extent, an increase in the ketones. The formation of decanols as major products whilst the hydroperoxides decompose is evidence that the decomposition at this temperature (178 °C) is occurring by homolytic fragmentation to produce alkoxyl radicals.

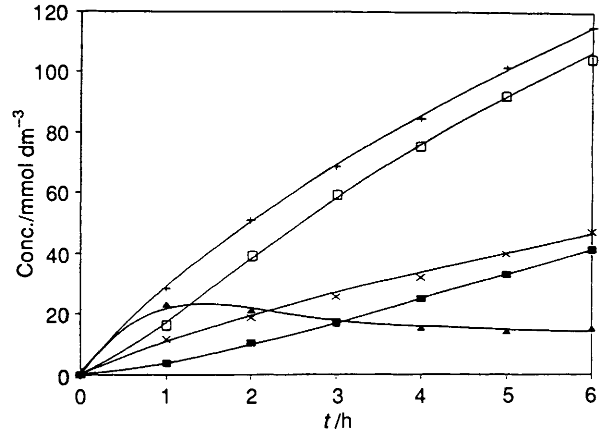

Fig. 1 Autoxidation of decane in the absence of an initiator: +, decanols after reduction; □, decanols before reduction; ■, decanones after reduction; ×, decanones before reduction; ▲, hydroperoxides

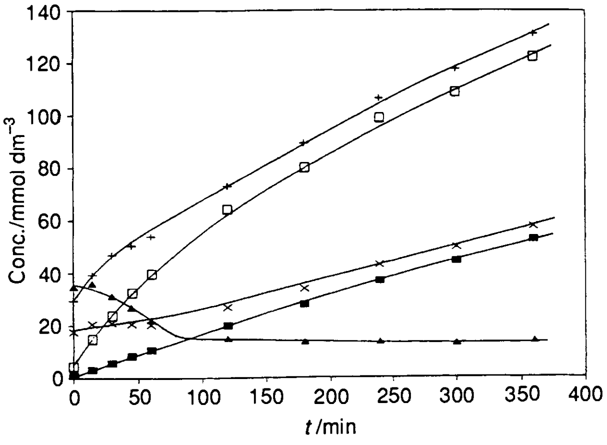

Fig. 2 Autoxidation of decane in the presence of 2-decyl hydroperoxide (0.2715 g, 31.21 mmol dm^{-3}): +, decanols after reduction; □, decanols before reduction; ■, decanones after reduction; ×, decanones before reduction; ▲, hydroperoxides

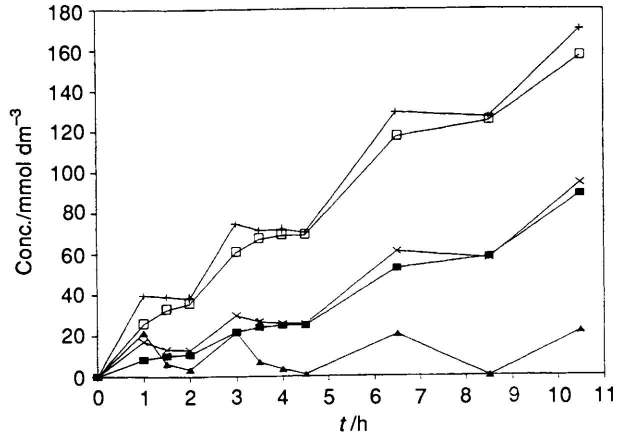

Fig. 3 Autoxidation of decane with intermittent pulses of oxygen and nitrogen (nitrogen from 1 to 2, 3 to 4.5 and 6.5 to 8.5 h): +, decanols after reduction; □, decanols before reduction; ■, decanones after reduction; ×, decanones before reduction; ▲, hydroperoxides

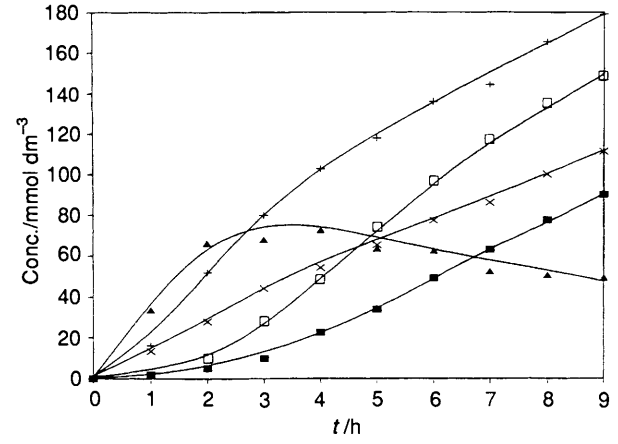

Fig. 4 Autoxidation of nonane using isooctane (0.32 g, 1 mol%) as the initiator: +, nonanols after reduction; □, nonanols before reduction; ■, nonanones after reduction; ×, nonanones before reduction; ▲, hydroperoxides

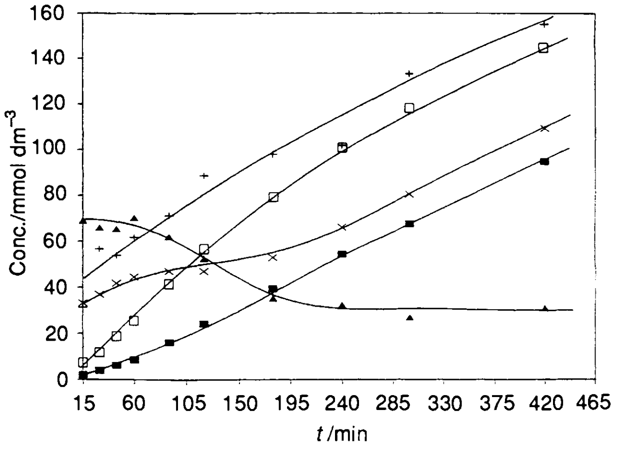

Fig. 5 Autoxidation of nonane using 2-nonyl hydroperoxide (0.3741 g, 46.69 mmol dm^{-3}, 0.83 mol%) as the initiator: +, nonanols after reduction; □, nonanols before reduction; ■, nonanones after reduction; ×, nonanones before reduction; ▲, hydroperoxides

A standard solution of 2-decyl hydroperoxide in decane, the concentration of which was similar to that produced in the autoxidation, was heated at 160 °C. Analysis of aliquots withdrawn at regular intervals showed that its half-life is *ca.* 3 h under these conditions. It has been shown[11,12] that the order of alkyl hydroperoxide decomposition is concentration-dependent. Differential scanning calorimetry of neat 2-decyl hydroperoxide in an aluminium boat gave exotherms at 90 and 108 °C showing that this technique is not useful in studying the behaviour of hydroperoxides in autoxidation reactions. These exotherms are probably due to dissociation of dimeric hyroperoxides and aluminium-reduction of the alkyl hydroperoxide, respectively.

Autoxidation of nonane at 151 °C with isooctane (Fig. 4) or hydrogen peroxide as initiators produced almost identical results. These showed that during the initial stage of the autoxidation, the main products are isomeric nonane hydroperoxides. During this period negligible amounts of the isomeric nonanols and nonanones are produced. The concentration of nonyl hydroperoxides produced was greater than the decyl hydroperoxides produced in decane autoxidation. After this initial stage in which hydroperoxides are being produced and particularly after the nonyl hydroperoxides have reached a maximum concentration, the isomeric nonanols and nonanones are formed. This is in accord with nonyl hydroperoxides being the precursors of the nonanols and nonanones. As with the experiment with decane, addition of a greater concentration of 2-nonyl hydroperoxide than that produced in the reaction led to its decomposition, albeit more slowly, until an almost steady-concentration was maintained (Fig. 5).

Bateman and Hughes[13] attributed the change in reaction order of hydroperoxide decomposition to be due to a bimolecular process at higher concentrations. However, Benson[14] pointed out that the bond dissociation energy E_d(RO–OH) ≃ 42 kcal mol^{-1} implies that homolysis of hydroperoxides would contribute negligibly to the observed kinetics of Bu^{t}OOH decomposition. Hiatt[11] supported the view that alkyl hydroperoxides do not significantly decompose below 150 °C and that they are susceptible to radical-induced chain decomposition. Hajdu, Emanuel and co-workers[12] have established that peroxyl radicals induced the decomposition of 1-phenylethyl hydroperoxide. The initially slow decomposition of the added nonyl hydroperoxide in our studies, which later increased prior to reaching an almost steady concentration, is best accounted for by a radical-induced decomposition of the alkyl hydroperoxide initiated by alkylperoxyl radicals as well as by radicals produced by the homolytic decomposition of the alkyl hydroperoxides.

The second stage of the autoxidation is reached when the alkyl hydroperoxide decomposes to produce alcohols and ketones. Since alcohol production is greater than ketone production in this stage, the induced decomposition must lead to alkoxyl radicals as the main chain-propagating species [eqns. (5) and/or (7) and (9)]. The ketones are formed in the second stage from alkylperoxyl radicals, generated from alkyl radicals [eqn. (2)] and induced decomposition of hydroperoxides [eqns. (6) and/or (7)] which subsequently form alkylperoxyl radicals. These peroxyl radicals terminate either *via* a Russell mechanism [eqn. (10)] or *via* reactions [eqns. (12), (13) and (14)]. A less likely process for ketone formation would be the heterolytic decomposition of alkyl hydroperoxides [eqn. (4)] since added 2-decyl hydroperoxide did not lead to a significant increase in decanone production.

A complicating factor in the analysis of alkane oxidations, which has also been observed by others,[15] is that the hydroperoxide content determined by titration exceeds the value obtained by GLC analysis for alcohols prior to and after triphenylphosphine reduction of the reaction mixture. Triphenylphosphine reduction of standard solutions of 2-nonyl and 2-decyl hydroperoxides afforded the corresponding alcohols in 80 and 90% yield, respectively. Mill and co-workers[15] suggested that peracids could be responsible but that they were produced in insufficient amounts to account for the

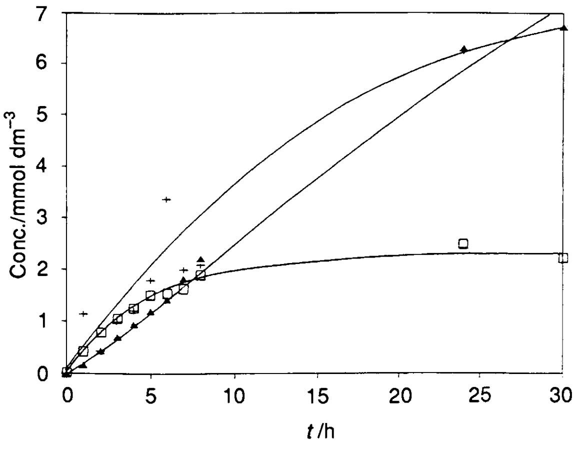

Fig. 6 Bifunctional products in the autoxidation of decane in the presence of 1 mol% isooctane (after Ph_3P reduction): ▲, octanoic lactone; +, decane-2,5-dione; □, decane-2,5-diol

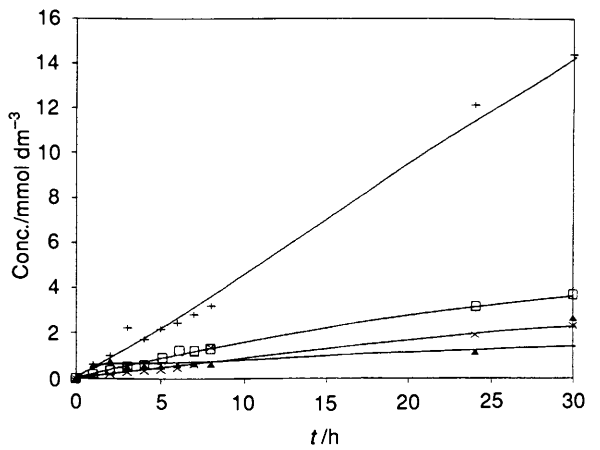

Fig. 7 Minor products in the autoxidation of decane in the presence of 1 mol% isooctane (after Ph_3P reduction): ▲, heptanal; +, octanal; ■, heptanol; ×, octanol

discrepancy. We postulated that the error might be due to the formation of alkyl hydroperoxide–hydrogen peroxide dimers which are not separated under the reaction conditions. However, when 2-decyl hydroperoxide in decane was shaken with aqueous hydrogen peroxide the concentration of 2-decyl hydroperoxide as determined by titration and GLC analysis after triphenylphosphine reduction was unchanged.

$$\text{R-H} + \text{O}_2 \longrightarrow \text{R}^{\cdot} + {}^{\cdot}\text{OOH} \quad (1)$$

$$\text{R}^{\cdot} + \text{O}_2 \longrightarrow \text{ROO}^{\cdot} \quad (2)$$

$$\text{ROO}^{\cdot} + \text{RH} \longrightarrow \text{ROOH} + \text{R}^{\cdot} \quad (3)$$

$$\text{R}^1\text{CH(OOH)R}^2 \longrightarrow \text{R}^1\text{COR}^2 + \text{H}_2\text{O} \quad (4)$$

$$\text{ROOH} \longrightarrow \text{RO}^{\cdot} + \text{HO}^{\cdot} \quad (5)$$

$$\text{RO}^{\cdot} + \text{ROOH} \longrightarrow \text{ROH} + \text{ROO}^{\cdot} \quad (6)$$

$$\text{ROO}^{\cdot} + \text{R}^1\text{CH(OOH)R}^2 \longrightarrow \text{ROH} + \text{R}^1\text{CH}\dot{\text{O}}\text{R}^2 + \text{O}_2 \quad (7)$$

$$2\,\text{ROO}^{\cdot} \rightleftharpoons [\text{ROOOOR}] \longrightarrow \text{R=O} + \text{O}_2 + \text{ROH} \quad (8)$$

$$2\,\text{ROO}^{\cdot} \rightleftharpoons [\text{ROOOOR}] \longrightarrow 2\,\text{RO}^{\cdot} + \text{O}_2 \quad (9)$$

$$2\,\text{ROO}^{\cdot} \rightleftharpoons [\text{ROOOOR}] \longrightarrow \text{R}^3\text{=O} + \text{ROH} + \text{O}_2 \quad (10)$$

$$\text{RO}^{\cdot} + \text{R}^1\text{CHOHR}^2 \longrightarrow \text{ROH} + \text{R}^1\dot{\text{C}}\text{(OH)R}^2 \quad (11)$$

$$\text{R}^1\dot{\text{C}}\text{(OH)R}^2 + \text{O}_2 \longrightarrow \text{R}^1\text{C(O}\dot{\text{O}}\text{)(OH)R}^2 \quad (12)$$

$$\text{R}^1\text{C(O}\dot{\text{O}}\text{)(OH)R}^2 + \text{RH} \longrightarrow \text{R}^1\text{C(OOH)(OH)R}^2 + \text{R}^{\cdot} \quad (13)$$

$$\text{R}^1\text{C(OOH)(OH)R}^2 \longrightarrow \text{R}^1\text{COR}^2 + \text{H}_2\text{O}_2 \quad (14)$$

$$2\text{ROO} \rightleftharpoons [\text{ROOOOR}] \longrightarrow 2\text{R=O} + \text{H}_2\text{O}_2 \quad (15)$$

The minor products, which included those produced by intramolecular propagation, were investigated in the autoxidation of decane. After the autoxidation had proceeded to *ca.* 8% conversion, *i.e.*, towards the end of the second stage of the autoxidation, the mixture contained decan-1-ol and γ-octanoic lactone (octane-4-olide) as the most significant minor components and they were both present as less than 1.25% of the monosubstituted products (Figs. 6 and 7). The reaction mixture contained a lower yield of γ-heptanoic lactone (heptan-4-olide).

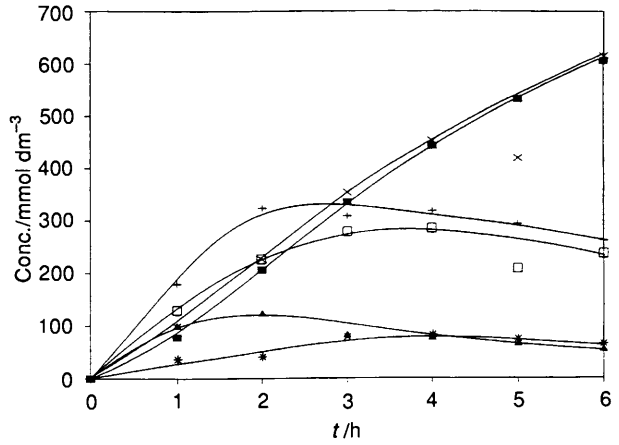

Fig. 8 Autoxidation of decane under conditions of higher oxygen concentration and with a Dean–Stark attachment: +, decanols after reduction; □, decanols before reduction; ■, decanones after reduction; ×, decanones before reduction; ▲, hydroperoxides; *, hydrogen peroxide

Monocarboxylic acids from pentanoic acid to decanoic acid were produced only in the latter stages of the autoxidation of decane and were each less than 2% of the reaction product. The reaction mixture also contained octanal in *ca.* 2% of the amounts of monosubstituted decanes and a significantly lesser amount of heptanal. Further minor products were heptanol and octanol. Negligible amounts of decane-2,4-dione and decane-2,4-diol were produced. However, both decane-2,5-dione and decane-2,5-diol were present. 1,4-Bifunctional product formation was also found in the autoxidation of nonane. No 1,3-bifunctional products, *viz.*, nonane-2,4-dione and nonane-2,4-diol could be detected by a selected ion profile GC–MS analysis of the products produced in the autoxidation of nonane. In accordance with Jensen *et al.*[16] it was found that the synthetic standard nonane-2,4-diol could not be eluted from a polar column but was readily eluted from a non-polar column. The formation of the 1,4-disubstituted products *viz.*, γ-lactones and 2,5-disubstituted alkanes, are in accord with alkoxyl- rather than peroxyl-radical intra-, and hence also inter-, molecular chain propagating reactions in the second and third stages of the autoxidation reaction.

When decane was oxidised under conditions of higher oxygen concentration with a Dean–Stark attachment, the third stage of the autoxidation, *i.e.*, above 10% formation of products, was reached after 2 h (Fig. 8). During this stage the alcohols were being oxidised in competition with the substrate. Acids could be

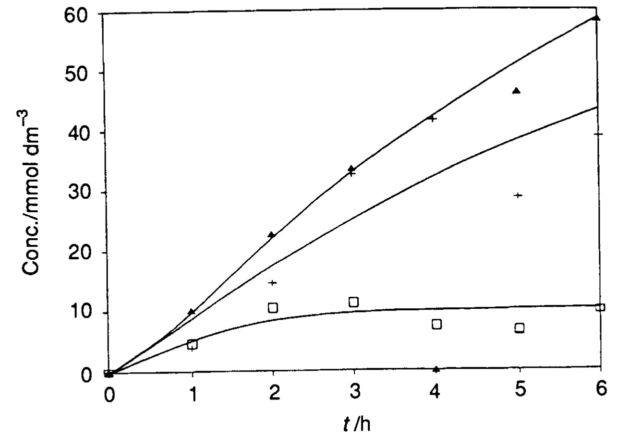

Fig. 9 Bifunctional products in the autoxidation of decane under conditions of higher oxygen concentration (after Ph_3P reduction): ▲, octanoic lactone; +, decane-2,5-dione; □, decane-2,5-diol

detected sooner (3 h) and all products (Figs. 8 and 9) were present in greater yields. This experiment clearly demonstrates the second and third phases of hydrocarbon autoxidation. The first phase which leads primarily to alkyl hydroperoxide formation is only observed at lower temperatures and with lower oxygen concentration. Another important feature of the reaction with higher oxygen concentration is that significantly larger amounts of water and hydrogen peroxide are produced. Hydrogen peroxide is, in all probability, produced when alcohols or hydroperoxides are oxidised to ketones [eqns. (7) and (11) followed by (12)–(14)]. Production of hydrogen peroxide by decomposition of the dialkyl tetraoxide[17] [eqn. (15)] is unlikely at this temperature since more alcohols than ketones are produced in the initial stages.

Since all the hydrogen peroxide was removed after each interval, the steady concentration in each aliquot (Fig. 7) indicates a steady production of hydrogen peroxide during the course of the reaction. Autoxidation of decane in the absence of the Dean–Stark attachment with a high oxygen concentration, produced significantly different results (Fig. 10). In this experiment the hydrogen peroxide produced was not removed but remained in the reactor for further reaction. Comparison of the yields of decanols prior to and after triphenylphosphine reduction showed that a high, almost steady-state concentration of alkyl hydroperoxide was present. After 2 h the rate of hydrogen peroxide and ketone formation was almost constant, whereas the rate of alkyl hydroperoxide and alcohol production were almost identical with their rate of decomposition. The lower conversion into products in the reaction without the Dean–Stark attachment is, in all probability, due to the fluctuation in temperature caused by the return of condensed aqueous phase.

Ketones have been shown[18] to be initiators in autoxidations. Addition of decan-2-one to an autoxidation reaction of decane was found to enhance the formation of heptan-1-ol and octanal (Fig. 11). However, after a short period the rate of octanal formation was equal to its rate of conversion into other products. The oxidation of aldehydes to carboxylic acids has been investigated[19,20] but their conversion into nor-alcohols has not been intimated. The formation of heptan-1-ol, the precursor of which, *viz.*, 1-heptyloxyl radical, generated either by decarboxylation or decarboxylation of a C_8-fragment from decan-2-one, supports our proposal that alkoxyl radicals are the main propagating species in the second stage of the autoxidation reactions. However, decan-2-one did not promote γ-octanoic lactone formation and the slight increase in 2,5-dione is most probably due to an intermolecular process.

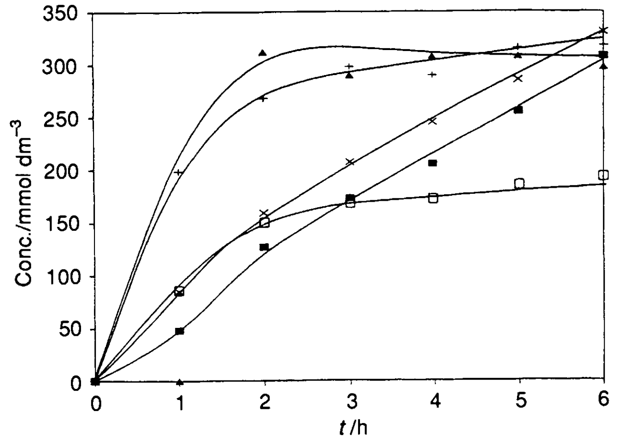

Fig. 10 Autoxidation of decane under conditions of higher oxygen concentration without the Dean–Stark attachment: +, decanols after reduction; □, decanols before reduction; ■, decanones after reduction; ×, decanones before reduction; ▲, peroxide

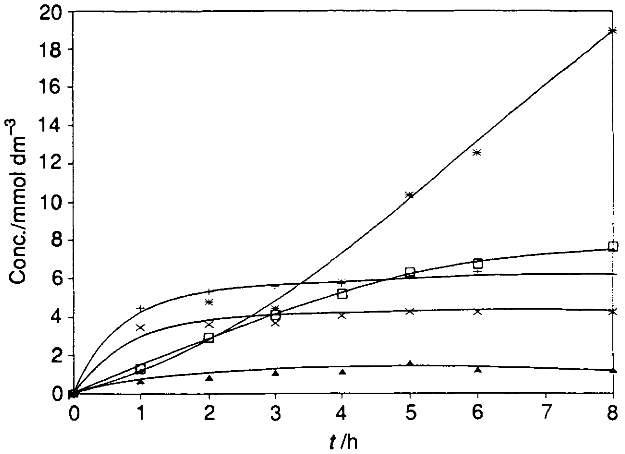

Fig. 11 Minor products in the autoxidation of decane in the presence of decan-2-one (after Ph_3P reduction): ▲, heptanal; +, octanal; *, octanoic acid; □, heptan-1-ol; ×, octan-1-ol

Only minor amounts of esters, apart from lactones, were produced in the autoxidations investigated. Trace amounts of the 2-decyl esters of octanoic, heptanoic and hexanoic acid were detected. Since octyl acetate could not be detected when decan-2-one was added to a decane autoxidation, ester formation by a Baeyer–Villiger reaction cannot be a major process. Further, it was found that addition of octanal, which could form peroctanoic acid and promote the Baeyer–Villiger, did not lead to octyl acetate formation. Addition of decan-2-one, however, did lead to the production of 2-decyl acetate which indicates that intermolecular esterification is taking place with acetic acid formed from decan-2-one.

Experimental

Infrared spectra were recorded on a Perkin-Elmer infrared spectrometer, Model 297 and a Perkin-Elmer 1600 Series Fourier transform infrared spectrometer. ^{1}H NMR spectra were recorded on a Perkin-Elmer R12A spectrometer with Me_4Si as an internal standard (60 MHz) and on a Varian Gemini 200 (200 MHz) in $CDCl_3$. Capillary GLC analyses were carried out on a Varian Model 3300 gas chromatograph using a flame ionisation detector linked to a Varian Model 4400 Integrator. Mass spectra were recorded on a Hewlett-Packard 5985A mass spectrometer linked to a Hewlett-Packard 5840A gas chromatograph with helium as the carrier gas. Differential scanning calorimetry was performed on a Du Pont 9000 thermal analyser which was purged with nitrogen. The heating rate was 10 °C min^{-1} and the compounds were sealed in aluminium DSC pans.

GLC conditions. Analyses were performed on a capillary column (Supelcowax TM10), 30 m, 0.25 mm i.d. The injector port and detector were held at 250 and 275 °C, respectively. Temperature programmes were 75 °C for 3 min, increasing at 6 °C min^{-1} to 150 °C which was held for 0.5 min, increased at either 12 or 8 °C min^{-1} to 180 or 220 °C which was held for 0.5 min before increasing at 20 °C min^{-1} to 250 °C which was held for 10 or 5 min. The column head pressure was 28 or 15 psi.

General Procedure for Autoxidations.—The hydrocarbon (50 cm^3) was heated under reflux with oxygen bubbling through the mixture at 23 cm^3 min^{-1} for nonane and 17.5 cm^3 min^{-1} for decane or in a reactor with oxygen bubbling through a frit (No. 3) at 58 cm^3 min^{-1}. The reactors were fitted with Dean–Stark adaptors.

Aliquots (1.5–1.9 cm^3) were withdrawn at regular intervals and cooled. To a portion (1 cm^3), an external standard (nitrobenzene for nonane and ethyl benzoate for decane) was added and the whole was then divided into two equal portions. One portion was analysed (GLC) then reduced (Ph_3P) and reanalysed. The yields of products were obtained from peak ratios using standard calibration graphs.

A fixed volume of the original aliquot was analysed for hydroperoxide by iodimetric titration.[21] Products were identified by comparison of GLC retention times with authentic samples. The results are summarised in the figures.

2-*Nonyl pentanoate* had b.p. 140 °C/1 mmHg; ν_{max}($CHCl_3$)/cm^{-1} 1718; δ_H(60 MHz; CCl_4) 0.9–1.6 (25 H, m), 2.22 (2 H, t) and 4.9 (1 H, m) (Found: C, 73.3; H, 11.9. Calc. for $C_{14}H_{28}O_2$: C, 73.6; H, 12.4%).

1-*Nonyl nonanoate* had b.p. 195 °C/0.9 mmHg; ν_{max}($CHCl_3$)/cm^{-1} 1730; δ_H(60 MHz; CCl_4) 0.85–1.65 (32 H, m), 2.3 (2 H, t) and 4.05 (2 H, t) (Found: C, 76.3; H, 13.25. Calc. for $C_{18}H_{36}O_2$: C, 76.0; H, 12.75%).

Nonane-2,4-*dione.*—Ethyl hexanoate (40.04 g, 0.28 mol), acetone (8.07 g, 0.14 mol) and 50% sodium hydride (13.34 g, 0.28 mol) were reacted according to a published procedure[22] to afford nonane-2,4-dione (5 g, 0.0321 mol, 23%), b.p. 78 °C/4 mmHg (lit.,[23] b.p. 101–103 °C/19 mmHg); ν_{max}(film)/cm^{-1} 1700 and 1660–1550; δ_H($CDCl_3$) 0.9 (3 H, t, CH_3CH_2), 1.3 (4 H, m, CH_2), 1.6 (2.7 H, m, CH_3–C=C), 2.06 (2.3 H, s, CH_3CO), 2.5 (0.25 H, t, CH_2COCH_2CO), 3.58 (0.3 H, s, $COCH_2CO$), 5.6 (0.8 H, s, –CH=C) and 15.6 (0.7 H, s, H-bonded enol); *m/z* 156 (M$^+$, 7.6%) 43 (*M* – 113, 13.4), 85 (*M* – 71, 100), 100 (*M* – 56, 57.6) and 113 (*M* – 43, 18.7) (Found: C, 69.0; H, 10.8. Calc. for $C_9H_{16}O_2$: C, 69.2; H, 10.3%).

Nonane-2,4-*diol.*—Sodium borohydride (1.5 g, 0.0405 mol) in isopropyl alcohol (10 cm^3) was added to nonane-2,4-dione (1.13 g, 0.0073 mol) in isopropyl alcohol (10 cm^3) and the mixture was stirred for 24 h. The reaction mixture was poured onto water and extracted with dichloromethane (3 × 50 cm^3). The dichloromethane extracts were washed with water (3 × 50 cm^3) and after concentration and microdistillation afforded nonane-2,4-diol (1.0 g, 0.0063 mol, 86%), bath temperature 150 °C/0.5 mmHg; ν_{max}($CHCl_3$)/cm^{-1} 3600–3200; δ_H($CDCl_3$) 0.98 (3 H, m), 1.2–1.6 (13 H, m), 2.4 (2 H, br s, OH) and 3.8–4.2 (2 H, m); *m/z* 142 (*M* – 18, 1.4%), 101 (*M* – 59, 42.2), 89 (*M* – 71, 100), 83 (*M* – 77, 77.9), 71 (*M* – 89, 76.5), 55 (*M* – 105, 40.9) and 45 (*M* – 115, 53.8) (Found: C, 67.9; H, 12.9. Calc. for $C_9H_{20}O_2$: C, 67.45; H, 12.6%).

Note: Nonane-2,4-diol was not eluted on a Supelcowax TM10 column but on Supelcowax SBP 5.

2-*Nonyl Hydroperoxide.*—2-Nonyl mesylate (30 g, 0.14 mol), 50% hydrogen peroxide (60.94 g, 0.90 mol) and potassium hydroxide (8.5 g, 0.15 mol) were reacted according to a published procedure[24] and TLC (SiO_2–CH_2Cl_2) afforded 2-nonyl hydroperoxide (3.7 g, 0.0231 mol, 17%); ν_{max}(film)/cm^{-1} 3600–3200; δ_H($CDCl_3$) 0.99 (3 H, m), 1.1–1.7 (15 H, m), 4.1 (1 H, m) and 7.5–8 (1 H, br s) (Found: C, 67.3; H, 12.2. Calc. for $C_9H_{20}O_2$: C, 67.45; H, 12.6%).

Octyl Acetate had b.p. 210 °C/760 mmHg (lit.,[25] b.p. 210 °C/760 mmHg); ν_{max}($CHCl_3$)/cm^{-1} 1726; δ_H($CDCl_3$) 0.98 (3 H, m), 1.2–1.7 (12 H, m), 2.05 (3 H, s) and 4.05 (2 H, t) (Found: C, 70.1; H, 12.2. Calc. for $C_{10}H_{20}O_2$: C, 69.75; H, 11.7%).

Decan-2-*ol* was microdistilled [bath temperature 150 °C/1.3 mmHg (lit.,[26] b.p. 211 °C/760 mmHg)]; ν_{max}($CHCl_3$)/cm^{-1} 3557–3400 and 1470; δ_H($CDCl_3$) 0.9–1.5 (2 H, m) and 3.8 (1 H, m) (Found: C, 76.0; H, 14.3. Calc. for $C_{10}H_{22}O$: C, 75.9; H, 14.0%).

Decan-3-*ol* was microdistilled [bath temperature 150 °C/1.3 mmHg (lit.,[27] b.p. 213 °C/760 mmHg)]; ν_{max}(film)/cm^{-1} 3500–3200; δ_H($CDCl_3$) 0.8–1.8 (20 H, m), 3.6 (1 H, m) (Found: C, 75.4; H, 13.9. Calc. for $C_{10}H_{22}O$: C, 75.9; H, 14.0%).

Decan-4-*ol* was microdistilled [bath temperature 130 °C/0.9 mmHg (lit.,[26] b.p. 210–211 °C/760 mmHg)]; ν_{max}(film)/cm^{-1} 3500–3200, 2950 and 1460; δ_H($CDCl_3$) 0.8–1.5 (20 H, m), 3.6 (1 H, m) (Found: C, 75.6; H, 13.6. Calc. for $C_{10}H_{22}O$: C, 75.9; H, 14.0%).

2-*Decyl acetate* was microdistilled [bath temperature 130 °C/0.9 mmHg (lit.,[27] b.p. 115 °C/15 mmHg)]; ν_{max}(film)/cm^{-1} 1740; δ_H($CDCl_3$) 0.8–1.6 (20 H, m), 2 (3 H, s) and 4.9 (1 H, m) (Found: C, 72.4; H, 12.5. Calc. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.1%).

2-*Decyl heptanoate* was microdistilled (bath temperature 200 °C/1 mmHg); ν_{max}(film)/cm^{-1} 1740; δ_H($CDCl_3$) 0.8–1.7 (31 H, m) 2.3 (2 H, t) and 4.9 (1 H, m) (Found: C, 75.95; H, 13.05. Calc. for $C_{17}H_{34}O_2$: C, 75.50; H, 12.7%).

2-*Decyl octanoate* was microdistilled (bath temperature 205 °C/1.3 mmHg); ν_{max}(film)/cm^{-1} 1740; δ_H($CDCl_3$) 0.8–1.7 (33 H, m), 2.3 (2 H, t) and 4.9 (1 H, m) (Found: C, 76.5; H, 12.9. Calc. for $C_{18}H_{36}O_2$: C, 76.0; H, 12.75%).

Ethyl heptanoate had b.p. 84–86 °C/3.5 mmHg (lit.,[28] b.p. 188.6 °C/760 mmHg); ν_{max}(film)/cm^{-1} 1740; δ_H($CDCl_3$) 0.98 (3 H, m), 1.2–1.4 (8 H, m), 1.7 (3 H, m), 2.3 (2 H, t) and 4.1 (2 H, q) (Found: C, 69.4; H, 10.7. Calc. for $C_9H_{18}O_2$: C, 69.25; H, 10.25%).

Decane-2,4-*dione.*—Ethyl heptanoate (23.72 g, 0.15 mol), acetone (4.36 g, 0.075 mol) and 50% sodium hydride (7.2 g, 0.15 mol) were reacted according to a published procedure[22] to afford decane-2,4-dione (4 g, 0.0235 mol; 31%), b.p. 130 °C/0.6 mmHg (lit.,[29] b.p. 130–131 °C/23 mmHg); ν_{max}(film)/cm^{-1} 1700 and 1680–1500; δ_H($CDCl_3$) 0.9 (3 H, t, CH_3CH_2), 1.3 (5.5 H, m, CH_2), 1.6 (3.7 H, m, CH_3–C=C), 2.09 (2 H, s, CH_3CO), 2.25 (1.77 H, m, CH_2CO), 2.5 (0.07 H, t, CH_2COCH_2CO), 3.58 (0.15 H, s, $COCH_2CO$), 5.6 (0.6 H, s, –CH=C) and 15.6 (0.7 H, s, H-bonded enol); *m/z* 170 (M$^+$, 10.2%), 43 (*M* – 127, 18.1), 85 (*M* – 85, 100), 100 (*M* – 70, 65.5) and 113 (*M* – 57, 24.6) (Found: C, 71.0; H, 11.10. Calc. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65%).

Decane-2,4-*diol.*—Sodium borohydride (0.22 g, 0.0059 mol) in ethanol (10 cm^3) was added to decane-2,4-dione (1.0 g, 0.0059 mol) in ethanol (10 cm^3) and stirred at room temperature for 24 h. The reaction mixture was poured onto water and extracted with dichloromethane (3 × 50 cm^3). The dichloromethane extracts were washed with water (3 × 50 cm^3) and concentrated to afford decane-2,4-diol (0.9 g, 0.0052 mol, 88%); ν_{max}($CHCl_3$)/

cm^{-1} 3600–3200; δ_H(CDCl$_3$) 0.98 (3 H, m), 1.2–1.7 (15 H, m), 2.1 (2 H, br s, OH) and 3.8–4.2 (2 H, m); m/z 156 (M − 18, 1%), 115 (M − 59, 35.1), 97 (M − 77, 51.4), 89 (M − 85, 100), 71 (M − 103, 73.5), 55 (M − 119, 43.9) and 45 (M − 129, 49.5) (Found: C, 68.6; H, 12.5. Calc. for $C_{10}H_{22}O_2$: C, 68.9; H, 12.7%).

5-*Nitrodecan*-2-*one*.—1-Nitrohexane (5.15 g, 0.393 mol), diisopropylamine (1.97 cm^3) and methyl vinyl ketone (2.74 g, 0.0394 mol) were reacted according to a published procedure[30] to afford 6.4 g, crude reaction mixture. The impure crude material was chromatographed on a column of silica gel (400 g) with chloroform as the eluent to give 5-nitrodecan-2-one (3.68 g, 0.0283 mol, 47%), a portion of which was microdistilled (bath temperature 170 °C/0.7 mmHg); ν_{max}(CHCl$_3$)/cm^{-1} 1716, 1548 and 1364; δ_H(CDCl$_3$) 0.99 (3 H, m), 1.2–2.2 (13 H, m), 2.5 (2 H, t) and 4.5 (1 H, m) (Found: C, 59.0; H, 9.5; N, 6.7. Calc. for $C_{10}H_{19}NO_3$: C, 59.7; H, 9.5; N, 7.0%).

Decane-2,5-*dione*.—5-Nitrodecan-2-one (1.5 g, 0.0075 mol) in THF (40 cm^3) was treated with 15% TiCl$_3$ solution (40 g, 0.0389 mol) under an N_2 atmosphere according to a published procedure.[30] The crude reaction mixture was chromatographed on a column of silica gel with chloroform as the eluent and microdistilled to give decane-2,5-dione (0.7 g, 0.0041 mol, 55%), bath temperature 150 °C/0.8 mmHg (lit.,[31] b.p. 132 °C/17 mmHg); ν_{max}(CHCl$_3$)/cm^{-1} 1710; δ_H(CDCl$_3$) 0.98 (3 H, m), 1.2–1.8 (6 H, m), 2.2 (3 H, s), 2.4 (2 H, t) and 2.7 (4 H, m); m/z 170 (M^+, 1.5%), 127 (M − 43, 6.6), 114 (M − 56, 81.7), 99 (M − 71, 100) and 43 (M − 127, 22.3) (Found: C, 70.7; H, 10.25. Calc. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.7%).

Decane-2,5-*diol*.—Decane-2,5-dione (0.5 g, 0.0029 mol) in tetrahydrofuran (THF) (5 cm^3) was added dropwise to a stirred solution of LiAlH$_4$ (0.22 g, 0.0061 mol) in THF and the resulting mixture was heated under reflux for 6 h after which it was poured onto crushed ice, acidified with dilute hydrochloric acid and extracted with ether (3 × 50 cm^3). The solvent was removed under reduced pressure to afford a solid which crystallised from light petroleum (b.p. 80–100 °C) to afford decane-2,5-diol (0.42 g, 0.0024 mol, 83%), m.p. 46–47 °C; ν_{max}(CHCl$_3$)/cm^{-1} 3600–3200; δ_H(CDCl$_3$) 0.98 (3 H, m), 1.2–1.7 (15 H, m), 3.6 (1 H, m) and 3.8 (1 H, s): m/z 156 (M − 18, 0.5%), 114 (M − 60, 3.7), 103 (M − 71, 12.1), 85 (M − 89, 100), 67 (M − 107, 17.1), 56 (M − 118, 25.8), 43 (M − 131, 13) and 29 (M − 145, 36) (Found: C, 68.5; H, 12.4. Calc. for $C_{10}H_{22}O_2$: C, 68.9; H, 12.7%).

2-*Decyl Hydroperoxide*.—2-Decyl mesylate (23 g, 0.0973 mol), 50% hydrogen peroxide (43.89 g, 0.65 mol) and potassium hydroxide (6.26 g, 0.11 mol) were reacted according to a published procedure[24] to yield 8 g crude material which was shown to contain unchanged 2-decyl mesylate, decan-2-ol and 2-decyl hydroperoxide. TLC (SiO$_2$–CH$_2$Cl$_2$) of 3 g of the crude reaction mixture yielded 0.62 g pure 2-decyl hydroperoxide; ν_{max}(CHCl$_3$)/cm^{-1} 3534–3300; δ_H(CDCl$_3$) 0.99 (3 H, m), 1–1.7 (17 H, m) and 4.1 (1 H, m) (Found: C, 69.3; H, 31.0. Calc. for $C_{10}H_{22}O_2$: C, 69.0; H, 12.6%).

γ-*Heptanoic Lactone*.—γ-Heptanoic lactone was synthesised according to a standard procedure[32] and gave ν_{max}(CHCl$_3$)/cm^{-1} 1765; δ_H(CDCl$_3$) 0.9 (3 H, t), 1.2–2.4 (6 H, m), 2.55 (2 H, m) and 4.5 (1 H, m); m/z 85 (M − 43).

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