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Autoxidation of Alkylnaphthalenes. 2. Inhibition of the Autoxidation of *n*-Hexadecane at 160 °C[1]

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Abstract: The rate of the self-initiated autoxidation of hexadecane at 160 °C under 760 Torr of O_2 is reduced by the addition of submolar concentrations of naphthalene or alkylnaphthalene. The kinetics of these (alkyl)naphthalene-modulated, self-initiated hexadecane autoxidations have been examined by monitoring hydroperoxide concentrations. Under similar conditions, the extent of the rate retardation is essentially identical for equal concentrations of naphthalene and 1- and 2-methylnaphthalene (and 2-*sec*-butylnaphthalene), which proves that retardation is due to chemistry associated with the naphthalene moiety. It is shown that the (alkyl)naphthalene produces both an increase in the rate constant for a bimolecular, peroxyl + peroxyl chain-termination process and a kinetically-first-order chain-termination reaction. Both of these termination processes are attributed to an initial addition of hexadecylperoxyl radicals to the naphthalene ring. Reaction of the resultant peroxycyclohexadienyl radical with O_2 produces the $HOO^•$ radical which is responsible for the increase in the rate constant for bimolecular termination. Unimolecular decomposition of the peroxycyclohexadienyl radical yields hexadecanol and an (alkyl)naphthoxyl radical, the latter being responsible for the kinetically-first-order termination process. A simplified scheme of 17 elementary reactions yields a kinetic expression which, via computer modeling, is shown to give a very satisfactory agreement between calculated and measured hydroperoxide yields under all experimental conditions surveyed. This simulation yields a rate constant k_{19} of ~ 70 M^{-1} s^{-1} for the addition of hexadecylperoxyl radicals to (alkyl)naphthalenes at 160 °C, a value which may be compared with the estimated rate constant for hydrogen abstraction from 1- or 2-methylnaphthalene under similar conditions, viz., $k_{15} = 34$ M^{-1} s^{-1}. The simulation also gives a satisfactory agreement between calculated and measured yields of organic hydroperoxides and hydrogen peroxide. That the naphthalene ring was oxidatively cleaved under the experimental conditions was demonstrated by the identification of phthalic acid and phthalic anhydride following the addition of naphthalene or a methylnaphthalene to autoxidizing hexadecane. Both 1- and 2-methylnaphthalene also yielded 2-acetylbenzoic acid. The possible mechanisms by which these naphthalene ring-cleaved products are formed are discussed.

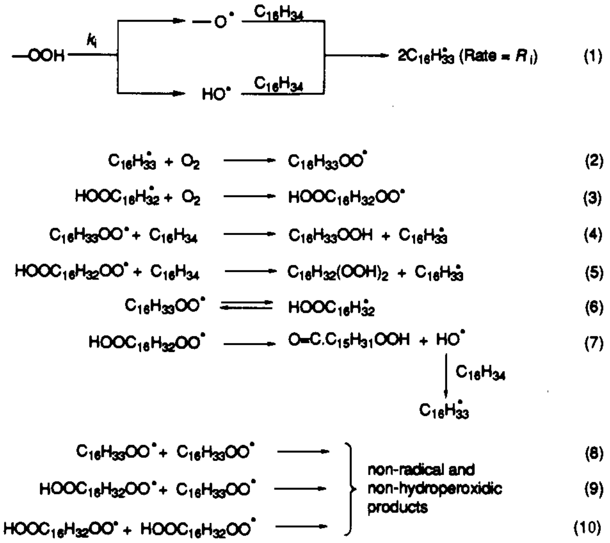
In the preceding paper[4] we demonstrated that the unexpectedly high resistance to autoxidation of 1- and 2-methylnaphthalene at temperatures from 30 to 60 °C is due to a combination of autoretardation and self-inhibition. The former effect can be attributed to the buildup of molecular oxidation products which can function as chain-breaking antioxidants. The latter effect was attributed to the addition of peroxyl radicals to the naphthalene ring which leads to chain-breaking by a kinetically-first-order chain-termination process. This addition reaction accompanies H-atom abstraction from the methyl group so that even the very initial stages of the autoxidation are inhibited.

In this paper we extend our kinetic studies to higher temperatures where the unusual resistance to autoxidation of alkylnaphthalenes has already been demonstrated,[5,6] a resistance which makes these compounds attractive as synthetic lubricating oils and heat transfer fluids. Specifically, we have examined the effect of the two methylnaphthalenes and of naphthalene itself (and of 2-*sec*-butylnaphthalene) on the rates of the self-initiated autoxidation of hexadecane at 160 °C. The results obtained are readily explained within the general framework of the reactions invoked at lower temperatures.[4]

Results

Self-Initiated Autoxidation of Hexadecane at 160 °C. Extensive studies by some of the present authors[7-13] have demonstrated that the autoxidation of hexadecane, $C_{16}H_{34}$, at 160 °C occurs "spontaneously" with chain-initiation being due to the unimolecular thermal decomposition of isomeric hexadecyl mono- and dihydroperoxides, –OOH.[14,15] The overall autoxidation process at relatively low extents of oxidation is shown in simplified form[16] in Scheme I. The various organic species shown in this scheme correspond, of course, to mixtures of isomers.

Scheme I



$$-OOH \xrightarrow{k_i} \left\{ \begin{array}{l} -O^• \xrightarrow{C_{16}H_{34}} \\ HO^• \xrightarrow{C_{16}H_{34}} \end{array} \right\} \longrightarrow 2C_{16}H_{33}^• \ (\text{Rate} = R_i) \quad (1)$$

$$C_{16}H_{33}^• + O_2 \longrightarrow C_{16}H_{33}OO^• \quad (2)$$

$$HOOC_{16}H_{32}^• + O_2 \longrightarrow HOOC_{16}H_{32}OO^• \quad (3)$$

$$C_{16}H_{33}OO^• + C_{16}H_{34} \longrightarrow C_{16}H_{33}OOH + C_{16}H_{33}^• \quad (4)$$

$$HOOC_{16}H_{32}OO^• + C_{16}H_{34} \longrightarrow C_{16}H_{32}(OOH)_2 + C_{16}H_{33}^• \quad (5)$$

$$C_{16}H_{33}OO^• \rightleftharpoons HOOC_{16}H_{32}^• \quad (6)$$

$$HOOC_{16}H_{32}OO^• \longrightarrow O{=}C.C_{15}H_{31}OOH + HO^• \quad (7)$$

$$HO^• \xrightarrow{C_{16}H_{34}} C_{16}H_{33}^•$$

$$\left. \begin{array}{ll} C_{16}H_{33}OO^• + C_{16}H_{33}OO^• \longrightarrow & (8) \\ HOOC_{16}H_{32}OO^• + C_{16}H_{33}OO^• \longrightarrow & (9) \\ HOOC_{16}H_{32}OO^• + HOOC_{16}H_{32}OO^• \longrightarrow & (10) \end{array} \right\} \text{non-radical and non-hydroperoxidic products}$$

Application of the usual steady-state approximations to Scheme I yields the following kinetic equations for hydroperoxide formation:

$$\frac{d[-OOH]}{dt} = k_4[C_{16}H_{33}OO^•][C_{16}H_{34}] + \{2k_5[C_{16}H_{34}] + k_7\}[HOOC_{16}H_{32}OO^•] \quad (I)$$

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(4) Igarashi, J.; Lusztyk, J.; Ingold, K. U. Preceding paper in this issue.

(5) Larsen, R. G.; Thorpe, R. E.; Armfield, F. A. *Ind. Eng. Chem.* **1942**, *34*, 183–193.

(6) Yoshida, T.; Watanabe, H. U.S. Patent 4,714,794, December 22, 1987.

(7) Jensen, R. K.; Korcek, S.; Mahoney, L. R.; Zinbo, M. *J. Am. Chem. Soc.* **1979**, *101*, 7574–7584.

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We now assume that $k_4 = k_5 = k_p$ and hence

$$\frac{d[\text{-OOH}]}{dt} = k_p[C_{16}H_{34}]\{1 + \Psi(2 + \theta)\}[C_{16}H_{33}OO^{\bullet}] \quad \text{(II)}$$

where

$$\psi = [HOOC_{16}H_{32}OO^{\bullet}]/[C_{16}H_{33}OO^{\bullet}] \quad \text{(III)}$$

and

$$\theta = k_7/k_p[C_{16}H_{34}] \quad \text{(IV)}$$

If we further assume that $k_8 = k_9 = k_{10} = k_t$, we can write:

$$2k_t\{[C_{16}H_{33}OO^{\bullet}] + [HOOC_{16}H_{32}OO^{\bullet}]\}^2 = 2k_i[\text{-OOH}] = R_i \quad \text{(V)}$$

Substituting into eq II we obtain:

$$\frac{d[\text{-OOH}]}{dt} = k_p\left(\frac{2k_i}{2k_t}\right)^{1/2}\phi[C_{16}H_{34}][\text{-OOH}]^{1/2} \quad \text{(VI)}$$

where

$$\phi = 1 + \psi(2 + \theta)/(1 + \psi) \quad \text{(VII)}$$

In eqs VI and VII the dimensionless parameter ϕ reflects the increased rate of formation of hydroperoxides due to the production of difunctional oxidation products. The magnitude of ϕ depends on the hexadecane and oxygen concentrations[17] and on the magnitude of various rate constants.[18] ϕ is always greater than unity ($\phi > 1.0$). At a given oxygen pressure and at low conversions where $[C_{16}H_{34}]$ remains approximately constant, ϕ is also a constant.[22-24]

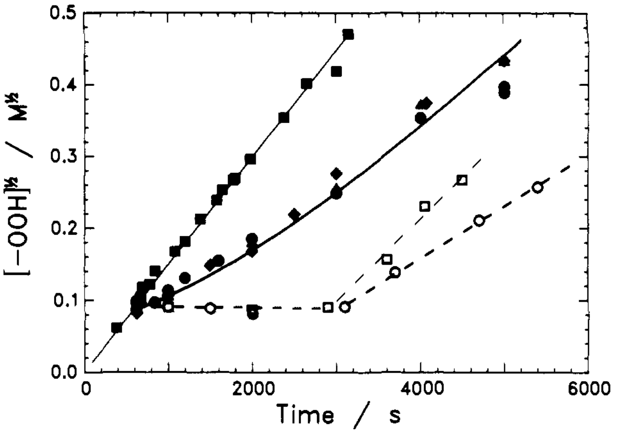

Figure 1. Plot of [hydroperoxide]$^{1/2}$ vs time for the self-initiated autoxidation of hexadecane at 160 °C under 760 Torr of O_2: no additives (■); with additives, 1-methylnaphthalene, 0.31 M, (●), 2-methylnaphthalene, 0.28 M (▲), naphthalene, 0.30 M (◆), BMP, 1.2 × 10^{-3} M (□), 1-methylnaphthalene, 0.31 M, and BMP, 1.2 × 10^{-3} M (○). All additives indicated above were introduced into autoxidizing hexadecane at t_0 = 620 s, $[\text{-OOH}]_{t_0} \approx 0.01$ M. The smooth, thick curve has been computed for the 1-methylnaphthalene modulated autoxidation of hexadecane as described in the text.

In a stirred-flow reactor eq VI has been shown to be obeyed during the early stages of hexadecane autoxidation.[7,10,13] For application to batch reactions, eq VI can be integrated from the start of the experiment at a time $t = t_0$ to the time t at which the measurement of the -OOH concentration has been made:

$$\int_{t=t_0}^{t=t}\frac{d[\text{-OOH}]}{[\text{-OOH}]^{1/2}} = \int_{t=t_0}^{t=t}k_p\left(\frac{2k_i}{2k_t}\right)^{1/2}\phi[C_{16}H_{34}]\,dt \quad \text{(VIII)}$$

$$[\text{-OOH}]_t^{1/2} - [\text{-OOH}]_{t_0}^{1/2} = K[C_{16}H_{34}](t - t_0) \quad \text{(IX)}$$

which, for $t_0 = 0$, simplifies to

$$[\text{-OOH}]_t^{1/2} = K[C_{16}H_{34}]t \quad \text{(X)}$$

where

$$K = \tfrac{1}{2}k_p\left(\frac{2k_i}{2k_t}\right)^{1/2}\phi \quad \text{(XI)}$$

A plot of $[\text{-OOH}]_t^{1/2}$ versus t for the self-initiated autoxidation of neat hexadecane (2.98 M) at 160 °C and 760 Torr of O_2 in a batch reactor is indeed linear (as predicted by eq X) during the early stages of the reaction (see filled squares and the straight line going through the origin in Figure 1). The slope of this line yields

$$K = 4.91 \times 10^{-5}\ M^{-1/2}\ s^{-1/2}$$

Using kinetic information which is available[18,20] we can calculate[22] that $\phi = 1.40$ under these experimental conditions and hence

$$k_p(2k_i/2k_t)^{1/2} = 7.03 \times 10^{-5}\ M^{-1/2}\ s^{-1/2}$$

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[8] Jensen, R. K.; Korcek, S.; Mahoney, L. R.; Zinbo, M. *J. Am. Chem. Soc.* **1981**, *103*, 1742–1749.

[9] Korcek, S.; Mahoney, L. R.; Jensen, R. K.; Zinbo, M.; Willermet, P. A.; Kandah, S. K. Report 1983, AFOSR-TR-83-0987; Order No. AD-A135464, 214 pp.

[10] Korcek, S.; Jensen, R. K.; Zinbo, M.; Mahoney, L. R. *PREPRINTS, Div. Petrol. Chem., Am. Chem. Soc.* **1987**, *32*, 833–840.

[11] Zinbo, M.; Jensen, R. K.; Johnson, M. D.; Korcek, S. *Ind. Eng. Chem. Res.* **1987**, *26*, 902–906.

[12] Jensen, R. K.; Johnson, M. D.; Korcek, S.; Zinbo, M. *Int. J. Chem. Kinet.* **1990**, *22*, 1095–1107

[13] Jensen, R. K.; Korcek, S.; Zinbo, M. Unpublished results.

[14] -OOH represents the totality of hydroperoxides produced during autoxidation.

[15] "Spontaneous" initiation at the start of each experiment may be due to a combination of a direct reaction between oxygen and hexadecane ($O_2 + C_{16}H_{34} \rightarrow HOO^{\bullet} + C_{16}H_{33}^{\bullet}$), thermal decomposition of -OOH present at concentrations too low to detect, and background γ and cosmic ray events.

[16] Reaction 6 involves both α,γ- and α,δ-intramolecular H-atom abstractions. Reaction 7 involves intramolecular α,γ- and α,δ-abstraction of the tertiary H-atom from the $-CH_2CH(OOH)CH_2-$ moiety to form the $-CH_2C^{\bullet}(OOH)CH_2-$ radical which undergoes immediate β-scission. A more comprehensive scheme[10,13] would include reaction 6′:

$$\alpha,\delta\text{-}HOOC_{16}H_{32}^{\bullet} \rightarrow CH_3(CH_2)_n\underbrace{CHCH_2CH_2CH}_{O}(CH_2)_{10-n}CH_3 + HO^{\bullet} \quad (6')$$

and the thermal decomposition of the relatively unstable $O{=}C{\cdot}C_{15}H_{31}OOH$.

[17] As previously defined:[10,13,16]

$$\psi = \frac{k_6^{\alpha,\gamma}}{k_p[C_{16}H_{34}] + k_7^{\alpha,\gamma}}\,\frac{1}{1 + k_{-6}^{\alpha,\gamma}/k_3[O_2]} + \frac{k_6^{\alpha,\delta}}{k_p[C_{16}H_{34}] + k_7^{\alpha,\delta}}\,\frac{1}{1 + (k_{-6}^{\alpha,\delta} + k_{6'})/k_3[O_2]} \quad \text{(A)}$$

At high oxygen pressures where all the $HOOC_{16}H_{32}^{\bullet}$ radicals are captured by O_2 (reaction 3) equation A simplifies to:

$$\psi = \frac{k_6^{\alpha,\gamma}}{k_p[C_{16}H_{34}] + k_7^{\alpha,\gamma}} + \frac{k_6^{\alpha,\delta}}{k_p[C_{16}H_{34}] + k_7^{\alpha,\delta}} \quad \text{(B)}$$

[18] For the autoxidation of hexadecane at 160 °C the following rate constants have been determined using a stirred-flow reactor:[13,19,20] $k_i = 2.82 \times 10^{-5}\ s^{-1}$, $k_p = 88.9\ M^{-1}\ s^{-1}$, $k_6^{\alpha,\gamma} = 83.6\ s^{-1}$, $k_{-6}^{\alpha,\gamma} = 6.28 \times 10^5\ s^{-1}$, $k_7^{\alpha,\gamma} = 1225\ s^{-1}$, $k_6^{\alpha,\delta} = 53.6\ s^{-1}$, $k_{-6}^{\alpha,\delta} = 1.05 \times 10^5\ s^{-1}$, $k_7^{\alpha,\delta} = 339\ s^{-1}$, $k_{6'}$ (see footnote 16) $= 1.7 \times 10^4\ s^{-1}$. It is assumed that $k_3 = 1 \times 10^9\ M^{-1}\ s^{-1}$.

[19] Jensen, R. K. Unpublished results.

[20] The value of k_p ($=88.9\ M^{-1}\ s^{-1}$) was calculated from the slope of a plot of $d[C_{16}H_{33}OOH]/dt$ versus $[\text{-OOH}]^{1/2}$, this slope being equal to $k_p[C_{16}H_{34}](2k_i/2k_t)^{1/2}/(1 + \Psi)$. The values of $k_i = 2.82 \times 10^{-5}\ s^{-1}$ and $2k_t = 1.12 \times 10^8\ M^{-1}\ s^{-1}$ used in deriving k_p were obtained from the Arrhenius parameters given for the relevant reactions in refs 12 and 21, respectively.

[21] Bennett, J. E.; Eyre, J. A.; Summers, R. *J. Chem. Soc., Perkin Trans. 2* **1974**, 797–800.

[22] The magnitude of ϕ can be calculated from eqs VII, IV, and A[17] or B.[17] The values of the rate constants used for this calculation at 160 °C are given in footnote 18. The concentration of O_2 was estimated from oxygen solubility data as equal to 2.65×10^{-3} M at 760 Torr of O_2.[23]

[23] Jensen, R. K.; Korcek, S.; Zinbo, M. *Oxid. Commun.* **1990**, *13*, 258–262.

[24] Boozer, C. E.; Hammond, G. S.; Hamilton, C. E.; Sen, J. N. *J. Am. Chem. Soc.* **1955**, *77*, 3233–3247.

The value of k_i can be derived using the "induction period method".[12,24] Thus, the addition of 1.2×10^{-3} M 2,6-di-*tert*-butyl-4-methylphenol (BMP) to autoxidizing hexadecane at t_0 = 620 s (corresponding to $[\text{–OOH}]^{1/2} \approx 0.1$ M$^{1/2}$, i.e., to [–OOH] $\approx$ 0.01 M)[25] completely prevented further oxidation for a period of 2555 s, after which time the oxidation rate returned to approximately its original value (see open squares in Figure 1). From the duration of this induction period it is possible to calculate the rate of chain initiation, R_i, by ca. 0.01 M [–OOH]. At lower temperatures BMP traps 2.0 peroxyl radicals per molecule,[24,26] but at 160 °C it traps an average of only 1.2 peroxyl radicals per molecule.[9] Hence, $R_i = 1.2 \times (1.2 \times 10^{-3})/2555 = 5.64 \times 10^{-7}$ M^{-1} s^{-1} at [–OOH] $\approx$ 0.01 M. Therefore, $k_i = 2.82 \times 10^{-5}$ s^{-1} and $k_p/(2k_t)^{1/2} = 0.94 \times 10^{-2}$ M$^{-1/2}$ s$^{-1/2}$, values which are in satisfactory agreement with 2.5×10^{-5} s^{-1} and 0.93×10^{-2} M$^{-1/2}$ s$^{-1/2}$, respectively, reported previously at this temperature.[12,13]

We also measured the rate of hydroperoxide formation at 160 °C under an oxygen partial pressure of 150 Torr using an oxygen/argon gas mixture. The results of these measurements and their comparison with results previously obtained using a stirred-flow reactor[13] indicate that oxidation in the batch reactor is controlled by mass transfer of oxygen at 150 Torr though not at 760 Torr.[27] For this reason, further studies at 150 Torr of O_2, including studies of the effects of added (alkyl)naphthalenes, were not undertaken. It is hoped that an investigation of the retardation of hexadecane autoxidation by alkylnaphthalenes will be pursued shortly in the stirred-flow reactor.

Retardation of the Autoxidation of Hexadecane by (Methyl)-naphthalene. The addition of 1- or 2-methylnaphthalene to hexadecane which had been preoxidized at 160 °C under 760 Torr of O_2 caused an immediate reduction in the rate of oxidation. However, in contrast to BMP, such additions did not bring the oxidation to a complete halt. Thus, addition of either 1- or 2-methylnaphthalene at the same time point as had been used for BMP, viz.,[25] at t_0 = 620 s, $[\text{–OOH}]_{t_0}^{1/2} \approx 0.1$ M$^{1/2}$, in quantities appropriate to produce a ca. 0.3 M solution of the methylnaphthalene in the oxidizing hexadecane, reduced the slope of the line in the plot of $[\text{–OOH}]_t^{1/2}$ versus t by about a factor of 2 (see filled circles and triangles in Figure 1). This reduction in K *must* be attributed to oxidation chemistry *specific* to the naphthalene nucleus and *not* to chemistry of the methyl group because an essentially identical reduction in K was produced by the addition of about the same molar concentration of naphthalene (see filled diamonds in Figure 1). The plots of $[\text{–OOH}]_t^{1/2}$ versus t subsequent to the addition of ca. 0.3 M (methyl)naphthalene at t_0 = 620 s are approximately linear until $t \geq 3000$ s (see Figure 1). After this time, the –OOH concentration increases at a slightly greater rate. This increase in the rate of formation of –OOH at longer times may be partly or entirely due to the volatility of the (methyl)naphthalene since volatility causes a substantial loss of the (methyl)naphthalene after a few thousand seconds (see Figure 2).[28]

The addition of ca. 0.3 M (methyl)naphthalene to hexadecane preoxidized under 760 Torr of O_2 to $[\text{–OOH}]_{t_0} \approx 0.01$ M and t_0 = 620 s[25] roughly halves the slope of the $[\text{–OOH}]_t^{1/2}$ versus t plot (see Figure 1). This means that K (eq XI) is approximately halved because the diluting effect of the added (methyl)naphthalene is almost negligible, viz., $[C_{16}H_{34}]$ = 2.98 M for the neat material and 2.83 M for hexadecane containing 0.3 M (methyl)naphthalene. This reduction in K is not due to any change in k_i because the simultaneous addition of 1.2×10^{-3} M BMP and ca. 0.3 M 1-methylnaphthalene (open circles in Figure 1) produced an induction period of the same length as had previously been obtained by the addition of 1.2×10^{-3} M BMP alone (open squares in Figure 1). Furthermore, because the concentration of the major oxidizable substrate, hexadecane, is virtually unchanged by the addition of ca. 0.3 M (methyl)naphthalene, the major chain-propagating reactions will remain unchanged. This means that both k_p and ϕ will be virtually unaffected by the (methyl)naphthalene. Since K is determined by the magnitude of k_i, k_p, ϕ, and k_t (see eq XI) and since the first three of these quantities will be little affected by the addition of ca. 0.3 M (methyl)naphthalene, it must be concluded that k_t has increased, and increased by about a factor of 4.

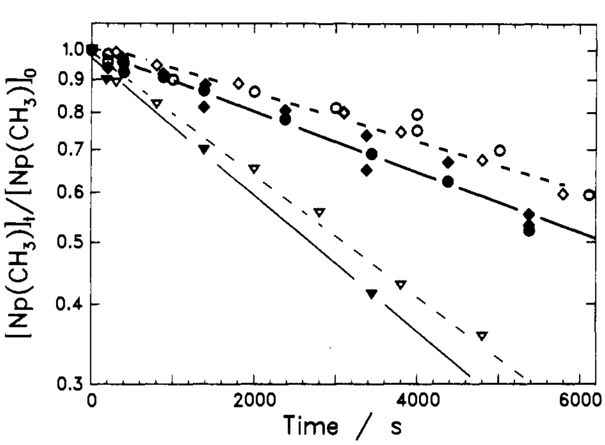

Figure 2. Semilogarithmic plot of the relative concentrations of naphthalene (▼ and ▽), 1-methylnaphthalene (● and ○), and 2-methylnaphthalene (◆ and ◇) as a function of time when added to hexadecane at 160 °C autoxidizing under 760 Torr of O_2 (solid symbols and lines) at t_0 = 620 s and when added to hexadecane at 160 °C which was being bubbled with argon at the same flow rate as oxygen in the autoxidizing hexadecane experiments (open symbols and interrupted lines). The thick lines are the best straight lines through the experimental points for both 1- and 2-methylnaphthalene. Concentrations of the additives were 0.27–0.31 M in all cases. On this plot, the time is measured from the time of addition of the additive to the reaction vessel.

The effective rate constant for chain-termination in the presence of ca. 0.3 M (methyl)naphthalene could increase because of the following: (i) The second-order rate constant for peroxyl + peroxyl chain-termination reactions is increased. (ii) There is a contribution from a *kinetically*-first-order chain-termination reaction. (iii) Both of the above phenomena occur.

With regard to possibility i, $2k_t$ has a value of about 1.12×10^8 M^{-1} s^{-1} at 160 °C,[20,21] which is well below the upper limit of ca. 5.3×10^9 M^{-1} s^{-1} which we calculate[29] for a radical + radical reaction which proceeds at the diffusion-controlled limit in hexadecane at this temperature. If, therefore, these (methyl)naphthalene retarded hexadecane autoxidations could be properly described by eqs IX and XI, i.e., if chain-termination were entirely a second-order process, then we can put limits on the (methyl)naphthalene modulated value of K, hereafter referred to as K'. These limits are $(1.12/53)^{1/2}K = 0.15K < K' < K$.

For the experiments described above (viz., addition of ca. 0.3 M (methyl)naphthalene at $[\text{–OOH}]_{t_0} \approx 0.01$ M, t_0 = 620 s, 760 Torr of O_2) we find a 2-fold decrease in rate, i.e., $K' \approx 0.5K$. Therefore, it is not essential to invoke a kinetically-first-order chain-termination process (possibility ii). *However*, such a first-order process must be invoked in order to account for the retardation which is observed when higher concentrations of

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(25) In these and analogous experiments a sample of hexadecane was removed from the reactor at 600 s and was titrated to measure [–OOH], which varied from a low of 7.7×10^{-3} M to a high of 11.3×10^{-3} M. Materials were added to the reactor 20 s later. Note that all concentrations have been corrected for the change in density with temperature and hence are actual concentrations at 160 °C.

(26) Horswill, E. C.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1966**, *44*, 985–991.

(27) For the autoxidation of neat hexadecane at 160 °C, ϕ is calculated to be equal to 1.28 at 150 Torr of O_2 from data obtained in the stirred-flow reactor.[13] The results obtained in the batch reactor used in the present study would have implied a much smaller value for ϕ at 150 Torr of O_2.

(28) The decrease in the concentration of naphthalene, in particular, is so substantial after 3000 s that an even more significant deviation from linearity of the $[\text{–OOH}]_t^{1/2}$ vs t plot for this additive might have been expected. We suggest that the rate accelerating effect caused by volatility of the (methyl)naphthalene is partially compensated for in the plots shown in Figure 1 by the fact that some (methyl)naphthalene oxidation products are more potent retarders of autoxidation than the parent hydrocarbons.[4] These retarders are probably (methyl)naphthoquinones.[4]

(29) Estimated from data given in: Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130–2164.

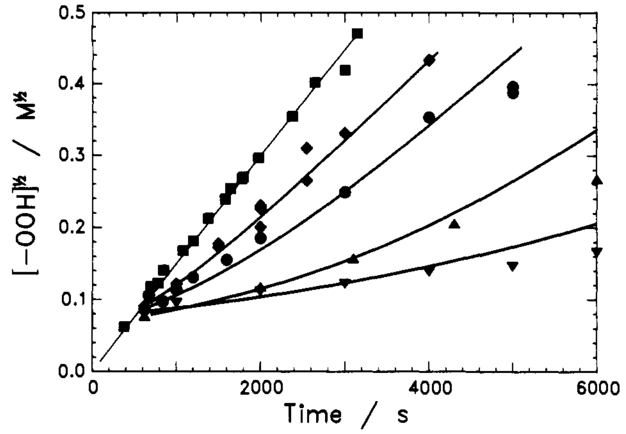


Figure 3. Plot of [hydroperoxide]$^{1/2}$ vs time for the self-initiated autoxidation of hexadecane at 160 °C under 760 Torr of O_2: no additives (■); with additive, 1-methylnaphthalene at concentrations of 0.15 (◆), 0.31 (●), 0.61 (▲), and 1.06 (▼). The 1-methylnaphthalene was introduced into the autoxidizing hexadecane at t_0 = 620 s (680 s for the highest concentration) and $[-OOH]_{t_0} \approx 0.01$ M. The curves shown for the 1-methylnaphthalene modulated autoxidation of hexadecane, corresponding to the above concentrations of 1-methylnaphthalene, have been computed as described in the text.

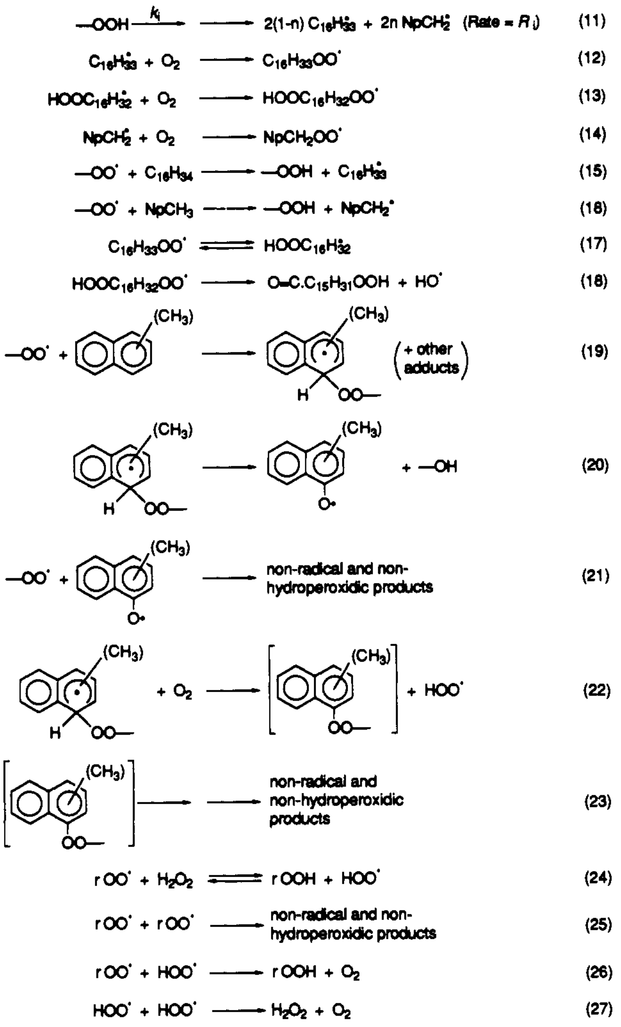
(methyl)naphthalene are added under similar experimental conditions. For example, the slope of the straight line which can be drawn through the experimental points for a plot of $[-OOH]_t^{1/2}$ versus t for an experiment in which 1.06 M 1-methylnaphthalene was added to preoxidized hexadecane at 160 °C under 760 Torr of O_2 ($[-OOH]_{t_0} \approx 0.01$ M, t_0 = 680 s, $[C_{16}H_{34}]_{t_0}$ = 2.45 M, see Figure 3) yields $K' \approx 0.10K$ which is lower than the limiting value of $0.15K$. First-order chain termination is also required to explain the very strong initial retardation observed when (methyl)naphthalene is added to hexadecane which has not been preoxidized (vide infra).

Despite the foregoing, the agreement between calculated and experimental data is not acceptable if a kinetically-first-order chain-termination process is introduced into a kinetic model in which the magnitude of the second-order rate constant for chain-termination remains invariant and equal to $2k_t$. Possibilities i and ii can therefore be ruled out.

Possibility iii provides a very satisfactory degree of agreement between theory and experiment with a kinetic model which includes both a first-order chain-termination and a second-order chain-termination for which the rate constant increases as the concentration of (methyl)naphthalene increases. These two requirements can be accommodated within a relatively simple reaction scheme, Scheme II.

In Scheme II, $NpCH_3$ represents methylnaphthalene, $NpCH_2^•$ the naphthylmethyl radical, rOO$^•$ represents all organic peroxyl radicals present in the system, i.e., rOO$^•$ = $\sum(C_{16}H_{33}OO^• + HOOC_{16}H_{32}OO^• + NpCH_2OO^•)$, and –OO$^•$ represents all the peroxyl radicals present, i.e., –OO$^•$ = $\sum$(rOO$^•$ + HOO$^•$). This scheme combines the main features of Scheme I with many of the features shown in a scheme in the preceding paper.[4,30] We attribute the increase in the second-order rate constant for chain-termination to the interaction of HOO$^•$ radicals in cross (reaction 26) and self (reaction 27) radical + radical reactions. The HOO$^•$ radicals are formed via reactions 19 and 22, so their rate of formation and, hence, the enhancement in the overall second-order rate constant for chain-termination increases with an increase in the (methyl)naphthalene concentration and oxygen partial pressure. We attribute the kinetically-first-order chain-termination, as before,[4] to peroxyl radical trapping by (methyl)naphthoxyl radicals (reaction 21) which are themselves produced by decomposition of the peroxycyclohexadienyl radical (reaction 20) formed by peroxyl addition to the (methyl)naphthalene (reaction 19).

Scheme II



Computer Simulation of the (Methyl)naphthalene Retarded Autoxidation of Hexadecane. A kinetic analysis of Scheme II is given as an Appendix in which it is shown that

$$\frac{d[-OOH]}{dt} = \{k_{15}[C_{16}H_{34}]\phi + k_{16}[NpCH_3]\}(1 + \delta)[HOO^•] + (k_{26}\delta + k_{27})[HOO^•]^2 - k_i[-OOH] \quad (XII)$$

where $\delta = [rOO^•]/[HOO^•]$. It is also shown in the Appendix that the HOO$^•$ radical concentration can be represented by

$$[HOO^•] = \left[-k_{19}[Np(CH_3)]\beta + \sqrt{(k_{19}[Np(CH_3)]\beta)^2 + 8k_i[-OOH]\{2k_{25}\delta^2 + 2k_{26}\delta + 2k_{27}\}}\right] \Big/ 2\{2k_{25}\delta^2 + 2k_{26}\delta + 2k_{27}\} \quad (XIII)$$

where $\beta = (2f + 2f\delta)$ and $f = k_{20}/(k_{20} + k_{22}[O_2])$.

From earlier work values of k_{15}, k_{16}, k_{25}, k_{26}, k_{27}, k_i, and ϕ at 160 °C (see Table I) are known or can be estimated on the basis of the assumptions indicated in this table.[4,18,20–22,29,31–40] Of the

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[30] In comparing the present Scheme II with the earlier Scheme in ref 4 used to describe the Me_3COOH modulated autoxidation of methylnaphthalene at much lower temperatures, it should be noted that the rOOH concentrations ($\approx$[–OOH]) generated by hexadecane autoxidation are very much lower (typically ca. 0.01–0.05 M) than the concentrations of Me_3COOH which were added earlier ($\geq$1.0 M). As a consequence, the quantitative conversion of HOO$^•$ into $Me_3COO^•$ via the reaction $HOO^• + Me_3COOH \rightarrow HOOH + Me_3COO^•$ has no parallel in the current experiments, i.e., reaction –24 is of much less importance than the other reactions which consume HOO$^•$, viz., reactions 15, 26, and 27 in particular. It should also be noted that the "nonradical and non-hydroperoxidic product" from reactions 21, 23, and 25 refers only to the absence of hydroperoxide formation from the –OO or rOO moiety. If the reaction in question involves the $HOOC_{16}H_{32}OO$ moiety then, of course, hydroperoxide-containing products will result. However, the concentration of hydroperoxide in the system will not change.

Table I. Kinetic Parameters for the (Methyl)naphthalene Modulated Autoxidation of Hexadecane at 160 °C

parameter	assumption
$k_{15} = k_p = 88.9\ \mathrm{M^{-1}\ s^{-1}}$	Since k_p is known[18,20] this assumes that all peroxyl radicals in the system have equal reactivity in intermolecular H-atom abstractions. Even if this assumption is not entirely valid,[31] the approximation is reasonable since the major abstracting species will be the hexadecylperoxyl radicals under all conditions.
$k_{16} = 34\ \mathrm{M^{-1}\ s^{-1}}$	Based on a value obtained by extrapolation of our low-temperature kinetic data[4] for the reaction: $NpCH_2OO^\bullet + NpCH_3 \rightarrow NpCH_2OOH + NpCH_2^\bullet$.[36]
$k_{25} = k_t = 5.6 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$	Since k_t is known[20,21] this assumes that the $NpCH_2OO^\bullet$ radicals react with the hexadecylperoxyl radicals and with themselves with the same rate constant as two hexadecylperoxyls.
$k_{26} = 2.5 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$	It is assumed that $k_{26} = k_{27}$.
$k_{27} = 2.5 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$	This reaction is assumed[37] to be diffusion-controlled[29] in hexadecane at this temperature, viz., $2k_{27} \approx 5 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$.
$k_i = 2.82 \times 10^{-5}\ \mathrm{s^{-1}}$	See refs 12 and 13.
ϕ	Calculated[22] for the hexadecane concentration present in each run after addition of the (methyl)naphthalene using an oxygen concentration of 2.65×10^{-3} M, i.e., the concentration appropriate for 760 Torr of O_2.[22,23]

remaining three unknowns in eqs XII and XIII, one, k_{19}, is a constant, one, $f\,(=k_{20}/(k_{20} + k_{22}[O_2]))$, varies only with a change in the oxygen pressure, and one, $\delta\ (=[rOO^\bullet]/[HOO^\bullet])$, depends primarily on the $[C_{16}H_{34}]/[Np(CH_3)]$ ratio. This last quantity, δ, is expected to change only rather slowly during an oxidation. It will change because of evaporative losses of the (methyl)naphthalene and because reactions 24 and −24 come to play an increasingly important role as the hydroperoxide concentration increases. With regard to the latter potential cause for a change in δ during a reaction, it should be noted that immediately following the (methyl)naphthalene addition the concentration of hydrogen peroxide is extremely low (ca. 4–5% of the total [−OOH])[41] and therefore reaction 24 can be ignored. At this point under typical experimental conditions, i.e., $t_0 = 620$ s, the [−OOH] concentration is ca. 0.01 M and so reaction −24 does occur to a small extent. That is, we estimate[43] that $k_{24} = k_{-24} = 5.4 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$ at 160 °C and hence the ratio of $HOO^\bullet$ radicals which react by H-atom abstraction from 0.01 M [−OOH] relative to those which abstract hydrogen from 2.8 M hexadecane is only $(5 \times 10^3) \times 0.01/89 \times 2.8 \approx 0.2$. The [−OOH] concentration must therefore rise to ca. 0.05 M before reactions −24 and 15 become equally important as routes for the conversion of $HOO^\bullet$ into $rOO^\bullet$ radicals.

Because eq XII is not readily integrated, a computer simulation was used to calculate [−OOH] as a function of time using the approximation

$$\frac{\Delta[-OOH]}{\Delta t} \approx \frac{d[-OOH]}{dt} \tag{XIV}$$

which will be valid for small Δt. For these simulations $\Delta t = 1$ s was used since smaller values of Δt had little effect on the results. The program calculated the accumulation of hydroperoxidic oxidation products on the basis of the kinetic analysis given above and the rate constants given in Table I and its associated footnotes. The assumption is made that $[C_{16}H_{34}]$ and $[O_2]$ do not change during the course of an experiment. However, it is known (see Figure 2) that the (methyl)naphthalene concentration declines during an experiment due to both evaporation and reaction. The $[Np(CH_3)]$ concentration was therefore estimated as a function of time by interpolation using the data presented in Figure 2.

To simplify the computational procedure a preliminary estimate of $\delta\ (=[rOO^\bullet]/[HOO^\bullet])$ was made under each initial set of experimental conditions as described below.

The ratio, a, of the rates of formation of $rOO^\bullet$ and $HOO^\bullet$ radicals is given by

$$a = \frac{k_{15}[C_{16}H_{34}] + k_{16}[NpCH_3]}{(1 - f)k_{19}[Np(CH_3)]} \tag{XV}$$

This equation indicates that $a \gg 1$ under all conditions. If we now neglect the first-order chain-termination reactions then, because $a \gg 1$, we can make the simplifying assumption that $HOO^\bullet$ radicals are destroyed in the very fast, bimolecular, $HOO^\bullet + rOO^\bullet$ cross-reaction (reaction 26) and that the large fraction of $rOO^\bullet$ radicals which remain are lost by their much slower bimolecular self-reaction (reaction 25). The ratio, b, of the rates of destruction of $rOO^\bullet$ and $HOO^\bullet$ radicals can therefore be approximated by

$$b = \frac{2k_{25}[rOO^\bullet]^2}{k_{26}[rOO^\bullet][HOO^\bullet]} \tag{XVI}$$

Since the rates of formation and destruction of the peroxyl radicals

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(31) In this connection, the limited evidence available suggests that the $HOO^\bullet$ radical does have about the same reactivity in hydrogen atom abstraction as a secondary alkylperoxyl radical. For example,[32] per reactive (bis-allylic) hydrogen atom the rate constant for H-atom abstraction, k/H, from 1,4-cyclohexadiene by $HOO^\bullet$ has been reported to be 85 $\mathrm{M^{-1}\ s^{-1}}$ in *n*-decane at 30 °C[33] and 40 $\mathrm{M^{-1}\ s^{-1}}$ in water at 25 °C,[34] while for abstraction of a bis-allylic H-atom from a polyunsaturated fatty acid by the corresponding secondary alkylperoxyl, $k/\mathrm{H} \approx 45\ \mathrm{M^{-1}\ s^{-1}}$ at 30 °C.[35]

(32) For a comprehensive listing of rate constants for reactions involving peroxyl radicals including the $HOO^\bullet$ radical, see: Howard, J. A.; Scaiano, J. C. *Radical Reaction Rates in Liquids*; Landolt-Börnstein, New Series. Springer-Verlag: Berlin, 1984; Vol. 13d, pp 193–422.

(33) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1967**, *45*, 785–792.

(34) Sawyer, D. T.; McDowell, M. S.; Yamaguchi, K. S. *Chem. Res. Toxicol.* **1988**, *1*, 97–100.

(35) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1967**, *45*, 793–802.

(36) Note that the hydrogen atoms in the methyl group of the methylnaphthalenes are, as expected, more readily abstracted by an attacking peroxyl radical than the secondary, parafinic hydrogen atoms in hexadecane, i.e., $k_{16}/\mathrm{H} = 34/3 = 11.3\ \mathrm{M^{-1}\ s^{-1}}$ vs $k_{15}/\mathrm{H} = 88.9/28 = 3.2\ \mathrm{M^{-1}\ s^{-1}}$.

(37) Values reported for k_{27} are very much greater in nonpolar solvents (and in the gas phase) than in polar solvents.[32] For example,[33] $k_{27} = 3.5 \times 10^9$, 2.8×10^9, 3.4×10^8, and $3.2 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ at 30 °C in CCl_4/fluorolube ($\eta^{20\,°C} = 8.0$ cP), CCl_4, *n*-decane, and chlorobenzene, respectively (and $1.5 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$ in the gas phase),[38] whereas its value is $2.2 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$ at 30 °C in acetonitrile[33] and ca. $1 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$ at room temperature in water.[34,39] (The reaction in the gas phase is known to yield H_2O_2 and O_2 only.)[40]

(38) See, e.g.: Burgess, R. H.; Robb, J. C. *Chem. Soc. London, Spec. Publ.* **1958**, *9*, 167.

(39) See, e.g.: Bielski, B. H. J.; Saito, E. *J. Phys. Chem.* **1962**, *66*, 2266–2268. Czapski, G.; Bielski, B. H. J. *J. Phys. Chem.* **1963**, *67*, 2180–2184. Currie, D. J.; Dainton, F. S. *Trans. Faraday Soc.* **1965**, *61*, 1156–1165. Adams, G. E.; Boag, J. W.; Michael, B. D. *Proc. R. Soc. London* **1966**, *289A*, 321–341.

(40) Ingold, K. U. *J. Phys. Chem.* **1988**, *92*, 4568–4569.

(41) Although there are several potential sources of the $HOO^\bullet$ radical, and hence of H_2O_2, in autoxidizing hexadecane, the major route probably involves the further oxidation of the alcohol products formed via the Russell termination of two *sec*-alkylperoxyl radicals.[42]

(42) Niu, Q. J.; Mendenhall, G. D. *J. Am. Chem. Soc.* **1992**, *114*, 165–172.

(43) Based on Arrenhius equation given for the reaction of *tert*-butylperoxyl radicals with tetralin hydroperoxide.[44] We also note that this Arrhenius equation[44] yields $k = 1.4 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$ at 70 °C, at which temperature the rate constant for the reaction $C_6H_5CH(CH_3)OO^\bullet + H_2O_2 \rightarrow C_6H_5CH(CH_3)OOH + HOO^\bullet$ has been estimated to have essentially the same value, viz.,[45] $1.56 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$.

(44) Chenier, J. H. B.; Howard, J. A. *Can. J. Chem.* **1975**, *53*, 623–627.

(45) Gol'denburg, V. I.; Denisov, E. T.; Ermakova, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 738–743.

must, according to the normal steady-state assumption, be equal, we have

$$\frac{2k_{25}[\mathrm{rOO^\bullet}]}{k_{26}[\mathrm{HOO^\bullet}]} \approx \frac{k_{15}[\mathrm{C_{16}H_{34}}] + k_{16}[\mathrm{NpCH_3}]}{(1 - f)k_{19}[\mathrm{Np(CH_3)}]} \qquad \text{(XVII)}$$

That is

$$\delta = \frac{[\mathrm{rOO^\bullet}]}{[\mathrm{HOO^\bullet}]} \approx \frac{k_{26}}{2k_{25}} \frac{k_{15}[\mathrm{C_{16}H_{34}}] + k_{16}[\mathrm{NpCH_3}]}{(1 - f)k_{19}[\mathrm{Np(CH_3)}]} \qquad \text{(XVIII)}$$

Equation XVIII becomes more reliable as the (methyl)naphthalene concentration is reduced and as the oxygen pressure is increased, i.e., under conditions where $[\mathrm{HOO^\bullet}] \ll [\mathrm{rOO^\bullet}]$ and first-order chain-termination is *relatively* unimportant.

It can be seen that eq XVIII provides an approximate relation between δ and the other two "unknowns", f and k_{19}. Values for f and k_{19} were assigned more-or-less arbitrarily in the early simulations but were modified in subsequent simulations in order to improve the overall "fit" between the calculated [–OOH] vs t curves and the experimental data. The final "best" values for these quantities were

$$k_{19} = 70\ \mathrm{M^{-1}\ s^{-1}}$$

$$f = 0.40$$

At each time point the program calculated ϕ (footnote 22), δ (eq XVIII), [HOO•] (eq XIII), and the increase in [–OOH] for the following one second interval (eqs XII and XIV). The increase in $[\mathrm{H_2O_2}]$ for the following one second interval was also calculated (eq XIX).

$$\Delta[\mathrm{H_2O_2}] = \frac{\Delta[\mathrm{-OOH}](1 - f)k_{19}[\mathrm{Np(CH_3)}]}{k_{15}\phi[\mathrm{C_{16}H_{34}}] + k_{16}[\mathrm{NpCH_3}]} \qquad \text{(XIX)}$$

Finally, the calculated changes are accumulated over time via

$$[\mathrm{H_2O_2}]_t = [\mathrm{H_2O_2}]_{t-1} + \Delta[\mathrm{H_2O_2}] \qquad \text{(XX)}$$

and

$$[\mathrm{-OOH}]_t = [\mathrm{-OOH}]_{t-1} + \Delta[\mathrm{-OOH}] \qquad \text{(XXI)}$$

The program then repeats the calculations for the next one second time interval.

The [–OOH] concentrations calculated as a function of time, as described above, were converted to curves showing $[\mathrm{-OOH}]_t^{1/2}$ vs t. These calculated curves are shown in Figures 1 and 3. It can be seen that there is a satisfactory to excellent agreement between the measured and calculated values of [–OOH] for the addition (at t_0 = 620 s, $[\mathrm{-OOH}]_{t_0} \approx 0.01$ M) of (methyl)naphthalene at ca. 0.3 M (Figure 1) and of 1-methylnaphthalene at 0.15, 0.31, 0.61, and 1.06 M (Figure 3). There is also a very satisfactory agreement between the theoretical curves for $[\mathrm{-OOH}]_t^{1/2}$ vs t calculated using the foregoing kinetic parameters and the results of experiments in which ca. 0.3 M (methyl)naphthalene was added to hexadecane which had not been preoxidized, i.e., t_0 = 0 s, $[\mathrm{-OOH}]_0$ assumed as 1×10^{-4} M, or had been only mildly preoxidized, t_0 = 300 s, $[\mathrm{-OOH}]_{t_0} \approx 1 \times 10^{-3}$ M (see Figure 4). The full experimental data and values of δ, $[\mathrm{H_2O_2}]$, and [–OOH] calculated at the same time points as those at which the experimental measurements were made are listed in the supplementary material.

The good agreement between calculated and measured total hydroperoxide concentrations, $[\mathrm{-OOH}]_t$ (see Figures 1, 3, and 4), provides strong support for not only the 17 reactions used to describe the (methyl)naphthalene modulated autoxidation of hexadecane (Scheme 2) but also the kinetic parameters used in the computations. Additional validification of Scheme II and of the magnitude of the kinetic parameters is provided by there being a reasonable agreement between the calculated and measured yields of hydrogen peroxide (vide infra). Further validification of our kinetic treatment is provided by the fact that when ca. 0.3 M 1- and 2-methylnaphthalene were added to autoxidizing hexadecane the yields of side chain (i.e., methyl group) oxidation products and of ring-opened products were found to be comparable (vide infra). This implies that at 160 °C k_{16} and k_{19} must be of roughly comparable magnitude, a conclusion which is fully consistent with our estimate that $k_{16} = 34\ \mathrm{M^{-1}\ s^{-1}}$ and $k_{19} = 70\ \mathrm{M^{-1}\ s^{-1}}$.

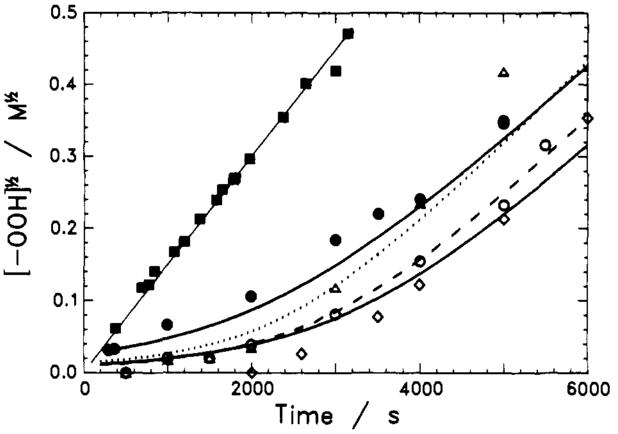


Figure 4. Plot of [hydroperoxide]$^{1/2}$ vs time for the self-initiated autoxidation of hexadecane at 160 °C under 760 Torr of O_2: no additives (■); with additives, 0.31 M 1-methylnaphthalene added at t_0 = 300 s (●) and at the beginning of the reaction t_0 = 0 s (○), 0.30 M naphthalene (▲), and 0.28 M 2-methylnaphthalene (◇), both also added at the beginning of the reaction, t_0 = 0 s, $[\mathrm{-OOH}]_{t_0}$ assumed as 1×10^{-4} M. The curves shown for the (methyl)naphthalene modulated autoxidation of hexadecane (solid curves for the 1-methylnaphthalene, dashed curve for 2-methylnaphthalene, and dotted curve for naphthalene) have been computed as described in the text.

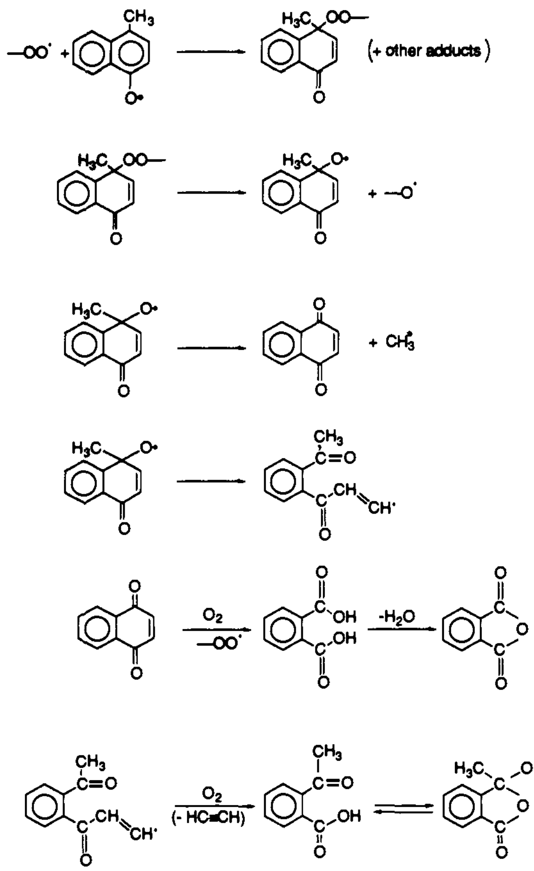
Peroxyl Radical Addition to (Methyl)naphthalene: Product Evidence. We have assumed (vide supra) that peroxyl radical addition to the (methyl)naphthalene ring, reaction 19, is responsible both for the enhanced rate constant for the kinetically-second-order, peroxyl + peroxyl chain-termination process, reactions 26 and 27, which involve HOO•, and for the kinetically-first-order peroxyl + (methyl)naphthoxyl chain-termination process, reaction 21.

If HOO• radicals are indeed produced in the (alkyl)naphthalene modulated autoxidation of hexadecane, then hydrogen peroxide must also be formed, in part via hydrogen atom abstraction from the oxidizing hydrocarbons and in part via reaction 27. Two experiments were performed in which the total H_2O_2 yields were measured. The gas stream exiting the reactor was bubbled through two consecutive water traps. At the end of each experiment iodiometric titration showed H_2O_2 only in the first trap. The oxidized hydrocarbon was also extracted with water so that the nonvolatilized H_2O_2 could also be determined.

In the first experiment 1.1 M 1-methylnaphthalene was added to hexadecane preoxidized under 760 Torr of O_2 to $[\mathrm{-OOH}]_{t_0} \approx$ 0.01 M, t_0 = 680 s. The autoxidation was continued for an additional 3320 s after which time titration gave [–OOH] = 23.2 mM and $[\mathrm{H_2O_2}]$ = 1.81 mM (0.91 mM in the first trap, 0.90 mM in the water extract). Thus, during the time the 1-methylnaphthalene was present the yield of rOOH was ca. 23.2 – (10.1 + 0.90) = 12.2 mM. The yield of H_2O_2 which is actually derived from the 1-methylnaphthalene is not the total H_2O_2. This is because of the small quantity of H_2O_2 (ca. 4–5% of the total [–OOH])[41] formed during the autoxidation of neat hexadecane. Since 12.2 mM [rOOH] was formed during the time in question, the yield of H_2O_2 which can be directly attributed to 1-methylnaphthalene autoxidation can be calculated to be ca. $1.81 - (0.04_5 \times 12.2) = 1.26$ mM. The calculated yields of rOOH and H_2O_2 during this same time interval are 14.2 – 1.6 = 12.6 mM and 1.6 mM, respectively (see supplementary material). Thus, under these conditions the calculated yields of rOOH and H_2O_2 are in excellent agreement with the experimental values, a fact which lends additional support both to the proposed reaction mechanism (Scheme 2) and to the derived kinetic parameters.

In a second experiment corresponding to more typical experimental conditions, 0.3 M 1-methylnaphthalene was added to

Scheme III



(28)

(29)

(30)

(31)

(32)

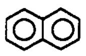
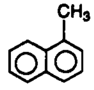
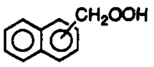
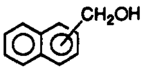
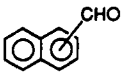
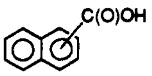
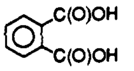
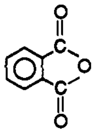
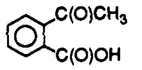
(33)

hexadecane preoxidized under 760 Torr of O_2 to $[-OOH]_{t_0} \approx 0.009$ M, $t_0 = 620$ s, and the oxidation was continued for an additional 2480 s, i.e., for a total of 3000 s. The measured hydroperoxide yields were $[-OOH] = 66.7_4$ mM and $[H_2O_2] = 5.12$ mM (trap 2.23 mM, reactor 2.89 mM). Thus, during the time in question the yield of rOOH was $66.7_4 - (9.0 + 2.89) = 54.8_5$ mM and the yield of H_2O_2 derived from the added 1-methylnaphthalene was $5.12 - (0.04_5 \times 54.8_5) = 2.65$ mM. The calculated yields of rOOH and H_2O_2 derived from oxidized 1-methylnaphthalene during this interval of time are $54.7 - 1.6 = 53.3$ mM and 1.6 mM, respectively (see supplementary material). In this case also, the estimated contribution to the measured total yield of H_2O_2 which is due to the 1-methylnaphthalene is in reasonable agreement with its calculated yield.

Let us now turn to the organic products arising from the trapping of a peroxyl radical by the (methyl)naphthoxyl radical. This reaction is expected to be an addition as shown by reaction 28 in Scheme III, a scheme which is specific for 1-methylnaphthalene. All the peroxides formed in reaction 28 will be thermally unstable at 160 °C and will decompose by scission of the O–O bond, reaction 29 (for example). The (methyl)naphthalene derived alkoxyl radicals formed via reaction 29 will also be thermally unstable and are expected to undergo β-scission with loss of a methyl radical, reaction 30, or with ring-opening, reaction 31.[46] Further oxidation of the 1,4-naphthoquinone formed in reaction 30 will lead, eventually, to phthalic acid and hence, possibly, to phthalic anhydride, reaction 32. Further oxidation of the vinylic radical formed in reaction 31 (or perhaps a direct loss of acetylene followed by oxidation) would be expected to lead to the formation of 2-acetylbenzoic acid, reaction 33.

It is clear that relatively stable ring-opened products such as phthalic acid and 2-acetylbenzoic acid are demanded by the peroxyl radical addition process (reaction 19) which we have invoked as the first step of the (methyl)naphthalene retarded autoxidation of hexadecane. We therefore decided to search for such products. In three separate experiments, naphthalene and the two methylnaphthalenes were added at concentrations of 0.35 M to hexadecane preoxidized to $[-OOH]_{t_0} \approx 0.01$ M, $t_0 = 620$ s, i.e., under the conditions shown in Figure 1, and the reactions were continued until $t = 5{,}600$ s. At this time the reactants were rapidly cooled to prevent further oxidation. Products remaining in the oxidized hexadecane were analyzed by methods described in the Experimental Section. Approximate product yields are given in Table II.

Table II. Products Derived from 0.35 M Naphthalene, 0.35 M 1-Methylnaphthalene, and 0.35 M 2-Methylnaphthalene following Their Addition to Hexadecane Preoxidized at 160 °C for 620 s (t_0) to $[-OOH]t_0 \approx 0.01$ M. Oxidation Was Continued to 5600 s, i.e., for an Additional 4980 s

Products (mM)			
Side-chain (total)		(13.5)	(≥ 9.2)
		7.1	3.8
		2.9	2.5
		1.7	a
		1.8	2.9
Ring-Scission (total)	(5.8)	(6.0)	(11.0)
	5.3[b]	1.8[c,d]	5.0[c,d]
	0.5[b]		
		4.2[c]	6.0[c]

[a] Present but a quantitative analysis proved impossible. [b] Single ion extraction procedure applied to LC/MS analysis to partition ring-scission products. [c] Single ion extraction procedure applied to GC/MS analysis to partition ring-scission products. [d] Phthalic anhydride may also be present and is included in this quantity.

An examination of Table II reveals that the methyl group of the methylnaphthalenes is oxidized to all the expected products, viz., hydroperoxide, alcohol, aldehyde and carboxylic acid. Of more importance in the present context, the naphthalene ring undergoes oxidative scission to form phthalic acid, traces of phthalic anhydride, and, from the two methylnaphthalenes, 2-acetylbenzoic acid. The formation of these last three products certainly implies that peroxyl radicals add to the naphthalene ring—just as we have assumed in order to account for both our low[4] and high temperature kinetic results. In view of the similar rate-retarding properties of naphthalene and the two methylnaphthalenes (see Figure 1) it is not surprising to find that the yields of ring-opened products from these three compounds are all of comparable magnitude. Of great importance is the fact that for the two methylnaphthalenes the yields of products derived from side chain oxidation and from oxidative ring-opening are com-

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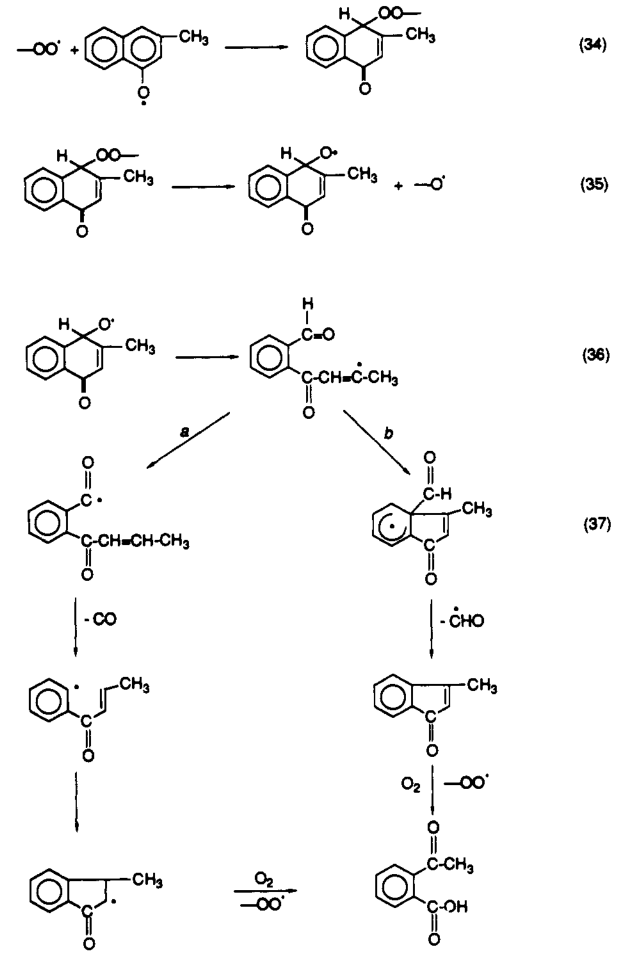
(46) Reactions 31 (Scheme III) and 36 (Scheme IV) may occur in stages, i.e., via an intramolecular addition of the oxyl radical to form an oxirane, followed by ring expansion and β-scission. We thank a referee for this suggestion.

Scheme IV



parable. As mentioned previously, this implies that k_{16} and k_{19} are of comparable magnitude, just as we had deduced from our kinetic analysis.

The absence of methyl-substituted phthalic acids suggests that such products suffer further oxidative degradation. The same would appear to be true for both naphthoquinone and methylnaphthoquinones since none of these compounds could be detected among the reaction products. In this connection, we note that 2-methyl-1,4-naphthoquinone was about 3 times as effective a retarder of hexadecane's autoxidation as were the (methyl)naphthalenes. This observation implies that any (methyl)naphthoquinones which are produced will be relatively rapidly consumed. Presumably the steady-state concentration of (methyl)naphthoquinones is lower than our limits of detection. Interestingly, the 2-methyl-1,4-naphthoquinone retarded autoxidation of hexadecane was itself autoretarding which indicates that even more effective antioxidants are generated from this compound.

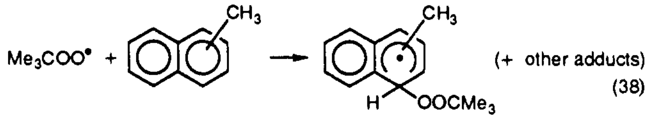
Finally, we note that 2-acetylbenzoic acid is a major product of the oxidative ring-scission of *both* 1- and 2-methylnaphthalene. For 1-methylnaphthalene this result can be rationalized via the reactions shown in Scheme III. However, it is less easy to rationalize for 2-methylnaphthalene since this compound was purified by recrystallization and contained no detectable quantity of 1-methylnaphthalene as an impurity. Two possible routes, *a* and *b*, for the conversion of the naphthoxyl radical derived from 2-methylnaphthalene to 2-acetylbenzoic acid are shown in Scheme IV.[46] These routes would appear to be chemically indistinguishable. Both require that the carbon atom located at the 1-position of the naphthalene ring is expelled and that the carbon atom originally located at the 2-position becomes attached to the phenyl ring as the carbonyl carbon of the acetyl group. Although such an interesting rearrangement of the naphthalene skeleton could be identified by ^{13}C labeling, such a study was deemed to be beyond the scope of our current objectives.

Discussion

The retardation of the self-initiated autoxidation of hexadecane at 160 °C by naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene has been very successfully modeled at various methylnaphthalene concentrations and with various times of addition using the minimum number of "adjustable" parameters which are required by our kinetic analysis of Scheme II (see Figures 1, 3, and 4). The principal assumption embodied in Scheme II is that peroxyl radicals add to the naphthalene ring (reaction 19) and that the resulting adduct radical subsequently (reactions 20–23) produces both an increase in the overall second-order rate constant for chain-termination (reactions 26 and 27) and a kinetically-first-order chain-termination process (reaction 21).[47] That peroxyl radicals add to (methyl)naphthalene under our experimental conditions is implied by the increased formation of hydrogen peroxide and has been confirmed by the identification of the oxidatively ring-opened products: phthalic acid, phthalic anhydride, and, from the methylnaphthalenes, 2-acetylbenzoic acid (see Table II and Schemes III and IV).

If we consider the true complexity of the self-initiated co-oxidation of hexadecane and (methyl)naphthalenes at 160 °C and the simplifications utilized in Scheme II in order to keep the number of elementary reactions manageable, we feel that the general agreement between experiment and calculation is not only extremely satisfactory but also rather remarkable. Despite this agreement, the precise magnitudes of the derived kinetic parameters are bound to be somewhat uncertain (i.e., they are rather "soft"). We therefore restrict our discussion of these quantities to a minimum.

The value estimated by curve fitting for k_{19} at 160 °C, viz., 70 M^{-1} s^{-1}, can be compared with a rate constant for the analogous addition, reaction 38, of the *tert*-butylperoxyl radical to 1- and 2-methylnaphthalene. The magnitude of k_{38} at 160 °C can be estimated by extrapolation of our low-temperature data.[4] The mean Arrhenius parameters found for the addition of *tert*-butylperoxyl to 1- and 2-methylnaphthalene over the temperature range 30–60 °C are $\log (A_{38}/M^{-1}\ s^{-1}) = 6.8$ and $E_{38} = 14.6_5$ kcal/mol, values which yield $k_{38} = 0.25\ M^{-1}\ s^{-1}$ at 160 °C. This value is considerably smaller than our estimated value for k_{19}, most probably because reaction 38 involves a *tertiary* alkylperoxyl radical whereas reaction 19 involves (mainly) *secondary* alkylperoxyl radicals. The latter are known to be considerably more reactive than *tertiary* alkylperoxyls, there being good evidence that *secondary* (and *primary*) alkylperoxyl radicals are both about 10 times as reactive as *tertiary* alkylperoxyl radicals in hydrogen atom abstractions from hydrocarbons.[48] For steric reasons an even larger difference in peroxyl radical reactivities might be expected in addition reactions. Indeed, we found[4] that at 60 °C the rate constants for the addition of the 1- and 2-naphthylmethylperoxyl radicals to the corresponding methylnaphthalenes, reaction 39, were about 60 times larger than k_{38} at this temperature, i.e., $k_{39}^{60°C} \approx 60k_{38}^{60°C}$. Thus, we might expect that at 160 °C $k_{39} \approx 60 \times 0.25 = 15\ M^{-1}\ s^{-1}$, a value which is only about a factor of 5 lower than our estimate that $k_{19} = 70\ M^{-1}\ s^{-1}$ at this temperature.



(38)

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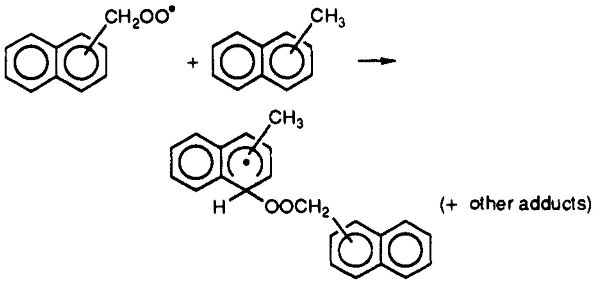
(47) If this assumption is correct, the kinetics of the self-initiated autoxidation of hexadecane retarded by other alkylnaphthalenes would be expected to be the same, both *qualitatively* and *quantitatively*. This prediction was tested with 2-*sec*-butylnaphthalene for which compound the experimental data were in gratifying agreement with the data computed using the kinetic parameters derived for the (methyl)naphthalene retarded autoxidation of hexadecane (see supplementary material).

(48) Korcek, S.; Chenier, J. H. B.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1972**, *50*, 2285–2297.



(39)

The ratio of the rate at which the peroxyl radicals present in autoxidizing hexadecane abstract hydrogen from the methylnaphthalenes to the rate at which they add to the naphthalene ring, i.e., k_{16}/k_{19}, would therefore appear to be ca. 34/70 = 0.5 at 160 °C. The corresponding rate constant ratio for attack of naphthylmethylperoxyl radicals on methylnaphthalene, k_{abs1}/k_{39}, is ca. 24 at 60 °C.[4] These results suggest that peroxyl radical addition to alkylnaphthalenes becomes more important relative to hydrogen abstraction from the alkyl group as the temperature is increased.[49] This has the practical consequence that chain-termination by alkylnaphthalenes will become of more rather than less importance at elevated temperatures. The resistance to oxidation of alkylnaphthalenes at high temperatures which makes these compounds attractive as synthetic lubricating oils and heat transfer fluids[5,6] is therefore explained.

The plots of $[\mathrm{-OOH}]_t^{1/2}$ vs t obtained following the addition of ca. 0.3 M (methyl)naphthalene to hexadecane which had not been deliberately preoxidized or had been only mildly preoxidized are strongly curved (see Figure 4) whereas the curvature is much less when the same quantity of (methyl)naphthalene was added to hexadecane which had been fairly extensively preoxidized (see Figure 1). The explanation for this difference lies in the relative importance of the kinetically-first- and second-order chain-termination processes. In the very earliest stages of the self-initiated autoxidation of hexadecane the rate of chain-initiation, R_i, is very small and, in the absence of (methyl)naphthalene, the chain length is consequently extremely long. However, the addition of (methyl)naphthalene introduces a kinetically-first-order chain-termination reaction into the overall oxidation process and, for small values of R_i, this reduces the chain length dramatically.[50] Hence, (methyl)naphthalene added to previously unoxidized hexadecane is a rather effective antioxidant. However, as the oxidation of the hexadecane progresses the hydroperoxide concentration rises which causes R_i to increase and this, in turn, increases the steady-state concentration of peroxyl radicals. As a consequence, the relative importance of the second-order chain-termination reaction increases with time and the (methyl)naphthalene (whether added at the start of the oxidation or after some preoxidation) becomes decreasingly effective as an inhibitor of hexadecane autoxidation. This produces the pronounced curvature in the plots of $[\mathrm{-OOH}]_t^{1/2}$ vs t obtained when the (methyl)naphthalene was added to unoxidized or mildly preoxidized hexadecane, a curvature which can be quite satisfactorily simulated using our kinetic analysis and applying it to these systems (see Figure 4).

In summary, alkylnaphthalenes are known to be highly resistant to autoxidation at elevated temperatures.[5,6] This class of compounds is far more resistant to oxidation than are the corresponding alkylbenzenes. They are, in fact, even more resistant to oxidation than "unactivated" paraffinic hydrocarbons. By combining detailed kinetic measurements and a theoretical kinetic analysis with product studies we have traced this oxidative resistance of alkylnaphthalenes to reaction 19 which involves peroxyl radical addition to the naphthalene ring. This addition reaction is not particularly fast, viz., at 160 °C, $k_{19} \approx 70\ \mathrm{M^{-1}\,s^{-1}}$ compared with the rate constants for hydrogen abstraction from hexadecane, $k_{15} = 89\ \mathrm{M^{-1}\,s^{-1}}$, and from methylnaphthalene, $k_{16} = 34\ \mathrm{M^{-1}\,s^{-1}}$. However, the addition leads both to a kinetically-first-order chain-termination process and to an enhanced value for the rate constant for a second-order, peroxyl + peroxyl chain-termination process. Thus, the resistance to oxidation of alkylnaphthalenes can be attributed to a high overall rate of chain-termination.

Experimental Section

The self-initiated autoxidation of hexadecane was carried out at 160 °C under 760 Torr of O_2. The apparatus and procedures have been described in detail in earlier publications.[7-13]

Product Analyses. Hydroperoxide yields were determined by titration on 1–2-mL aliquots removed from the reaction mixture using an iodometric procedure.[7]

The aromatic oxidation products formed at t = 5600 s following the addition of 0.35 M naphthalene, 0.35 M 1-methylnaphthalene, and 0.35 M 2-methylnaphthalene to preoxidized hexadecane ($[\mathrm{-OOH}]_{t_0} \approx 0.01$ M, t_0 = 620 s) were analyzed quantitatively as described below.

A 0.2-mL sample from the reaction mixture was eluted through a Sep-pak (C-18) cartridge with methanol in order to remove most of the hexadecane (and probably some of its oxidation products). Sufficient methanol was employed to elute essentially all the aromatic compounds. The methanolic solution of products was then analyzed by liquid chromatography (200 × 2.1 mm ODS (C-18) RP column) with UV (280 nm) detection *and* by LC/MS (HP 5988/thermospray system) using total ion current for detection. The following compounds were used as standards: 1-naphthylcarbinol, 1-naphthaldehyde, 1-naphthoic acid, phthalic acid, phthalic anhydride, and 2-acetylbenzoic acid. It was assumed that the UV extinction coefficients of the side chain oxidation products from 2-methylnaphthalene were the same as the corresponding products from 1-methylnaphthalene and that the naphthyl hydroperoxides had the same extinction coefficients as the alcohols. The yields of side chain oxidation products given in Table II are based on UV detection, but only the total yield of the three ring oxidized products (phthalic acid, phthalic anhydride, and 2-acetylbenzoic acid, all of which fortunately have very similar UV extinction coefficients) could be obtained by this method since these compounds were not separated on the column we employed. Their identities and, in the case of the naphthalene modulated oxidation, the approximate ratio of phthalic acid to anhydride were determined by the single ion extraction technique.

The acidic oxidation products were examined further by GC/MS analysis of their methyl esters on an HP 5890 GC/MS using a 10 m × 0.2 mm i.d. methylsilicone capillary column (HP Ultra 1). Product mixtures were extracted with aqueous alkali, and the aqueous extract was concentrated, acidified, and esterified with methanol. 1-Naphthoic acid, phthalic acid, and 2-acetylbenzoic acid were esterified in the same way to provide analytical standards. The naphthoic acid and phthalic acid gave the expected mono- and dimethyl esters, respectively. However, 2-acetylbenzoic acid yielded two products, 3-methoxy-3-methylphthalide and 2-acetylmethylbenzoate in order of elution and in a ratio of ca. 45:55. The formation of these two products in a roughly 1:1 ratio provided good confirmatory evidence that 2-acetylbenzoic acid was an oxidation product from 1-methylnaphthalene (as expected) *and* was a product from 2-methylnaphthalene (quite unexpected). Single ion extraction was used to determine the dimethylphthalate/(3-methoxy-3-methylphthalide + 2-acetylmethylbenzoate) ratios. The principal peaks in the mass spectra of the esterified acids, m/e (%), were the following: 1-methylnaphthoate, 186 (M^+, 63), 155 (100), 127 (74); dimethylphthalate, 194 (M^+, 6), 163 (100); 3-methoxy-3-methylphthalide, 163 (55), 147 (100), 133 (27); and 2-acetylmethylbenzoate, 178 (M^+, 0.4), 163 (100), 147 (21).

Because of the analytical methods employed the product yields given in Table II are only approximate.

Acknowledgment. We thank D. A. Lindsay for most valuable technical assistance. One of us (K.U.I.) also thanks the Alexander von Humboldt Foundation and the organic chemists at the Universities of Freiburg and Essen, Germany, for their generous hospitality during the time that this work was written up.

Appendix: Kinetic Analysis of Scheme II

Application of the usual steady-state approximations yields the following kinetic equations:

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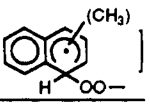
(49) This trend with temperature is consistent with our observation that the activation energy for the addition of *tert*-butylperoxyl to the methylnaphthalenes is greater than the activation energy for hydrogen atom abstraction.[4]

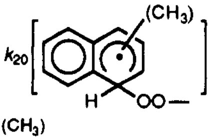
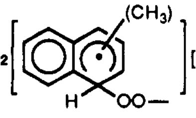
(50) In this system, the "maximum chain length"[4] will be given by

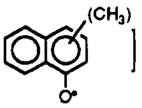
$$\nu_{\max} = \frac{k_{15}[\mathrm{C_{16}H_{34}}]\phi + k_{16}[\mathrm{NpCH_3}]}{2fk_{19}[\mathrm{Np(CH_3)}]}$$

d 

dt

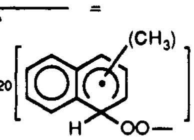
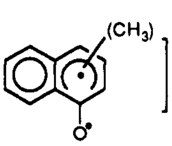
$= 0 = k_{19}[\text{-OO}^\bullet][\text{Np(CH}_3)] -$

k_{20}  $- k_{22}$  $[\text{O}_2]$ (1)

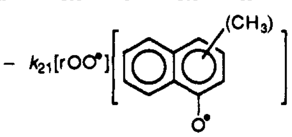
d 

dt

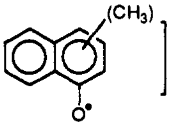
$=$

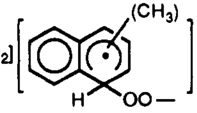
$0 = k_{20}$  $- k_{21}$  $[\text{-OO}^\bullet]$ (2)

$$\frac{d[\text{rOO}^\bullet]}{dt} = 0 = k_{15}[\text{HOO}^\bullet][\text{C}_{16}\text{H}_{34}] + k_{16}[\text{HOO}^\bullet][\text{NpCH}_3] + k_{24}[\text{HOO}^\bullet][\text{rOOH}] - k_{24}[\text{rOO}^\bullet][\text{H}_2\text{O}_2] - 2k_{25}[\text{rOO}^\bullet]^2 - k_{26}[\text{rOO}^\bullet][\text{HOO}^\bullet] + 2k_i[\text{-OOH}] - k_{19}[\text{rOO}^\bullet][\text{Np(CH}_3)] - k_{21}[\text{rOO}^\bullet]$$

 (3)

$$\frac{d[\text{HOO}^\bullet]}{dt} = 0 = -k_{15}[\text{HOO}^\bullet][\text{C}_{16}\text{H}_{34}] - k_{16}[\text{HOO}^\bullet][\text{NpCH}_3] + k_{24}[\text{rOO}^\bullet][\text{H}_2\text{O}_2] - k_{24}[\text{HOO}^\bullet][\text{rOOH}] - k_{26}[\text{rOO}^\bullet][\text{HOO}^\bullet] - 2k_{27}[\text{HOO}^\bullet]^2 - k_{19}[\text{HOO}^\bullet][\text{Np(CH}_3)] - k_{21}[\text{HOO}^\bullet]$$

 $+$

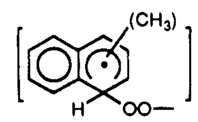
$k_{22}[\text{O}_2]$  (4)

and

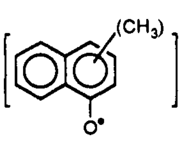
$$\frac{-d[\text{-OOH}]}{dt} = k_{15}[\text{-OO}^\bullet][\text{C}_{16}\text{H}_{34}]\phi + k_{16}[\text{-OO}^\bullet][\text{NpCH}_3] + k_{26}[\text{rOO}^\bullet][\text{HOO}^\bullet] + k_{27}[\text{HOO}^\bullet]^2 - k_i[\text{-OOH}] \quad (5)$$

where ϕ reflects the increased rate of formation of hydroperoxides due to the production of difunctional oxidation products.

From (1)

 $= \dfrac{k_{19}[\text{-OO}^\bullet][\text{Np(CH}_3)]}{k_{20} + k_{22}[\text{O}_2]}$ (6)

Substitution of (6) into (2) yields

 $= k_{19}[\text{Np(CH}_3)]\dfrac{k_{20}}{k_{21}\{k_{20} + k_{22}[\text{O}_2]\}}$ (7)

Substitution of (6) and (7) into (3) and (4) yields

$$\frac{d[\text{rOO}^\bullet]}{dt} = 0 = k_{15}[\text{HOO}^\bullet][\text{C}_{16}\text{H}_{34}] + k_{16}[\text{HOO}^\bullet][\text{NpCH}_3] + k_{24}[\text{HOO}^\bullet][\text{rOOH}] - k_{24}[\text{rOO}^\bullet][\text{H}_2\text{O}_2] - 2k_{25}[\text{rOO}^\bullet]^2 - k_{26}[\text{rOO}^\bullet][\text{HOO}^\bullet] + 2k_i[\text{-OOH}] - k_{19}[\text{rOO}^\bullet][\text{Np(CH}_3)]\left\{1 + \frac{k_{20}}{k_{20} + k_{22}[\text{O}_2]}\right\} \quad (8)$$

and

$$\frac{d[\text{HOO}^\bullet]}{dt} = 0 = -k_{15}[\text{HOO}^\bullet][\text{C}_{16}\text{H}_{34}] - k_{16}[\text{HOO}^\bullet] \times [\text{NpCH}_3] - k_{24}[\text{HOO}^\bullet][\text{rOOH}] + k_{24}[\text{rOO}^\bullet][\text{H}_2\text{O}_2] - k_{26}[\text{rOO}^\bullet][\text{HOO}^\bullet] - 2k_{27}[\text{HOO}^\bullet]^2 - k_{19}[\text{HOO}^\bullet][\text{Np(CH}_3)] \times \left\{1 + \frac{k_{20}}{k_{20} + k_{22}[\text{O}_2]}\right\} + k_{22}[\text{O}_2]\left\{\frac{k_{19}[\text{-OO}^\bullet][\text{Np(CH}_3)]}{k_{20} + k_{22}[\text{O}_2]}\right\} \quad (9)$$

Adding eqs 8 and 9 yields

$$\frac{d[\text{rOO}^\bullet]}{dt} + \frac{d[\text{HOO}^\bullet]}{dt} = \frac{d[\text{-OO}^\bullet]}{dt} = 0 = 2k_i[\text{-OOH}] - 2k_{25}[\text{rOO}^\bullet]^2 - 2k_{26}[\text{rOO}^\bullet][\text{HOO}^\bullet] - 2k_{27}[\text{HOO}^\bullet]^2 + k_{22}[\text{O}_2]\left\{\frac{k_{19}[\text{-OO}^\bullet][\text{Np(CH}_3)]}{k_{20} + k_{22}[\text{O}_2]}\right\} - k_{19}[\text{-OO}^\bullet][\text{Np(CH}_3)]\left\{1 + \frac{k_{20}}{k_{20} + k_{22}[\text{O}_2]}\right\} \quad (10)$$

Let

$$\frac{k_{20}}{k_{20} + k_{22}[\text{O}_2]} = f, \quad \text{i.e.} \quad \frac{k_{22}[\text{O}_2]}{k_{20} + k_{22}[\text{O}_2]} = 1 - f$$

and

$$\frac{[\text{rOO}^\bullet]}{[\text{HOO}^\bullet]} = \delta, \quad \text{i.e.} \quad [\text{-OO}^\bullet] = [\text{rOO}^\bullet] + [\text{HOO}^\bullet\} = (1 + \delta)[\text{HOO}^\bullet]$$

Substituting for f and δ into (10) yields

$$0 = 2k_i[\text{-OOH}] - 2k_{25}\delta^2[\text{HOO}^\bullet]^2 - 2k_{26}\delta[\text{HOO}^\bullet]^2 - 2k_{27}[\text{HOO}^\bullet]^2 - (2f + 2f\delta)k_{19}[\text{HOO}^\bullet][\text{Np(CH}_3)] \quad (11)$$

Solving eq 11 with $(2f + 2f\delta) = \beta$ leads to eq XIII:

$$[\text{HOO}^\bullet] = \left[-k_{19}[\text{Np(CH}_3)]\beta + \sqrt{\{k_{19}[\text{Np(CH}_3)]\beta\}^2 + 8k_i[\text{-OOH}](2k_{25}\delta^2 + 2k_{26}\delta + 2k_{27})}\right] / 2(2k_{25}\delta^2 + 2k_{26}\delta + 2k_{27})$$

Substitution for δ in eq 5 yields eq XII:

$$\frac{d[\text{-OOH}]}{dt} = \{k_{15}[\text{C}_{16}\text{H}_{34})\phi + k_{16}[\text{NpCH}_3]\}(1 + \delta)[\text{HOO}^\bullet] + (k_{26}\delta + k_{27})[\text{HOO}^\bullet]^2 - k_i[\text{-OOH}]$$

Supplementary Material Available: Measured total hydroperoxide yields, calculated hydrogen peroxide yields, and calculated values of δ for the naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, and 2-*sec*-butylnaphthalene modulated autoxidation of *n*-hexadecane at 160 °C (Tables III–VI) and a plot of [hydroperoxide]$^{1/2}$ vs time for the self-initiated autoxidation of hexadecane in the presence of 2-*sec*-butylnaphthalene (Figure 5) (9 pages). Ordering information is given on any current masthead page.