J. Am. Chem. Soc. 1992, 114, 7719-7726

Autoxidation of Alkylnaphthalenes. 1. Self-Inhibition during the Autoxidation of 1- and 2-Methylnaphthalenes Puts a Limit on the Maximum Possible Kinetic Chain Length[1]

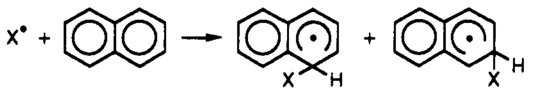
J. Igarashi,[2] J. Lusztyk,* and K. U. Ingold

Contribution from the Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. Received January 10, 1992

Abstract: The kinetics of the azobis(isobutyronitrile) initiated autoxidation of 1- and 2-methylnaphthalene have been studied from 30 to 60 °C in the presence of sufficient *tert*-butyl hydroperoxide (1.0 M) to ensure that the *tert*-butylperoxyl radical totally dominates chain propagation and bimolecular peroxyl/peroxyl chain termination. Initial rate measurements demonstrate that these oxidations do not follow the kinetic rate law which applies to alkylbenzenes and other hydrocarbons. Specifically, in addition to the usual second-order peroxyl/peroxyl termination there is a kinetically first-order chain termination reaction, the relative importance of which increases as the oxygen partial pressure is reduced. As a consequence, these autoxidations are self-inhibiting. The major reaction between *tert*-butylperoxyl and the methylnaphthalenes is hydrogen abstraction from the methyl group (rate constant, k_p^{BR}). Self-inhibition is a consequence of a competing, peroxyl radical addition to the aromatic ring, reaction 8. This is a very minor process, e.g., $k_8^{BR}/k_p^{BR} = 0.0036$ at 30 °C, and it does not entirely lead to chain termination. That is, the adduct radical formed in reaction 8 may react with O_2, a process which leads to chain propagation, or it may decompose to yield *tert*-butyl alcohol and a methylnaphthoxyl radical (reaction 9). It is the methylnaphthoxyl radical that is responsible for the kinetically first-order termination process (via its reaction with a second peroxyl). Reaction 9 is also responsible for the existence of a maximum chain length, ν_{max}, in these autoxidations. That is, at a given temperature and oxygen partial pressure ν cannot be increased indefinitely by reducing the rate of chain initiation as is the case for most hydrocarbons. Thus, at 60 °C in the presence of 1.0 M *tert*-butyl hydroperoxide $\nu_{max} \approx 88 \pm 4$ and 161 ± 23 at 160 and 760 Torr of O_2, respectively, while in the absence of the hydroperoxide ν_{max} is only ca. 12 and does not depend on the oxygen pressure. Our detailed kinetic results and mechanistic conclusions explain why alkylnaphthalenes are so much more resistant to autoxidation than the corresponding alkylbenzenes.

It is well-known that methyl-, *n*-alkyl-, and *sec*-alkyl-substituted benzenes undergo autoxidation much more readily than alkanes,[3,4] a phenomenon that can be attributed to the fact that benzylic C–H bonds are ca. 10 kcal/mol weaker than alkane C–H bonds. In this context, a very surprising report by Larsen et al.,[5] which appeared half-a-century ago, has been largely overlooked. These workers reported that at temperatures above 100 °C certain alkylated naphthalenes were very significantly (~1/30) less reactive toward atmospheric oxygen than alkylated benzenes, paraffins, and cycloalkanes,[5] yet there can be no doubt that the α-C–H bonds in alkylnaphthalenes are 2–3 kcal/mol weaker than those in structurally related alkylbenzenes.[6] Larsen et al.[5] attributed the oxidative stability of alkylated naphthalenes to the formation of inhibitors during the oxidation. In support of this suggestion, they reported that the rate of oxidation of *n*-amylbenzene was reduced by the addition of ca. 10% of preoxidized 1-methylnaphthalene but that it was unaffected by a similar addition of unoxidized 1-methylnaphthalene (vide infra, however).

Despite the reported oxidative stability of alkylnaphthalenes[5] these compounds received little or no attention as potential synthetic lubricating oils[9] until recently when Yoshida and Watanabe[10] confirmed their remarkable oxidation stability at temperatures above 100 °C. Inhibitors of autoxidation (such as naphthols) could not be detected.[10] Of particular importance, and in contrast to the report of Larsen et al,[5] Yoshida and Watanabe[11] also discovered that unoxidized 1- or 2-methylnaphthalene significantly retarded the autoxidation of saturated hydrocarbons. This result suggests that the alkylnaphthalenes themselves can act as antioxidants, which is not unreasonable since it has long been known that polycyclic aromatics have chain-breaking, radical-trapping activity.[12,13] In particular, it has been shown that peroxyl radicals can add to anthracene[14-19] (and to more highly condensed polycyclic aromatics)[14,15,16,19] and that anthracene can inhibit the autoxidation of organic compounds, e.g., benzaldehyde[14,15] and cumene.[16,17] Although the rate of addition of peroxyl radicals to naphthalene proved too slow to measure,[17] a study of the Co/Mn/Br catalyzed autoxidation of 2,6-dimethylnaphthalene would seem to imply that this reaction is self-inhibiting since the yield of the 2,6-dicarboxylic acid increased as the hydrocarbon's concentration was decreased.[20] In general terms, the inhibition of radical-chain processes by unoxidized polycyclic aromatics can be attributed to their ability to add reactive, chain-carrying radicals so as to produce resonance-stabilized, relatively unreactive benzocyclohexadienyl radicals, e.g.,



---

[1] Issued as NRCC No. 33305.

[2] On leave from the Nippon Oil Company, Japan.

[3] For books on hydrocarbon autoxidation, see e.g.: Scott, G. *Atmospheric Oxidation and Antioxidants*; Elsevier: Amsterdam, 1965. Emanuel, N. M.; Denisov, E. T.; Maizus, Z. K. *Liquid Phase Oxidation of Hydrocarbons*; Hazzard, B. J., Translator; Plenum Press: New York, 1967. Reich, L.; Stivila, S. S. *Autoxidation of Hydrocarbons and Polyolefins*; Dekker: New York, 1969.

[4] For general reviews on hydrocarbon autoxidation, see e.g.: Ingold, K. U. *Chem. Rev.* **1961**, *61*, 563–589. Ingold, K. U. *Acc. Chem. Res.* **1969**, *2*, 1–9. Mayo, F. R. *Acc. Chem. Res.* **1968**, *1*, 193–201. Howard, J. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 12.

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

[6] D[1-NpCH$_2$–H] = 86 kcal/mol[7] vs D[PhCH$_2$–H] = 88.2–89 kcal/mol.[8]

[7] McMillen, D. F.; Trevor, P. L.; Golden, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 7400–7402.

[8] (a) Meot-Ner, M. *J. Am. Chem. Soc.* **1982**, *104*, 5–10. (b) Zavitsas, A. A.; Fogel, G.; Halwagi, K. E.; Legotte, P. A. D. *J. Am. Chem. Soc.* **1983**, *105*, 6960–6962. (c) Hayashibara, K.; Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5441–5443.

[9] In part because many of these compounds have undesirable viscosity-temperature characteristics.

[10] Yoshida, T.; Watanabe, H. U.S. Patent 4,714,794, Dec. 22, 1987.

[11] Yoshida, T.; Watanabe, H. Unpublished results.

[12] Magat, M.; Bonême, R. *Compt. Rend.* **1951**, *232*, 1657–1659. Magat, M. *Discuss. Faraday Soc.* **1951**, *10*, 226.

[13] Kooyman, E. C.; Farenhorst, E. *Trans. Faraday Soc.* **1953**, *49*, 58–67.

[14] Dunn, J. R.; Waters, W. A.; Roitt, I. M. *J. Chem. Soc.* **1954**, 580–586 and references cited therein.

[15] Turner, A. H.; Waters, W. A. *J. Chem. Soc.* **1956**, 879–888.

[16] Mahoney, L. R. *J. Am. Chem. Soc.* **1964**, *86*, 444–449.

[17] Mahoney, L. R. *J. Am. Chem. Soc.* **1965**, *87*, 1089–1096.

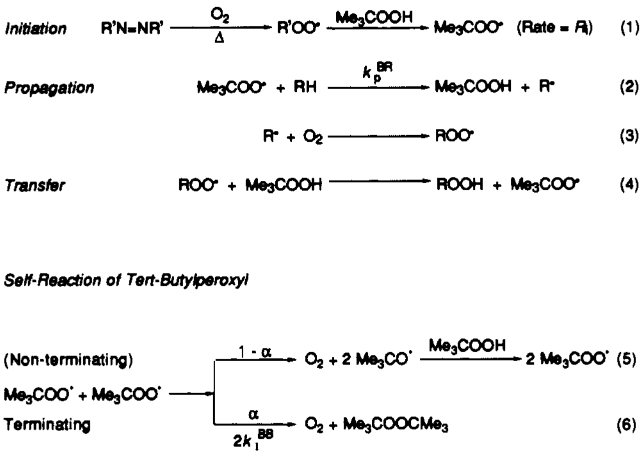
[18] Opeida, I. A.; Nechitailo, L. G. *Kinet. Katal.* **1978**, *19*, 1581–1585.

[19] Caceres, T.; Guaiquil, S.; Lissi, E. A. *Bol. Soc. Chil. Quim.* **1988**, *33*, 177–186.

[20] Kamiya, Y.; Taguchi, T.; Futamura, S. *Nippon Kagaku Kaishi* **1987**, 1772–1778.

0002-7863/92/1514-7719$03.00/0 Published 1992 by the American Chemical Society

Scheme I



In the present paper, we report rate constants for the reactions of peroxyl radicals with 1- and 2-methylnaphthalene at temperatures in the range 30–60 °C and show that their resistance to oxidation can be attributed to two phenomena. In the first place, the autoxidations of both methylnaphthalenes are strongly autoretarding which indicates that one or more of the oxidation products is a retarder (inhibitor) which reduces the oxidation rate by radical trapping to an increasing extent as its concentration builds up. Secondly, and very much more interestingly, these oxidations are autoinhibited from their very start! That is, measurements of the initial rates of autoxidation prove that these reactions are self-inhibited. The self-inhibition leads to the novel and quite unexpected discovery that at a given oxygen partial pressure and temperature there is a maximum possible chain length for these autoxidations. Thus, reducing the initiation rate, for example, does not increase the chain length indefinitely as is the case for the autoxidation of all other hydrocarbons that have, to our knowledge, been examined. In kinetic terms self-inhibition can be adequately accounted for by assuming that peroxyl radical addition to the naphthalene ring accompanies, but is much slower than, hydrogen atom abstraction from the methyl group. In the following paper, we extend these studies to the inhibition of *n*-hexadecane autoxidation at 160 °C by naphthalene, the two methylnaphthalenes, and 2-*sec*-butylnaphthalene.[21]

Results

At 30 °C the α,α-azobis(isobutyronitrile) (AIBN, 0.01 M) initiated autoxidations of both 1- and 2-methylnaphthalene were much too slow to measure conveniently. In fact, under comparable conditions both compounds oxidized even more slowly than toluene.[22] We therefore turned to the "hydroperoxide method"[23] which, with appropriate precautions, allows substrates even as unreactive as *n*-alkanes to be autoxidized at 30 °C with a reasonable chain length.[24,25] This method involves the addition to the substrate of *tert*-butyl hydroperoxide at a sufficient concentration (1.0 M) that *all* peroxyl radical attack on the substrate and *all* peroxyl radical + peroxyl radical termination involve only the *tert*-butylperoxyl radical.[23-27] Although the *tert*-butylperoxyl radical is only ca. 10% as reactive toward hydrocarbon substrates as are secondary and primary alkylperoxyl radicals,[23a,24,27,28] a more rapid autoxidation of a substrate yielding secondary or primary alkylperoxyl radicals is achieved[23-28] because of the relatively small rate constant for the chain-terminating bimolecular self-reaction of *tert*-butylperoxyl radicals.[29]

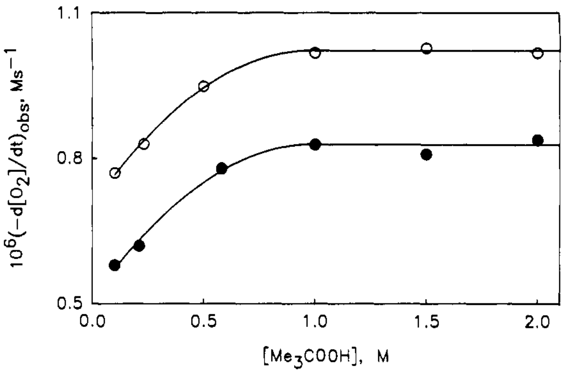


Figure 1. Rate of autoxidation of 1-methylnaphthalene (4.8 M in chlorobenzene) initiated with 0.018 M AIBN in the presence of *tert*-butyl hydroperoxide at 40 °C: 160 Torr of O_2 (●); 760 Torr of O_2 (○).

The AIBN-initiated autoxidation of a hydrogen-donating substrate, RH, in the presence of ca. ≥1.0 M *tert*-butyl hydroperoxide can be represented by the reactions shown in Scheme I.

According to Scheme I, the observed overall rate of autoxidation is given by

$$\left(\frac{-d[O_2]}{dt}\right)_{obs} = \frac{k_p^{BR}[RH]R_i^{1/2}}{(2k_t^{BB})^{1/2}} - c \qquad (I)$$

where c is a correction which allows for N_2 evolution by the initiator, O_2 absorbed by the initiating radicals, R'•, and O_2 evolved in the nonterminating and terminating bimolecular self-reactions of *tert*-butylperoxyl radicals.[24] This correction becomes negligible, i.e.,

$$\left(\frac{-d[O_2]}{dt}\right)_{corr} = \left(\frac{-d[O_2]}{dt}\right)_{obs} - c = \left(\frac{-d[O_2]}{dt}\right)_{obs} = \frac{k_p^{BR}[RH]R_i^{1/2}}{(2k_t^{BB})^{1/2}} \qquad (II)$$

at chain lengths, $\nu = (-d[O_2])/R_i$, greater than ca. 20, a situation that obtained in most of the present work. The rate constant of interest, k_p^{BR}, is easily obtained from the measured rate of the AIBN initiated autoxidation since values of $2k_t^{BB}$ have been determined previously over a wide range of temperatures[30c] and R_i can be measured for each individual experiment by the "induction period method".[31]

The AIBN-initiated autoxidation of 1- and 2-methylnaphthalene in the presence of adequate (≥1.0 M, see, e.g., Figure 1) *tert*-butyl hydroperoxide showed no induction period, which indicates that the low rates of autoxidation of these compounds in the absence of hydroperoxide were not due to inhibition by trace impurities. In the presence of the hydroperoxide (or, for that matter, in its

---

(21) Igarashi, J.; Jensen, R. K.; Lusztyk, J.; Korcek, S.; Ingold, K. U. *J. Am. Chem. Soc.* Following paper in this issue.

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

(23) (a) Howard, J. A.; Schwalm, W. J.; Ingold, K. U. *Adv. Chem. Ser.* **1968**, *No. 75*, 6–23. (b) For a review of the hydroperoxide method, see: Howard, J. A. *Isr. J. Chem.* **1984**, *24*, 33–37.

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

(25) Howard, J. A.; Chenier, J. H. B. *Int. J. Chem. Kinet.* **1974**, *6*, 527–530.

(26) Howard, J. A.; Chenier, J. H. B.; Holden, D. A. *Can. J. Chem.* **1978**, *56*, 170–175.

(27) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1969**, *47*, 3809–3815.

(28) Howard, J. A.; Chenier, J. H. B. *J. Am. Chem. Soc.* **1973**, *95*, 3054–3055.

(29) The rate constant, $2k_t^{RR}$, for the reaction ROO• + ROO• → nonradical products for R = Me₃C is ≪1% of the values found for R = primary alkyl or secondary alkyl.[22,30]

(30) See e.g.: (a) Howard, J. A.; Adamic, K.; Ingold, K. U. *Can. J. Chem.* **1969**, *47*, 3793–3795. (b) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1969**, *47*, 3797–3801. (c) Adamic, K.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1969**, *47*, 3803–3808. (d) Howard, J. A. In *Organic Free Radicals*; Pryor, W. A., Ed.; ACS Symp. Ser. No. 69; American Chemical Society: Washington, DC, 1978; Chapter 25.

(31) This involves addition to the system of a known quantity of a phenolic antioxidant and measurement of the length of the induction period, τ, that it produces.[32] Each molecule of a suitable phenol traps two peroxyl radicals so R_i = 2[ArOH]/τ. The phenol may be added either before or after measuring the rate of the uninhibited autoxidation.

(32) Boozer, C. E.; Hammond, G. S.; Hamilton, C. E.; Sen, J. N. *J. Am. Chem. Soc.* **1955**, *77*, 3233–3247.

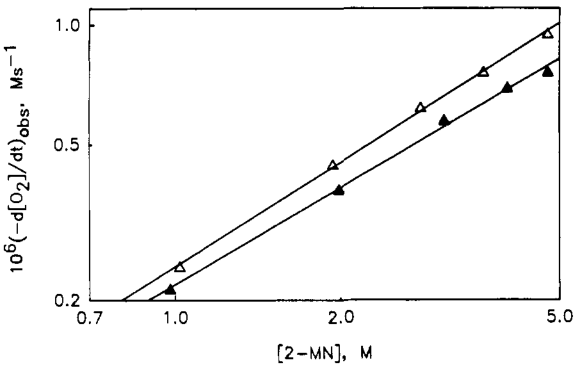


Figure 2. Rate of autoxidation of 2-methylnaphthalene in chlorobenzene initiated with 0.018 M AIBN in the presence of 1.0 M *tert*-butyl hydroperoxide at 40 °C: 160 Torr of O_2 (▲); 760 Torr of O_2 (△).

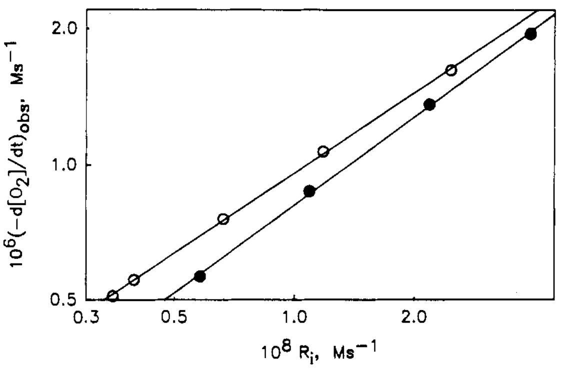


Figure 3. Rate of autoxidation of 1-methylnaphthalene (4.5–4.9 M in chlorobenzene) initiated with 4.7×10^{-3} to 6.3×10^{-2} M AIBN in the presence of 1.0 M *tert*-butyl hydroperoxide at 40 °C: 160 Torr of O_2 (●); 760 Torr of O_2 (○).

absence) the autoxidation reaction is very strongly autoretarding. For example, at 40 °C with 5 M 1-methylnaphthalene in chlorobenzene and with an initial [AIBN] = 9.2×10^{-3} M (corresponding to $R_i = 6.6 \times 10^{-9}$ M s^{-1}) the initial rate of autoxidation was 7.4×10^{-7} M s^{-1}, but after 4, 8, 13, and 24 h (which correspond to the absorption of 0.011, 0.019, 0.027, and 0.040 M oxygen, respectively) the rates of autoxidation had declined to 78%, 61%, 49%, and 36%, respectively, of the initial rate. (Over this period of time R_i had fallen only 10% to 6.1×10^{-9} M s^{-1}.) In a similar experiment at 60 °C (with [AIBN] = 4.7×10^{-3} M corresponding to $R_i = 8.2 \times 10^{-8}$ M s^{-1}) the initial rate of autoxidation was 4.6×10^{-6} M s^{-1}, but after 40, 80, and 120 min (which correspond to the absorption of 0.011, 0.020, and 0.027 M oxygen, respectively) the rates of autoxidation had declined to 80%, 67%, and 59%, respectively, of the initial rate (R_i at 120 min = 7.2×10^{-8} M s^{-1}).

Autoretardation in hydrocarbon autoxidations is a rather common phenomenon.[3,4] It can be attributed to the formation of oxidation products which are retarders (inhibitors) of the reaction. Typically, these retarders will build up to some approximately steady-state concentration (at constant R_i) so that autoretardation becomes progressively less obvious as the reaction progresses. This was certainly the case for 1- and 2-methylnaphthalene. However, the very small extent of oxidation of the methylnaphthalenes which is required to produce a very substantial reduction in the rate is somewhat unusual. It seems probable that autoretardation is due to the formation of methylnaphthoquinones since quinones, particularly those derived from polycyclic aromatics, have long been recognized as retarders of autoxidation.[14,15,33] It was, no doubt, the production of retarders in the preoxidized 1-methylnaphthalene which made this material an effective retarder of the autoxidation of *n*-amylbenzene in Larsen et al.'s[5] experiments which were described in the Introduction. Furthermore, we have found that naphthoquinones do retard the autoxidation of alkylbenzenes. For example, with neat (7.2 M) cumene and 9.2×10^{-3} M AIBN at 30 °C, the initial rate of autoxidation is 3.55×10^{-7} M s^{-1} under 160 and 760 Torr of O_2; the addition of 0.1 M 2-methylnaphthoquinone reduced the initial rate to 2.78×10^{-7} M s^{-1} at 760 Torr of O_2 and to 2.50×10^{-7} M s^{-1} at 160 Torr of O_2. The greater degree of retardation at the lower oxygen pressure can be simply attributed to the known fact that quinones trap alkyl radicals, R•, very much more effectively than peroxyl radicals, ROO•.

While autoretardation is not without interest we shall henceforth ignore this aspect of the autoxidation of the methylnaphthalenes and confine the remainder of this paper to *initial* rate measurements (which are available in detail as supplementary material) and to the novel and interesting kinetic effects the initial rates exhibit. In brief, even the initial rates of autoxidation of the methylnaphthalenes in the presence of 1.0 M *tert*-butyl hydroperoxide do not obey the expected kinetic equation (eq II). In the first place, initial rates are not directly proportional to the methylnaphthalene concentration but are instead proportional to $[RH]^m$, where $m < 1.0$. For example, $m = 0.83 \pm 0.03$ at 160 Torr of O_2 and $m = 0.87 \pm 0.02$ at 760 Torr of O_2 for the AIBN-initiated autoxidation of 2-methylnaphthalene at 40 °C in the presence of 1.0 M *tert*-butyl hydroperoxide (see Figure 2). Secondly, initial rates of autoxidation were not proportional to $R_i^{1/2}$ but to R_i^n, with $0.5 \leq n \leq 1.0$, and thirdly, *n* was dependent on the partial pressure of oxygen. The results obtained with ca. 4.7 M 1-methylnaphthalene and 1.0 M *tert*-butyl hydroperoxide in chlorobenzene at 40 °C which demonstrate the unusual dependence on R_i are shown in Figure 3. It can be seen that for a particular rate of initiation the initial rate of oxidation is higher under 760 than under 160 Torr of O_2 (see also Figure 1). The value of *n* calculated from the slopes of the lines in Figure 3 is 0.59 ± 0.01 for 760 Torr of O_2 and 0.64 ± 0.02 for 160 Torr of O_2.

Rates of autoxidation measured at ambient or slightly higher temperatures which increase with an increase in the oxygen partial pressure from 160 to 760 Torr have frequently been reported for substrates which yield strongly resonance-stabilized R• radicals.[34] They arise from the reversibility of reaction 3, i.e.,

$$ROO^\bullet \rightarrow R^\bullet + O_2 \qquad (-3)$$

and the fast cross termination,

$$R^\bullet + ROO^\bullet \rightarrow ROOR \qquad (7)$$

However, it is unlikely that the 1- or 2-naphthylmethylperoxyl radicals would undergo reaction −3 under our conditions. That is, naphthylmethyl radicals are thermodynamically slightly more stabilized than benzyl radicals,[6] have about the same stabilization energy as cumyl radicals,[6,41] and are slightly less stabilized than diphenylmethyl radicals.[6,41] Nevertheless, we have confirmed earlier studies[43,44] which indicated that the rates of autoxidation of *p*-xylene, cumene, and diphenylmethane at 40 °C are the same under 160 and 760 Torr of oxygen.[45]

---

(33) Dunn, J. R.; Waters, W. A. *J. Chem. Soc.* **1953**, 2993–2998.

(34) Mainly for radicals of the pentadienyl type see refs 35–38 and for even more highly conjugated radicals see refs 17, 39, and 40.

(35) Bateman, L. *Q. Rev. Chem. Soc.* **1954**, *8*, 147–167.

(36) Porter, N. A.; Weber, B. A.; Weenen, H.; Khan, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 5597–5601. Porter, N. A.; Lehman, L. S.; Weber, B. A.; Smith, K. J. *J. Am. Chem. Soc.* **1981**, *103*, 6447–6455. Porter, N. A.; Wujek, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 2626–2629.

(37) Chan, W. S.; Levett, G.; Matthew, J. A. *Chem. Phys. Lipids* **1979**, *24*, 245–256.

(38) Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 6478–6485.

(39) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1968**, *46*, 2655–2660.

(40) Burton, G. W.; Ingold, K. U. *Science* **1984**, *224*, 569–573.

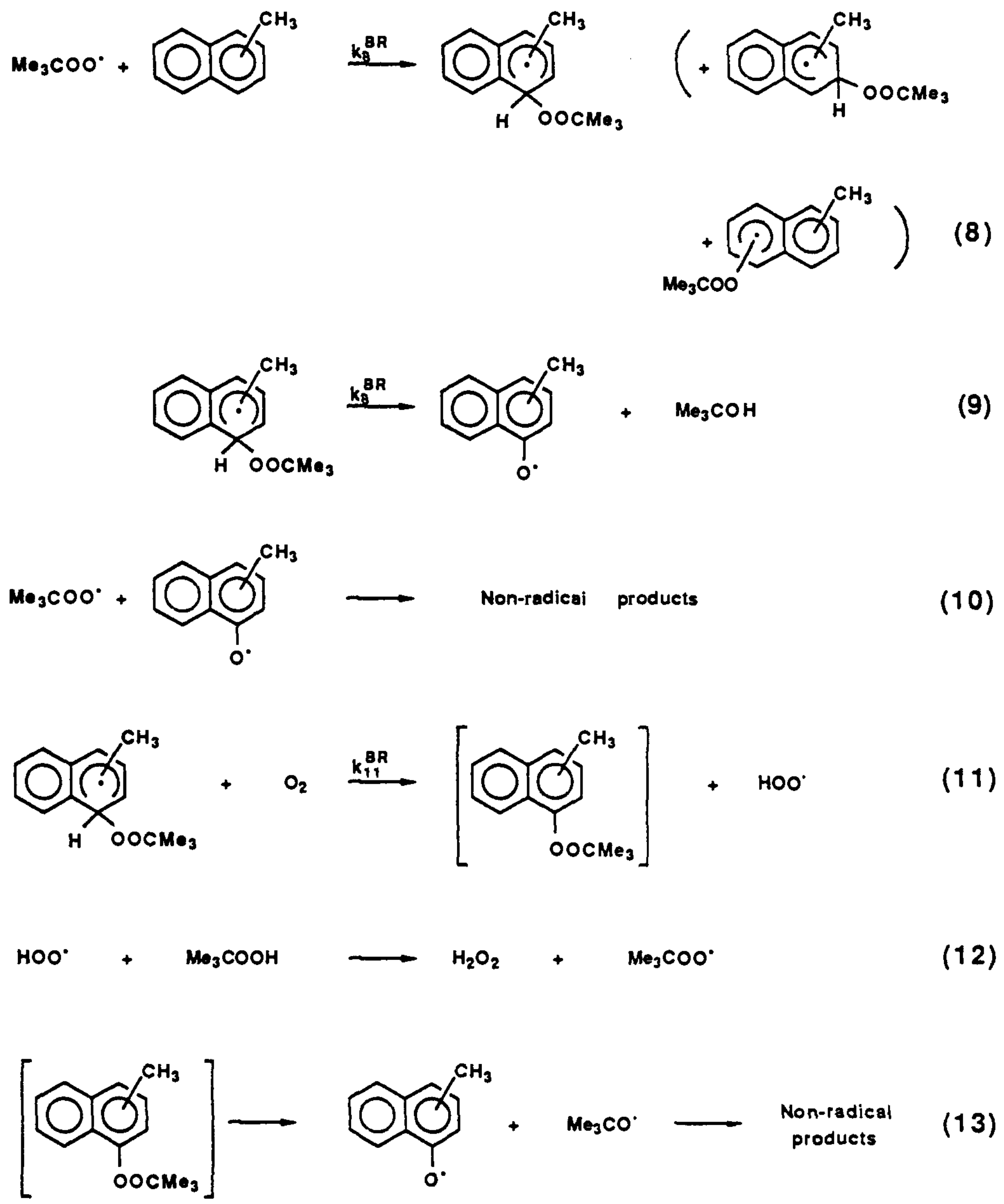
(41) $D[PhC(CH_3)_2\text{-}H]$ = 86.1 kcal/mol[8a] and $D[Ph_2CH\text{-}H]$ = 81.4,[42a] 81.8[42b] kcal/mol.

(42) (a) Rossi, M. J.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 5031–5039. (b) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229–1231.

(43) (a) See e.g., ref 22. (b) See also: Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1966**, *44*, 1119–1130.

(44) Howard, J. A.; Bennett, J. E.; Brunton, G. *Can. J. Chem.* **1981**, *59*, 2253–2260.

Scheme II



Hydrocarbon autoxidation kinetics with rates proportional to R_i^n and with $0.5 < n < 1.0$ were first reported for styrene ($n = 0.60 \pm 0.02$ at 50 and 65 °C),[47] but for this hydrocarbon the rate of oxidation did not depend upon the oxygen pressure (50–760 Torr).[48] The unusual dependence of the rate on R_i was attributed to a first-order chain termination process occurring concurrently with the normal second-order termination. It was also pointed out[49] that any minor reaction which gave a peroxyl radical trapping agent (such as a phenol or a phenoxyl radical) would yield a kinetically first-order termination which would contribute to the overall termination process.

Discussion

Reaction Mechanism, Kinetics, and Kinetic Parameters for the Low-Temperature Autoxidation of 1- and 2-Methylnaphthalene in the Presence of 1.0 M *tert*-Butyl Hydroperoxide. The *simplest* reaction scheme[50] which will accommodate our experimental results for the AIBN-initiated autoxidation of 1- and 2-methylnaphthalene in the presence of 1.0 M *tert*-butyl hydroperoxide at temperatures in the range 30–60 °C requires eqs 1–6 (Scheme I, RH = methylnaphthalene and R˙ = naphthylmethyl radical) together with the reactions shown in Scheme II. It should be noted that under the low conversion conditions employed the only products detected were the corresponding naphthylmethyl hydroperoxides.

With regard to Scheme II it should be understood that addition reaction 8 can give various benzocyclohexadienyl radicals all of which (except the ipso adduct) are expected to undergo reactions analogous to reactions 9, 10, 11, and 13. The essential feature of Scheme II is that the adduct radicals formed in reaction 8 undergo two competing reactions, 9 and 11. Reaction 9 is an oxygen-independent, unimolecular decomposition which yields a naphthoxyl radical possibly via a fragmentation–disproportionation route or via a proton-catalyzed decomposition. This reaction is a chain-ending step since the naphthoxyl radical will trap a peroxyl radical to form nonradical products (reaction 10). Reaction 11 is an oxygen-dependent, bimolecular reaction which is not

---

(45) The rate constants for loss of O_2 from $PhC(CH_3)_2OO^\bullet$ and $Ph_2C(CH_3)OO^\bullet$ have been estimated to be ca. 2 s^{-1} and ca. 1700 s^{-1}, respectively, at 30 °C.[44,46]

(46) Howard, J. A.; Chenier, J. H. B.; Yamada, T. *Can. J. Chem.* **1982**, *60*, 2566–2572.

(47) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1962**, *40*, 1851–1864.

(48) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1965**, *43*, 2729–2736.

(49) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1965**, *43*, 2737–2743.

(50) A variety of more complex schemes were considered but we have applied Occam's razor to cut out kinetically unnecessary, though chemically possible, or even probable, reactions.

Table I. Kinetic Parameters for the Autoxidation of 1-Methylnaphthalene in the Presence of 1.0 M *tert*-Butyl Hydroperoxide

temp (°C)	n^a		$10^4 f^{BR}k_8^{BR}$ (M^{-1} s^{-1})		$10^2 k_p^{BR}$ (M^{-1} s^{-1})	$10^4 k_8^{BR}$ (M^{-1} s^{-1})	k_{11}^{BR}/k_9^{BR} (M^{-1})
	160 Torr of O_2	760 Torr of O_2	160 Torr of O_2	760 Torr of O_2			
30	0.69 ± 0.01	0.60 ± 0.02	1.5	0.7	6.1	2.2	220
35	0.67 ± 0.03		2.4		8.0		
40	0.64 ± 0.02	0.59 ± 0.01	3.1	1.5	10.0	4.5	210
45	0.63 ± 0.01		4.0		12.2		
50	0.64 ± 0.02	0.57 ± 0.01	6.0	2.9	15.0	8.4	190
60	0.66 ± 0.02	0.61 ± 0.01	12.8	6.4	23.6	17.6	175
log (A/M^{-1} s^{-1})					5.2 ± 0.1	6.2 ± 0.3	
E (kcal/mol)					8.9 ± 0.1	13.7 ± 0.5	1.6 ± 0.2[b]

[a] Kinetic order in rate of initiation, R_i^n, obtained from data given in Tables VII and VIII (supplementary material) with the measured rates of oxidation corrected for the (small) changes in methylnaphthalene concentration with the different concentrations of initiator. [b] $E_9^{BR} - E_{11}^{BR}$.

Table II. Kinetic Parameters for the Autoxidation of 2-Methylnaphthalene in the Presence of 1.0 M *tert*-Butyl Hydroperoxide

temp (°C)	n^a		$10^4 f^{BR}k_8^{BR}$ (M^{-1} s^{-1})		$10^2 k_p^{BR}$ (M^{-1} s^{-1})	$10^4 k_8^{BR}$ (M^{-1} s^{-1})	k_{11}^{BR}/k_9^{BR} (M^{-1})
	160 Torr of O_2	760 Torr of O_2	160 Torr of O_2	760 Torr of O_2			
30	0.64 ± 0.02	0.59 ± 0.01	1.1	0.5	4.7	1.7	230
35	0.64 ± 0.02		1.9		6.3		
40	0.63 ± 0.03	0.58 ± 0.01	2.8	1.4	9.0	3.9	180
45	0.61 ± 0.01		3.6		10.5		
50	0.65 ± 0.02	0.58 ± 0.02	6.5	3.9	13.9	8.5	130
60	0.65 ± 0.02	0.61 ± 0.01	14.1	8.6	23.8	17.2	100
log (A/M^{-1} s^{-1})					6.4 ± 0.2	7.4 ± 0.1	
E (kcal/mol)					10.8 ± 0.3	15.6 ± 0.1	5.7 ± 0.3[b]

[a] Kinetic order in rate of initiation, R_i^n, obtained from data given in Tables X and XI (supplementary material) with the measured rates of oxidation corrected for the (small) changes in methylnaphthalene concentration with the different concentration of initiator. [b] $E_9^{BR} - E_{11}^{BR}$.

chain-ending since an HOO$^\bullet$ radical is formed which will continue the chain by reaction with Me_3COOH (reaction 12). The *tert*-butyl methylnaphthyl peroxide formed in reaction 11 will be very short lived. However, its decomposition products (reaction 13) will not cause chain-branching since the methylnaphthoxyl radical will trap the *tert*-butoxyl radical either directly (as shown, possibly as an "in cage" process) or indirectly after conversion of the $Me_3CO^\bullet$ radical to a $Me_3COO^\bullet$ radical. Thus, the additional reactions of Scheme II provide, from a common intermediate radical, for a kinetically first-order chain-termination process (reactions 9 and 10) the importance of which relative to the second-order chain-termination process (reaction 6) will decrease as the oxygen partial pressure is increased (reactions 11, 12, and 13).

The foregoing equations lead to the following rate law for the autoxidation of the methylnaphthalenes in the presence of ≥1.0 M *tert*-butyl hydroperoxide:

$$\left(\frac{-d[O_2]}{dt}\right)_{corr} = \frac{k_p^{BR}[RH](\{(2f^{BR}k_8^{BR}[RH])^2 + 8k_t^{BB}R_i\}^{1/2} - 2f^{BR}k_8^{BR}[RH])}{4k_t^{BB}} \tag{III}$$

where $f^{BR} = k_9^{BR}/(k_9^{BR} + k_{11}^{BR}[O_2])$ and represents the fraction of the adduct radical formed in reaction 8 which is chain-terminating. The 2 in the $2f^{BR}k_8^{BR}$ terms appears because two of the chain-carrying *tert*-butylperoxyl radicals are destroyed via reactions 9 and 10.

Equation III is most readily utilized in the rearranged form

$$\left(\frac{\nu}{\tau[RH]}\right)^2 = (k_p^{BR})^2 - 2f^{BR}k_p^{BR}k_8^{BR}\nu \tag{IV}$$

where the chain length (ν) is $(-d[O_2]/dt)/R_i$ and τ (which would represent the lifetime of an average chain in the absence of first-order termination) is equal to $(2k_t^{BB}R_i)^{-1/2}$. At sufficiently high oxygen pressures the methylnaphthalenes will obey normal autoxidation kinetics since $f^{BR} \to 0$ as $[O_2] \to \infty$, i.e., eq III will reduce to eq II and eq IV will reduce to:

$$\nu/\tau[RH] = k_p^{BR} \tag{V}$$

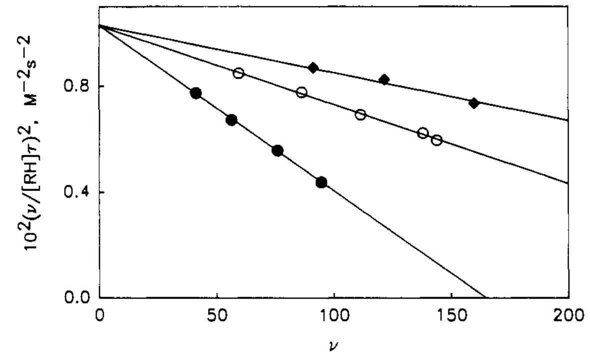


Figure 4. Plots of $(\nu/[RH]\tau)^2$ against ν for the autoxidation of 4.5–4.9 M 1-methylnaphthalene in chlorobenzene initiated with AIBN (R_i = (0.35–3.7) × 10^{-8} M s^{-1}) in the presence of 1.0 M *tert*-butyl hydroperoxide at 40 °C: 160 Torr of O_2 (●); 760 Torr of O_2 (○); 1460 Torr of O_2 (◆).

Autoxidation chain lengths, ν, always depend on the rate of chain-initiation, R_i, and the concentration of the oxidizable substrate, [RH]. In the case of the methylnaphthalenes, ν also depends on the oxygen pressure. However, at constant oxygen pressure, plots of $(\nu/\tau[RH])^2$ against ν should, according to eq IV, yield straight lines with a common intercept equal to $(k_p^{BR})^2$. Three such plots, in which ν was changed by changing R_i while [RH] was held constant, are shown for 1-methylnaphthalene at 40 °C in Figure 4. It can be seen that eq IV is obeyed. The values of k_p^{BR} derived from such plots for 1- and 2-methylnaphthalene at temperatures from 30 to 60 °C are given in Tables I and II, respectively, together with values of $f^{BR}k_8^{BR}$ calculated from the slopes of these plots. A related plot, in which R_i was held constant while ν was changed by varying the concentration of 2-methylnaphthalene (at 40 °C), is given in the supplementary material. There is gratifying agreement between the experimental points in this plot and the straight lines constructed from data obtained via a figure analogous to Figure 4, i.e., from kinetic parameters obtained by varying R_i at constant [RH].

Values for k_8^{BR} and for the rate constant ratio k_{11}^{BR}/k_9^{BR} are also summarized in Tables I and II. They were obtained via eq VI

$$\frac{1}{f^{BR}k_8^{BR}} = \frac{1}{k_8^{BR}} + \frac{k_{11}^{BR}[O_2]}{k_8^{BR}k_9^{BR}} \tag{VI}$$

Table III. Rate Constants and Arrhenius Parameters for Hydrogen Atom Abstraction from Some Alkylaromatic Hydrocarbons by the *tert*-Butylperoxyl Radical at 30 °C

hydrocarbon	$10^2k_p^{BR}/H$[a] (M^{-1} s^{-1})	E_p^{BR} (kcal/mol)	log ($A_p^{BR}/H/M^{-1}$ s^{-1})[a]
1-methylnaphthalene	2.0	8.9 ± 0.1	4.7 ± 0.1
2-methylnaphthalene	1.6	10.8 ± 0.3	5.9 ± 0.2
toluene	1.0[b]	11.4[c] (19.8)[d]	6.1[c] (8.7)[e]
p-xylene[f]	1.5	11.0	6.1
cumene[g]	16	13.2 ± 0.4	8.7 ± 0.3

[a] Statistically corrected for the number of active hydrogens. [b] Reference 28. [c] Based on an estimated Arrhenius equation for the propagation step in the autoxidation of *m*-xylene in the absence of *tert*-butyl hydroperoxide[22] it having been further assumed that the ca. 10-fold lower reactivity of $Me_3COO^\bullet$ in H-atom abstraction relative to a primary alkylperoxyl radical is due to a 1.4-kcal/mol increase in the activation energy. [d] Activation energy suggested in ref 22b based on an assumed log ($A_p^{BR}/H/M^{-1}$ s^{-1}) of 8.7. [e] Assumed in ref 22b. [f] Reference 24. [g] Reference 26.

Table IV. Maximum Kinetic Chain Lengths, ν_{max}, for the Autoxidation of Methylnaphthalenes in the Presence of 1.0 M *tert*-Butyl Hydroperoxide

	1-methylnaphthalene		2-methylnaphthalene	
temp (°C)	160 Torr of O_2	760 Torr of O_2	160 Torr of O_2	760 Torr of O_2
30	203	436	214	470
40	165	333	156	321
50	125	259	107	178
60	92	184	84	138

by plotting $1/f^{BR}k_8^{BR}$ against the oxygen concentration in solution at oxygen partial pressures of 160, 760 ($[O_2] = 1 \times 10^{-2}$ M),[44] and 1460 Torr.

Comparison of Hydrogen Atom Abstraction by *tert*-Butylperoxyl Radicals from Methylnaphthalenes and Alkylbenzenes. Values of k_p^{BR} at 30 °C, statistically corrected for the number of active hydrogen atoms, are given in Table III for the methylnaphthalenes and for toluene,[28] *p*-xylene,[24] and cumene.[26] The methylnaphthalenes are slightly more reactive toward the $Me_3COO^\bullet$ radical than toluene as would be expected because of their slightly weaker $ArCH_2$–H bonds.[6,51]

Although the 30 °C range of temperatures used to study the $Me_3COO^\bullet$/methylnaphthalene reactions is too small to derive accurate Arrhenius parameters, these parameters have been included in Table III for comparison with earlier data. The preexponential factors for the methylnaphthalenes are uncomfortably small.[53] It is not clear whether the measured values are correct and are a consequence of severe geometric constraints in the transition state, as previously suggested for *p*-xylene,[24] or whether there is a systematic error in the measurements.

The Maximum Chain Length Phenomenon. The kinetics of autoxidation of most hydrocarbons in the presence of 1.0 M *tert*-butyl hydroperoxide can be described by eq II. According to this equation, the chain length can be increased indefinitely simply by reducing the rate of chain-initiation. This is not true for the methylnaphthalenes as is graphically illustrated for 1-methylnaphthalene in Figure 4. The methylnaphthalenes obey eq IV which predicts that there will be a maximum chain length, ν_{max}, at the point where the apparent rate constant for propagation, ν/τ[RH], has dropped to zero, i.e.,

$$\nu_{max} = \frac{k_p^{BR}}{2f^{BR}k_8^{BR}} \qquad \text{(VII)}$$

Values of ν_{max} are given in Table IV. Under the same conditions of temperature and oxygen pressure the ν_{max} values for 1- and 2-methylnaphthalene are rather similar and, in view of our probable experimental uncertainties, we will treat them as being equal in the following discussion.

At a given temperature, v_{max} increases as the oxygen pressure increases (i.e., as $[O_2] \rightarrow \infty, f^{BR} \rightarrow 0$ and hence $v_{max} \rightarrow \infty$). At a given oxygen pressure, v_{max} decreases as the temperature increases, a phenomenon which we attribute to two causes. The first, and probably the more important, is that the addition of the *tert*-butylperoxyl radical to the naphthalene ring (reaction 8) has a higher activation energy than does hydrogen atom abstraction from the methyl group (reaction 2), i.e., $E_8^{BR} - E_p^{BR} \approx 4.8$ kcal/mol (cf. Tables I and II). Second, the activation energy for the chain-ending, unimolecular decomposition of the peroxyl/naphthalene adduct radical to form the naphthoxyl radical and *tert*-butyl alcohol (reaction 9) appears to be higher than the activation energy for the chain-propagating reaction of this adduct radical with molecular oxygen (reaction 11), i.e., $E_9^{BR} - E_{11}^{BR} \approx$ 1.6–5.7 kcal/mol (cf. Tables I and II).

Methylnaphthalene and other alkylnaphthalenes[5,10] are less readily autoxidized at elevated temperatures than the corresponding alkylbenzenes for the foregoing reasons combined with the fact that alkylnaphthalene autoxidations are, as mentioned earlier, very strongly autoretarding. In the absence of the *tert*-butyl hydroperoxide, the rates of autoxidation of methylnaphthalenes, *n*-alkylnaphthalenes (and even *sec*-alkylnaphthalenes), and the rates of autoxidation of the corresponding alkylbenzenes are greatly reduced. This is because chain termination via the bimolecular self-reaction of primary and secondary alkylperoxyl radicals (and even the tertiary dialkylarylmethylperoxyl radicals), viz.

$$\mathrm{ROO^\bullet + ROO^\bullet} \xrightarrow{2k_t^{RR}} \text{nonradical products} \qquad (14)$$

is more rapid (generally much more rapid) than chain termination via the bimolecular self-reactions of *tert*-butylperoxyl radicals (reaction 6).

Autoxidation of Methylnaphthalenes at 60 °C. Initial rates for the AIBN-initiated autoxidation of 1- and 2-methylnaphthalene could be measured at 60 °C. Unfortunately, the errors involved in determining the corrected rates of autoxidation were rather large. This was due to the low experimental rates of autoxidation combined with very short chain lengths (vide infra) which made the corrections for N_2 evolution and O_2 absorption by the initiator and O_2 evolution in termination a significant fraction of the observed rates. For these reasons, the kinetics were not explored in detail. However, for both methylnaphthalenes the order, *n*, in R_i was found to be greater than 0.5 which indicates that a kinetically-first-order chain-termination process also plays a role in these reactions. The normal bimolecular termination via two naphthylmethylperoxyl radicals, $ROO^\bullet$, reaction 14, was also important since $0.5 < n < 1.0$.

However, there is a difference between the oxidations carried out in the presence of *tert*-butyl hydroperoxide and in its absence. In the latter case, within our experimental accuracy the initial rates of the AIBN-initiated autoxidation of 1-methylnaphthalene (neat, 7.0 M) and 2-methylnaphthalene (5.0 M in chlorobenzene) did not depend on the oxygen partial pressure in the range 160–760 Torr (see Figure 5). The identified products were naphthylmethyl hydroperoxide, naphthylmethanol, and naphthaldehyde.

The simplest explanation[50,54] for the apparent lack of effect of oxygen pressure on the initial rates of autoxidation of the methylnaphthalenes is that the hydroperoxyl radical, $HOO^\bullet$, formed in reaction 11′, generally becomes a chain-terminating species via reaction 15 because the chain-propagating step involving reaction

---

(51) Alkylnaphthalenes are also more reactive than alkylbenzenes toward the cumylperoxyl radical.[52]

(52) Gerasimova, S. A.; Matvienko, A. G.; Opeida, I. A.; Smirnov, Yu. I. *Neftekhimiya* **1989**, *29*, 251–256.

(53) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(54) We do not rule out the possibility that the rate of a reaction akin to reaction 9 increases relative to reaction 11′ as the steric protection of the relevant oxygen atom decreases with the change from a *tert*-butyl group to a naphthylmethyl group. We also note that intramolecular cyclizations of naphthylmethylperoxyl radicals would appear to be a distinct possibility in the absence of the good hydrogen donor, *tert*-butyl hydroperoxide.

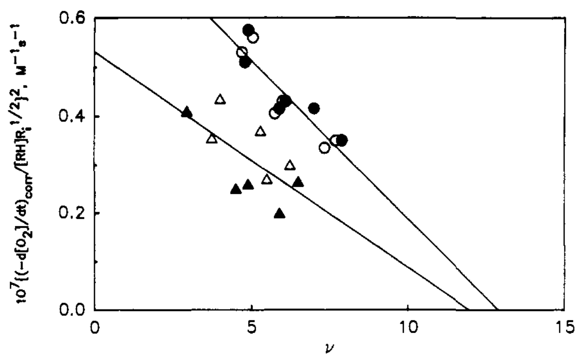
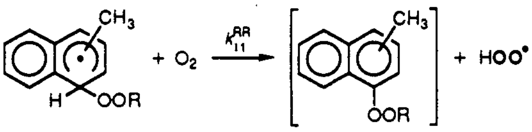


Figure 5. Plots of $[(-d[O_2]/dt)_{corr}/[RH]R_i^{1/2}]^2$ against ν for the autoxidation of neat (7.0 M) 1-methylnaphthalene and 5.0 M 2-methylnaphthalene in chlorobenzene initiated with (1.4–9.2) × 10^{-3} M AIBN (R_i = (0.15–1.1) × 10^{-7} M s^{-1}) at 60 °C: 1-methylnaphthalene, 160 Torr of O_2 (●), 760 Torr of O_2 (○); 2-methylnaphthalene, 160 Torr of O_2 (▲), 760 Torr of O_2 (△).

12 is not available in the absence of *tert*-butyl hydroperoxide. It is, of course, well established that chain-termination rate constants are very large in the autoxidations of a variety of organic substrates that involve HOO• radicals.[55,56] That is, k_{15} will be substantially greater than $2k_t^{RR}$ (reaction 14).



(11')

$$\mathrm{HOO^\bullet + ROO^\bullet \longrightarrow nonradical\ products} \qquad (15)$$

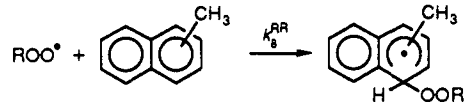
A kinetic analysis which includes the chain-propagating step

$$\mathrm{ROO^\bullet + RH \xrightarrow{k_p^{RR}} ROOH + R^\bullet} \qquad (16)$$

and which assumes that reactions 11′ and 15 are responsible for the observed lack of any appreciable effect of oxygen pressure on initial rates yields the equation

$$\left(\frac{(-d[O_2]/dt)_{corr}}{[RH]R_i^{1/2}}\right)^2 = \frac{(k_p^{RR})^2 - k_p^{RR}k_8^{RR}\nu}{2k_t^{RR}} \qquad \text{(VIII)}$$

The foregoing assumptions imply that reaction 8′ is always chain-terminating.



(8')

In Figure 5 the left-hand side of eq VIII has been plotted against ν for the initial (corrected) rates of autoxidation of 1- and 2-methylnaphthalene at 60 °C. The values found for $k_p^{RR}/(2k_t^{RR})^{1/2}$, $k_8^{RR}/(2k_t^{RR})^{1/2}$, and ν_{max} from these plots are given in Table V. The small magnitude of ν_{max} (~12) is particularly striking.

Since a direct measurement of $2k_t^{RR}$ for the methylnaphthalenes by the usual rotating sector technique[48] is completely ruled out by the extremely limited maximum chain lengths of these autoxidations, we have simply assumed that this rate constant will have a value of 1 × 10^8 M^{-1} s^{-1}, a value which is fairly typical for primary alkylperoxyl radicals.[22,43b] This assumption yields the k_p^{RR} and k_8^{RR} values also listed in Table V. It is gratifying to note that for both methylnaphthalenes the k_p^{RR} values are ca. 10 times larger than the k_p^{BR} values measured at this temperature since it is well established that primary and secondary alkylperoxyl radicals are ca. 10 times as reactive in hydrogen atom abstractions as *tert*-butylperoxyl radicals.[23a,24,27,28,57]

Table V. Kinetic Parameters for the Autoxidation of Neat (7.0 M) 1-Methylnaphthalene and 5.0 M 2-Methylnaphthalene in Chlorobenzene at 60 °C

parameter	1-methyl-naphthalene	2-methyl-naphthalene
$10^4k_p^{RR}/(2k_t^{RR})^{1/2}$ ($M^{-1/2}$ $s^{-1/2}$)	(2.8 ± 0.1)	(2.2 ± 0.3)
k_p^{RR} (M^{-1} s^{-1})	$2.8^{a,b}$	$2.2^{a,b}$
$10^4k_8^{RR}/(2k_t^{RR})^{1/2}$ ($M^{-1/2}$ $s^{-1/2}$)	0.11 ± 0.02	0.10 ± 0.04
k_8^{RR} (M^{-1} s^{-1})	$0.11^{a,c}$	$0.10^{a,c}$
ν_{max}	13 ± 2	12 ± 4

[a] Calculated with the assumption that $2k_t^{RR}$ = 1 × 10^8 M^{-1} s^{-1}. [b] For comparison k_p^{BR} = 0.24 M^{-1} s^{-1}. [c] For comparison k_8^{BR} = (1.7–1.8) × 10^{-3} M^{-1} s^{-1} (see Tables I and II).

For both methylnaphthalenes k_8^{RR} is ca. 60 times as large as k_8^{BR} (see Table V and footnote *b*). That is, at 60 °C the naphthylmethylperoxyl radicals add to their parent methylnaphthalenes some 60 times more rapidly than do *tert*-butylperoxyl radicals. Such enhanced reactivity for addition to condensed ring aromatic compounds of primary vs tertiary alkylperoxyl radicals is not without precedent. Thus, Opeida and Nechitailo[18] have measured Arrhenius parameters for the addition to anthracene of $PhCH_2OO^\bullet$, $PhCH(CH_3)OO^\bullet$, and $PhC(CH_3)_2OO^\bullet$ and, at 60 °C, their reported rate constants were 3550, 1290, and 80 M^{-1} s^{-1}, respectively,[58] i.e., their primary alkylperoxyl radical is some 44 times as reactive in addition as their tertiary alkylperoxyl. We attribute the greater reactivity in additions to (electron rich) polycyclic aromatics of primary alkylperoxyls relative to tertiary alkylperoxyls to polar contributions to the transition state for this reaction, viz.,

$$[\mathrm{ROO^\bullet Ar \leftrightarrow ROO^{-\,+\bullet}Ar}]^{\ddagger}$$

Primary alkylperoxyl radicals are more electrophilic than tertiary alkylperoxyls[59] and hence will add to aromatics more rapidly. Indeed, our results imply that at 60 °C the primary naphthylmethylperoxyl radicals have a ca. 25-fold preference for reacting with the methylnaphthalenes by hydrogen abstraction rather than by addition whereas for the *tert*-butylperoxyl radicals this pref-

---

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

(56) Howard, J. A.; Yamada, T. *J. Am. Chem. Soc.* **1981**, *103*, 7102–7106.

(57) Howard, J. A.; Ingold, K. U.; Symonds, M. *Can. J. Chem.* **1968**, *46*, 1017–1022.

(58) The Arrhenius parameters given in ref 18 are obviously unreliable since values of log (A/M^{-1} s^{-1}) for these three peroxyl radicals range from 6.0 to 13.1. Fortunately, 60 °C is within the temperature range employed in ref 18 so that the rate constants we have given may be reasonably reliable. This is further indicated by Mahoney's[16] value of 62 M^{-1} s^{-1} for $PhC(CH_3)_2OO^\bullet$ + anthracene at 60 °C.

(59) ESR spectroscopy[60] and calculated[61] and measured[62] dipole moments suggest that the electron distribution in peroxyl radicals can be represented as having contributions from two canonical structures:[63]

$$\mathrm{R-\ddot{O}-\dot{O} \longleftrightarrow R-\overset{\bullet+}{O}-\overset{\bullet\bullet}{O}^-}$$

The dipolar structure will be favored by an electron-releasing R group, i.e., it is more favored for R = *tert*-alkyl than for R = primary alkyl. The more electrophilic canonical structure

$$\mathrm{R-\ddot{O}-\dot{O}}$$

therefore makes a greater contribution when R is a primary alkyl group and such peroxyl radicals are therefore more reactive in general (less electron delocalization) and, in particular, when the electrophilicity of the radical is important.

(60) Adamic, K.; Ingold, K. U.; Morton, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 922–923. Howard, J. A. *Can. J. Chem.* **1972**, *50*, 1981–1983; **1979**, *57*, 253–254. Melamud, E.; Silver, B. L. *J. Phys. Chem.* **1973**, *77*, 1896–1900.

(61) Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 6478–6485.

(62) Fessenden, R. W.; Hitachi, A.; Nagarajan, V. *J. Phys. Chem.* **1984**, *88*, 107–110.

(63) Recent theoretical calculations[64] have suggested that the direction of the dipole is reversed, i.e., that it should be $RO^{\delta-}O^{\bullet\delta+}$. However, these calculations do not reproduce the experimentally observed spin densities on the inner oxygen (ca. 35%) and outer oxygen (ca. 65%) atoms, giving instead ca. 10% and 90% spin density on the inner and outer oxygen, respectively.

(64) Boyd, S. J.; Boyd, R. J.; Barclay, L. R. C. *J. Am. Chem. Soc.* **1990**, *112*, 5724–5730.

erence has increased to ca. 130.

Summary

In the 30–60 °C temperature range the autoxidation of both 1- and 2-methylnaphthalene in the presence of 1.0 M *tert*-butyl hydroperoxide is autoretarding and self-inhibiting. The major reaction between the *tert*-butylperoxyl radicals and the methylnaphthalenes is hydrogen atom abstraction from the methyl group (reaction 2, rate constant k_p^{RR}). Self-inhibition is a consequence of a competing process involving the addition of *tert*-butylperoxyl to the naphthalene ring (reaction 8). Reaction 8 is a very minor process relative to reaction 2, e.g., $k_8^{BR}/k_p^{BR} = 0.0036$ and 0.0074 at 30 and 60 °C, respectively, and it does not lead automatically to chain termination. Instead, the adduct radical formed in reaction 8 may react with oxygen (reaction 11) to form the $HOO^\bullet$ radical which is a chain-propagating species or, alternatively, it may decompose to yield *tert*-butyl alcohol and a methylnaphthoxyl radical (reaction 9). Reaction 9 is responsible for a kinetically first-order chain termination since the naphthoxyl radical can trap another peroxyl radical.

Reaction 9 is also responsible for the existence of a maximum chain length, ν_{max}, in the autoxidation of the methylnaphthalenes. That is, at a given temperature and oxygen partial pressure the chain length cannot be increased more or less indefinitely by reducing the rate of chain initiation, R_i, as is the case for the autoxidation of most hydrocarbons, e.g., for 1-methylnaphthalene at 40 °C $\nu_{max} \approx 165$, 330, and 510 at O_2 partial pressures of 160, 760, and 1460 Torr. The rate constant ratio, k_{11}^{BR}/k_9^{BR}, has a value of ca. 200 M^{-1} at 30–40 °C. Since k_{11}^{BR} is likely to be comparable to the rate constant measured for the reaction of O_2 with the cyclohexadienyl radical, viz.[65] 1.6×10^9 M^{-1} s^{-1} at 27 °C, we can conclude that the unimolecular decomposition of the *tert*-butylperoxyl/methylnaphthalene adduct radical is rapid ($k_9^{BR} \sim 10^7$ s^{-1} at these temperatures).

The importance of the reaction leading to self-inhibition relative to the normal chain-propagation step of H-atom abstraction (i.e., k_8^{BR}/k_p^{BR}) increases as the temperature increases, for which reason ν_{max} at a given oxygen pressure decreases as the temperature rises. Furthermore, in the absence of *tert*-butyl hydroperoxide, self-inhibition of the autoxidation of 1- and 2-methylnaphthalene at 60 °C becomes more important relative to propagation than it was in the presence of the hydroperoxide. This is due to two effects. First, in the absence of hydroperoxide ν_{max} does not depend on the oxygen partial pressure, probably because the $HOO^\bullet$ radical (formed by reaction of O_2 with the peroxyl/methylnaphthalene adduct radical) is more likely to enter into a chain-terminating reaction with a naphthylmethylperoxyl radical than it is to abstract hydrogen from the methylnaphthalene and propagate the chain. Second, the addition of the primary naphthylmethylperoxyl radical to the naphthalene ring occurs ca. 60 times as rapidly as does the addition of *tert*-butylperoxyl (i.e., $k_8^{RR} \approx 60k_8^{BR}$), whereas the primary peroxyl radical is only ca. 10 times as active as the tertiary peroxyl in hydrogen abstraction from the methyl group of the methylnaphthalenes (i.e., $k_p^{RR} \approx 10k_p^{BR}$).

Our results and mechanistic conclusions serve to explain the well-established fact that alkylnaphthalenes are highly resistant to autoxidation, *particularly* at elevated temperatures.[5,10,11] In the following paper we show that these compounds are fairly effective retarders of the autoxidation of *n*-hexadecane at 160 °C and that the mechanism of retardation involves peroxyl radical addition to the naphthalene ring.

Experimental Section

Materials. 1-Methylnaphthalene (99%, Aldrich) was used after fractional distillation and percolation through alumina. 2-Methylnaphthalene (98%, Aldrich) was purified by careful recrystallization from isopropyl alcohol. *tert*-Butyl hydroperoxide (90%, Aldrich) was purified by fractional distillation, α,α'-azobis(isobutyronitrile) (AIBN, Aldrich) was recrystallized from warm methanol. Cumene (99%, Aldrich) was treated with concentrated H_2SO_4, passed through basic alumina, and fractionally distilled. 2-Methylnaphthoquinone (Aldrich, vitamin K_3) was purified by recrystallization from methanol. The two naphthylmethanols and naphthaldehydes used to help identify oxidation products were commercial samples employed without further purification.

Kinetic Procedure. Rates of autoxidation were determined (generally to within ±3%) by monitoring the decrease in oxygen pressure in a constant volume apparatus using a pressure transducer and an automatic recording system.[27,66] Rates of chain initiation, R_i, were measured for all kinetic experiments by the induction period method[31] using 6-hydroxy-2,2,5,7,8-pentamethylchroman (a vitamin E analogue) as the phenolic antioxidant. For a given concentration of AIBN and given temperature R_i was always ca. 10% greater under 760 Torr of O_2 than under 160 Torr of O_2, e.g., for [AIBN] = 0.018 M at 40 °C, $R_i = 1.09 \times 10^{-8}$ M s^{-1} under 160 Torr of O_2 and $R_i = 1.18 \times 10^8$ M s^{-1} under 760 Torr of O_2. We attribute this difference in R_i to a reduced rate for geminate radical/radical reactions at the higher oxygen pressure.

Registry No. $Me_2C(CN)N{=}NC(CN)Me_2$, 78-67-1; $Me_3COOCMe_2$, 75-91-2; 1-methylnaphthalene, 90-12-0; 2-methylnaphthalene, 91-57-6.

Supplementary Material Available: Initial rates and other kinetic data for the AIBN initiated autoxidation of 1-methylnaphthalene and 2-methylnaphthalene in the presence and absence of *tert*-butyl hydroperoxide (Tables VI–XIII) and a plot of $(\nu/[RH]\tau)^2$ against ν for the autoxidation of 1.0–4.8 M 2-methylnaphthalene in chlorobenzene containing 1.0 M *tert*-butyl hydroperoxide at 40 °C (Figure 6) (9 pages). Ordering information is given on any current masthead page.

---

(65) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095–5099.

(66) Wayner, D. D. M.; Burton, G. W. In *Handbook of Free Radicals and Antioxidants in Biomedicine*; CRC Press Inc.: Boca Raton, FL, 1989; Vol. III, pp 223–232.