Inhibition Kinetics of Initiated Autoxidations

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In the kinetic analysis of the inhibition of initiated autoxidations, it has to be taken into account that peroxyl radicals derived from the initiator ($R'O_2^{\bullet}$), as well as those generated from the substrate ($RO_2^{\bullet}$), may participate in the reaction. They become increasingly important the shorter the kinetic chain. This manifests itself in deviations of the rate constants calculated by usual analyses. If $R'O_2^{\bullet}$ is more reactive towards the substrate RH than $RO_2^{\bullet}$, the calculated rate constants for the reaction of $RO_2^{\bullet}$ with the inhibitor AH are too small, and decrease with increasing antioxidant concentration.

Kinetic equations are derived which take into account the participation of peroxyl radicals derived from the initiator and which allow the estimation of consistent rate constants from the rates of inhibited oxidations. The application of these equations to the oxidation of tetralin and cumene inhibited by t-butylphenols is demonstrated.

Kinetics of Inhibited Autoxidation.—It is well established that initiated autoxidations inhibited by chain-breaking antioxidants, *e.g.* sterically hindered phenols, proceed at ambient temperatures according to Scheme 1.[1,†]

$$\mathrm{I} \longrightarrow 2a\mathrm{R}^{\bullet} \qquad (1)$$

I = initiator a = initiator efficiency

$$\mathrm{R}^{\bullet} + \mathrm{O_2} \longrightarrow \mathrm{RO_2}^{\bullet} \qquad (2)$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R}^{\bullet} \qquad (3)$$

$$2\mathrm{RO_2}^{\bullet} \longrightarrow \text{products} + \mathrm{O_2} \qquad (4)$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{AH} \longrightarrow \mathrm{ROOH} + \mathrm{A}^{\bullet} \qquad (7)$$

$$\mathrm{RO_2}^{\bullet} + \mathrm{A}^{\bullet} \longrightarrow \mathrm{ROOA} \qquad (8)$$

Scheme 1.

From this mechanism, the rate of oxygen absorption is given by equation (9), when oxygen generation in the termination reaction (4) is disregarded. Substituting k_4 for the rate of uninhibited oxidation r_u, *i.e.* equation (10), gives equation (11),

$$r = \frac{\mathrm{d}[\mathrm{O_2}]_{\mathrm{abs}}}{\mathrm{d}t} = r_i + k_3[\mathrm{RH}]\left\{\left[\left(\frac{k_7[\mathrm{AH}]}{2k_4}\right)^2 + \frac{r_i}{2k_4}\right]^{\frac{1}{2}} - \frac{k_7[\mathrm{AH}]}{2k_4}\right\} \qquad (9)$$

$$r_u = r_i + \left(\frac{r_i}{2k_4}\right)^{\frac{1}{2}} k_3[\mathrm{RH}] \qquad (10)$$

$$r = r_i + (r_u - r_i)\left\{\left[\left(\frac{r_u - r_i}{r_i}\right)^2\left(\frac{k_7[\mathrm{AH}]}{k_3[\mathrm{RH}]}\right)^2 + 1\right]^{\frac{1}{2}} - \left(\frac{r_u - r_i}{r_i}\right)\frac{k_7[\mathrm{AH}]}{k_3[\mathrm{RH}]}\right\} \qquad (11)$$

which can be rewritten as (12). In these equations the differences $r - r_i$ and $r_u - r_i$ change into r and r_u when the kinetic chains are long ($r \gg r_i$).[2]

$$\frac{r_i}{r - r_i}\left[1 - \left(\frac{r - r_i}{r_u - r_i}\right)^2\right] = \frac{2k_7[\mathrm{AH}]}{k_3[\mathrm{RH}]} \qquad (12)$$

If the 'quadratic' termination (4) can be neglected in comparison with the termination reaction (7) ($k_4[\mathrm{RO_2}^{\bullet}] \ll k_7[\mathrm{AH}]$, which holds good for short kinetic chains at high concentrations of antioxidant), equations (9) and (12) reduce to (13). Equation (13) is usually used to estimate k_7 from measured initial rates of inhibited oxidations.

$$r = r_i\left(1 + \frac{k_3[\mathrm{RH}]}{2k_7[\mathrm{AH}]}\right) \qquad (13)$$

The rate of antioxidant consumption is in every case given by equation (14), from which equation (15) follows after integration (if r_i = constant). Thereby one obtains equation (16) for the induction period t_{in}, equation (17) for the antioxidant concentration, and equations (18) and (19) for the oxygen uptake after integration of equation (12). If $r \gg r_i$ (at low [AH]), then the first term in equations (18) and (19) can be omitted and the relationships given by Denisov *et al.*[3] result.

$$-\frac{\mathrm{d}[\mathrm{AH}]}{\mathrm{d}t} = \frac{r_i}{2} \qquad (14)$$

$$[\mathrm{AH}] = [\mathrm{AH}]_0 - r_i t/2 \qquad (15)$$

$$t_{\mathrm{in}} = 2[\mathrm{AH}]_0/r_i \qquad (16)$$

$$[\mathrm{AH}] = [\mathrm{AH}]_0(1 - t/t_{\mathrm{in}}) \qquad (17)$$

$$[\mathrm{O_2}]_{\mathrm{abs}} = r_i t - \frac{k_3}{k_7}[\mathrm{RH}]\ln\left(1 - \frac{r_i{}^t}{2[\mathrm{AH}]_0}\right) \qquad (18)$$

$$= 2[\mathrm{AH}]_0\frac{t}{t_{\mathrm{in}}} - \frac{k_3}{k_7}[\mathrm{RH}]\ln\left(1 - \frac{t}{t_{\mathrm{in}}}\right) \qquad (19)$$

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† Some modified schemes are valid for inhibition by non-hindered phenols and other chain-breaking antioxidants and for autoxidations at higher temperatures leading to more complicated rate equations. For a discussion of various cases see, *e.g.*, E. T. Denisov and I. V. Khudyakov, *Chem. Rev.*, 1987, **87**, 1313. The problems dealt with in the present paper are not affected by this.

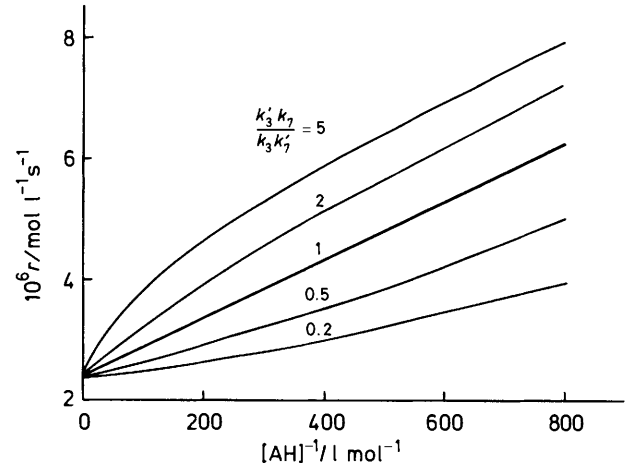

Figure 1. Rates of inhibited oxidations calculated according to equation (26) with $r_i = 2.4 \times 10^{-6}$ mol l^{-1} s^{-1}, k_3[RH] = 40 s^{-1}, and $k_7 = 1 \times 10^4$ l mol^{-1} s^{-1}

At high antioxidant concentrations, the induction periods are long and the rate of initiation r_i decreases in the course of reaction [equation (20)]

$$r_i = 2ak_1[\mathrm{I}]_0 \exp(-k_1t) \tag{20}$$

Then follow equations (21)—(25).

$$t_{in} = -\frac{1}{k_1}\ln\left(1 - \frac{[\mathrm{AH}]_0}{a[\mathrm{I}]_0}\right) \tag{21}$$

$$[\mathrm{AH}] = [\mathrm{AH}]_0 - a[\mathrm{I}]_0[1 - \exp(-k_1t)] \tag{22}$$

$$= [\mathrm{AH}]_0\left[1 - \frac{1 - \exp(-k_1t)}{1 - \exp(-k_1t_{in})}\right] \tag{23}$$

$$[\mathrm{O_2}]_{abs} = 2a[I]_0[1 - \exp(-k_1t)] - \frac{k_3}{k_7}[\mathrm{RH}]\ln\left\{1 - \frac{a[\mathrm{I}]_0}{[\mathrm{AH}]_0}[1 - \exp(-k_1t)]\right\} \tag{24}$$

$$= 2[\mathrm{AH}]_0\frac{1 - \exp(-k_1t)}{1 - \exp(-k_1t_{in})} - \frac{k_3}{k_7}[\mathrm{RH}]\ln\left[1 - \frac{1 - \exp(-k_1t)}{1 - \exp(-k_1t_{in})}\right] \tag{25}$$

A plot of $[\mathrm{O_2}]_{abs} - 2a[1 - \exp(-k_1t)]$ or of $[\mathrm{O_2}]_{abs} - 2[\mathrm{AH}]_0[1 - \exp(-k_1t)]/[1 - \exp(-k_1t_{in})]$ against $-\ln\{1 - a[\mathrm{I}]_0[1 - \exp(-k_1t)]/[\mathrm{AH}]_0\}$ or $-\ln\{1 - [1 - \exp(-k_1t)]/[1 - \exp(-k_1t_{in})]\}$ gives a straight line with slope $k_3[\mathrm{RH}]/k_7$, from which k_7 can be estimated when k_3 is known.

Inhibition of Autoxidation with Participation of Peroxyl Radicals derived from the Initiator.—Scheme 1 supposes the radicals R$^\bullet$ generated in the initiation reaction (1) to be identical with those formed from RH according to equation (3). If this is *not* the case, the equations derived so far are valid only when the radicals R$''$ generated from the initiator do not react predominantly with oxygen to give R$'$O$_2^\bullet$ but with RH to give R$^\bullet$, *or* when the reactivities of RO$_2^\bullet$ and R$'$O$_2^\bullet$ towards RH and AH are equal, *or* when the kinetic chains are long. None of these suppositions is fulfilled in autoxidations initiated by azo compounds (R$'$N=NR$'$) and arylalkanes (R$'$R$'$) in the presence of relatively high antioxidant concentrations. In these cases the reaction must be described by the more complicated Scheme 2.

$$\mathrm{I} \longrightarrow 2a\mathrm{R''} \tag{1}$$

$$\mathrm{R''} + \mathrm{O_2} \longrightarrow \mathrm{R'O_2^\bullet} \tag{2'}$$

$$\mathrm{R'O_2^\bullet} + \mathrm{RH} \longrightarrow \mathrm{R'OOH} + \mathrm{R^\bullet} \tag{3'}$$

$$\mathrm{R^\bullet} + \mathrm{O_2} \longrightarrow \mathrm{RO_2^\bullet} \tag{2}$$

$$\mathrm{RO_2^\bullet} + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R^\bullet} \tag{3}$$

$$2\mathrm{R'O_2^\bullet} \longrightarrow \text{products} + \mathrm{O_2} \tag{4''}$$

$$\mathrm{R'O_2^\bullet} + \mathrm{RO_2^\bullet} \longrightarrow \text{products} + \mathrm{O_2} \tag{4'}$$

$$2\mathrm{RO_2^\bullet} \longrightarrow \text{products} + \mathrm{O_2} \tag{4}$$

$$\mathrm{R'O_2^\bullet} + \mathrm{AH} \longrightarrow \mathrm{R'OOH} + \mathrm{A^\bullet} \tag{7'}$$

$$\mathrm{RO_2^\bullet} + \mathrm{AH} \longrightarrow \mathrm{ROOH} + \mathrm{A^\bullet} \tag{7}$$

$$\mathrm{R'O_2^\bullet} + \mathrm{A^\bullet} \longrightarrow \mathrm{R'OOA} \tag{8'}$$

$$\mathrm{RO_2^\bullet} + \mathrm{A^\bullet} \longrightarrow \mathrm{ROOA} \tag{8}$$

Scheme 2.

The aforementioned premises are also not fulfilled in uninhibited autoxidations of short kinetic chain. The chain reaction is then propagated not only by RO$_2^\bullet$ but also by R$'$O$_2^\bullet$, and equation (10) cannot be applied. Rate equations for *un*inhibited autoxidations, which consider chain propagation by peroxyl radicals derived from the initiator, have been published by Soviet authors.[4,5]

The rate equations derived from Scheme 2 can be numerically integrated and the dependences of the reactant concentrations on the initial concentrations and rate constants of the reaction steps may be simulated by computer. But the essential consequences can be recognized already under certain simplifying conditions. Thus, if termination reactions (4) to (4$''$) are neglected in comparison with (7) and (7$'$) (which holds for higher antioxidant concentrations) and if the reactivities of both the radicals RO$_2^\bullet$ and R$'$O$_2^\bullet$ towards phenoxyl radicals are equal ($k_8' = k_8$), the rate of oxygen absorption is given by equation (26). It follows that the deviations of kinetic behaviour from equation (12) depend on the ratio of the quotients k_3'/k_3 and k_7'/k_7 (Figure 1). When $k_3'/k_3 = k_7'/k_7$, equation (12) is valid, a plot of the rate of oxygen uptake against [RH]/[AH] is linear, and the slope equals $k_3/2k_7 = k_3'/2k_7'$. When $k_3'/k_3 > k_7'/k_7$, the plot of r *vs.* [RH]/[AH] is concave and the rate constants 'k_7' calculated by equation (12) are smaller than the

$$r = \frac{d[\mathrm{O_2}]_{abs}}{dt} = r_i \left[1 + \frac{1 + k_3[\mathrm{RO_2^\bullet}]/k_3'[\mathrm{R'O_2^\bullet}]}{\dfrac{(k_7 + k_7')[\mathrm{AH}](1 + 2[\mathrm{R'O_2}]/[\mathrm{RO_2^\bullet}])}{k_3'[\mathrm{RH}](1 + [\mathrm{R'O_2^\bullet}]/[\mathrm{RO_2^\bullet}])}}\right] \tag{26}$$

$$\frac{[\mathrm{R'O_2^\bullet}]}{[\mathrm{RO_2^\bullet}]} = \left[\frac{(k_7 + k_7')[\mathrm{AH}]}{2k_3'[\mathrm{RH}]} - 1\right] \left[\left(\frac{(k_7 + k_7')[\mathrm{AH}]}{2k_3'[\mathrm{RH}]} - 1\right)^2 + \frac{2k_7[\mathrm{AH}]}{k_3'[\mathrm{RH}]}\right]^{\frac{1}{2}} \tag{27}$$

true k_7 values and decrease with increasing [AH]/[RH]. When, on the other hand, $k_3'/k_3 < k_7/k_7$, the plot of r *vs.* [RH]/[AH] is convex, the 'k_7' values calculated by equation (12) are between k_7 and k_7' and decrease with increasing [RH]/[AH]. In the case $k_7' = k_7$, equations (27) and (26) change into the lucid relationships (28) and (29). The rate of antioxidant consumption is the same as before [equation (14)].

$$\frac{[\mathrm{R'O_2^{\bullet}}]}{[\mathrm{RO_2^{\bullet}}]} = \frac{2k_7[\mathrm{AH}]}{k_3'[\mathrm{RH}]} \tag{28}$$

$$r = \frac{\mathrm{d}[\mathrm{O_2}]_{\mathrm{abs}}}{\mathrm{d}t} = r_{\mathrm{i}}\left(1 + \frac{1 + k_3[\mathrm{RH}]/2k_7[\mathrm{AN}]}{1 + 2k_7[\mathrm{AH}]/k_3'[\mathrm{RH}]}\right) \tag{29}$$

With the help of equation (29), the rate constants $k_7 \approx k_7'$ can be estimated at known k_3 and k_3', or k_3' can be calculated at known k_3 and k_7. Both coefficients k_3' and k_7 can be estimated from the dependence of r on [AH]/[RH] when only k_3 is known. Integration of equations (29) and (24) gives, if r_i and [RH] are constant, the relationship (16) for the period of induction t_{in}, equations (15) and (17) for [AH](t), and equations (30) and (31) for the concentration of absorbed oxygen.

$$[\mathrm{O_2}]_{\mathrm{abs}} = r_{\mathrm{i}}t + \frac{k_3'[\mathrm{RH}]}{k_7}\ln\frac{1 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0}{1 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0 - r_{\mathrm{i}}t/2[\mathrm{AH}]_0} - \frac{k_3[\mathrm{RH}]}{k_7}\ln\frac{(1 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0)(1 - r_{\mathrm{i}}t/2[\mathrm{AH}]_0)}{1 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0 - r_{\mathrm{i}}t/2[\mathrm{AH}]_0} \tag{30}$$

$$= 2[\mathrm{AH}]_0\frac{t}{t_{\mathrm{in}}} + \frac{k_3'[\mathrm{RH}]}{k_7}\ln\frac{1 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0}{1 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0 - t/t_{\mathrm{in}}} - \frac{k_3[\mathrm{RH}]}{k_7}\ln\frac{(1 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0)(1 - t/t_{\mathrm{in}})}{1 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0 - t/t_{\mathrm{in}}} \tag{31}$$

If the rate of initiation is not constant, equations (21)—(23) result for t_{in} and [AH], respectively, and (32) and (33) for $[\mathrm{O_2}]_{\mathrm{abs}}$.

$$[\mathrm{O_2}]_{\mathrm{abs}} = 2a[\mathrm{I}]_0[1 - \exp(-k_1t)] + \frac{k_3'[\mathrm{RH}]}{k_7}\ln\frac{1 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0}{1 - a[\mathrm{I}]_0[1 - \exp(-k_1t)]/[\mathrm{AH}]_0 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0} - \frac{k_3[\mathrm{RH}]}{k_7}\ln\frac{2k_7[\mathrm{AH}]_0/k_3'[\mathrm{RH}]}{1/\{1 - a[\mathrm{I}]_0[1 - \exp(-k_1t)]/[\mathrm{AH}]_0\} + 2k_7[\mathrm{AH}]_0/k_3'[\mathrm{RH}]} \tag{32}$$

$$= 2[\mathrm{AH}]_0\frac{1 - \exp(-k_1t)}{1 - \exp(-k_1t_{\mathrm{in}})} + \frac{k_3'[\mathrm{RH}]}{k_7}\ln\frac{1 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0}{1 - [1 - \exp(-k_1t)]/[1 - \exp(-k_1t_{\mathrm{in}}) + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]_0} - \frac{k_3[\mathrm{RH}]}{k_7}\ln\frac{1 + 2k_7[\mathrm{AH}]_0/k_3'[\mathrm{RH}]}{1/\{1 - [1 - \exp(-k_1t)]/[1 - \exp(-k_1t_{\mathrm{in}})\} + 2k_7[\mathrm{AN}]_0/k_3'[\mathrm{RH}]} \tag{33}$$

Equation (29) assumes a simpler form for certain [RH]/[AH] ratios. At low [antioxidant] and high [RH] ($k_3[\mathrm{RH}] \gg k_7[\mathrm{AH}] \ll k_3'[\mathrm{RH}]$) it changes into the familiar equation (13), and chain propagation by $\mathrm{R'O_2^{\bullet}}$ plays no role. On the other hand, equation (34) results at very high antioxidant concentrations

$$r = r_{\mathrm{i}}(1 + k_3'[\mathrm{RH}]/2k_7[\mathrm{AH}]) \tag{34}$$

and/or low [RH] ($k_3[\mathrm{RH}] \ll k_7[\mathrm{AH}] \gg k_3'[\mathrm{RH}]$), and only $\mathrm{R'O_2^{\bullet}}$ (and no $\mathrm{RO_2^{\bullet}}$) takes part in the reaction.

Inhibition of the Autoxidation of Cumene and Tetralin by t-Butylphenols.—Application of equations (29), (32), and (33) will be demonstrated by some examples.

Table 1. Inhibition of the 2,2,3,3-tetraphenylbutane (R′R′)-initiated oxidation of tetralin by tri-t-butylphenol in chlorobenzene at 30 °C

10^3[RH]/[AH]	$10^6r/2[\mathrm{R'R'}]$[a] $\mathrm{s^{-1}}$	10^{-4}'k_7'[b] $\mathrm{l\ mol^{-1}\ s^{-1}}$	$10^{-4}k_7$[c] $\mathrm{l\ mol^{-1}\ s^{-1}}$
0	2.2		
5.7	4.9	1.43	2.51
11.2	6.8	1.66	2.35
24.4	10.2	2.08	2.54
			mean 2.47 ± 0.10

[a] From ref. 6. [b] From equation (13) with $k_3 = 6.4\ \mathrm{l\ mol^{-1}\ s^{-1}}$. [c] From equation (29) with $k_3' = 25\ \mathrm{l\ mol^{-1}\ s^{-1}}$.

The 2,2,3,3-tetraphenylbutane-initiated oxidation of tetralin inhibited by 2,4,6-tri-t-butylphenol has been studied by Mahoney and DaRooge.[6] A non-linear $r/[\mathrm{AH}]^{-1}$ plot is reproduced in their paper but was not used to estimate k_7. If one calculates 'k_7' from their data with the help of equation (13), values result which decrease with increasing [AH] (Table 1). If one calculates k_7 with equation (29) and chooses k_3' so that k_7 becomes independent of [AH], one obtains $k_3' = 25\ \mathrm{l\ mol^{-1}\ s^{-1}}$ and $k_7 = 2.4 \pm 10^4\ \mathrm{l\ mol^{-1}\ s^{-1}}$. The value of k_7 corresponds (within the limits of error) to that estimated in the presence of tetralin hydroperoxide [$k_7 = 2.9 \times 10^4\ \mathrm{l\ mol^{-1}\ s^{-1}}$ (ref. 6)]. The value of k_3' is larger than that of k_3 [$= 6.4\ \mathrm{l\ mol^{-1}\ s^{-1}}$ (ref. 7)], demonstrating that 1,1-diphenylethylperoxyl radicals are more reactive towards tetralin than α-tetralylperoxyls.

We ourselves studied, among other things, the inhibition of the azobisisobutyronitrile (AIBN)-initiated autoxidation of tetralin and cumene by 2.6-di-t-butyl-4-methylphenol (BHT) at relatively high inhibitor concentrations.[8] The initial rate of oxygen uptake in the BHT-inhibited oxidation of tetralin is not linearly dependent on 1/[BHT] (Figure 2) and the rate constants 'k_7' calculated according to equation (24) slightly decrease with increasing $[\mathrm{BHT}]_0$ (Table 2). Altogether they are smaller than the rate constants for the reaction of tetralylperoxyl radicals with BHT given by Mahoney and Berger *et al.* ($k_7 = 2.8 \times 10^4\ \mathrm{l\ mol^{-1}\ s^{-1}}$ at 40 °C[6,9]). However, when one analyses the $[\mathrm{O_2}](t)$ data with equation (32) and fits k_3' so that k_7 becomes independent of $[\mathrm{BHT}]_0$, one obtains $k_3' = 120\ \mathrm{l\ mol^{-1}\ s^{-1}}$ and $k_7 = 2.6 \times 10^4\ \mathrm{l\ mol^{-1}\ s^{-1}}$. The k_7 value so calculated is in good agreement with the literature value already mentioned.[6,9] Here, too, $k_3' > k_3$, indicating that 1-cyano-1-

Table 2. Inhibition of the AIBN-initiated oxidation of tetralin by 2,6-di-t-butyl-4-methylphenol in chlorobenzene at 65 °C[a]

$10^3[AH]$ / mol l^{-1}	$10^6 r_0$ / mol l^{-1} s^{-1}	10^{-4}'k_7'[b] / l mol^{-1} s^{-1}	$10^{-4}k_7$[c] / l mol^{-1} s^{-1}
4	3.68	0.99	3.1
5	3.76	0.74	2.3
7	3.36	0.75	2.7
20	2.88	0.52	2.2
50	2.59	0.63	3.0
			mean 2.6 ± 0.4

[a] [RH] = 1.75 mol l^{-1}; [AIBN] = 0.1 mol l^{-1}. [b] From equation (24) with k_3 = 24 l mol^{-1} s^{-1}. [c] From equation (32) with k_3' = 120 l mol^{-1} s^{-1}.

Table 3. Inhibition of the AIBN-initiated oxidation of cumene by 2,6-di-t-butyl-4-methylphenol in chlorobenzene at 65 °C[a]

$10^3[AH]$ / mol l^{-1}	$10^6 r_0$ / mol l^{-1} s^{-1}	10^{-4}'k_7'[b] / l mol^{-1} s^{-1}	$10^{-4}k_7$[c] / l mol^{-1} s^{-1}
4	2.88	0.16	0.9
5	2.80	0.16	1.4
7	2.59	0.23	1.4
10	2.54	0.22	1.5
		mean 0.19 ± 0.04	1.3 ± 0.3

[a] [RH] = 1.71 mol l^{-1}; [AIBN] = 0.1 mol l^{-1}. [b] From equation (24) with k_3 = 1.5 l mol^{-1} s^{-1}. [c] From equation (32) with k_3' = 10 l mol^{-1} s^{-1}.

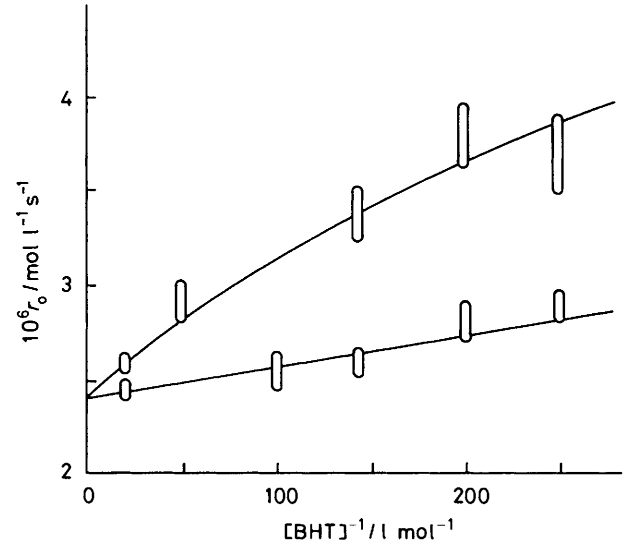

Figure 2. Rates of AIBN-initiated oxidations of tetralin and cumene inhibited by 2,6-di-t-butyl-4-methylphenol in chlorobenzene at 65 °C; [AIBN] = 0.1 mol l^{-1}, [tetralin] = 1.75 mol l^{-1}, [cumene] = 1.71 mol l^{-1}

methylethylperoxyl radicals are more reactive towards tetralin than α-tetralylperoxyls.

In the AIBN-initiated oxidation of cumene inhibited by BHT, the rate of oxidation depends linearly on 1/[BHT] (Figure 2) and the 'k_7' values calculated according to equation (24) are independent of [BHT] within experimental error (Table 3). However, they are six times smaller than the rate constant of the reaction of cumylperoxyl radicals with cumene determined by Berger *et al.*[9] Here, at the high BHT concentrations used, $k_3[RH] \ll k_7[AH] \gg k_3'[RH]$ holds and therefore equation (34) rather than (13) is valid. From this equation [with k_7 = 1.3 × 10^4 l mol^{-1} s^{-1} (refs. 9 and 10)], the rate constant of the reaction of 1-cyano-1-methylethylperoxyl radicals with cumene follows as k_3' = 10 l mol^{-1} s^{-1}. This value agrees well with that (k_3' = 7 l mol^{-1} s^{-1} at 60 °C) calculated from $k_3'/(2k_4')^{\frac{1}{2}}$ = 1.1 × 10^{-3} l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$ given by Vichutinskii,[5] with $2k_4'$ = 4 × 10^5 l mol^{-1} s^{-1}.[11] Thus 1-cyano-1-methylethylperoxyl radicals are also more reactive towards cumene then cumylperoxyls [k_3 = 1.5 l mol^{-1} s^{-1} at 65 °C (ref. 12)].

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