Absolute rate constants for hydrocarbon autoxidation. VI. Alkyl aromatic and olefinic hydrocarbons[1]

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Absolute rate constants have been measured for the autoxidation of a large number of hydrocarbons at 30 °C. The chain-propagating and chain-terminating rate constants depend on the structure of the hydrocarbon and also on the structure of the chain-carrying peroxy radical. With certain notable exceptions which are mainly due to steric hindrance, the rate constants for hydrogen-atom abstraction increase in the order primary < secondary < tertiary; and, for compounds losing a secondary hydrogen atom, the rate constants increase in the order unactivated < acyclic activated by a single π-electron system < cyclic activated by a single π-system < acyclic activated by two π-systems < cyclic activated by two π-systems. The rate constants for chain termination by the self-reaction of two peroxy radicals generally increase in the order tertiary peroxy radicals < acyclic allylic secondary $\leqslant$ cyclic secondary $\leqslant$ acyclic benzylic secondary < primary peroxy radicals < hydroperoxy radicals.

INTRODUCTION

Early work on the liquid phase autoxidation of hydrocarbons suggested that the rate constant for the chain-terminating interaction of two peroxy radicals ($2k_t$),

$$RO_2\cdot + RO_2\cdot \xrightarrow{2k_t} \text{inactive products},$$
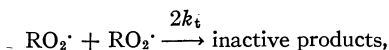
was insensitive to the structure of R, the hydrocarbon portion in the radical (1). It was therefore assumed that variations in oxidation rates reflected changes in the rate constants for chain propagation,

$$RO_2\cdot + RH \xrightarrow{k_p} ROOH + R\cdot .$$
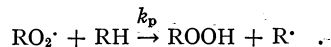
Bolland (2) utilized an "average" termination constant of $6 \times 10^5\ M^{-1}\ s^{-1}$ to develop a set of rules relating olefinic structure to the ease of hydrogen-atom abstraction in chain propagation. These empirical rules have been successfully applied to the prediction of the gross reactivities of olefins containing *primary* or *secondary* allylic hydrogens but they predict too great a reactivity for olefins with *tertiary* allylic hydrogen (3, 4).

This simple picture of hydrocarbon autoxidation which was based on an invariant termination constant became unlikely when Melville and Richards (5) showed that the rate constant for the interaction of the tertiary peroxy radicals from cumene was only about $3 \times 10^4\ M^{-1}\ s^{-1}$. Russell (6) utilized the difference in the termination constants of *secondary* and *tertiary* peroxy radicals to explain the minimum that occurred in plots of the oxidation rate against composition for mixtures of cumene with a number of hydrocarbons giving secondary peroxy radicals. However, in the absence of evidence to the contrary, Russell was forced to assume that all *secondary* and all *primary* peroxy radicals terminate at the same rate. We have recently presented some rather limited evidence (Part IV of this series (7)) that not only do *primary* peroxy radicals terminate more rapidly than *secondary* peroxy radicals but that there is also a fairly wide variation in the rate constants for the termination of *secondary* peroxy radicals. The present paper extends the measurement of termination rate constants to a much wider variety of hydrocarbons. In addition, the propagation rate constants have been used to compare the relative rates of hydrogen abstraction by peroxy radicals with the relative rates reported for abstraction by some other free radicals.

EXPERIMENTAL

Reagents

None of the hydrocarbons and esters used in this work had purities of less than 99.5% as determined by gas–liquid chromatography (g.l.c.). All compounds except neopentylbenzene were passed through alumina immediately before use.

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Experimental Procedure

The experimental technique and theory of the rotating sector method have been described in previous papers in this series (7–10). None of the compounds studied showed any variation of the rate with oxygen pressure (200–730 mm). Unreactive liquid substrates were used in the pure state. The solid hydrocarbons and the more reactive liquids were used as solutions in chlorobenzene, their concentrations ranging as low as 0.1 mole/l for the very reactive substrates. In calculations of rate constants for 1,3- and 1,4-cyclohexadiene, 1,2- and 1,4-dihydronaphthalene, and 9,10-dihydroanthracene in chlorobenzene it was assumed that the rate of chain initiation was equal to the value found under similar conditions with less reactive hydrocarbons (see preceding paper (11)). The hydroperoxide yield was determined by the iodine–thiosulfate method so that the rate of hydrogen-atom abstraction (k_{abstr}) could be separated from the other chain-propagating steps such as addition (k_{add}) (10).

Although it is nearly impossible to assign specific errors to absolute rate constants, the sources of such errors were discussed in some detail in earlier papers (8, 10). In the present work, particular attention was paid to the chain lengths (ν) of the reactions. All the results represent averages of reasonably consistent data which were obtained at not less than two chain lengths. Most of the compounds oxidized quite readily and gave no particular difficulty. For these compounds it is probably safe to assume that k_t should be accurate to within a factor of 2 and k_p should be accurate to within $\pm 50\%$. Certain compounds exhibited specific problems which are outlined below. The calculation of absolute rate constants from measurements at short chain lengths is also described below.

Compounds Presenting Special Problems

(i) Toluene and m-Xylene

Toluene and m-xylene both oxidized at rather too low a rate for satisfactory rotating sector measurements at our standard temperature of 30 °C. Fortunately, all the available evidence indicates that k_t is probably not significantly affected by polar factors (6, 9, 12). It is therefore fairly safe to assume that k_t for these two hydrocarbons will be close to the value found for p-xylene, i.e. 1.5×10^8 M^{-1} s^{-1}. Propagation rate constants for toluene and m-xylene were calculated using this assumed termination constant.

(ii) Methyl Linolenate

The rate of oxygen absorption decreased sharply as the reaction proceeded. This was not observed with the simple monoolefins (see Fig. 1). The decreased rate was attributed to a decrease in the rate of chain initiation (R_i) resulting from the formation of a conjugated triene (these compounds absorb strongly at the initiating wavelength, 365 mμ). The results for methyl linolenate are therefore much less reliable than those obtained with most other compounds. A much smaller autoretardation was observed with methyl linoleate, indene, and

2,5-dimethyl hexene-3. In contrast, diphenylmethane, octene-1, 1,3-cyclohexadiene, decyne-5, and 1,2-dihydronaphthalene were slightly autocatalytic. For the remaining hydrocarbons, the rates of oxygen absorption were constant for the duration of the experiments.
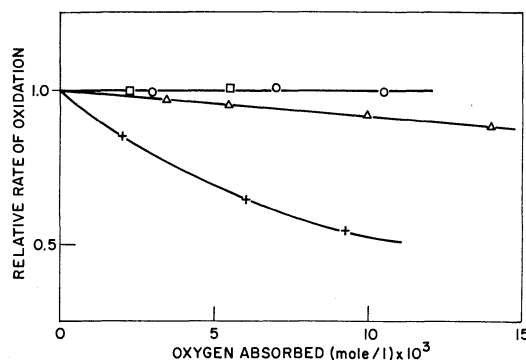

FIG. 1. Relative rates of oxygen absorption at 30 °C vs. amount of oxygen absorbed for some unsaturated compounds. ($\bigcirc$) Heptene-3; ($\square$) methyl oleate; ($\triangle$) methyl linoleate; ($\times$) methyl linolenate.

(iii) 9,10-Dihydroanthracene, Decyne-5, and Octyne-1

9,10-Dihydroanthracene, decyne-5, and octyne-1 underwent oxidation in the dark. For the first two compounds the relative importance of this thermally initiated reaction could be reduced sufficiently to permit rotating sector studies by oxidizing them as 1.0 M solutions in chlorobenzene. For octyne-1 the thermal rate, even in the absence of hydroperoxide, was 30–40% of the photochemical rate under the standard experimental conditions and absolute rate constants could not be obtained.

(iv) 1,2-Dihydronaphthalene

1,2-Dihydronaphthalene forms both polyperoxides and hydroperoxides (cf. indene (10, 13)). It also behaves like other hydrocarbons which contain a styrene skeleton with a hydrogen atom in the α-position in that there is a kinetically first-order chain-termination process (rate constant k_x) as well as the usual bimolecular termination process (8–10). This renders the accurate determination of k_p and k_t quite difficult. The first-order process is a fairly important source of chain termination and its importance increases during the oxidation (cf. β-methylstyrene (10)). The first-order rate constant in chlorobenzene at 30 °C is about 0.9 s^{-1} which can be compared with values of 0.24, 0.61, and 1.24 s^{-1} for styrene, β-methylstyrene, and indene, respectively, under the same conditions (10). The first-order termination process could be effectively eliminated by the addition of D$_2$O (8, 10), the overall rate of oxidation increasing by about 35%. In the presence of D$_2$O the measured propagation and termination rate constants were 415 M^{-1} s^{-1} and

1.2×10^8 M^{-1} s^{-1} respectively, whereas in the absence of D$_2$O the measured values were 190 M^{-1} s^{-1} and 3.5×10^7 M^{-1} s^{-1}. The former values are considered the more accurate because the first-order correction has been eliminated and so they are quoted in Table III.

(v) 9,10-Dihydrophenanthrene

9,10-Dihydrophenanthrene had a kinetically first-order chain-termination process which increased in importance as the reaction proceeded. In the initial stages of the reaction k_x was about 0.3 s^{-1}. Since the addition of D$_2$O reduced, but did not eliminate, this process, it is possible that only part of the first-order termination was due to the formation of a phenolic inhibitor (9[2]). The increase in k_x during the reaction may result from the slow accumulation of the weak inhibitor phenanthrene.

Calculation of Rate Constants at Short Chain Lengths

At short chain lengths the usual assumption that the measured rate of gas absorption is proportional to the peroxy radical concentration is no longer valid. This is because the quantities of gas absorbed and evolved in the initiation and termination processes become significant compared with the amount absorbed in the propagation process. It was assumed that for each molecule of initiator (azo-bis-cyclohexylnitrile) decomposed, one molecule of nitrogen was evolved, $2e$ molecules of oxygen were absorbed by the initiating radicals, and e molecules of oxygen were finally evolved in the chain-ending step. By using this correction[3] it was found that absolute rate constants obtained at chain lengths as low as 3.0 were not significantly different from those obtained at long chain lengths.

Reactions with t-Butoxy Radicals

In order to extend the comparison of hydrocarbon reactivity towards peroxy and alkoxy radicals we measured the relative reactivity of a few hydrocarbons towards *t*-butoxy radicals. The radicals were generated photolytically from *t*-butyl hypochlorite using the general techniques and competitive procedures developed by Walling and co-workers (16–18). The reactions were carried out in dilute solutions in CCl$_4$ at 40 °C as we have described previously (19). Analyses were by gas chromatography and selective solvolysis (19). Where comparison is possible, the present results are generally

[2]The oxidation products gave a positive response to the phosphomolybdic acid spot test for phenols (14). The parent hydrocarbon and phenanthrene both gave a negative response to this test.

[3]Under intermittent illumination this correction is independent of the speed of rotation of the sectored disc. That is, for our experimental arrangement with a light/dark ratio of 3.0, the correction under intermittent illumination is 1/4 of the correction under steady illumination. In similar circumstances, Tsepalov and Shlyapintokh (15) have used a correction which varies with the sector's rotation speed. We believe our method of correcting the measured rates is more precise.

in quite good agreement with the data of Walling (see Table IV).

In Part IV (7), deuterium isotope effects were reported for the oxidation of α,α-d_2-diphenylmethane and perdeuterotetralin at 30 °C. The measured values of $(k_p)_H/(k_p)_D$ were 5.1 for diphenylmethane, which is of about the expected magnitude, but > 50 for tetralin. It was suggested that this high value might be due to an impurity in the deuterated compound which retarded its oxidation. Such an impurity should not affect a relative reactivity determined by a competitive procedure. In competition with toluene, the isotope effects for the reaction with *t*-butoxy radicals were 1.7 for diphenylmethane and 2.4 for tetralin, both values being in good agreement with our previous value of 2.4 for toluene itself (19).

RESULTS

Rate constants for the autoxidation of alkyl aromatic hydrocarbons, olefins, and alkenyl aromatic hydrocarbons at 30 °C are given in Tables I, II, and III respectively. The tables include data from the previous papers in this series. Values of $k_p/(2k_t)^{1/2}$ are in reasonable agreement, after allowing for the 15° temperature difference, with Bolland's results at 45 °C (2). The agreement is good for 2,3-dimethyl butene-2, methyl oleate, heptene-3, octene-1, and allylbenzene, but only fair for tetralin, cyclohexene, linoleate, linolenate, and crotylbenzene. Rate constants for hydrogen-atom abstraction are given on an available hydrogen basis, e.g. $k_{abstr}/H = k_p/3$ for toluene, $k_p/2$ for ethylbenzene, etc. Compounds which did not contain benzylic or allylic hydrogens, e.g. *t*-butylbenzene, cyclohexane, *n*-decane, and methyl palmitate, did not oxidize under the present conditions. The error involved in ignoring the unactivated hydrogen atoms when calculating k_{abstr}/H is therefore negligible. Although several alkenes did not give 100% yields of hydroperoxide, the values of k_{abstr}/H were only corrected when the measured yields fell below 75%. The hydroperoxide yields were generally not measured for those compounds for which yields of over 80% at higher temperatures have been reported. All rate constants are in units of mole^{-1} s^{-1}.

In the tables the compounds from which a *primary* hydrogen atom is abstracted are listed ahead of those from which a *secondary*

TABLE I

Rate constants for the autoxidation of alkyl aromatic hydrocarbons at 30 °C*

Hydrocarbon	$k_p/(2k_t)^{1/2} \times 10^5$	k_{abstr}/H	$k_t \times 10^{-6}$
Primary			
Toluene	1.4	0.08	150†
m-Xylene	2.8	0.08	150†
o-Xylene	3.3	0.07	77
p-Xylene	4.9	0.14	150
Secondary			
Neopentylbenzene‡	2.0	—	—
n-Butylbenzene	8.1	0.28	25
Bibenzyl	13	0.14	10
Ethylbenzene (ref. 7)	21	0.65	20
Indan	170	1.2	4.1
Tetralin (ref. 7)	230	1.6	3.8
9,10-Dihydrophenanthrene	720	14	30
Diphenylmethane (ref. 7)	38	2.4	80
9,10-Dihydroanthracene	5 850	44	4.6
Tertiary			
sec-Amylbenzene	11	0.07	0.22
Phenylcyclohexane	15	0.06	0.08
sec-Butylbenzene	18	0.08	0.09
1,1-Diphenylethane	110	0.34	0.047
Isopropylbenzene	150	0.18	0.0075

*In mole⁻¹ s⁻¹ units.
†Assumed, see text.
‡Oxidized too slowly for a rotating sector study.

TABLE II

Rate constants for the autoxidation of alkenes at 30 °C†

Olefins‡	Hydroperoxide yield (%)	$k_p/(2k_t)^{1/2} \times 10^5$	k_{abstr}/H	$k_t \times 10^{-6}$
Primary				
2,3-Me₂-butene-2*(p,t)	67	320	0.14	0.32
Secondary (s,s)				
Methyl oleate	>81§	89	0.22	0.53
Heptene-3	100	54	0.35	3.2
Octene-1*(s,p)	80	6.2	0.50	130
Cyclopentene	86‖	280	1.7	3.1
Cyclohexene (ref. 7)	88‖	230	1.5	2.8
1,3-Cyclohexadiene	27	10 000	55	33
1,4-Pentadiene*(s,p)	100	42	7.0	540
Methyl linoleate*	98§	2 100	31	4.4
Methyl linolenate*	~100¶	3 900	59	18
1,4-Cyclohexadiene* (ref. 11)	97	3 900	370	630
Tertiary				
2,5-Me₂-hexene-3(t,s)	100	540	1.2	0.09
Acetylenes				
Octyne-1	—	12	—	—
Decyne-5	80	74	0.7	7.0

*A rearranged peroxy radical is probably involved in the reactions. See text.
†In mole⁻¹ s⁻¹ units.
‡(p,t) refers to a reaction in which a primary hydrogen is abstracted to give an allylic radical in which the odd electron is delocalized between a primary and a tertiary carbon, (s,s) a secondary hydrogen abstracted and the electron delocalized between two secondary carbon atoms, etc.
§Reference 20.
‖Reference 21.
¶Assumed to be ~ 100% by analogy with methyl linoleate. Titration actually gives only 48%, probably because the hydroperoxide is rather unstable under our conditions.

TABLE III

Rate constants for the autoxidation of alkenyl aromatic hydrocarbons at 30 °C[†]

Hydrocarbon	$k_p/(2k_t)^{1/2} \times 10^5$	k_{abstr}/H	k_{add}	$k_t \times 10^{-6}$
Secondary				
Styrene (ref. 9)	890	—	41	21
β-Methyl styrene (ref. 10)	1 300	—	51	16
Allylbenzene* (ref. 7)	49	5.0	—	220
Crotylbenzene*,‡	420	4.1	—	1.9
Indene (ref. 10)	2 840	7.0	128	25
1,2-Dihydronaphthalene	2 750	26§	291	115
1,4-Dihydronaphthalene* (ref. 11)	3 500	225	—	350
Tertiary				
α-Methyl styrene (ref. 10)	1 300	—	10	0.3

*A rearranged peroxy radical is probably involved in the reactions. See text.
[†]In mole^{-1} s^{-1} units.
‡C$_6$H$_5$CH$_2$CH=CHCH$_3$.
§Assumed to have four active hydrogen atoms.

hydrogen is abstracted and these precede the *tertiary* hydrogen donors. Those compounds losing *secondary* hydrogens are arranged in the order: acyclic activated by a single π-electron system (i.e. $\rangle$C—CH$_2$—R); cyclic activated by a single π-system; acyclic activated by two π-systems (i.e. $\rangle$C—CH$_2$—C$\langle$); and cyclic activated by two π-systems. This order corresponds approximately with the order of increasing ease of hydrogen-atom abstraction. It must be emphasized that classification as *primary*, *secondary*, or *tertiary* does *not* imply that the same *primary*, *secondary*, or *tertiary* peroxy radical is produced and is involved in the abstraction and (or) termination processes. That is, oxygen may add to either end of an allylic radical formed by hydrogen abstraction from an alkene. This can lead, for example, to the production of mainly *primary* peroxy radicals after the abstraction of a *secondary* hydrogen from allylbenzene (22) and 1-octene (23).

RCH$_2$CH=CH$_2$ → RĊHCH=CH$_2$ →
RCH=CHCH$_2$OO·

Rearrangement of the allylic radical also occurs for methyl linoleate and linolenate (24), although in these cases the peroxy radical remains a secondary radical.

R′CH=CHCH$_2$CH=CHR →
R′CH=CHCH=CHCHROO·
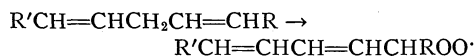
In a similar way, 1,4-pentadiene should give a *primary* peroxy radical. All the obvious cases where oxygen does not add at

the position from which hydrogen was abstracted because of the migration of a double bond are marked with an asterisk in the tables. 1,4-Cyclohexadiene and 1,4-dihydronaphthalene give mainly the HOO· radical under the conditions employed (11). In addition to these changes in the monomeric peroxy radicals, compounds containing the styrene skeleton and compounds with conjugated double bonds form polymeric peroxy radicals, R(OOR)$_n$OO·. These polymeric radicals are certainly the main hydrogen-atom-abstracting species from indene, 1,2-dihydronaphthalene, and 1,3-cyclohexadiene (2).

The rate of the photochemically initiated autoxidation of *m*-xylene was measured from 30 to 65 °C. The results could be represented by

$$k_p/(2k_t)^{1/2} = 1.7 \times 10^2$$
$$\exp(-9400/RT) \ (M^{-1} s^{-1})^{1/2}.$$

Since k_t for this hydrocarbon is probably quite large (Table I) the chain-termination process cannot be associated with a big activation energy. If we assume it has a value of 1.2 kcal/mole[4] then

$$k_{abstr}/H = 1.3 \times 10^6$$
$$\exp(-10000/RT) \ M^{-1} s^{-1}$$

for *m*-xylene and also for toluene.

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[4]This is purposely chosen to be slightly smaller than the value of 1.8 kcal/mole found previously for the autoxidation of styrene (8) because k_t is probably larger for *m*-xylene than for styrene.

The rate of the azo-bis-isobutyronitrile thermally initiated oxidation of cyclohexane was measured at 65 °C. By using a low concentration of AIBN (5.2×10^{-4} M) a chain length of 2.4 was attained. The measured rate gave $k_p/(2k_t)^{1/2} = 2.75 \times 10^{-5}$ $(M^{-1}\,s^{-1})^{1/2}$. Taking McCarthy and MacLachlan's (25) value of 1.4×10^6 $M^{-1}\,s^{-1}$ for k_t at 25 °C and assuming E_t ~ 4.5 kcal/mole (cf. tetralin (7)) gives $k_t = 3.5 \times 10^6$ $M^{-1}\,s^{-1}$ at 65 °C. Therefore, at 65 °C $(k_{abstr}/H)_{cyclohexane} = 6.1 \times 10^{-3}$ $M^{-1}\,s^{-1}$ and hence $(k_{abstr}/H)_{cyclohexane}/(k_{abstr}/H)_{toluene} = 0.014$. This small value indicates that peroxy radicals have a high selectivity in hydrogen-atom abstraction reactions (cf. Table IV and the results for a number of additional radicals collected in ref. 26).

DISCUSSION

The compounds listed in Tables I, II, and III exhibit wide differences in the ease with which their activated hydrogen atoms can be abstracted by the chain-carrying peroxy radicals and in the rates at which the peroxy radicals interact with one another to terminate reaction chains. These differences must arise from a variety of mechanistic, steric, polar, and radical stabilization effects. Small differences produced by small changes in reactant structure could often be attributed to several of these factors. For this reason, an attempt has been made to restrict the following discussion of chain termination and hydrogen abstraction to those results for which the relation between structure and rate constant appears to be fairly straightforward.

Chain Termination

Secondary and, presumably, primary peroxy radicals terminate reaction chains by transfer of an α-hydrogen atom (27). The ease with which this atom is transferred plays a very important role in determining the rate constant for termination.

(i) Primary Peroxy Radicals

Primary peroxy radicals derived from alkylbenzenes and 1-olefins (allylbenzene (22) and octene-1 (23)) give k_t values in the range 0.8–1.5×10^8 $M^{-1}\,s^{-1}$. As we had predicted (7), previously reported

values of k_t for octene-1 (i.e. 0.8–1.5×10^5 $M^{-1}\,s^{-1}$ (1), and 4.6×10^6 $M^{-1}\,s^{-1}$ (25)) were too small. The larger termination constant for 1,4-pentadiene (which can be assumed to give mainly *primary* peroxy radicals) indicates that a peroxy radical adjacent to a conjugated system of double bonds terminates more readily than one adjacent to a single double bond, possibly because the α-hydrogen is more loosely bound and thus more readily transferred.

The low termination constant for 2,3-dimethyl butene-2 (3.2×10^5 $M^{-1}\,s^{-1}$) suggested that tertiary rather than primary peroxy radicals are involved in the oxidation, i.e.
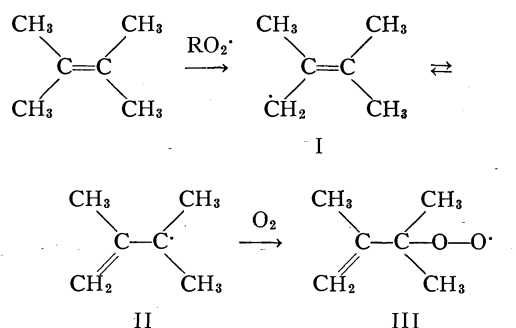
The allylic radical should have a greater electron density at the *tertiary* carbon (structure II) than at the *primary* carbon (structure I).[5] Oxygen should therefore add mainly to the tertiary position. It has been shown previously that the hydroperoxide derived from III (1,1,2-trimethylallylhydroperoxide) is the main product of the Rose Bengal photosensitized autoxidation (28) and the singlet oxygen oxidation (29) of 2,3-dimethyl butene-2. The same hydroperoxide is produced under our experimental conditions and the low termination rate constant for this olefin is thus explained.

(ii) Secondary Peroxy Radicals

Secondary peroxy radicals show wide variations in k_t for comparatively small changes in structure. Most secondary benzylic peroxy radicals ($C_6H_5C(H,R)OO \cdot$)

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[5]This is due to the greater stability of tertiary radicals. Moreover, repulsion between the methyl groups will be reduced by an increase in the central CC bond length, i.e. by an increase in its single bond character.

have values in the range 1.0–3.0×10^7 $M^{-1} s^{-1}$ which is about an order of magnitude smaller than the values found with the xylenes. This difference can be partly attributed to the greater steric hindrance to termination for secondary than for primary peroxy radicals. A number of m- and p-substituted styrenes have k_t values in the range 2.2–5.4×10^7 $M^{-1} s^{-1}$ (9). Diphenylmethane has the highest k_t value $(8.0 \times 10^7$ $M^{-1} s^{-1})$ of all the secondary benzylic compounds examined, possibly because the α-hydrogen is activated by a second phenyl group.

The difference in termination rate constants for methyl oleate and heptene-3 can presumably be attributed to steric effects. The fact that k_t for heptene-3 is smaller than for secondary benzylic hydrocarbons may be partly related to steric effects and partly to the rapid isomerization of acyclic allylic peroxy radicals (30). Steric effects must be nearly equal for methyl oleate and methyl linoleate. Comparison of their termination constants again suggests that a peroxy radical adjacent to a conjugated system of double bonds terminates more readily than one adjacent to a single double bond.

It is rather more difficult to interpret the termination constants for cyclic hydrocarbons. We have previously attributed the comparatively low k_t values for cyclohexene and tetralin ($\sim 3 \times 10^6$ $M^{-1} s^{-1}$) to the fact that these compounds have non-planar, six-membered rings (7). This leads to steric hindrance in termination because one radical must have its peroxy group in the unfavorable axial position in order for its α-hydrogen to be in the most favored position for transfer. Rather surprisingly cyclopentene and indan also have small termination rate constants. Since these five-membered rings will be virtually planar, these low values suggest that there is an increase in ring strain in the transition state for termination. The $HOO^{\cdot}$ radical is responsible for the very high termination constants observed in the oxidation of dilute solutions of 1,4-cyclohexadiene and 1,4-dihydronaphthalene (11). Steric hindrance to termination is probably more important for 9,10-dihydroanthracene ($k_t = 4.6 \times 10^6$ $M^{-1} s^{-1}$) than for the remaining cyclic compounds 1,3-cyclohexadiene, indene, 1,2-dihydronaphthalene, and 9,10-dihydrophenanthrene, which have k_t values in the range 2.5–11.5×10^7 $M^{-1} s^{-1}$.
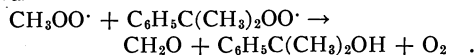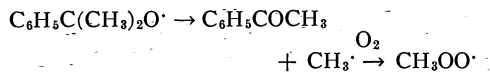
The termination and propagation rate constants for decyne-5 are slightly higher than the values found for comparable olefins.

(iii) Tertiary Peroxy Radicals

Tertiary peroxy radicals, having no α-hydrogens, generally terminate chains more slowly than secondary peroxy radicals. The self-reaction of t-peroxy radicals has received considerable attention in recent years (see e.g. refs. 31–33). Oxygen is evolved in both a chain-terminating and a non-terminating interaction.

$$[1] \qquad RO_2^{\cdot} + RO_2^{\cdot} \rightarrow ROOR + O_2$$

$$[2] \qquad RO_2^{\cdot} + RO_2^{\cdot} \rightarrow RO^{\cdot} + O_2 + RO^{\cdot}$$
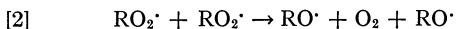
Both processes involve significant activation energies (33, 34). The alkoxy radicals may undergo β-scission to give a ketone and a new radical which, if it contains an α-hydrogen atom, may become important in the overall termination process, e.g. (32)

$$C_6H_5C(CH_3)_2O^{\cdot} \rightarrow C_6H_5COCH_3$$
$$+ CH_3^{\cdot} \xrightarrow{O_2} CH_3OO^{\cdot}$$

$$CH_3OO^{\cdot} + C_6H_5C(CH_3)_2OO^{\cdot} \rightarrow$$
$$CH_2O + C_6H_5C(CH_3)_2OH + O_2 \quad .$$

The relative importance of the direct termination (reaction [1]) and the indirect termination (via β-scission) cannot be obtained by rotating sector measurements.

Rather surprisingly the measured termination constants decrease as the size of the groups on the *tertiary* carbon decrease (see, *sec*-amyl-, *sec*-butyl-, and isopropylbenzene). Unfortunately, it was not possible to measure k_t for triphenylmethane because its rate of oxidation depends on the oxygen pressure (6). The differences in the k_t values for the various tertiary hydrocarbons may be associated with differences in the relative importance of the two termination processes.

The k_t value for cumene is only about half the value of 1.8×10^4 M^{-1} s^{-1} obtained as the rate constant for reaction [1] at this temperature by electron spin resonance (34), which suggests that the indirect termination process, via $CH_3OO^{\cdot}$, is unimportant under our experimental conditions. This was confirmed by showing that added cumene hydroperoxide had a comparatively small effect on the rate constants for the oxidation of cumene at 30 °C. The presence of 1.6 M cumene hydroperoxide in cumene gave $k_p/(2k_t)^{1/2} = 1.05 \times 10^{-3}$ $M^{-1/2}$ $s^{-1/2}$, $k_p = 0.14$ M^{-1} s^{-1}, and $k_t = 8.3 \times 10^3$ M^{-1} s^{-1}. The differences in the absolute rate constants from the values found in the absence of added hydroperoxide are not significant. The fact that k_t is unchanged under conditions designed to suppress termination via β-scission (32) again implies that this process is not important at 30 °C. The small decrease in $k_p/(2k_t)^{1/2}$ produced by added cumene hydroperoxide contrasts with its accelerating effect at 60 °C (32).

Hydrogen Abstraction

The rate constants in Tables I, II, and III indicate that singly activated benzylic and allylic hydrogen atoms have similar reactivities in compounds of similar structure. This point is brought out more clearly in Table IV which compares the rates of hydrogen abstraction (per activated hydrogen) from a number of compounds with the rate of abstraction from toluene. The similarity in the reactivity of indan and cyclopentene and of tetralin and cyclohexene is remarkable. In the analogous straight chain compounds the allylic hydrogens seem to be slightly more reactive than the benzylic. This might be due to a lower steric hindrance for the abstraction of an allylic hydrogen or to the greater stability of the resultant allylic radical. The greater reactivity of allylic positions is most clearly apparent for hydrogen atoms activated by two π-systems in the series diphenylmethane, allylbenzene, and 1,4-pentadiene.

We have recently discussed some of the factors which may contribute to the greater reactivity of cyclic hydrocarbons compared with their straight chain analogues (34), cf. tetralin and indan vs. ethylbenzene, cyclohexene and cyclopentene vs. heptene-3. The difference appears to be due to a combination of radical stabilization, steric effects, and polar factors rather than to one overriding process. The rather high reactivities of 1,4-cyclohexadiene and 1,4-dihydronaphthalene compared with indene and 9,10-dihydroanthracene suggest that the $HOO^{\cdot}$ radical is more active than the secondary peroxy radicals derived from the indene and 9,10-dihydroanthracene. This is probably due more to steric effects than to differences in the HOO—H and ROO—H bond strengths (35).

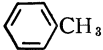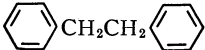The polar and radical stabilizing effects of the alkyl groups not directly involved in the reaction are probably mainly responsible for the greater reactivities of 2,3-dimethyl butene-2 and 2,5-dimethyl hexene-3 compared with toluene and cumene respectively (cf. toluene and p-xylene in Table I). A similar explanation probably applies to the difference in reactivity of methyl linoleate and 1,4-pentadiene.
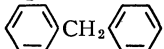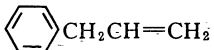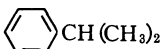
Steric effects can be invoked to explain the lower reactivity of methyl oleate compared with heptene-3 and of *sec*-amyl- and *sec*-butylbenzene compared with cumene. The *tertiary* hydrogen in cumene is itself remarkably unreactive when compared with the *secondary* hydrogens of ethylbenzene. When cumene and ethylbenzene are attacked by the same free radical, the reactivity of cumene (per benzylic hydrogen) is *always* greater than the reactivity of ethylbenzene (cf. Table IV and the literature data collected in ref. 34). The low reactivity of cumene in the present work must therefore be attributed to steric factors associated with the attacking *tertiary* peroxy radical. That is, the *tertiary* cumylperoxy radical is a less reactive radical than the secondary α-phenethylperoxy radical. This difference in the reactivities of *secondary* and *tertiary* peroxy radicals appears to be a fairly general phenomenon (34, 36). It has an important bearing on the relative rates of consumption of different hydrocarbons during the autoxidation of hydrocarbon mixtures.

TABLE IV

Reactivities of α-hydrogen atoms toward abstraction by some free radicals
(reactivity per active hydrogen relative to toluene)

Compound	$RO_2\cdot$, 30 °C	$(CH_3)_3CO\cdot^a$, 40 °C	$C_6H_5\cdot^b$, 60 °C
(benzene)CH_3	1.00^c	1.00^c	1.00^c
$(CH_3)_2C{=}C(CH_3)_2$	2.6	2.0^d	2.1
(benzene)CH_2CH_3	8.1	3.2	4.6
(benzene)CH_2CH_2(benzene)	2.0	$1.8^{e,f}$	2.8^g
$CH_2{=}CH(CH_2)_5CH_3$	6.3	6.1^h	3.4
$R'CH{=}CHCH_2R$	4.4^i	9.2^j	3.3^k
(indane)	15	19^e	8.0
(cyclopentene)	21	38	9.7
(tetralin)	20	$16^{e,l}$	12
(cyclohexene)	18	37	11
(benzene)CH_2(benzene)	30	$3.5^{e,m}$	7.7
(benzene)$CH_2CH{=}CH_2$	63	$8.3^{e,n}$	10
$CH_2{=}CHCH_2CH{=}CH_2$	88	—	6.6^g
(benzene)$CH(CH_3)_2$	2.3	6.8	9.7
$R'CH{=}CHCH(CH_3)_2$	15	18°	16°
(cyclohexane)	0.014^p	1.5	1.0

^{a}References 16 and 17.
^{b}Reference 26.
^{c}By definition.
^{d}cis-Butene-2 and trans-butene-2.
^{e}This work.
^{f}A value of 4.1 was obtained for n-butylbenzene.
^{g}G. A. Russell. Private communication.
^{h}Butene-1.
^{i}Heptene-3.
^{j}cis-Pentene-2 and trans-pentene-2.
^{k}An average value for a secondary allylic hydrogen derived from several 1- and 2-olefins.
^{l}A value of 9.2 is given in ref. 18.
^{m}A value of 4.7 is given in ref. 16.
^{n}A value of 5.4 is given in ref. 18.
^{o}3-Methyl-butene-1.
^{p}At 65 °C.

In Table IV the reactivities of the hydrocarbons towards their own peroxy radicals are compared with their reactivities towards two more active radicals, *t*-butoxy (16–18) and phenyl (26). The most remarkable aspect of this comparison is the general similarity (with the exception of cumene) in the relative reactivities of singly activated hydrogen atoms towards the three radicals. This similarity does not extend to hydrogen atoms activated by two π-systems, the peroxy radicals showing a greater preference for these more weakly bound hydrogens. In a similar way, peroxy radicals are much more reluctant to abstract an unactivated hydrogen atom from cyclohexane than are the *t*-butoxy or phenyl radicals. Since only small differences are observed in the relative reactivities of hydrocarbons containing hydrogens activated by a single π-system for radicals of widely different absolute reactivity, some caution must be employed when relative reactivities are used to identify abstracting radicals.[6] When this method is employed the structures of the reactants and their relative reactivities should cover a wide range. The present results indicate that secondary peroxy radicals are more selective than chlorine, *t*-butoxy, phenyl, and methyl, and less selective than bromine, trichloromethyl, and polystyryl (see Table IV and refs. 26, 38, and 40).

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[6]For example, this technique has been used to show that bromine atoms are the abstracting species in N-bromosuccinimide brominations (37–39), and that trichloromethyl radicals are not the abstracting species in the aralkyl hydrocarbon retarded telomerization of 1-hexadecene and CCl$_4$ (38).

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