

RATE CONSTANTS FOR SOME REACTIONS OF OXY RADICALS

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INTRODUCTION

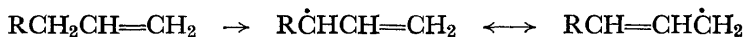
The term oxy radicals is used to refer to those radicals in which the odd electron is located mainly on an oxygen atom as it is, for example, in an alkoxy radical ($\text{RO}\cdot$) or a peroxy radical ($\text{ROO}\cdot$).

Oxy radicals enter into all of the four major classes of free radical reactions, i.e., unimolecular reactions and bimolecular reactions with molecules, with radicals and with one electron transfer reagents. These processes can be illustrated by the following examples.

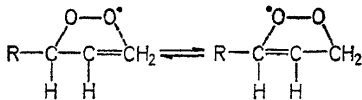
1. UNIMOLECULAR REACTIONS

(a) *Rearrangement*

Moss and Steiner¹ have recently shown that all the unsaturated oxidation products formed during the autoxidation of 1-hexene are derivatives of 2-hexene. In this reaction the peroxy radical abstracts a hydrogen atom from the 3-position of the olefin to produce an allylic radical which then rapidly adds a molecule of oxygen.



Two isomeric peroxy radicals could be formed. Moss and Steiner have suggested that these may be rapidly interconverted by way of a five-membered cyclic transition state.



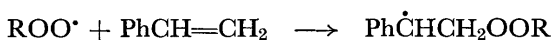
A similar rearrangement of allylic peroxy radicals has also been observed by Brill². If both peroxy radicals are in fact formed from 1-hexene then the isolation of derivatives of 2-hexene implies that the 1-peroxy radical (primary) is more stable or, at least, is more reactive than the 3-peroxy radical (secondary).

(b) Decomposition

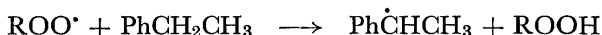
Unimolecular radical decomposition can be illustrated by the well-known β -scission of the *tert*-butoxy radical to acetone and a methyl radical.

**2. BIMOLECULAR REACTIONS WITH MOLECULES***(a) Addition*

This involves attack of the radical on the π electrons of an unsaturated molecule with the formation of a new radical. Successive addition reactions can produce long chain polymers. This reaction can be illustrated by the slow propagating step in the oxidation of styrene.

*(b) Abstraction*

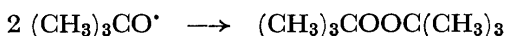
This generally involves peripheral monovalent atoms such as hydrogen or halogen, e.g., the slow step in the oxidation of ethylbenzene.

**3. BIMOLECULAR REACTIONS WITH RADICALS**

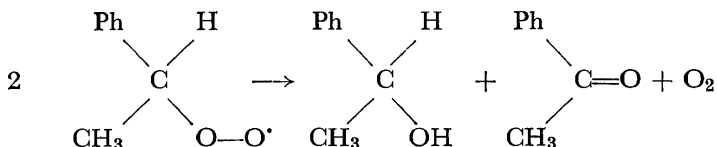
Bimolecular reactions with a second radical generally lead to the destruction of both radicals.

(a) Combination

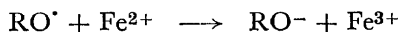
Radical combination is the reverse of homolytic fission, e.g.,

*(b) Disproportionation*

The disproportionation of two radicals into saturated and unsaturated molecules is illustrated by the chain terminating reaction in oxidizing ethylbenzene by which two secondary peroxy radicals interact to give an alcohol, a ketone, and oxygen³.

**4. BIMOLECULAR REACTIONS WITH ONE-ELECTRON TRANSFER AGENTS**

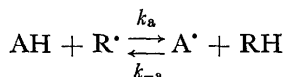
Radical destruction can also occur by transfer of an electron, e.g.



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After this quick survey of oxy radical reactions I want to concentrate on two main topics for the rest of this lecture, namely hydrogen atom abstraction by oxy radicals and the mutual destruction of oxy radicals in their reactions with one another. That is, I will be dealing mainly with the chain reactions involving alkoxy and peroxy radicals as chain carriers and in which a propagation step involves hydrogen atom abstraction and termination involves radical combination or disproportionation. In particular, I will be concentrating on the rates and rate constants of these reactions.

For the general hydrogen atom abstraction process



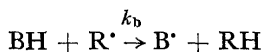
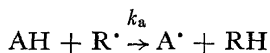
the rate constants for the forward and reverse reactions can be represented by

$$\ln k_a = \ln A_a - E_a/RT$$

$$\ln k_{-a} = \ln A_{-a} - E_{-a}/RT$$

Since the activation energy, E , cannot be less than the heat of reaction and since a reaction can only proceed rapidly if the activation energy is small, it is clear that the forward reaction is only likely to be rapid if the reaction is exothermic. That is, if the R—H bond strength is greater than the A—H bond strength [i.e., if $D(\text{R—H}) > D(\text{A—H})$]. If AH is replaced by a compound which has a higher bond strength the rate of the forward reaction will, in general, decrease while that of the back reaction will, in general, increase.

In recent years, the relative rates with which a wide variety of free radicals react with very many compounds in the liquid phase have been determined, chiefly by the extensive studies of Brown, Kharasch, Kooyman, Mayo, Russell, Szwarc and Walling. Relative rates have generally been obtained by the method of competing reactions since this avoids the difficulties which are nearly always involved in the measurement of absolute rates. That is, in order to obtain an absolute rate, and hence a rate constant, it is necessary to know the concentration of the free radical, R^{\bullet} . In contrast, the competitive technique enables relative rate constants to be obtained without determining the radical concentration. This can be illustrated by considering radical generation in the presence of two reactants



Their rates of consumption are given by

$$-d[\text{AH}]/dt = k_a [\text{R}^{\bullet}] [\text{AH}]$$

$$-d[\text{BH}]/dt = k_b [\text{R}^{\bullet}] [\text{BH}]$$

and hence their relative rates of consumption are proportional to the relative rate constants and concentrations of the two reactants

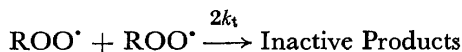
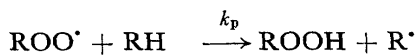
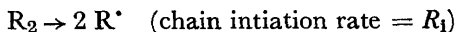
$$\frac{-d[AH]}{-d[BH]} = \frac{k_a[AH]}{k_b[BH]}$$

If R^{\cdot} is a very reactive atom or radical, i.e. if the $R-H$ bond strength is very high, then R^{\cdot} will not readily differentiate between AH and BH even though the $A-H$ and $B-H$ bond strengths may be quite different. However, as the $R-H$ bond strength is decreased the attacking radical becomes more selective and reacts preferentially with the compound containing the most weakly bound hydrogen atom. Thus, fluorine and chlorine atoms are very unselective reagents [$D(H-F) = 134$ kcal/mole and $D(H-Cl) = 102.2$ kcal/mole⁴] that attack hydrocarbons in a rather indiscriminate manner. In contrast, the bromine atom [$D(H-Br) = 86.5$ kcal/mole⁴] is a relatively discriminating species with a strong preference for weakly bound benzylic or allylic hydrogen atoms compared with the more strongly bound aliphatic hydrogen atoms.

Current interest in determining free radical selectivities stems from both theoretical and practical considerations. A list of selectivities can be important in solving many problems faced by both synthetic organic chemists and manufacturing chemists. For example, the information can be used to choose the most suitable free radical for preferentially attacking one compound in a mixture or a single compound at a particular position.

Now if bond strengths were the sole factors that determined reaction rates it would be possible to place every compound into a specific position in relation to every other compound. That is, it would be possible to make a unique list of compounds in the order of their reactivities and this order would not depend on the attacking radicals. Fortunately, or unfortunately, depending upon how one views these matters, such a monotonous situation does not exist. Thus, cyclohexane is more reactive than toluene towards *t*-butoxy radicals, but toluene is more reactive than cyclohexane towards peroxy radicals. Such variations can be attributed to polar and to steric effects, the importance of which are becoming increasingly obvious as more data are accumulated. There are now quite extensive lists in the literature on the relative reactivities of organic compounds in the liquid phase towards atoms such as chlorine and bromine and radicals such as methyl, phenyl, *t*-butoxy, polystyryl, polyvinylacetate, etc. Most of this data has been obtained by the competitive method. However, there is a startling lack of information on relative reactivities towards the peroxy radical, a situation that is even more amazing when you consider that oxidation with the cheapest of all reagents, molecular oxygen, consumes more hydrocarbons than all the other reactions of hydrocarbons put together. The reason for this gap in our knowledge is chiefly that the competitive technique is difficult to employ in autoxidation because of the analytical problems associated with the wide variety of oxidation products, many of which are thermally unstable. Simple measurement of the oxidation rate of a pure compound is not very helpful because it depends on the rate at which two peroxy radicals interact to terminate reaction chains as well as on the rate at which they attack the substrate. That is, if the elementary steps of autoxidation are represented by:

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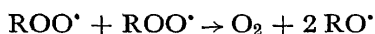
then the rate of oxidation is given by

$$-\frac{d[O_2]}{dt} = k_p [RH] \left(\frac{R_1}{2 k_t} \right)^{1/2}$$

Thus, the rate is proportional to the propagation rate constant divided by the square root of the termination rate constant. The measured rates of oxidation of two pure compounds do not, therefore, necessarily tell us which will be most rapidly consumed if they are oxidized together, i.e., they do not tell us which compound has the higher propagation rate constant.

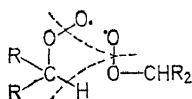
Up to the present, the most fruitful approach to the problem of obtaining the relative reactivities of different substrates towards peroxy radicals has been to determine k_p and k_t separately for each pure substrate by one of the non-stationary state techniques, such as the rotating sector method or the thermocouple method⁵. By these non-stationary state methods the average lifetime of a free radical chain can be determined, i.e. these methods measure how long the average chain† lasts from the time it is started to the moment of its destruction in the termination process. The rate constant for chain termination, k_t , is easily calculated from the measured lifetime provided the rate of chain initiation, R_1 , is known. Substituting k_t and R_1 into the expression for the steady rate of oxidation, the rate constant for chain propagation, k_p , is obtained.

Before considering some of the absolute rate constants for autoxidation that we have obtained by the rotating sector method it is worthwhile re-examining the chain termination process which was simply represented in the kinetic scheme as two peroxy radicals interacting to form inactive products. For the secondary peroxy radicals from ethylbenzene, Russell³ showed that the products of termination were a ketone and, presumably, an alcohol and oxygen. The fact that equal amounts of alcohol and ketone are formed in chain termination has since been demonstrated by analysis of the products formed after the pulse radiolysis of cyclohexane saturated with oxygen⁶. Chain termination may be either a two-step process involving the formation of alkoxy radicals and their rapid disproportionation while still in the solvent cage



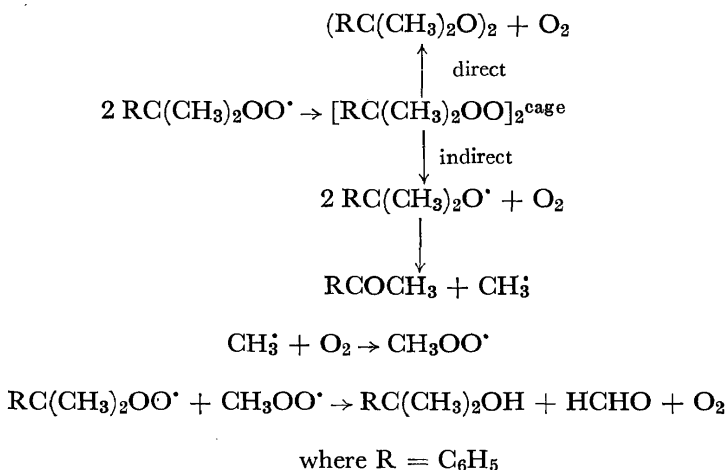
† Not the average radical, since each chain may involve hundreds or thousands of individual radicals.

or, as originally suggested by Russell³, a concerted process by way of a cyclic transition state.



Primary peroxy radicals can presumably interact by the same mechanism as secondaries. For primaries the rate of termination should be accelerated for statistical reasons since there are twice as many hydrogen atoms available for transfer and, moreover, any steric retardation of the rate should be smaller for primary than for secondary peroxy radicals. On the other hand, the α -hydrogen atom of a primary peroxy radical should be more firmly bound than the α -hydrogen of a secondary and it will therefore be more slowly transferred *if* transfer in the termination involves any activation energy. In the absence of experimental data it does not seem possible to predict whether primary peroxy radicals will interact with one another faster or slower than secondary peroxy radicals.

It is obvious that α -hydrogen atom transfer is an impossible termination mechanism for two tertiary peroxy radicals and these radicals do, in fact, generally terminate chains rather slowly. Recent work by several investigators has shed a good deal of light on this reaction. In particular, Traylor⁷ has shown that chain termination in the oxidation of cumene occurs by two distinct processes which can be represented by the following reactions:



Thomas⁸ has used an ingenious e.s.r. technique to show that for *t*-butylperoxy radicals ($\text{R} = \text{CH}_3$) the measured activation energy of the direct termination process is somewhat less than that of the reaction producing two *t*-butoxy radicals. The latter reaction has an activation energy of about 9 kcal/mole and the direct termination has an activation energy of about

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6 kcal/mole⁹. The activation energies of the direct and indirect processes for cumylperoxy radicals differ by about 2 kcal/mole⁹. These differences in the measured activation energies may be associated with the diffusion of the alkoxy radicals from the solvent cage.

Until recently it was generally assumed that all primary and secondary peroxy radicals terminate at the same rate, this rate being much faster than the rate for tertiary peroxy radicals. Some of our recent results on the rate constants for peroxy radical termination which are summarized in *Table 1* show that this assumption was fairly good as a first approximation.

Table 1. Chain termination constants for hydrocarbon autoxidation at 30°C

<i>Peroxy Radical</i>	$k_t(\text{M}^{-1} \text{sec}^{-1})$
Primary: $\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{O}-\text{O}\cdot \\ \\ \text{H} \end{array}$	0.8-2.0 $\times 10^8$
Secondary: $\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{C}-\text{O}-\text{O}\cdot \\ \\ \text{H} \end{array}$	Benzylic 1.0-3.0 $\times 10^7$ Allylic 0.5-5.0 $\times 10^6$ Cyclic 1.0-4.0 $\times 10^6$
Tertiary: $\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{C}-\text{O}-\text{O}\cdot \\ \\ \text{R}'' \end{array}$	0.2-30 $\times 10^4$
Hydroperoxy: $\text{H}-\text{O}-\text{O}\cdot$	1.0 $\times 10^6$

For hydrocarbons which give primary peroxy radicals directly such as *ortho*- and *para*-xylene, k_t was found to be in the range 1.0-2.0 $\times 10^8$ l./mole sec. A similar value was also found for allylbenzene and 1-octene, two hydrocarbons which give primary peroxy radicals after rearrangement of the secondary allylic radical which is produced in the hydrogen abstraction process.

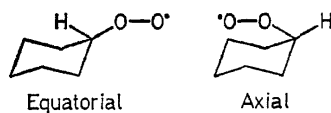
Hydrocarbons that give secondary peroxy radicals exhibit a wide variation in termination constants. However, with a few exceptions they can be roughly classified according to whether the peroxy radical is derived from a benzylic, allylic or cyclic system. In the benzylic group are compounds such as ethylbenzene, *n*-butylbenzene, styrene and bibenzyl with $k_t \sim 1.0-3.0 \times 10^7$ l./mole sec. Diphenylmethane has a higher termination constant ($\sim 8 \times 10^7$ l./mole sec), possibly because the α -hydrogen is flanked by two activating phenyl groups. Peroxy radicals from olefins terminate more slowly than the benzylic peroxy radicals. This must be at least partly due to steric effects associated with R and R' since we have found that k_t increases as the size of the olefin is decreased, thus k_t increases from 5×10^5 l./mole sec for methyl oleate to 3×10^6 l./mole sec for heptene-3. The cyclic hydrocarbons with

k_t values in the range $1.0\text{--}4.0 \times 10^6$ l./mole sec include cyclohexene, tetralin, cyclopentene, indan and 9,10-dihydroanthracene. Cyclohexane can also be included in this group of compounds since McCarthy and MacLachlan have obtained a value for k_t of 1.4×10^6 l./mole sec by the technique of pulse radiolysis¹⁰. In this technique the hydrocarbon is first saturated with oxygen and then given a powerful pulse of ionizing radiation from a linear accelerator. The alkyl radicals which are formed initially are rapidly converted to peroxy radicals, which have an absorption at about 2900 Å. This allows their bimolecular decay to be followed spectroscopically. The absolute rate constant can be calculated from the decay rate once the radical concentration has been determined. To judge from McCarthy and MacLachlan's data this interesting technique may only give results comparable with those obtained in slow thermal oxidations for those compounds such as cyclohexane that can give only one type of peroxy radical. For compounds in which the hydrogen atoms are not all equivalent the decay kinetics after pulse radiolysis will not necessarily represent chain termination of the same peroxy radicals as are formed in the thermal reaction. For example, pulse radiolysis of 1-octene gave $k_t = 4.6 \times 10^6$ l./mole sec¹⁰ whereas the value we find by thermal oxidation is 1.3×10^8 l./mole sec which is in good agreement with our values for other primary peroxy radicals.

Hydrocarbons giving tertiary peroxy radicals which we have studied by the rotating sector method show a variation in k_t from 3×10^5 l./mole sec for α -methyl styrene to 8×10^3 l./mole sec for cumene. The direct termination of *t*-butylperoxy radicals (i.e., the reaction giving di-*t*-butylperoxide) has a rate constant of roughly 2×10^3 l./mole sec at 30°C⁹.

Finally, *Table 1* includes a recent determination by Currie and Dainton¹¹ of k_t for the simplest of all peroxy radicals, namely the hydroperoxy radical $\text{HOO}\cdot$. This rate constant was obtained by the radiolysis of a concentrated aqueous solution of hydrogen peroxide at about room temperature. A similar value has been obtained by Adams *et al.* by the same method¹². Bielski and Saito¹³, using e.s.r. spectroscopy, obtained a value of $\sim 3 \times 10^6$ l./mole sec by the oxidation of acidified hydrogen peroxide with ceric sulphate in a flow system. The rather surprisingly low value of k_t for $\text{HOO}\cdot$ may be partly connected with the solvent since we have found that k_t is noticeably decreased in solvents of high polarity such as acetonitrile or dimethyl sulphoxide¹⁴. The k_t values given in *Table 1* for the alkylperoxy radicals were obtained in relatively non-polar media such as the hydrocarbons themselves or their solutions in chlorobenzene.

The low termination rate constants for peroxy radicals on cyclohexane and cyclohexene ring systems can perhaps be attributed to steric factors since the reaction may require one of the radicals to have its peroxy group in the unfavourable axial position while the other has its peroxy group in the more favoured equatorial position. Rather surprisingly our results suggest that



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cyclopentene and indan also have small termination rates ($\sim 4 \times 10^6$ l./mole sec). Since these 5 membered rings will be virtually planar these low values must probably be attributed to an increase in ring strain in the transition state for termination.

Both the rotating sector¹⁴ and e.s.r.^{8, 9, 13} methods have been used to measure k_t over a range of temperature. The results indicate that differences in k_t for various peroxy radicals can be mainly assigned to differences in the activation energies rather than to differences in the activation entropies (cf. ref. 10). Some representative results for the self reaction (mutual destruction) of peroxy radicals (i.e., both the direct and indirect reactions for *t*-peroxy radicals) are give in *Table 2*.

Table 2. Self reaction of peroxy radicals

<i>Radical</i>	k_t at 30° (M ⁻¹ sec ⁻¹)	<i>E</i> (kcal/mole)	$\log_{10}A$ (M ⁻¹ sec ⁻¹)
<i>t</i> -Butylperoxy ⁹	1.8×10^3	9.5	10.4
Cumylperoxy ⁹	6.5×10^4	7.8	10.7
Hydroperoxy ^{13†}	2.7×10^6	4.7	9.8
<i>α</i> -Tetralylperoxy ¹⁴	3.8×10^6	4.3	9.6
Polystyrylperoxy ¹⁴	2.1×10^7	1.8	8.7

† Bielski and Saito¹³ give $E = 5.9$ kcal/mole. However, a least squares calculation on their rate constants gives $E = 4.7$ kcal/mole.

The wide variation in k_t for hydrocarbons giving primary, secondary and tertiary peroxy radicals can have quite a dramatic effect when the overall rate of oxidation is compared with the rate constant for chain propagation. This is illustrated in *Table 3*. The hydrocarbons have been arranged in order of increasing oxidation rate, i.e., increasing $k_p/\sqrt{2k_t}$. The wide variation in k_t precludes any possibility of correlating k_p with the rate although this has frequently been attempted in the past.

Table 3. Oxidation of some hydrocarbons at 30°C

<i>Hydrocarbon</i>	$k_p/\sqrt{2k_t} \times 10^5$ M ^{-1/2} sec ^{-1/2}	k_p M ⁻¹ sec ⁻¹	k_t M ⁻¹ sec ⁻¹
<i>p</i> -Xylene (primary)	5	0.84	1.5×10^8
Ethylbenzene (sec.)	21	1.3	2.0×10^7
Allylbenzene (primary)	50	10	2.2×10^8
Cumene (tert.)	150	0.18	7.5×10^3
Cyclohexene (sec.)	230	5.6	3.0×10^6

I would particularly like to draw your attention to the fact that the propagation rate constant for isopropylbenzene (i.e., cumene) is smaller than the values for ethylbenzene and *p*-xylene. That the rate of hydrogen atom abstraction from a tertiary position should be less than that from a comparable secondary position is almost unprecedented in free radical reactions as can be seen from *Table 4*.

Table 4. Relative reactivity of toluene, ethylbenzene and isopropylbenzene (Per Benzylic Hydrogen)

Radical	Temperature (°C)	PhCH ₃	PhCH ₂ CH ₃	PhCH(CH ₃) ₂	References
ROO·	30	1	8.1	2.3	This work
Cl·	40	1	2.5	5.6	15
(CH ₃) ₃ CO·	40	1	3.2	6.8	16
CH ₃ ·	65	1	4.1	13	17
C ₆ H ₅ ·	60	1	4.6	9.7	18
Polystyryl·	60	1	7.7 (6.3)	19 (16.8)	19 (19a)
Br·	40	1	17	37	20†
Cl ₃ C·	40	1	50	260	20

† Compare relative reactivities of 1.0: 24:50 found for bromine atoms at 80°²¹.

This Table gives data from the literature on the relative rates of abstraction of benzylic hydrogen atoms from toluene, ethylbenzene and isopropylbenzene by a number of free radicals and atoms. Our own data on hydrogen abstraction by peroxy radicals is also included. The three hydrocarbons have been compared on an "active" hydrogen basis. That is, the measured reactivities have been corrected to avoid statistical factors that would otherwise make toluene appear 50 per cent more reactive than ethylbenzene and three times as reactive as isopropylbenzene.

Although the experimental reactivities may depend somewhat on the technique that is employed in measuring them, the overall picture is quite clearly one in which the reactivity per benzylic hydrogen increases from primary (toluene), through secondary (ethylbenzene) to tertiary (cumene) for all radicals and atoms except the peroxy radical. Obviously the low reactivity of cumene must be connected with the fact that the reactivities towards peroxy radicals were not obtained by the competitive method which was used with all the other radicals. The peroxy radical reactivities are based on absolute rate measurements on reactions in which a primary benzylperoxy radical attacks toluene, a secondary 1-phenylethylperoxy radical attacks ethylbenzene and a tertiary cumylperoxy radical attacks cumene. That is, steric hindrance to the abstraction of the tertiary hydrogen atom by the tertiary peroxy radical is sufficient to outweigh the normal increase in the reactivity at a tertiary position. It is rather surprising that such a relatively large steric effect should be so easily observed when the only structural change in the radical has been the replacement of a hydrogen atom by a methyl group on a carbon which is separated by two oxygen atoms from the active end of the radical. One might well expect steric effects for the *t*-butoxy radical or trichloromethyl radical to be so much larger than for a cumylperoxy radical that cumene would be less reactive than ethylbenzene towards these radicals also, but this is clearly not the case. In this connection, there is data in the literature on the co-oxidation of cumene with ethylbenzene²² (and tetralin²³) which suggests that secondary peroxy radicals may attack cumene 2 or 3 times as fast as it is attacked by the tertiary cumylperoxy radical. However, this data is probably not very accurate and I think one should expect a cumene reactivity of more than just 4-6. That is, on the basis of the reactivity of ethylbenzene relative to toluene one might



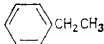




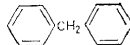
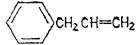
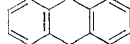

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expect that cumene should have a value rather similar to that for the polystyryl radical¹⁹.

The apparently anomalous reactivity of cumene towards peroxy radicals prompted us to measure the relative reactivities of these three hydrocarbons towards the same peroxy radical by a competitive procedure similar to that employed for the other radicals in this Table. Preliminary results using the tertiary peroxy radical from cumene as the attacking reagent give relative reactivities (per benzylic hydrogen) of 1:6:14 for toluene, ethylbenzene and cumene, respectively. Similar relative reactivities have been obtained with the primary peroxy radical from allylbenzene and the secondary peroxy radical from tetralin. The results suggest that the primary peroxy radical attacks a hydrocarbon nearly twice as fast as a secondary peroxy radical and the secondary peroxy radical attacks a hydrocarbon about four times as fast as a tertiary peroxy radical. This variation in the reactivities of peroxy radicals emphasizes the difficulties involved in trying to predict the behaviour of hydrocarbon mixtures on oxidation.

Table 5 gives some of our results on the relative reactivities (per active hydrogen) of some primary and secondary hydrocarbons towards the corresponding peroxy radicals.

Table 5. Relative reactivities towards peroxy radicals at 30°C
(Per Active Hydrogen)

	1		1.8
	8.1	$\text{CH}_2=\text{CHCH}_2\text{R}$	6.3
	15		21
	20		18
	30		63
	550		88

Data on hydrocarbons giving tertiary peroxy radicals have not been included because of the importance of steric effects in these reactions. For the primary and secondary hydrocarbons in Table 5 it seems likely that the relative reactivities should not be affected too much by the use of a different peroxy radical for each compound. The main points to note in this Table are that a phenyl group and a double bond have roughly similar activating effects on secondary hydrogen atoms, as can be seen by comparing ethylbenzene and 1-octene. This is also true of ring systems, e.g., cyclopentene and

indan, or cyclohexene and tetralin have similar reactivities. However, the reactivities of the ring compounds are about 3 or 4 times as great as those of the straight chain compounds. This phenomenon has been observed and commented on in several studies of hydrogen atom abstraction and various explanations have been proposed. The simplest explanation is that the secondary hydrogens in ethylbenzene have an unusually low reactivity because of steric inhibition of resonance in the incipient α -phenylethyl free radical which arises from an interaction between the CH_3 group and the *ortho*-hydrogens on the ring¹⁷. However, the importance of this interaction has probably been overemphasized and it certainly cannot play any significant role in olefins. Some of the increased reactivity of the ring compounds can be attributed to polar effects and to the increased stability of the radical¹⁵. (Thus substitution of a methyl group in the *para*-position increases the reactivity of a primary benzylic hydrogen in *p*-xylene by a factor of nearly two relative to toluene.) In addition to these effects, steric hindrance should be decreased by holding the β -carbon in a fixed position out of the way of the approaching radical. Furthermore, a cyclic compound will lose fewer degrees of freedom than a noncyclic compound on entering the rigid transition state²⁴ and this will tend to increase the pre-exponential factor.

When a secondary hydrogen is activated by two groups it has a very high reactivity, e.g., diphenylmethane, allylbenzene, indene and 9,10-dihydroanthracene. The high reactivity of 9,10-dihydroanthracene can be attributed to the fact that the hydrogen atoms are activated by two aromatic rings and each ring is further activated by an *ortho*-alkyl substituent.

Table 6 shows that most of these general observations on reactivities also apply to other radical abstraction reactions. For example, *p*-xylene is always more reactive than toluene (which can be attributed to polar effects and radical stabilization effects) and ethylbenzene and 1-olefins have rather similar reactivities. However, if we take the data in the literature at face value we might note that cyclopentene and cyclohexene are much less reactive towards methyl radicals and much more reactive towards bromine atoms than are indan and tetralin although towards phenyl and *t*-butoxy radicals the reactivities of all four hydrocarbons are fairly similar. The enhancement in reactivity for a compound containing two activating groups is much greater for peroxy radicals than for any of the other radicals. This is because the peroxy radical is relatively unreactive and this makes it very sensitive to small changes in the R—H bond strength.

Table 7 lists absolute rate constants for hydrogen atom abstraction from toluene at 40°C by seven radicals and two atoms. The radicals and atoms fall into different groups with preexponential factors (A factors) of about 10^7 – 10^8 l./mole sec for the radicals and 10^{10} – 10^{11} for the atoms. In each group the increase in the rate constant roughly parallels the increase in the strength of the new bond which is being formed between the attacking radical and hydrogen [D(R—H)]. There is a parallel decrease in the activation energies of the reactions.



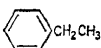




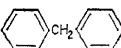
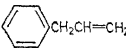
The rate constant for hydrogen abstraction by *t*-butoxy radicals was obtained directly by Dr. Carlsson by an interesting experimental method that is described below. This rate constant (8.3×10^3 l./mole sec at 40°C) was found to be in surprisingly good agreement with a rough indirect estimate

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of 2.6×10^3 l./mole sec which was derived from the relative rates of hydrogen atom abstraction by the *t*-butoxy radical and its β -scission to acetone and a methyl radical[†].

The radical-hydrogen bond strengths given in *Table 7* suggest that peroxy radicals will be fairly unreactive and therefore quite selective. They might

Table 6. Relative reactivities towards some free radicals
(Per Active Hydrogen)

Hydrocarbon	ROO [•] (30°)	(CH ₃) ₃ CO [•] (40°) ^{a,b}	C ₆ H ₅ [•] (60°) ^e	CH ₃ [•] (65°) ^f	Br [•] (40° ^g & 80° ^g)
	1	1	1	1	1
	1.8	1.5	1.5	1.2	2.6
	8.1	3.2	4.6	4.1	20
CH ₂ =CHCH ₂ R	6.3	6.1	3.3	6 ^g	45
	21	38	10	1 ^h	100 ^h -600 ^h
	15	19 ^c	8	8	36
	18	37	11	0.2 ^h	145
	20	16 ^c	12	12	25 ^h -36 ^h
	30	4.7	8	—	10
	63	7 ^d	10	—	28

^a Reference 16.

^b Reference 25.

^c Unpublished results from this laboratory.

^d Reference 26. There seems to be some doubt as to the accuracy of this number and some of the other values listed in this column^g. The values which have been chosen for this Table are those which were obtained by direct measurement, rather than indirectly from the acetone/*n*-butanol ratio.

^e Reference 18.

^f Reference 17.

^g Reference 28.

^h Reference 29.

ⁱ References 20 and 30.

^j Reference 21.

be expected to be slightly less selective than bromine atoms and a lot less selective than polystyryl radicals but more selective than methyl, *t*-butoxy or chlorine. *Table 8* shows that these predictions are only roughly fulfilled when toluene is compared with cyclohexane, a compound with a carbon-hydrogen bond strength which is at least 10 kcal/mole greater than the bond

[†] The rate constant for hydrogen abstraction from cyclohexane can be represented by $k_a = 10^{5.9} e^{-2440/RT}$, giving $k_a = 1.58 \times 10^4$ l./mole sec at 40°. Since cyclohexane is six times as reactive as toluene¹⁶ the rate constant for toluene is $1.58 \times 10^4/6 = 2.6 \times 10^3$ l./mole sec.

Table 7. Hydrogen atom abstraction from toluene at 40°C

Radical	Log k M ⁻¹ sec ⁻¹	Log A M ⁻¹ sec ⁻¹	E kcal/mole	$D(R-H)$ kcal/mole
Polystyryl ^a	-3.7	~ 6.9	~15	~ 80 ^b
Peroxy	-0.39	6.6	10 ^c	~ 88 ^d
Cyanomethyl ^e	0.11	7.1	10	79 ^f
Trichloromethyl ^e	0.15	8.3	11.6	96 ^g
Acetonyl ^e	0.21	6.7	9.3	92 ^h
Methyl ⁱ	2.3	7.5	7.4	103.8 ^j
<i>t</i> -Butoxy	3.7	7.6	5.6 ^k	104 ^l
Bromine	5.5 ^m -6.0 ⁿ	~10.5	7.2 ⁿ	86.5 ^o
Chlorine	9.6 ^p	~10.5	1-2 ^q	102.2 ^o

^a Reference 19. Both log A and E are very uncertain. The activation energy of 15 kcal/mole for this hydrogen abstraction process is based on an activation energy of 7.3 kcal/mole for chain propagation in the polymerization of styrene³¹ combined with a value of 7.8 kcal/mole for the activation energy for the chain transfer constant for toluene in styrene. The activation energy for chain transfer represents the difference in the activation energies for hydrogen abstraction from toluene and for the normal propagation step. The value of 7.8 kcal/mole has been chosen from the data of Gregg and Mayo¹⁹ as an average of their values of 10.1 kcal/mole for toluene (based on measurements at two temperatures) and 5.5 kcal/mole for ethylbenzene (based on measurements at three temperatures). The rate constant at 40° was calculated from the chain transfer constant at 60°¹⁹ and the propagation rate constant at this temperature³¹ using 15 kcal/mole as the activation energy for the hydrogen abstraction.

^b Assumed to be slightly less than $D(C_6H_5CH_2-H)$.

^c The measured activation energy for oxidation, i.e., $E_p-1/2E_t$, was found to be 9.4 kcal/mole. It was assumed that E_t had a value of 1.2 kcal/mole¹⁴.

^d Reference 32.

^e Reference 33.

^f Reference 34.

^g Reference 35.

^h Reference 36.

ⁱ Reference 37. Reaction in the gas phase. The data have been calculated using a value of 2.2×10^{10} l./mole sec³⁸ as the rate constant for combination of CH_3^* radicals in the gas phase (i.e., $2k_t$). The data of Cher *et al.*³⁹ gives log $k = 2.0$, log $A = 8.6$ and $E = 9.5$ for hydrogen atom abstraction by CH_3^* from the side chain of toluene.

^j Reference 40.

^k This activation energy is in good agreement with the value of 4.7 kcal/mole given by Wagner and Walling³⁷ which is based on an activation energy of 10.6 kcal/mole for the β -scission of *t*-butoxy radicals in chlorobenzene.

^l Reference 41.

^m Reference 20. This rate constant is based on the assumption that the tertiary hydrogen atoms of isobutane in the gas phase and 2,3-dimethyl butane in the liquid phase have an equal reactivity towards bromine atoms.

ⁿ Reference 42. Data in the gas phase which have been criticized⁴⁸.

^o Reference 4.

^p Reference 15. This rate constant is based on the assumption that cyclopentane has the same reactivity towards chlorine atoms in the gas phase as in non-complexing solvents.

^q Estimated to be in this range from reference 44.

strength of the benzylic hydrogen's in toluene. That is, although peroxy radicals are slightly less selective than bromine atoms and much less selective than methyl, *t*-butoxy and chlorine they appear to be more selective than the polystyryl radical. The relative reactivities in this Table emphasize the point that a single scale of reactivities towards free radicals does not exist.

While discussing different radicals it is interesting to compare some of the

Table 8. Reactivity of cyclohexane relative to toluene (Per Active Hydrogen)

Radical	Temperature (°C)	Relative reactivity	References
Polystyryl	60	0.048 (0.105)	19 (19a)
Peroxy	65	~0.014	46
Methyl	100	1.6 (0.45)	47 (47a)
<i>t</i> -Butoxy	40	1.5	16
Bromine	80	0.003	21
Chlorine	40	1.9	15

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available data on hydrogen abstraction from atoms other than carbon. One way of doing this is to compare toluene with other compounds of the type C_6H_5XH , such as phenol and aniline. This comparison is shown in Table 9.

Table 9. Relative reactivities of C_6H_5XH
(Per Active Hydrogen)

Compound	ROO· (65°) ^a	$(CH_3)_3CO·$ (122°) ^e	$C_6H_5·$ (60°) ^f	Polystyryl· (60°)
$C_6H_5CH_3$	1	1	1	1
$C_6H_5NH_2$	—	—	—	24 ^g
C_6H_5OH	1.1×10^{4b}	5×10^3	—	336 ^h
$(C_6H_5)_2CH_2$	30 ^c	—	7.7	27 ⁱ
$(C_6H_5)_2NH$	4.4×10^{4d}	—	25.5	—

^a Based on a value of k_p for toluene = 1.35 l./mole sec at 65°C⁴⁴.

^b The rate constant for the reaction of polystyryl peroxy radicals with phenol at 65°C given in ref.⁴⁸, i.e., 2.3×10^3 l./mole sec, was based on an estimated rate constant of 7.95×10^3 l./mole sec for the reaction of these peroxy radicals with 2,6-di-*t*-butyl-4-methyl phenol. We have now revised the latter rate constant to 17.8×10^3 l./mole sec as a result of our absolute rate measurements on oxidizing styrene⁴⁴. This gives an absolute rate constant of 5×10^3 l./mole sec for phenol and hence a rate constant of 1.1×10^4 relative to one hydrogen atom of toluene if it is assumed that benzylperoxy and styrylperoxy radicals attack toluene at equal rates.

^c At 30°C⁴⁴.

^d Based on an absolute rate constant of 2.0×10^4 l./mole sec for the reaction with polystyryl peroxy radicals⁴⁹.

^e Based on ratios of the rate constants at 122° for hydrogen abstraction to β -scission of 0.116 for toluene⁴⁹ per active hydrogen and 540 for phenol in CCl_4 ⁵¹.

^f Reference 18.

^g Reference 52.

^h Reference 53.

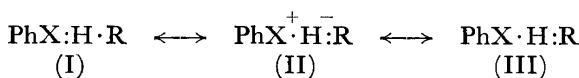
ⁱ Reference 19.

The results for the two oxy radicals, both of which have fairly high electron affinities, show that a hydrogen atom is removed from oxygen or nitrogen at a rate which is several orders of magnitude greater than its rate of removal from carbon. The differences between oxygen, nitrogen and carbon are much less for non-polar radicals whether they are reactive like phenyl or unreactive like polystyryl.

The importance of polar effects in oxy radical abstraction reactions is emphasized by the influence that *meta* and *para* substituents have on the reaction rates. Their effect can be roughly correlated by means of the Hammett equation

$$\log k/k_0 = \rho\sigma$$

where k and k_0 are the rate constants for the substituted and unsubstituted compounds, respectively. σ is a substituent constant that depends on the substituent but not on the reaction. The sign and magnitude of ρ gives a measure of the sensitivity of the reaction to polar effects. It has been found that most hydrogen atom abstraction reactions can be better correlated by Brown's electrophilic substituent constants, σ^+ , than by the normal Hammett substituent constants⁵⁴. This fact in itself emphasizes the importance of polar effects in hydrogen abstraction reactions, i.e. it emphasizes the importance of dipolar contributions to the transition state (structure II).



K. U. INGOLD

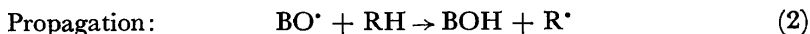
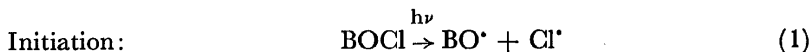
The negative values of ρ for all the reactions listed in *Table 10* mean that they are all facilitated by electron donating substituents on the ring. There is clearly a much larger polar effect for the oxy radical abstraction from phenols† than for the abstraction from hydrocarbons. Rates of hydrogen atom abstraction by radicals of low electron affinity, such as the phenyl radical, are almost uninfluenced by polar effects¹⁸.

Table 10. Correlation with the Hammett $\rho\sigma^+$ equation

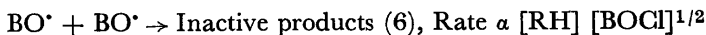
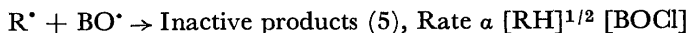
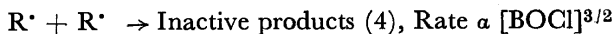
ROO [•]	Temperature (°C)	ρ	References
C ₆ H ₅ CH ₃	90	-0.7	54, 55
C ₆ H ₅ CH(CH ₃) ₂	60	-0.4	56
C ₆ H ₅ OH	65	-1.5	54
(C ₆ H ₅) ₂ NH	65	-0.9	57
(CH ₃) ₃ CO [•]			
C ₆ H ₅ CH ₃ ^a	40	-0.7	58
C ₆ H ₅ OH	122	-1.2	51

^a Our own correlation of substituent effects with σ^+ constants for this reaction contrasts with the earlier work of Gilliom and Ward⁹.

Turning now to the reactions of alkoxy radicals we find that although the literature contains a very large number of relative rate constants for hydrogen atom abstraction by *t*-alkoxy radicals there are no reliable absolute rate constants. We have been able to obtain some absolute values by a kinetic study of the photochemically initiated chain reaction between *t*-butyl hypochlorite and toluene. In this reaction *t*-butoxy radicals are chain carriers. The initiation and propagation steps can be represented by:



There are three possible chain terminating processes which all lead to different kinetic expressions for the overall rate of reaction, i.e.



† This may also be true for the simple anilines since ρ will almost certainly be larger for them than for the diphenylamines (cf. substituted toluenes and cumenes with peroxy radicals in *Table 10*).

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The reaction was followed by measuring the temperature rise which occurred at the centre of a cylindrical cell when the initiating light was switched on. The cell has a volume of about 30 ml. and at its centre no heat is lost for the first 10–20 sec. As long as the conditions remain adiabatic the temperature rise gives a direct measure of the reaction rate. The temperature is measured with a thermocouple. The rate of reaction can be obtained either indirectly from a knowledge of the heat of reaction and the heat capacities of the reactants or, directly, by a calibration of the extent of reaction against the rise in temperature.

Table 11. Radical combination in solution at 20–30°C

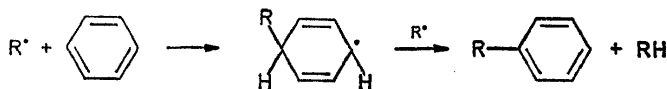
<i>Radical</i>	<i>Rate Constant (2k_t) × 10⁻⁸ (M⁻¹ sec⁻¹)</i>	<i>References</i>
H•	130	61, 62
Br•	100	63
HO•	60	61, 62
C ₆ H ₅ O•	56	64
(CH ₃) ₃ CO•	2.1	—
Cl ₃ C•	1.0	65, 66, 67 ^a
Polystyryl•	0.048 ^b	31

^a Tedder and Walton⁶⁸ give a value of 3×10^{10} l./mole sec at 175°C in the gas phase.

^b Combination and disproportionation.

Using light of a suitable wavelength and under carefully controlled experimental conditions it has been found that the rate of reaction of toluene with the hypochlorite in CCl₄ is proportional to the square root of the light intensity. Chain termination is, therefore, a bimolecular reaction. The rate is also roughly proportional to the square root of the hypochlorite concentration and to the first power of the toluene concentration in the ranges of concentration that were studied. The main chain termination process must, therefore, involve two *t*-butoxy radicals (reaction 6) and reaction 2 must be the rate controlling propagation step.

Under certain experimental conditions, a competing first order chain terminating process can partly or completely dominate the reaction. At the present time, it seems most likely that this process is due to the addition of a radical to an aromatic ring. This will give an unreactive cyclohexadienyl radical which apparently cannot readily continue the chain but can react with a second radical to end a second chain. By placing a rotating sector



between the light source and the reaction vessel the absolute rate constants for propagation and termination have been determined. For toluene in carbon tetrachloride at 24°C k_p is about 5×10^8 l./mole sec and $2k_t$ is about 2.1×10^8 l./mole sec. At first sight the termination rate constant for

the interaction of two *t*-butoxy radicals seemed to be surprisingly large† so it was reassuring to find that Batt and Benson⁶⁰ had estimated a value of about 1.6×10^8 l/mole sec from their study of the pyrolysis of di-*t*-butylperoxide in the gas phase.

The termination rate constant for *t*-butoxy radicals is compared in *Table 10* with a few representative rate constants for atom and radical combination reactions in solution. The rate constants for atoms and simple radicals such as ·OH are those of diffusion controlled processes, i.e., these species react with one another at every encounter. The larger radicals do not necessarily react at every encounter⁶⁹ and the rate constant tends to decrease as the radical becomes more complex. The high rate constant for the combination of phenoxy radicals may be connected with the extensive delocalization of the unpaired electron which gives a significant spin density at the *ortho*- and *para*- positions of the ring as well as on the oxygen atom⁷⁰. There are, therefore, a large number of different ways in which two phenoxy radicals can couple⁷¹. As might be expected, sterically hindered di- and tri-alkyl substituted phenoxy radicals couple at a significantly smaller rate than the unsubstituted radicals.⁷²

It is a great pleasure for me to thank Dr. J. A. Howard for his many contributions to this lecture. I should also like to acknowledge the contributions of Dr. I. T. Brownlie, Dr. D. J. Carlsson, Dr. B. R. Kennedy, and Dr. B. S. Middleton.

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† cf. Traylor's recent work on the oxidation of cumene⁷, which suggests that bimolecular termination between cumyloxy radicals is not an important chain termination process even though cumyloxy radicals may be fairly important chain carriers under certain conditions.

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