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Reactivity of hydrocarbons and their individual C – H bonds with peroxy radicals

W W Pritzkow, V Ya Suprun

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Abstract. The possibility of determining relative rates of oxidation of hydrocarbons and of their individual C – H bonds by competitive oxidation has been demonstrated. Data on the reactivities of C – H bonds of various hydrocarbons are discussed. Information about relative reactivities of the C = C double bonds of cyclic alkenes and of some styrene derivatives is presented. The bibliography includes 42 references.

I. Introduction

Competitive reactions have been widely used to obtain data concerning the relative rates of chlorination of various hydrocarbons.[1–6] If these data and also the compositions of the isomeric chloro-derivatives formed from the individual hydrocarbons are known, it is possible to calculate the relative reactivities of individual C – H bonds with chlorine atoms.

In the chlorination of mixtures of hydrocarbons only one radical capable of attacking C – H bonds is present, namely the chlorine atom. In the liquid-phase oxidation of a mixture of two hydrocarbons, individual C – H bonds may be attacked by at least two different peroxy radicals, each derived from one of the starting hydrocarbons (Scheme 1). It has been assumed that

Scheme 1

$$R^1\text{—H} + R^1\text{—O—O}^{\cdot} \xrightarrow{k_{11}} \dot{R}^1 + R^1\text{—O—O—H}$$
$$R^1\text{—H} + R^2\text{—O—O}^{\cdot} \xrightarrow{k_{12}} \dot{R}^1 + R^2\text{—O—O—H}$$
$$R^2\text{—H} + R^1\text{—O—O}^{\cdot} \xrightarrow{k_{21}} \dot{R}^2 + R^1\text{—O—O—H}$$
$$R^2\text{—H} + R^2\text{—O—O}^{\cdot} \xrightarrow{k_{22}} \dot{R}^2 + R^2\text{—O—O—H}$$

$k_{11} : k_{12} = k_{21} : k_{22} = k_1 : k_2$. Here k_1 and k_2 are the rate constants for the oxidation of the hydrocarbons R^1H and R^2H, respectively. In competitive oxidation correct data for k_1/k_2 can be obtained only if the relative reaction rates of peroxy radicals with different C – H bonds are independent of the nature of the attacking radical.[7] If the cooxidation is accomplished in the presence of a large excess of an individual hydroperoxide then all peroxy radicals formed from the starting hydrocarbons will react with it (Scheme 2).[8]

Scheme 2

$$R^1\text{—O—O}^{\cdot} + C\text{—O—O—H} \longrightarrow R^1\text{—O—O—H} + C\text{—O—O}^{\cdot}$$
$$R^2\text{—O—O}^{\cdot} + C\text{—O—O—H} \longrightarrow R^2\text{—O—O—H} + C\text{—O—O}^{\cdot}$$
$$R^1\text{—H} + C\text{—O—O}^{\cdot} \xrightarrow{k_1} \dot{R}^1 + C\text{—O—O—H}$$
$$R^2\text{—H} + C\text{—O—O}^{\cdot} \xrightarrow{k_2} \dot{R}^2 + C\text{—O—O—H}$$
$$\dot{R}^1 + O_2 \longrightarrow R^1\text{—O—O}^{\cdot}$$
$$\dot{R}^2 + O_2 \longrightarrow R^2\text{—O—O}^{\cdot}$$

In this case the relative reactivities of hydrocarbons and their individual C – H bonds with respect to the peroxy radical derived from the added hydroperoxide can be calculated by the methods used in chlorination.[8,9]

Table 1 presents the relative rates of oxidation of certain aromatic hydrocarbons in the presence of different individual

Table 1. The relative rates of reaction of various peroxy radicals with aromatic alkyl-substituted hydrocarbons.

Radical	Hydrocarbon			
	toluene	ethyl-benzene	cumene	tetralin
$Bu^t\text{—O—O}^{\cdot}$	0.23	0.91	1	9.1
$Pr^iC_6H_4\text{—O—O}^{\cdot}$	0.17	1.00	1	9.2
$C_2H_5C(C_6H_5)(CH_3)\text{—O—O}^{\cdot}$	0.33	1.47	1	8.7
$Bu^n\text{—O—O}^{\cdot}$	0.25	1.25	1	16.0
$Bu^s\text{—O—O}^{\cdot}$	0.25	1.25	1	10.5
$\alpha\text{-}C_{10}H_{12}\text{—O—O}^{\cdot}$ [a]	0.20	1.00	1	12.5

[a] The α-tetralinylperoxy radical.

W W Pritzkow, V Ya Suprun Institut für Technische und Makromolekulare Chemie der Martin-Luther-Universität, Geusaer Strasse, D-06217 Merseburg, Germany. Fax (49-3461) 46 20 73

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Table 2. The relative rates of oxidation of the R^1H and R^2H pairs of hydrocarbons as a function of their initial molar ratio.

R^1H	R^2H	k_1/k_2 for different molar ratios $R^1H:R^2H$				
		25:75	30:70	40:60	50:50	60:40
Cyclodecane	Cumene	0.60	0.62	0.60	0.59	0.48
Cyclooctane	"	0.79	0.75	0.74	0.72	0.72
	Cycloheptane	1.80	2.05	2.14	1.94	2.41
cis-Decalin	Cumene	0.67	0.72	0.67	0.66	0.63
cis-Pinane	"	1.55	1.52	1.62	1.49	1.64
	Cycloheptane	6.27	6.18	7.48	7.52	7.98
	Cyclooctane	3.94	3.58	3.25	3.29	3.39
Diphenylmethane	Cumene	1.86	1.97	1.69	1.97	1.82
1,2-Diphenylethane	"	0.68	0.58	0.73	0.76	0.74
Tetralin	"	4.44	5.14	6.19	5.06	5.31
p-Xylene	"	0.43	0.47	0.53	0.46	0.42
p-Di(*tert*-butyl)benzene	"	0.19	0.18	0.20	0.19	0.18
1,1-Diphenylethane	"	1.39	1.35	1.30	1.42	1.39

hydroperoxides. The data confirm the assumption that the relative rates do not depend strongly on the nature of the attacking peroxy radical.[8]

The ratios of oxidation rates of hydrocarbons R^1H and R^2H (i.e. their relative reactivities with peroxy radicals) were calculated from the equation

$$\frac{k_1}{k_2} = \frac{\Sigma[R^1OH][R^2H]}{\Sigma[R^2OH][R^1H]}.$$

Binary mixtures of hydrocarbons were oxidised at molar ratios ranging from 25:75 to 60:40, temperatures of 90–110 °C, and oxygen absorptions up to 10 mmol per 100 mmol of the sum of both hydrocarbons. After oxidation was complete, the reaction mixture was reduced with lithium aluminium hydride, and the alcohols formed were analysed gas chromatographically. For all the mixtures investigated k_1/k_2 ratios identical within the limits of error were obtained (Table 2). This demonstrates the validity of the assumption that the relative rates of reaction of peroxy radicals with hydrocarbons are independent of the nature of the radical. One must take into account the fact that at high concentrations of R^1H the fraction of its peroxy radical $R^1OO^\bullet$ in the reaction mixture must be higher than at low concentrations.

The independence of the relative rates of oxidation of a mixture of two hydrocarbons of a given initial ratio demonstrates that the relative rates of the individual C–H bonds with attacking peroxy radicals are independent of the nature of the latter. If this is the case, the rates of oxidation relative to any other partner can be calculated indirectly by employing the oxidation of two pairs of hydrocarbons (e.g. $R^1H + R^3H$ and $R^2H + R^3H$) in accordance with the equation

$$\frac{k_1}{k_2} = \frac{k_1/k_3}{k_2/k_3}.$$

The results of such calculations do agree with data obtained by direct cooxidations (of R^1H and R^2H) (Table 3). This constitutes yet another confirmation of the independence of the relative rates of oxidation of various hydrocarbons (or different C–H bonds) of the nature of the attacking peroxy radicals.

Evidently, it is necessary to select a certain hydrocarbon as a standard and to refer to its oxidation rate the oxidation rates (reactivities) of all other compounds. In the present review, the highly reactive tertiary C–H bond of cumene was chosen as the standard. This means that in most cases cumene was used as the second component of the starting mixture in the cooxidation experiments. Cyclooctane can also be used as a convenient reference hydrocarbon; its reactivity is relatively high, and only one alcohol (cyclooctanol) is formed from its oxidation products on reduction with lithium aluminium hydride.

Table 3. A test of the possibility of the indirect determination of the relative rates of oxidation of the $R^1H + R^2H$ pairs of hydrocarbons under the conditions of their cooxidation.

$R^1H + R^2H$	k_1/k_2	
	directly determined	indirectly determined
cis-Pinane + cycloheptane	7.09	–
Cumene + cycloheptane	2.24	–
cis-Pinane + cumene	2.29	2.29
cis-Pinane + cyclooctane	3.52	–
Cumene + cyclooctane	1.40	–
cis-Pinane + cumene	2.29	2.51
Ethylbenzene + indane	0.18	–
Cumene + indane	0.25	–
Ethylbenzene + cumene	0.84	0.72
3-Phenylbutane + cumene	0.18	–
n-Butylbenzene + cumene	0.44	–
3-Phenylbutane + n-butylbenzene	0.35	0.41
2-Phenylbutane + cumene	0.51	–
n-Propylbenzene + cumene	0.57	–
2-Phenylbutane + n-propylbenzene	0.85	0.89

II. Reactivities of alkylbenzenes and their activated α-C–H bonds

The reactivities of activated (α-position to the benzene ring) and nonactivated C–H bonds of alkylbenzenes have been investigated in detail.[7, 10–12] Table 4 presents data on the relative rates of oxidation of alkyl-substituted benzene and also on the relative reactivities of their individual C–H bonds. Evidently, the reactivities of both the primary and secondary C–H bonds at the α-position in most cases do not depend significantly on the presence of additional alkyl substituents in the benzene ring. A similar conclusion can also be reached concerning the reactivities of tertiary α-C–H bonds. Table 4 shows that the reactivities of the α-C–H bonds increase in the sequence primary (0.08) < secondary (0.29) < tertiary (0.82) in the ratio of approximately 1:3:10 (Table 5). The mean deviation of the reactivity data increases in the same sequence. The reason for this is obviously the steric hindrance caused by the alkyl groups linked to the α-carbon atoms.

Table 4. The relative rates of oxidation of aromatic alkyl-substituted hydrocarbons and the relative reactivities of their α-C–H bonds.

Hydrocarbon	Rate of oxidation (rel. units)	Reactivity of C–H bonds (rel. units)[a]		
		primary	secondary	tertiary
Toluene	0.189 ± 0.012	0.06	–	–
p-(*tert*-Butyl)-toluene	0.189 ± 0.003	0.06	–	–
o-Xylene	0.509 ± 0.009	0.08	–	–
m-Xylene	0.411 ± 0.020	0.07	–	–
p-Xylene	0.460 ± 0.019	0.08	–	–
Mesitylene	0.674 ± 0.043	0.07	–	–
Durene	1.472 ± 0.080	0.12	–	–
Ethylbenzene	0.805 ± 0.014	–	0.42	–
p-Ethyltoluene	1.89 ± 0.07	0.13	0.75	–
n-Propyl-benzene	0.573 ± 0.047	–	0.29	–
n-Butyl-benzene	0.436 ± 0.030	–	0.22	–
Isobutyl-benzene	0.494 ± 0.027	–	0.16	–
3-Methyl-1-phenylbutane	0.618 ± 0.021	–	0.26	–
3-Methyl-1-*p*-tolylbutane	0.866 ± 0.045	0.06	0.32	–
Cumene	1	–	–	1
p-Isopropyl-toluene	1.875 ± 0.015	0.13	–	1.50
p-Isobutyltoluene	0.81 ± 0.02	0.08	0.23	–
2-Phenylbutane	0.507 ± 0.003	–	–	0.51
3-Phenylpentane	0.184 ± 0.003	–	–	0.18
Diphenylmethane	1.861 ± 0.052	–	–	–
2-*p*-Tolylbutane	1.316 ± 0.086	0.13	–	0.93
Phenyl-*p*-tolyl-methane	2.06 ± 0.14	0.05	–	–
Bis(*p*-tolyl)-methane	2.235 ± 0.067	0.06	–	–
Fluorene	4.35 ± 0.13	–	–	–
1,2-Diphenyl-ethane	0.695 ± 0.033	–	0.17	–
1,2-Bis(*p*-tolyl)-ethane	1.367 ± 0.078	0.06	0.25	–
1,3-Diphenyl-propane	0.645 ± 0.022	–	0.17	–
1,1-Diphenyl-ethane	1.370 ± 0.021	–	–	–
1,1-Diphenyl-propane	0.626 ± 0.015	–	–	–
1,1-Diphenyl-butane	0.524 ± 0.022	–	–	–
Indane	3.973 ± 0.087	–	–	–
Tetralin	5.23 ± 0.28	–	–	–

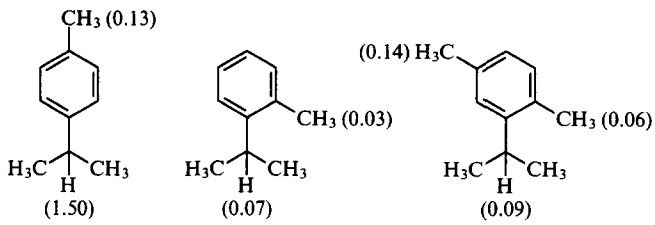
[a] The average reactivities of the C–H bonds are 0.083 ± 0.008 for the primary bond, 0.294 ± 0.051 for the secondary bond, and 0.82 ± 0.23 relative units for the tertiary bond.

Table 5. Relative reactivities of the C–H bonds[a] nonactivated and activated by one phenyl group.

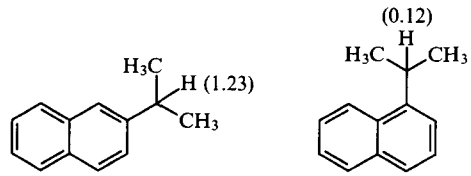
C–H bond	Nonactivated	Activated	Activation factor
Primary	0.00133	0.083	64
Secondary	0.011	0.29	26
Tertiary	0.10	0.82	8

[a] With respect to the tertiary C–H bond of cumene.

It is known from the literature[13–15] that *ortho*-substituted cumene derivatives are very difficult to oxidise; this is caused by steric hindrance of the coplanar arrangement of the methyl groups of the intermediate 2-arylisopropyl radical and the *ortho*-substituted benzene ring. Our data on the relative reactivities of the tertiary C–H bonds of two cumene derivatives containing *ortho*-methyl groups confirm this qualitative conclusion (the relative reactivities of the C–H bonds are indicated in brackets in the formulae presented).[12]



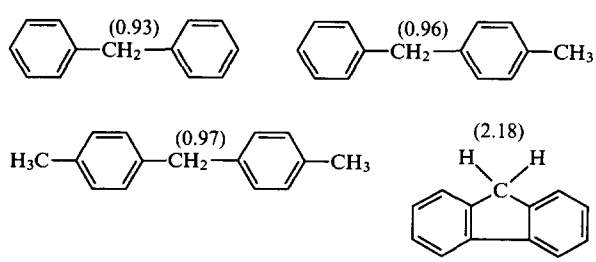
A similar decrease in reactivity is also observed in the case of α-isopropyl naphthalene,[12] which can be regarded as an *ortho*-substituted cumene derivative.

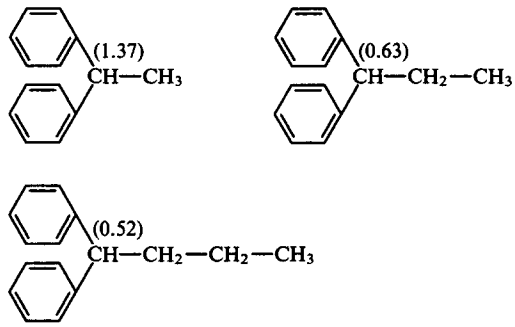


The tertiary C–H bonds in *ortho*-substituted cumenes and the inactivated tertiary C–H bonds have approximately the same reactivities in relation to the tertiary C–H bond of cumene (on average 0.10 ± 0.03):

Compound	Relative reactivity of the tertiary C–H bond
Isobutylbenzene	0.17
p-Isobutyltoluene	0.12
3-Methyl-1-phenylbutane	0.07
3-Methyl-1-*p*-tolylbutane	0.04

Only the question of the reactivities of the C–H bonds activated by a single benzene ring has been discussed hitherto, but Table 4 also contains data on diphenylmethane derivatives and 1,1-diphenylalkanes, i.e. hydrocarbons possessing C–H groups activated by two phenyl groups.





From the data presented in the formulae shown above, it follows that the second phenyl group induces only a small additional activation of the secondary C—H bonds and influences even less the reactivity of the tertiary C—H bonds. The cause of the influence of the phenyl groups on the reactivities of α-C—H groups is known to be the stabilisation of the corresponding carbon radicals and of the transition states during their formation. A prerequisite to such mesomeric stabilisation is the coplanar arrangement of the benzene rings with all the substituents at the α-carbon atom. Since two benzene rings at one radical (sp^2) carbon atom cannot be located in one plane, it follows that the second phenyl group is unable to induce a significant additional activation of the α-C—H bonds. On the other hand, if both benzene rings are forcibly accommodated in one plane, as in the case of fluorene, then the reactivity of α-C—H bonds is indeed increased (2.18).

III. Relative reactivities of aliphatic C—H bonds

Numerous studies of the cooxidation of n-alkanes with cumene carried out in our laboratory made it possible to determine their relative oxidation rates and also the reactivities of their individual C—H bonds (Table 6).[16] The secondary C—H bonds of n-alkanes are appreciably more reactive than the primary bonds in oxidation as well as in other radical substitution reactions.[5] The reactivity of the secondary C—H bond is lower the more remote its position from the end of the hydrocarbon chain. In the oxidation of normal paraffins a side reaction takes place, the intramolecular hydrogen transfer in the intermediate peroxy radicals, which results in the formation of up to 20% of bifunctional products.[16–18] In the case of branched paraffins, the contribution of the intramolecular H-transfer is much higher, so that the determination of relative reactivities of such hydrocarbons and their C—H bonds is difficult. In the oxidation of aromatic compounds containing bulky alkyl groups, the non-activated C—H bonds are also attacked by peroxy radicals. It follows from Table 7 that the ratios of the reactivities of the primary, secondary, and tertiary aliphatic C—H bonds in alkanes and alkylaromatic hydrocarbons are $0.0013:0.011:0.10 \approx 1:8.5:80$. This was in fact to be expected, since the reactivities of aliphatic C—H bonds increase in precisely this sequence in all radical substitution reactions.

The reactivities of activated and nonactivated C—H bonds are collated in Table 5. The ratio of these quantities constitutes the activation factor. The data presented in Table 5 show that the activating effect of the phenyl group at the α-position decreases in the sequence primary > secondary > tertiary C—H bond. The cause is probably steric hindrance of the coplanar arrangement of the alkyl groups linked to the α-carbon atom with the atoms of the benzene ring. The coplanar arrangement gives rise to strain which increases with the increase in the number and the size of the alkyl groups. In indane and tetralin the groups linked to the α-carbon atoms are located in approximately the same plane as the benzene ring, and this causes an increase in the reactivities of their α-C—H bonds.

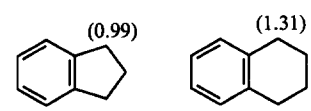


Table 6. Relative rates of oxidation of n-alkanes and relative reactivities of their C—H bonds.

n-Alkane	Rate of oxidation [b]	x [a]	Reactivity [b] of one C—H group (rel. units) in position:			
			1	2	3	4–x [c]
n-Nonane	0.181±0.005	5	0.0016	0.015	0.012	0.010
n-Decane	0.181±0.002	5	0.0014	0.014	0.011	0.009
n-Undecane	0.179±0.004	6	0.0010	0.013	0.010	0.008
n-Dodecane	0.200±0.011	6	0.0015	0.013	0.010	0.008
n-Tridecane	0.183±0.010	7	0.0006	0.011	0.009	0.007
n-Tetradecane	0.194±0.010	7	0.0009	0.011	0.009	0.007
n-Pentadecane	0.202±0.003	8	0.0008	0.010	0.008	0.007
n-Hexadecane	0.207±0.011	8	0.0007	0.009	0.007	0.007

[a] Position most remote from the chain end. [b] With respect to the tertiary C—H bond of cumene. [c] Mean value for the positions 4 to x. The corresponding secondary alcohols could not be separated by capillary gas chromatography.

Table 7. The relative reactivities of the nonactivated C—H bonds in n-alkanes and in aromatic alkyl-substituted compounds.

Hydrocarbon	Relative reactivity of one C—H bond [a,b] (rel. units)			
	primary	secondary		tertiary
		position	value	
n-Nonane	0.0016	2	0.015	–
		3	0.012	
n-Decane	0.0014	2	0.014	–
		3	0.011	
n-Undecane	0.0010	2	0.013	–
		3	0.010	
n-Dodecane	0.0015	2	0.013	–
		3	0.010	
n-Tridecane	0.0006	2	0.011	–
		3	0.009	
n-Tetradecane	0.0009	2	0.010	–
		3	0.009	
n-Pentadecane	0.0008	2	0.010	–
		3	0.008	
n-Hexadecane	0.0007	2	0.009	–
		3	0.007	
1-Phenylpropane	–	2	0.011	–
1-Phenylbutane	–	2	0.009	–
		3	0.011	
2-Phenylbutane	–	3	0.011	–
2-*p*-Tolylbutane	–	3	0.013	–
3-Phenylpentane	–	2	0.013	–
3-Methyl-1-phenylbutane	–	2	0.023	0.07
3-Methyl-1-*p*-tolylbutane	–	2	0.010	0.04
Ethylbenzene	0.0020	–	–	–
n-Propylbenzene	0.0015	–	–	–
n-Butylbenzene	0.0018	–	–	–
Isobutylbenzene	–	–	–	0.17
p-Isobutyltoluene	–	–	–	0.12

[a] With respect to the tertiary C—H bond of cumene. [b] The average reactivities of one C—H bond are 0.00125±0.00014 for the primary bond, 0.011±0.001 for the secondary bond, and 0.10±0.03 relative units for the tertiary bond.

IV. Ring strain effects in the oxidation of cycloalkanes and their derivatives

The change in the hybridisation of one carbon atom of a carbocyclic compound from sp^3 to sp^2 is always associated with a change of the ring strain, which depends on the size of the ring.[19] Therefore the rates of the reactions in which cycloalkyl radicals are formed are determined to a large extent by the ring size.[20] A similar dependence is characteristic also for the radical bromination (but not for the chlorination) of cycloalkanes.[4]

The cooxidation of cycloalkanes and their methyl-, ethyl-, and phenyl-substituted derivatives with cumene made the determination of the relative reactivities of their individual C–H bonds possible (Table 8).[21,22] As is to be expected,[4,19,20] the reactivities of the C–H bonds in six-membered rings are especially low, whilst those in five-, seven-, and eight-membered rings are much higher. In cyclododecane, the C–H bonds have about the same reactivity as the secondary C–H bonds in normal paraffins (Table 6).

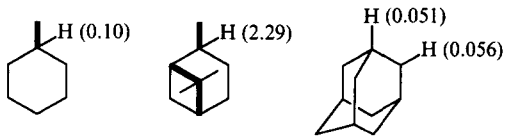
Table 8. Dependence of the reactivities of the C–H bonds of cycloalkane derivatives on ring size.

Number of carbon atoms in the ring	Relative reactivity[a] of one C–H bond (rel. units)			
	secondary C–H bond in cyclo-alkanes	tertiary C–H bond in methyl-cyclo-alkanes	tertiary C–H bond in ethyl-cyclo-alkanes	tertiary C–H bond in phenyl-cyclo-alkanes
4	–	–	–	1.1
5	–	–	0.128	5.3
6	–	0.102	0.072	0.8
7	0.032	0.261	0.122	1.5
8	0.045	0.258	0.148	2.6
9	0.038	0.115	0.128	–
10	0.029	–	–	–
11	0.028	–	–	–
12	0.011	–	–	–

[a] With respect to the tertiary C–H bond of cumene.

It must be expected that ring strain effects observed in saturated carbocyclic compounds also occur in cycloalkenes and benzocycloalkenes and that the reactivity of the C–H bonds at the α-position to the double bond in cycloalkenes and benzocycloalkenes depends on the ring size. Such dependence has indeed been observed in the oxidation of cycloalkenes.[23] This also gives an explanation for the particularly high reactivity of indane and tetralin.[7]

Ring strain effects should also determine ther reactivities in the oxidation of bicyclic and tricyclic compounds. The cooxidation of *cis*-pinane and cumene yields an unexpected result: the tertiary C–H bond in position 2 is 22 times more reactive than the analogous tertiary C–H bond of methylcyclohexane.[24] It is even more reactive than the tertiary C–H bond of cumene.



The tertiary C–H bonds at the bridgehead carbon atoms of *cis*-pinane do not react with peroxy radicals in accordance with Bredt's rule.[24,25] In adamantane both the secondary and the tertiary C–H bonds have approximately the same reactivities as the corresponding bonds in n-paraffins and in alkylaromatic hydrocarbons (Table 7).

V. Reactivities of the equatorial and axial C–H bonds in cyclohexane derivatives

The rates of oxidation of the *cis*- and *trans*-isomers of decalin[26] and dimethyl cyclohexanes[27] are substantially different. Obviously, tertiary C–H bonds in the equatorial position react more readily with peroxy radicals than similar C–H bonds in the axial position.[28] The cooxidation of the isomeric dimethyl cyclohexanes and of the decalins made it possible to determine the relative reactivities of the tertiary and secondary C–H bonds in these hydrocarbons (Table 9).[29] We were able to calculate separately the reactivities of the equatorial and axial C–H bonds from the overall reactivities of the tertiary C–H bonds (Table 10).

Table 9. Reactivities of the *cis*- and *trans*-isomers of dimethylcyclohexane and decalin and of their individual C–H bonds relative to cumene.

Compound	Relative reactivity (rel. units)		
	overall	tertiary C–H bond	secondary C–H bond[a]
cis-1,2-Dimethylcyclohexane	0.541	0.227	0.0087
trans-1,2-Dimethylcyclohexane	0.217	0.064	0.0113
cis-1,3-Dimethylcyclohexane	0.344	0.150	0.0059
trans-1,3-Dimethylcyclohexane	0.545	0.239	0.0085
cis-1,4-Dimethylcyclohexane	0.556	0.245	0.0082
trans-1,4-Dimethylcyclohexane	0.267	0.108	0.0065
cis-Decalin	0.671	0.262	0.0094
trans-Decalin	0.235	0.056	0.0078

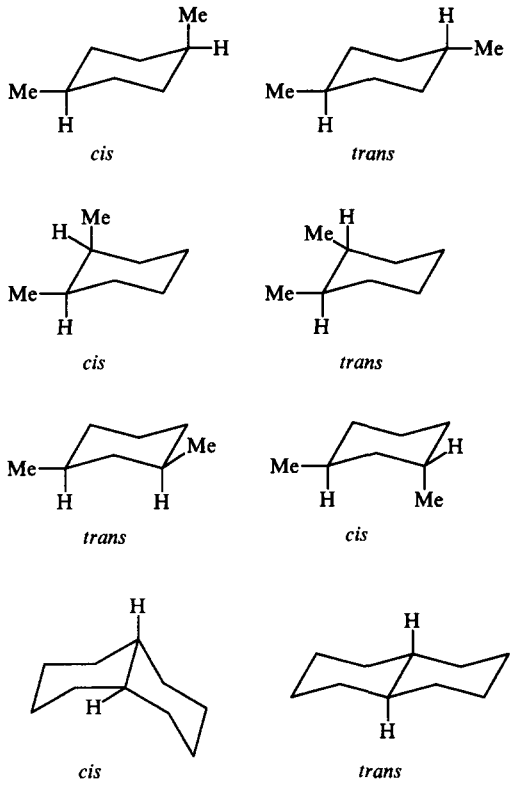
[a] The average reactivity is 0.0083 ± 0.0006 rel. units.

Table 10. Relative reactivities of axial and equatorial C–H bonds in cyclohexane derivatives.

Compound	Overall reactivity of tertiary C–H bond	Equation for the calculation of the reactivity of an individual C–H bond[a]	Reactivity of one tertiary C–H bond (rel. units)[b]	
			a	e
cis-1,2-Dimethylcyclohexane	0.227	a + e = 0.454	0.064	0.390
trans-1,2-Dimethylcyclohexane	0.064	2a = 0.128		
cis-1,3-Dimethylcyclohexane	0.150	2a = 0.300		
trans-1,3-Dimethylcyclohexane	0.239	a + e = 0.478	0.150	0.328
cis-1,4-Dimethylcyclohexane	0.245	a + e = 0.490	0.108	0.382
trans-1,4-Dimethylcyclohexane	0.108	2a = 0.216		
cis-Decalin	0.262	a + e = 0.524	0.056	0.468
trans-Decalin	0.056	2a = 0.112		

[a] Designations: (a) reactivity of axial tertiary C–H bond; (e) reactivity of equatorial C–H bond. [b] The average reactivities are 0.095 ± 0.022 for the axial bond and 0.392 ± 0.029 relative units for the equatorial bond.

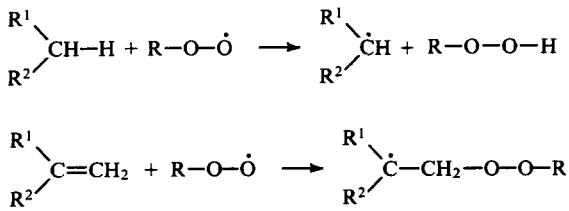
This was possible because one of the tertiary C–H bonds in *cis*-1,2- and *cis*-1,4-disubstituted cyclohexanes is in an equatorial whilst the other is in an axial position. In the corresponding *trans*-isomers, both tertiary C–H bonds are in axial positions. In *cis*-1,3-dimethylcyclohexane, both tertiary C–H bonds are axial, in *trans*-1,3-dimethylcyclohexane one of the tertiary C–H bonds is axial, the other is equatorial.



The reactivities of the secondary C–H bonds of disubstituted cyclohexane derivatives (Table 9) are similar to those of the secondary C–H bonds in acyclic hydrocarbons (Table 7). The equatorial tertiary C–H bond is approximately four times more reactive than the tertiary C–H bond in an axial position (Table 10). The reason for this difference is still not quite clear.[29] On the one hand, attack by peroxy radicals on the axial C–H bond is more hindered than on the equatorial bond. On the other hand, the internal strain in compounds with axial C–alkyl bonds is greater than in compounds with analogous equatorial bonds. It must be expected that the internal strain of cyclohexane derivatives diminishes if one H-atom is abstracted from a tertiary C–H bond and that the decrease of strain is higher if the geminal alkyl group is axial than if it is equatorial.

VI. Reactivities of cycloalkenes

In the oxidation of cycloalkenes, peroxy radicals do not only attack C–H bonds but also the C=C double bond.



We studied the cooxidation of certain cyclic alkenes with cumene and determined their relative reactivities (Table 11).[23] The reactivity of the allylic C–H bonds diminishes in the cyclopentene–cyclooctene sequence. The reactivity of these bonds is particularly high in the case of five- and six-membered rings. The reactivities of cyclopentene and cyclohexene are comparable with the reactivities of the corresponding indane and tetralin bonds. The reactivity of the C=C double bond also depends on the ring size and increases from cyclopentene to cyclooctene. The data presented in Table 11 make it possible to explain the results obtained previously in the oxidation of individual cycloalkenes.[30]

Table 11. The reactivities of certain cycloalkenes and their individual bonds relative to cumene.

Alkene	Overall reactivity (rel. units)	Reactivity (rel. units)	
		of C=C bond	of allylic C–H bond
Cyclopentene	8.2	0.24	1.98
Cyclohexene	6.6	0.56	1.62
Cycloheptene	4.9	1.02	0.97
Cyclooctene	1.6	1.16	0.10
Norbornene	6.5	6.5	0.00

The bicyclic olefin norbornene has an unusually high reactivity[31] and is attacked by peroxy radicals exclusively at the C=C double bond.[32,33] It is noteworthy that in the cooxidation of cycloalkenes and norbornene with cumene, the only products from the interaction of the peroxy radicals with the C=C double bond are the corresponding epoxy compounds.

VII. Reactivities of styrene derivatives

The study of the cooxidation of certain styrene derivatives with cumene made the estimation of relative reactivities of their double bonds possible (Table 12). The C=C bond of styrene is much more reactive than the double bonds in monocyclic alkenes, and its reactivity is comparable to that of the C=C bond of norbornene. A methyl group at the α-position increases the reactivity of the double bond and the effect induced by it is only slightly weaker than the effect of the α-phenyl group. The introduction of a phenyl group at the α-position increases only insignificantly the reactivity of the double bond in comparison with α-methylstyrene because a coplanar arrangement of two phenyl groups linked with one radical carbon atom is not possible. A *tert*-butyl group at the α-position diminishes the reactivity of styrene since in this case it is not possible to achieve a planar structure of the intermediate carbon radical. Further studies showed that the reactivity of the double bond in styrene derivatives usually increases if an electron-donating substituent is introduced in the α- or *para*-position.[34,35]

Table 12. The relative rates of oxidation of certain styrene derivatives.

Substituents in styrene molecule		Reactivity of the C=C bond (rel. units)
α-position	*para*-position	
H	H	6.98 ± 0.40
Me	H	12.78 ± 0.54
Bu^t	H	0.75 ± 0.05
Ph	H	15.6 ± 0.9
Me	Bu^t	14.0 ± 0.2

In the cooxidation of styrene and its derivatives with cumene, not only the corresponding epoxides but also oligomeric peroxides and products of an oxidative degradation are formed.[34–36] The proportion of the particular product depends on the nature of the substituent and on the reaction conditions.

VIII. Conclusion

Thus the oxidation of binary hydrocarbon–cumene mixtures makes it possible to determine both the relative overall rates of interaction of hydrocarbons with peroxy radicals and the relative reactivities of their individual C–H bonds without the addition of an individual hydroperoxide. For this purpose, the oxidation products are subjected to total quantitative analysis after preliminary reduction of the oxidation products by lithium aluminium hydride. Reproducible and mutually consistent

relative reactivities of hydrocarbons, which in most cases agree with the theoretical predictions, can be obtained in this way.

In the studies[37–42] the absorption of oxygen was followed during liquid-phase cooxidations. Relative and absolute rate constants for the interaction of peroxy radicals with hydrocarbons were determined with the aid of the copolymerisation equation without taking into account the formation of various isomeric peroxy radicals from each hydrocarbon. For this reason, in all the studies it was assumed that the rates of reaction of isomeric peroxy radicals with various hydrocarbons are equal. It is noteworthy that in most cases the data obtained in the studies[37–42] for the relative rates of interaction of hydrocarbons with peroxy radicals agree well with our results.[7] It must be stressed, however, that relative reactivities of individual C–H bonds cannot be determined by the methods described in Refs 37–42.

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