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Structural and Steric Factors Determining the Rate of Autoxidation of α-Methylene Groups in Alkylarenes and Alkenes

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Data on structural and steric effects in the autoxidation of alkylarenes and alkenes are summarised. Special attention is paid to the effect of steric hindrance on the rate of oxidation of an α-CH bond in various hydrocarbons—alkylbenzenes, alkylnaphthalenes, alkenes, alkylindanes, and tetrahydronaphthalenes—and data are given on the relation between their refractions, ultraviolet spectra, and rate of oxidation. The role of the molecular conformation of the hydrocarbons in the conjugation of single bonds is demonstrated, together with the effect of this conjugation on the rate of autoxidation of the α-CH bond. A list of 91 references is included.

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1. Introduction

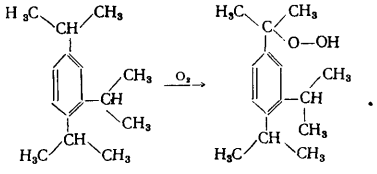
Oxidation with molecular oxygen (autoxidation) provides the basis for the large scale production of several synthetic organic products. Hence the publication of a number of reviews and monographs [1-4] on the autoxidation of hydrocarbons is not accidental. However, these works make no detailed examination of the influence of structural and steric factors on the rate of autoxidation. Yet recent investigations prove fairly convincingly [5-8] that the rate of autoxidation is determined in considerable measure by the chemical and three-dimensional structure of the molecules and by the presence of steric hindrance. Investigation of these effects is of value in understanding the mechanism of the oxidation of hydrocarbons.

2. Alkylbenzenes

The early experimental papers, which contained information on the influence of steric factors on the rate of autoxidation of alkylated aromatic compounds and their derivatives, reported investigations by Remsen [9-13] and by Ciamician and Silber [14]. Remsen noted that the ease of oxidation of a methyl group attached to an aromatic ring depends on the space occupied by the adjacent substituent. The latter workers studied the autoxidation of the isomeric xylenes, and concluded that *o*-xylene is the most resistant to oxidation, and the *para*-isomer the most unstable (the *meta*-isomer occupies an intermediate position). Mowry obtained similar results for the oxidation of the diethylbenzenes [15]. Erofeev and Chirco [16] found that the rate of autoxidation of the α-methylidyne group in *o*-cymene is half that in the *para*-isomer. Eventova and Mashkina [17] studied the oxidation of the di-isopropylbenzenes, and found that the tendency to oxidation increased in the sequence *ortho*—*meta*—*para*. The same order occurs with the cyclohexyltoluenes [18].

The spatial proximity of the adjacent alkyl groups in *o*-dialkylbenzenes is responsible not only for a decrease in the rate of oxidation of the α-methylene groups but also the formation of new oxygen-containing derivatives—α-lactones—during oxidation. Volkov and his coworkers [19-21] found that phthalans (0.2–0.3%) are formed in the earliest stages of the oxidation of *o*-alkyltoluenes and their homologues.

Thus the diminished rate of autoxidation of *o*-dialkylbenzenes and the accompanying formation of α-lactones are due to *ortho*-substitution (the "*ortho*-effect"). This effect determines the path and the rate of oxidation of other polyalkylbenzenes. Thus in the liquid-phase oxidation of 1,2,4-tri-isopropylbenzene [19,20] only the isolated isopropyl group undergoes oxidation, while the other two groups (located side by side) remain almost unoxidised:



The use of chromatographic methods of analysis made it possible to refine quantitatively the laws of the autoxidation of polyalkylbenzenes. For example, the relative rates of reaction of isopropylbenzene, 1-isopropyl-3,4-dimethylbenzene, 1-isopropyl-2,5-dimethylbenzene, and 1-isopropyl-2,3-dimethylbenzene with tertiary peroxy-radicals were 1, 2.1, 0.92, and 0.91 [21]. It is interesting that even in the early work Weissberger [22,23], who investigated the autoxidation of benzoin and its homologues, noted that the reaction velocity is greatly dependent on the nature and position of substituents in the benzene ring (Table 1).

In this case steric hindrance due to *ortho*-substitution is shown in a marked decrease in the rate of oxidation, as in the *o*-dialkylbenzenes. Here the *ortho*-effect could be assessed numerically, because, according to Weissberger [23], the autoxidation rate coefficients which would be expected in the absence of an *ortho*-effect could be calculated.

The diminished rate of autoxidation in *ortho*-substituted alkylbenzenes was explained solely by mechanical factors—repulsion of substituents or shielding of the α-carbon atom by adjacent alkyl groups[24]. This interpretation of the influence of substituents does not indicate why the *meta*-isomer, in which there is no shielding of the α-carbon atom, is oxidised just as slowly as the *ortho*-isomer. An alternative explanation was based on the mechanism of autoxidation and the geometry of the transition state for hydrocarbons[5].

Table 1. Rates of autoxidation of substituted benzoins.

Ar^1-C(=O)-CH(OH)-Ar^2	$10k_{20}$, observed
Ar^1 = Ar^2 = *o*-diethoxyphenyl	7.32
Ar^1 = Ar^2 = *p*-diethoxyphenyl	29.4
Ar^1 = Ar^2 = *o*-dimethoxyphenyl	20.4
Ar^1 = Ar^2 = *p*-dimethoxyphenyl	36.6
Ar^1 = phenyl; Ar^2 = *o*-tolyl	260.0
Ar^1 = *o*-tolyl; Ar^2 = phenyl	29.4
Ar^1 = Ar^2 = *o*-chlorophenyl	725.0
Ar^1 = Ar^2 = *p*-chlorophenyl	900.0

The liquid-phase autoxidation of alkylated aromatic hydrocarbons takes place by a free-radical chain mechanism, the attack usually occurring at hydrogen attached to a carbon atom in the α-position with respect to the aromatic ring. This is explained by the relative inactivity of the peroxy-radical ROO· in the main chain-propagation reaction.

$$ROO\cdot + R'H \rightarrow ROOH + R\cdot \qquad (I)$$

so that it acts fairly selectively: it attacks preferentially highly reactive bonds—homolytically conjugated C–H bonds of the α-carbon atom[25,26]. The rate of homolytic detachment of hydrogen in reaction (I) is determined by the strength of the α-C–H bond and the stability of the resulting radical. The strength of the bond under attack depends substantially on its σπ-conjugation with the aromatic ring. Thus, for example, the energy of rupture of a C–H bond in methane, where there is no σπ-conjugation, is 23–24 kcal mole^{-1} greater than that for a similar bond in toluene, a compound with well defined σπ-conjugation[27].

Thus decreased σπ-conjugation between the benzene ring and the α-C–H bond under attack in the alkyl group should lead to a corresponding increase in its energy, and hence to an increase in the activation energy and a decrease in the rate of oxidation[28]. The diminished reactivity of the C–H bond in *o*-dialkylbenzenes indicates weakening of its conjugation with the benzene ring and diminished polarisability of molecules of this type. This conclusion is supported by the lower molar refraction MR_D of *o*-dialkylbenzenes compared with the *para*-isomers (Table 2).

Since molar refraction is proportional to the volume of the atoms, its dimunution in *o*-dialkylbenzenes indicates that their atoms are more compactly arranged than in the molecules of the *para*-isomers[29]. This is supported by the fact that the former isomers have higher densities, refractive indices, and boiling points[30].

The compaction of the alkyl groups in *o*-dialkylbenzenes (in *o*-cymene, for example, the methyl group forces the adjacent isopropyl group out of the plane of the benzene ring) destroys the σπ-conjugation of the α-C–H bond with the benzene ring. This is apparent in a decreased polarisability, and hence a decrease in the electron mobility of *o*-dialkylbenzenes compared with the *para*-isomers[31–38]. For the same reasons changes occur in electronic (ultraviolet) absorption spectra in dialkylbenzenes[39–43].

Table 2. Molar refraction of dialkylbenzenes.

Hydrocarbon	MR_D	ΔMR_D
p-Xylene	36.02	0.25
o-Xylene	35.77	—
p-Cymene	45.34	—
o-Cymene	45.04	0.30
p-Diethylbenzene	48.82	—
o-Diethylbenzene	48.53	0.29
p-Di-isopropylbenzene	54.65	—
o-Di-isopropylbenzene	54.35	0.30

The changes occurring in the electronic spectra of benzenes as a result of introducing an alkyl group into the ring are due to displacement of the electrons of the α-C–H bonds towards the ring, i.e. to σπ-conjugation. The presence of steric hindrance in the molecule weakens the conjugation of the alkyl group with the benzene ring to a greater or lesser extent. This weakening results in a shift of the electronic spectra to shorter wavelengths accompanied by a diminution in the intensity of absorption. On the other hand, displacement to longer wavelengths with increase in intensity indicates an increase in the conjugation of the system. Such spectra are distinguished by a steep rise to high extinctions with fine structure (Fig. 1).

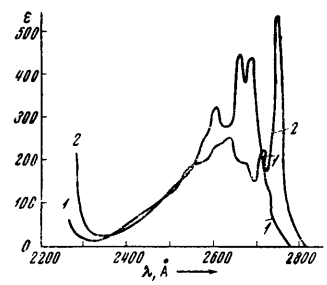
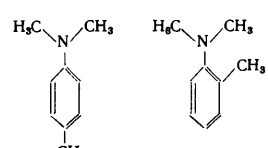


Figure 1. Ultraviolet absorption spectra of: 1) *o*-cymene; 2) *p*-cymene.

For dialkylbenzenes containing hydrogen atoms attached to the α-carbon atom the shift to longer wavelengths accompanied by increased strength of absorption occurs in the sequence—*ortho*, *meta*, *para*—as is clearly evident from Table 3. The same applies to the isomeric *NN*-dimethyl-*o*- and -*p*-toluidines[44]



(λ_{max} in μm, $10^{-3}\varepsilon$).

It has been remarked earlier that the dialkylbenzenes form the sequence—*ortho*–*meta*–*para*—according to their tendency to liquid-phase autoxidation. The absorption coefficients of the electronic spectra and also the exaltation of molar refraction—constants which characterise the mobility of the electrons in the dialkylbenzene molecules—increase in the same sequence. Thus there is a direct connection between the oxidisability of a C–H bond involving an α-carbon atom and its capacity for $\sigma\pi$-conjugation (electronic delocalisation): a high degree of $\sigma\pi$-conjugation between the bond and the benzene ring leads to greater oxidisability of the bond.

Table 3. Ultraviolet spectra of *o*- and *p*-dialkylbenzenes [39]*.

Compound	λ_{max}	ϵ_{max}
p-Xylene	2740	600
o-Xylene	2630	275
p-Diethylbenzene	2730	420
o-Diethylbenzene	2635	245
p-Cymene	2735	530
o-Cymene	2630	250
p-Di-isopropylbenzene	2715	370
o-Di-isopropylbenzene	2635	245

* The values of λ_{max} and ϵ_{max} for *m*-dialkylbenzenes are very close to the corresponding values for *o*-dialkylbenzenes.

This is confirmed by the kinetics of the autoxidation of dialkylbenzenes. Fig. 2 gives rate curves for the absorption of oxygen during the autoxidation of *o*- and *p*-cymenes [5], which show appreciable differences in the rates, *p*-cymene being oxidised considerably more rapidly than the *ortho*-isomer. A similar difference in rates of autoxidation is observed with a mixture of *o*- and *p*-dialkylbenzenes [45,46] and a mixture of isomeric alkylchlorobenzenes (Fig. 3). In particular the relative rate constants for the oxidation of the chloroisopropylbenzenes [6] are $k_p : k_m : k_o = 10 : 7 : 1$.

The hindrance to conjugation in *o*-diaklylbenzenes exists not only in the initial molecule but also in the transition state and in the radical. The geometry of the transition state in the autoxidation of hydrocarbons, e.g. cumene, can be represented by the scheme in Fig. 4. This shows that, during attack by the radical ROO• on the C–H bond, all three angles of the σ-bonds at the α-carbon atom change from 109° (the tetrahedral angle) to 120° in the radical, in which the three valences of the α-carbon atom are coplanar with the benzene ring. In this case maximum delocalisation of the unpaired *p*-electron is accomplished, with creation of a single "through" conjugated system covering the whole radical. A stable radical, capable of continuing the oxidation chain, is thereby formed. However, formation of a planar radical becomes difficult if *ortho*-substituents are present in the aromatic ring. Fig. 5 shows that coplanarity of the radical is impeded by overlapping of the van der Waals spheres [47,48] of the methyl and *o*-isopropyl groups, which are not directly bound to one another. In this case there is no gain in energy due to conjugation, which might have partly balanced (diminished) the energy required to break a C–H bond involving the α-carbon atom of the alkyl. For the same reason a stable radical capable of continuing the oxidation chain is not obtained.

Thus the steric hindrance ("*ortho*-effect") in the autoxidation of alkylated aromatic hydrocarbons consists essentially in destruction of the coplanarity of the system, which results in breakdown in the $\sigma\pi$-conjugation of the α-C–H bond with the benzene ring ("steric inhibition of mesomerism").

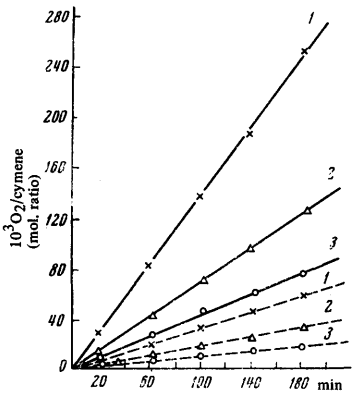


Figure 2. Rate curves for the absorption of oxygen in the presence of 4 wt. % of isopropylbenzene hydroperoxide at (°C): 1) 120; 2) 110; 3) 100. Full lines represent *p*-cymene; broken lines represent *o*-cymene.

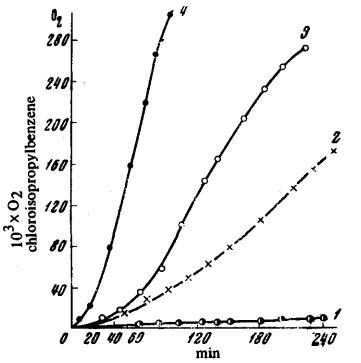


Figure 3. Effect, on rate of oxidation of chloroisopropylbenzene (with 0.6 wt. % of Na stearate + 4 wt. % of CaO at 120°C), of isomeric composition (wt. %): 1) 83 *o* + 13 *p*; 2) 34.3 *o* + 19.8 *m* + 45 *p*; 3) 23.55 *o* + 7.25 *m* + 69.2 *p*; 4) 7.42 *o* + 4.13 *m* + 88.5 *p*.

Similar conclusions were reached by Kooyman and Strang [49–51] in a study of the reactivity of α-methylene [and methylidyne (Ed. of Translation)] groups in various hydrocarbons towards the $^{\bullet}CCl_3$ radical. They found that the reactivity of the α-hydrogen atoms was greatly dependent on the coplanarity of the benzene ring and the α-carbon atom in the transition state. A quite close correlation was observed in the relative activities of $^{\bullet}CCl_3$ and ROO• radicals towards the same α-hydrogen atoms (Table 4).

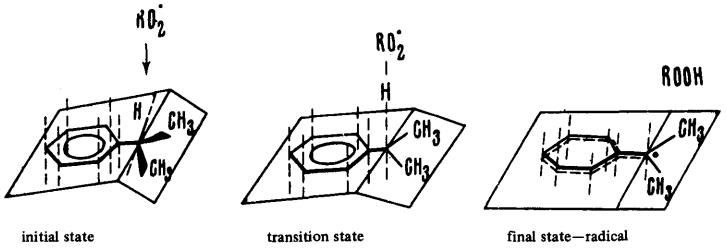


Figure 4. Graphical representation of transition state in the oxidation of cumene.

The rate of autoxidation of an α-C–H bond is, of course, governed not only by the position but also by the nature of alkyl groups present in the benzene ring. Thus Russell[52], who studied the autoxidation of hydrocarbons in the presence of an initiator at 90°C, showed that (*a*) the relative rates of oxidation of cumene, ethylbenzene, and toluene were respectively 1 : 0.59 : 0.075; and (*b*) electron-donor substituents, e.g. methyl, accelerate autoxidation, whereas electron-acceptor substituents (COOH, NO_2, Cl, Br, etc.) slow it down.

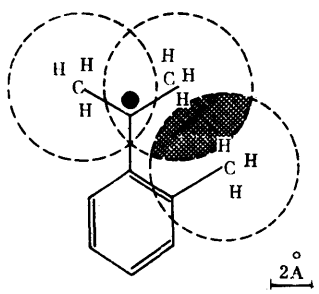


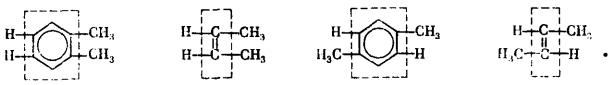
Figure 5. Effect of steric hindrance in the radical of *o*-cymene.

Similar results were obtained by Ingold[53], who found that the rates of autoxidation of *p*-nitrocumene, cumene, and *p*-cymene were approximately in the proportions 1 : 2 : 4. He also gave interesting data on the relative reactivities of the α-C–H bond in several alkylated aromatic hydrocarbons towards various radicals (Table 5). It is seen that the rate of abstraction of hydrogen from the α-carbon atom increases from toluene to cumene for all radicals other than ROO·. Although this radical removes hydrogen attached to the tertiary carbon atom in cumene, the rate of oxidation is lower than in ethylbenzene. A probable explanation is that the peroxy-radical formed from ethylbenzene is more active than that formed from cumene.

The autoxidation of alkylbenzenes is sensitive not only to the steric hindrance of $\sigma\pi$-conjugation in the molecule but also to such a delicate electronic effect in hydrocarbon molecules as the "alternation effect". This was shown by the work of Eventova and her coworkers[54] on the oxidation of the diphenylalkanes $C_6H_5[CH_2]_nC_6H_6$, the rates of which alternate with increase in *n*: i.e. the rate increases with an even number of carbon atoms in the polymethylene chain, but then decreases with an odd number (Table 6); this suggests that the chain is conjugated.

3. Alkenes

From the point of view of molecular symmetry *o*-dialkylbenzenes (I) correspond to the analogous *cis*-ethylene (I*a*)[55–60], and *para*-substituted benzenes (II) to the analogous *trans*-compounds (II*a*):



(Ia) (II) (IIa)

Table 4. Relative reactivity of hydrogen atoms in hydrocarbons towards radicals.

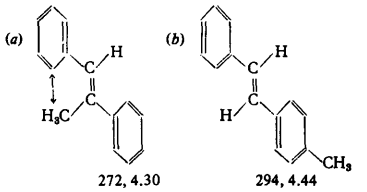
Hydrocarbon	$\cdot CCl_3$[49,51]	ROO·[5,51]
Toluene	1	1
Isopropylbenzene	12.5	13.3
o-Cymene	1.1	1.3
p-Cymene	5.6	4.0

Table 5. Relative reactivities of hydrocarbons towards radicals.

Radical	Ethylbenzene	Cumene
$(CH_3)_3CO\cdot$	3.2	6.8
$C_6H_5\cdot$	4.6	9.7
ROO·	8.1	2.3
Br·	17.0	37.0
$Cl_3C\cdot$	50.0	260.0

In fact, the alkyl groups in *cis*-alkenes, like those in *o*-dialkylbenzenes, are squeezed together as a consequence of their proximity (Fig. 6). This results in increases in density and refractive index, rise in boiling point[30], and decrease in molar refraction in comparison with *trans*-alkenes (Table 7).

The relation between the ultraviolet spectra of *cis*- and *trans*-alkenes is similar to that between those of *o*- and *p*-dialkylbenzenes. For example, the absorption maximum of methyl-*trans*-stilbene (*a*), which exhibits "*cis*-packing" between methyl and phenyl, lies at a shorter wavelength than that of the *para*-isomer (*b*):



(λ_{max} in μm, $\log \epsilon$). In general *cis*-isomers have their maximum absorption at rather shorter wavelengths, and the absorption coefficient is in all cases considerably smaller than for the *trans*-forms [43].

Table 6.

No. of C atoms n = 1	2	3	4	5	6
Oxidation, % = 11.8	21.5	17.0	26.0	23.0	42.0

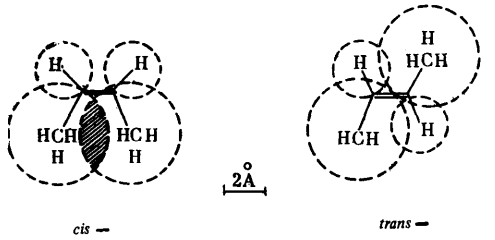
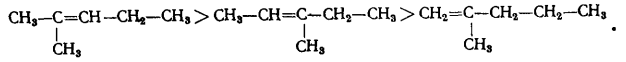


Figure 6. Interaction of atomic groupings, not directly combined together, in *cis*- and *trans*-but-2-ene.

Thus the "packing" in the *cis*-alkene molecule, like that in the *o*-dialkylbenzene molecule, destroys the coplanarity of the double bond with the trigonal α-carbon atom, thereby diminishing the degree of $\sigma\pi$-conjugation of the α-C–H bond. This leads to an increase in the energy of rupture of this bond compared with that of a C–H bond in *trans*-alkenes. This was shown initially in homolytic chlorination, which, like liquid-phase oxidation, has a radical-chain mechanism. Walling and Thaler [61] found that the homolytic chlorination of *trans*-but-2-ene with t-butyl hypochlorite yields 83% of *trans*-1-chlorobut-2-ene, whereas that of *cis*-but-2-ene under comparable conditions gives 65% of *cis*-1-chlorobut-2-ene. A similar difference in reactivity is apparent in the liquid-phase oxidation of isomeric *cis*- and *trans*-alkenes. The oxidation of a mixture of *cis*- and *trans*-4-methylpent-2-ene by oxygen shows [62] that the oxidisability of an α-C–H bond is considerably greater in the *trans*-alkene than in the *cis*-isomer (Figs. 7 and 8). The oxidation rate constants at 70°C were respectively 0.00385 and 0.0086 M min^{-1} for *trans*- and *cis*-forms.

Comparison of data obtained by various workers [63-67] on the autoxidation of branched alkenes clearly reveals that the oxidisability of α-methylene groups, e.g. in methylpentenes, diminishes in the sequence



The molar refraction and the exaltation decrease in the same sequence. Nevertheless, it is evident that enhanced oxidisability of α-methylene groups is observed where the methyl and the oxidisable α-methylene group are in the *trans*-position (parallel).

Table 7. Molar refraction of *cis*- and *trans*-alkenes.

Hydrocarbon	MR_D	ΔMR_D
trans-Pent-2-ene	25.61	0.25
cis-Pent-2-ene	25.38	
trans-Hex-2-ene	25.59	0.24
cis-Hex-2-ene	29.34	
trans-Hex-3-ene	29.61	0.21
cis-Hex-3-ene	29.40	
trans-3-Methylpent-2-ene	29.96	0.25
cis-3-Methylpent-2-ene	29.71	
trans-4-Methylpent-2-ene	29.75	0.24
cis-4-Methylpent-2-ene	29.51	
p-Xylene (*trans*)	36.02	0.25
o-Xylene (*cis*)	35.77	

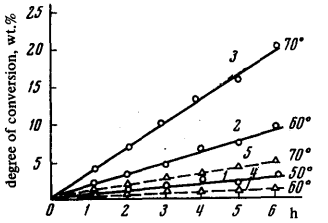
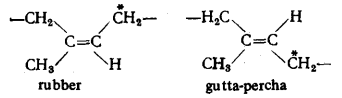


Figure 7. Variation in degree of conversion (with 0.5 mole % of 2-methylpent-2-ene hydroperoxide at 50–70°C):
1)–3) *trans*-4-methylpent-2-ene; 4, 5) *cis*-4-methylpent-2-ene.

These results, which support Nesmeyanov's conclusion [68] that the single bonds are more highly conjugated in *trans*-alkenes, make it possible to estimate the oxidisability of certain polymeric hydrocarbons, e.g. rubber and gutta-percha



Comparison of the three-dimensional structures of these two polymeric isomers makes it clear why rubber is more readily oxidisable than is gutta-percha: in natural rubber the oxidisable α-methylene and the methyl groups are in the *trans*-position, in which steric hindrance is absent; in gutta-percha, however, these two groups are in the *cis*-position, causing steric hindrance to conjugation, and hence a decrease in the reactivity of the α-methylene group.

4. Monoalkylnaphthalenes

Isomeric 1- and 2-alkylnaphthalenes differ in physical properties in the same way as *o*- and *p*-dialkylbenzenes. This is shown by their boiling points, specific gravities, refractive indices, and molecular refraction[69]. Comparison of the latter shows that the 1-isomer possess a lower refraction than their 2-analogues. Table 8 gives these data for the liquid hydrocarbons and their solutions[29].

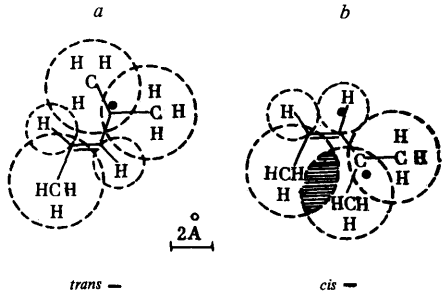


Figure 8. Radicals obtained by autoxidation of: *a*) *trans*-4-methylpent-2-ene; *b*) *cis*-methylpent-2-ene.

The diminished refraction of 1-alkylated naphthalenes in liquid and dissolved states supports the view that intramolecular factors—interaction between adjacent alkyl groups which are not directly bound to one another—are responsible for the regular variation in refraction, as in the case of *o*- and *p*-dialkylbenzenes and *cis*- and *trans*-alkenes. Fig. 9 illustrates such interaction for 1- and 2-monoalkylnaphthalenes.

Table 8. Molar refraction of 1- and 2-monoalkylated naphthalenes.

Substituent	Liquids		Solutions	
	MR_D	ΔMR_D	MR_D	ΔMR_D
2-Methyl	49.24	0.42	49.42	0.40
1-Methyl	48.82		49.02	
2-Ethyl	53.88	0.42	53.86	0.41
1-Ethyl	53.46		53.45	
2-Isopropyl	58.89	0.41	—	—
1-Isopropyl	58.48		—	
2-Butyl	63.31	0.43	—	—
1-Butyl	62.88		—	
2-Iodo	57.88	1.34	57.65	1.14
1-Iodo	56.54		56.51	

1-Alkylnaphthalenes have a lower optical exaltation as well as a lower refraction than the 2-isomers. This is all because the packing of the "*peri*-hydrogen" in 1-alkylnaphthalenes forces the adjacent $C_{Ar}-C_{Alk}$ bond out of the plane of the naphthalene ring, with a resultant breakdown in $\sigma\pi$-conjugation of the ring with an α-C–H bond in the alkyl group[70,71]. Thus steric hindrance to $\sigma\pi$-conjugation arises not only from the influence of bulky *ortho*-substituents but also from that of hydrogen in the *peri*-position with respect to the substituent in the 1-position of naphthalene. The occurrence of steric hindrance to $\sigma\pi$-conjugation in 1-alkylnaphthalenes is indicated also by the fact that the electronic absorption spectra of 2-alkylnaphthalenes, like those of *p*-dialkylbenzenes, possess a more intense long-wavelength maximum than do the 1-isomers.

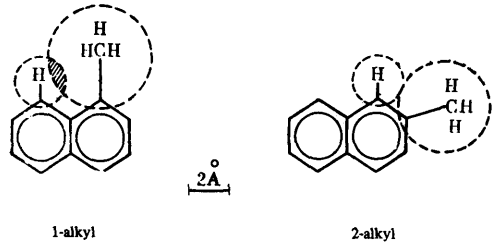


Figure 9. Interaction of unlinked groups in monoalkylnaphthalenes.

For the same reason the degree of conjugation of the unpaired *p*-electron of a new 1-alkylnaphthalene radical is lower and its stabilisation diminished, so that the radical is unable to continue the oxidation chain. This conclusion is supported by the oxidation rate curves for 1- and 2-monoalkylnaphthalenes illustrated in Fig. 10.

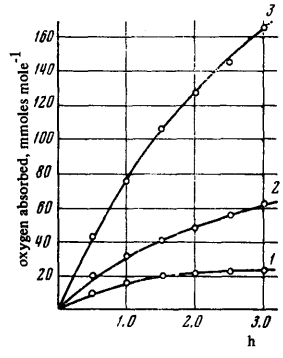
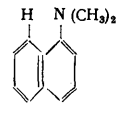
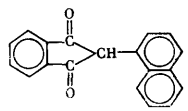
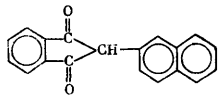


Figure 10. Variation in rate of oxidation of isopropylnaphthalene (with 0.01 wt.% of manganese resinate at 110°C) with amount (wt.%) of 1-isopropyl compound mixed with the 2-isomer: 1) 70; 2) 55; 3) 12.

It is interesting that analogous hindrance to conjugation[72] arises also in compounds of the type



The above concepts can obviously explain also the difference in oxidisability of the tetrahydro-5(and 6)-isopropylnaphthalenes[73] and between 2-naphth-1'-ylindane-1,3-dione (*a*) and the corresponding 2-naphth-2'-yl derivative (*b*)[74].

(*a*)  (*b*) 

Whereas 1-alkylnaphthalenes are less reactive in reactions involving autoxidation of an α-C–H bond in the alkyl, they are more reactive in the radical polymerisation of 1-vinylnaphthalenes. For example, 1-vinylnaphthalene polymerises about 2.5 times as fast as styrene[75]. It is interesting that the increase in reactivity in this case coincides with the increase in dissociation (the Gomberg series) of hexa-arylethanes[76] as a function of these substituents—phenyl < 2-naphthyl < 1-naphthyl—which means the alkyls having a greater steric effect on the α-carbon atom also show a greater degree of dissociation. This conclusion is supported not only by the Gomberg series but also by Theilacker and Ewald's data[77] on the dissociation of substituted hexa-arylethanes in benzene solution at 25°C (Table 9).

Table 9.

Hexa-arylethane	Degree of dissociation, %
Hexaphenylethane	2.5
Tetraphenyl-1,2-di-*o*-tolylethane	25.2
Hexa-*o*-tolylethane	90.8

The above cases of the effect of steric hindrance on rate of autoxidation in alkylated aromatic compounds and in alkenes constitute some of the most important specific examples of interaction between atoms which are not directly attached to one another in the molecule, a problem which was first formulated by Butlerov[78] and developed by Markovnikov.

The existence of such interaction is indicated by a mechanical model of the molecule. This was stated as early as 1904 by Chugaev[79]: "Chemical molecules represent a mechanism involving a known store of energy. In order to understand the action of these mechanisms, it is equally necessary to know their internal structure and the distribution of energy in them... We are indebted to organic chemistry for the first information on the nature of these mechanisms. Perhaps it is destined to make a further step and show how these mechanisms act, indicating the relation between them and the rate of chemical reactions. Is not this possibility evident in the cases of stereochemical hindrance, a large number of which are known in organic chemistry?". The above correlating data on the autoxidation of hydrocarbons confirm the validity of the ideas expressed by this remarkable Russian chemist.

5. Homologues of Indane and Tetreahydronaphthalene—Role of Molecular Conformation of Hydrocarbons in Conjugation of Single Bonds

The oxidation of homologues of indane and tetrahydronaphthalene has been studied in detail by Volkov and his coworkers[80], who have shown in particular that alkylindanes and alkyltetrahydronaphthalenes react far more readily than do the corresponding alkylbenzenes with a peroxy-radical ROO•. The difference between the rates of oxidation of these hydrocarbons is easily explained by the influence of rotational isomerism on the degree of coplanarity of the α-carbon atom with the benzene ring. In fact, the trigonal α-carbon atom lies in the plane of the ring in both the transition state and the radical of the oxidisable hydrocarbon (Fig. 4). The oxidisable α-C–H bond is then perpendicular to the plane of the ring: i.e. this bond has an axial orientation, which corresponds to the maximum degree of σπ-overlapping of the orbitals[81]. If this or a closely similar conformation is already present in the hydrocarbon molecule, conjugation (delocalisation of electrons) is readily accomplished, without the consumption of energy. This leads to an increase in the reactivity of the compound. Indane and its alkyl derivatives possess such a favourable conformation owing to the "rigid" fixation of the atoms of the alicyclic ring. The conformation of tetrahydronaphthalene is closely similar to that of indane. On the other hand, with e.g. di-isopropylbenzene the favourable conformation constitutes a small proportion among other conformations. In order to detach hydrogen from an α-carbon atom in di-isopropylbenzene, therefore, additional energy must be expended to bring the molecule into a coplanar condition in the transition state and in the radical (Fig. 4). Hence it follows that the autoxidation of alkylated aromatic hydrocarbons should have a higher activation energy, and hence a lower rate, than that of alkyl derivatives of indane and tetrahydronaphthalene.

Thus Webster[82] found that the relative rates of oxidation of *m*-di-isopropylbenzene, tetrahydro-1,4-dimethylnaphthalene, and 1,1,3-trimethylindane—compounds having the same hindrance and forming tertiary radicals of similar structure—were 2 : 9 : 10. Hence indane derivatives show the highest rate of oxidation. It is interesting that the same sequence applies to the long-wavelength shift of the absorption maximum in the electronic spectra of these hydrocarbons. Since electronic spectra characterise the degree of delocalisation of electrons, it is obvious that the greatest delocalisation occurs in indane compounds.

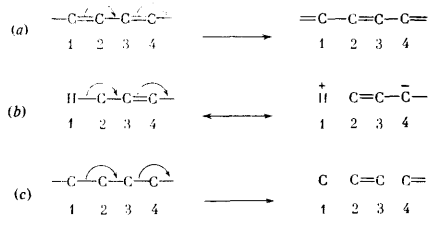
The above oxidation results show that alkylindanes are rather more reactive than are alkyltetrahydronaphthalenes. The explanation is that the alicyclic ring of tetrahydronaphthalene is not so flat as that of indane because of its slight conformational distortion (the former has the "half chair" shape[83]), and therefore requires a definite though small additional energy to produce a favourable conformation. It is interesting to note a similar regularity in reactions involving heterolytic rupture of an α-C–H bond[84].

Numerous facts accumulated from the study of the autoxidation of alkenes and alkylarenes confirm the suggestion that conformation plays an important part in the conjugation of single bonds[85-87]. As early as 1950 Nesmeyanov[25] showed for the first time the possibility of such conjugation. He put forward the following principles for heterolytic conjugation: "The complete conjugation of two single bonds requires that they should be parallel (or nearly parallel) to one another. However, this condition is insufficient. ... It is also necessary (at least in heterolytic conjugation phenomena) that one of the con-

jugating σ-bonds should be of donor character and the other of acceptor character, and that they should be located *trans* to one another". This quotation shows that the first requirement for conjugation is a favourable conformation.

The same stereochemical laws apply to the homologous as to the heterolytic development of conjugation[25]. An actual case of the former is σπ-conjugation, on the stereochemistry of which several papers have been published by Nesmeyanov[88] and also by Shorygin[89,90] and their coworkers. This work shows that, whereas two single bonds are conjugated when mutually parallel, conjugation occurs between a single and a multiple bond when they are perpendicular. This clearly opposite character of the stereochemistry of the two types of conjugation obviously has the same origin: the most favourable conformation is produced, in which delocalisation of electrons can be achieved with minimum energy.

This principle of the role of a favourable conformation can be justified by fairly simple theoretical arguments. The interaction of single and multiple bonds involved in conjugation in saturated and unsaturated compounds can be represented as the displacement of electron density along a chain of atoms:



A common feature here is the formation of a new double bond 2–3. In the first case this change in electronic structure should not result in a change in the molecular conformation. In the second and third cases changes would occur in the configuration of the molecule. In particular, formation of the double bond 2–3 requires that substituents in this portion of the molecule should have a planar (or nearly planar) arrangement. If such conformation is already present, as in the dienes (*a*), electron transfer occurs freely. On the other hand, where a favourable conformation (*b*) and (*c*) must be created, additional energy is obviously needed.

In alicyclic hydrocarbon molecules the atoms may be rigidly fixed. Conjugation is therefore more clearly developed here, as is confirmed by the increased tendency of alicyclic compounds, e.g. indane and tetrahydronaphthalene, compared with alkylated aromatic compounds, e.g. isopropylbenzene, to undergo autoxidation. Data on the autoxidation of hydrocarbons indicate that the conjugation of single bonds is similar in character to that of double bonds and is due to a quantum-mechanical effect[91].

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