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Effect of a Strained Double Bond on the Behaviour of Hydrocarbons Towards Oxygen

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The reasons for strain in a double bond are considered, and the effect of the stress on the behaviour of hydrocarbons in liquid-phase oxidation and in oxidative polymerisation is discussed. The list of references contains 39 items.

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I. INTRODUCTION

The oxidation of hydrocarbons by molecular oxygen is currently attracting the attention of many research workers. The literature on this process [1–4] indicates that the scientific problems of oxidation are indissolubly linked with general aspects of structure and reactivity. I have therefore examined the effect of a strained double bond on the behaviour of hydrocarbons in reactions with oxygen.

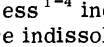
All substituents adjacent to a double bond are in the same plane as the alkene group and the angle [5]



is normally taken to be 120°. Departure from this angle requires the consumption of energy: i.e. it increases the internal energy of the system. Thus a strained double bond is understood to be one which, in contrast to the "ideal" geometry, is subject to strong angular distortions with enhanced energy of the system. Such systems were discussed comprehensively in a review by Zefirov and Sokolov [6]. However, they did not consider the effect of a strained double bond on the reactivity of hydrocarbons towards oxygen, a gap to be filled in the present Review.

II. OXIDATION OF A DOUBLE BOND WITH "CISOID REPULSIVE STRESS"

Hecht and Victor [7] found by proton magnetic resonance spectroscopy that rotation of the methyl groups in *cis*-but-2-ene was hindered compared with that in the *trans*-isomer. They also proved that the skew conformation of *cis*-but-2-ene, obtained from the form with the methyl protons shielding the double bond, was energetically the most favourable. Such a conformation exhibits fairly strong overlapping of the van der Waals spheres (Fig. 1), leading into an increase in the angle θ. It must be borne in mind that the deformation of this angle between the bonds is not localised, but distributed over the other angles, as a result of which the energy of the system as a whole is minimised. This involves deformation of the remaining angles and an increase in the strain in the double bond ("cisoid repulsive stress").

The strain in a double bond can be assessed experimentally from thermodynamic data by comparing the negative heats of hydrogenation of the alkenes. Table 1 shows that increase in the volume of *cis*-alkyl groups in an alkene produces an increase in the negative heat of hydrogenation, which corresponds to greater stress in the  bond, and so to greater deviation of the valency angle θ, which becomes 136° in *cis*-di-t-butylethylene [*cis*-2,2,5,5-tetramethylhex-3-ene]. The main consequence of such stress in the double bond is enhanced reactivity.

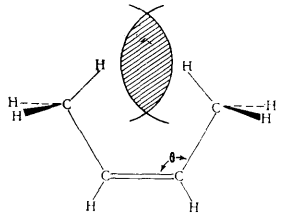


Figure 1. Diagram of overlapping of van der Waals spheres in *cis*-but-2-ene (from proton magnetic resonance data [7]) with distances (Å) C=C 1.38, C–C 1.54, and C–H 1.06 and angles CCC 120° and CCH 109.5°.

Table 1. Negative heats of hydrogenation of isomeric *cis*- and *trans*-alkenes [6].

Alkene	$-\Delta H_{hydr}$, kcal mole^{-1}	Alkene	$-\Delta H_{hydr}$, kcal mole^{-1}
cis-But-2-ene	28.57	*cis*-Methyl-t-butylethylene	30.8
trans-But-2-ene	27.62	*trans*-Methyl-t-butylethylene	26.5
cis-Methylisopropylethylene	28.60	*cis*-Di-t-butylethylene	36.2
trans-Methylisopropylethylene	27.76	*trans*-Di-t-butylethylene	26.87

In the epoxidation of alkenes by hydroperoxides in the presence of a molybdenum catalyst, represented by the general scheme

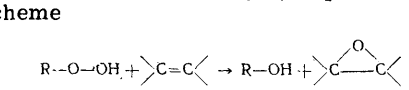


Table 2. Reactivities of isomeric butenes (4.0 M) in epoxidation on a molybdenum catalyst [8] (0.0001 M) at 50°C.

Alkene	Rate constant, $M^{-1}\ s^{-1}$	Relative rate
But-1-ene	$0.076 \cdot 10^{-3}$	1.00
trans-But-2-ene	$1.08 \cdot 10^{-3}$	14.2
cis-But-2-ene	$2.74 \cdot 10^{-3}$	36.0

for example, the reactivity of *cis*-but-2-ene is considerably greater than that of the *trans*-isomer (Table 2). A similar rule is observed in the epoxidation of cycloalkenes: those having a strained double bond (norbornene, cyclopentene) are epoxidised far more readily than are cycloalkenes not containing a strained double bond (cyclohexene) [9]. *cis*-Polybutadiene is oxidised by oxygen more vigorously than is *trans*-polybutadiene [10].

III. OXIDATION OF A DOUBLE BOND WITH "TORSIONAL STRESS"

"Torsional or twisting stress" in a double bond results from a fragment of the molecule turning about the double bond (Fig. 2), which reduces the degree of overlap of the p_z atomic orbitals. Quantum-mechanical calculations show that the energy of a π-bond is greatest with maximum overlap of these orbitals, which occurs when they lie in the same plane. Deflection of the axes of the orbitals from coplanarity decreases their degree of overlap, ultimately with the appearance of a biradical triplet state.

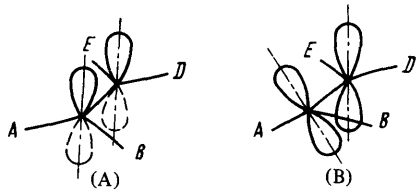
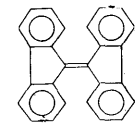


Figure 2. Diagram of the overlap of p_z orbitals in model of: A) coplanar state; B) strained state.

The graph shows (Fig. 3) how the energies of the ground level N, the first triplet level T, and an excited level V in ethylene vary with mutual rotation of the moieties of the molecule [11,39]. With increase in the angle of deflection the $N-V$ transitions require less energy: i.e. excitation occurs at longer wavelengths, and at an angle of 90° the triplet state now becomes energetically more favourable than the singlet state.

One mode of homolysis of an ethylenic bond, i.e. of mutual approach of ground and triplet levels N and T, is a decrease in the degree of overlap of the p_z atomic orbitals of the π-bond (Fig. 2). Such a state arises in ethylenic bonds with "torsional stress", e.g. in 9,9′-bifluorenylidene [12]



(I)

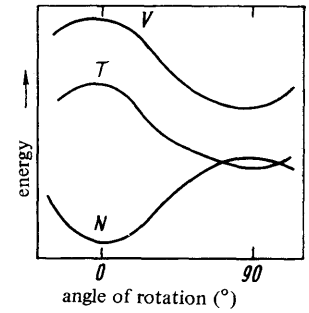
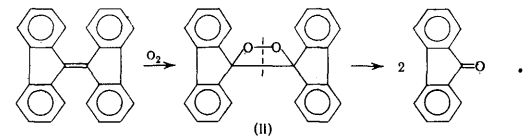


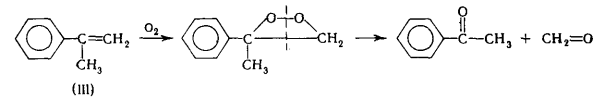
Figure 3. Variation of ground level N, first triplet level T, and excited level V of ethylene during rotation about the double bond [11].

Here the double bond is strained because left-hand and right-hand moieties of the molecules are turned apart by the repulsion of the non-bonded *peri*-hydrogen atoms. This leads to decreased overlap of the p_z atomic orbitals, i.e. to diminished coupling (overlapping) of the electrons forming π-bond and to an increased degree of homolysis of this bond. Such bonds exhibit an enhanced tendency to undergo homolytic (radical) reactions. This is supported by the fact that 9,9′-bifluorenylidene readily terminates reaction chains in the oxidation of benzaldehyde, thereby being oxidised to fluorenone. It is also extremely readily oxidised to fluorenone by atmospheric oxygen in ethereal or alcoholic solution. The sensitised photochemical oxidation of 9,9′-bifluorenylidene occurs highly selectively to give a 91% yield of fluorenone [13]. The oxidation probably involves intermediate formation of 1,2-dioxetans:



(II)

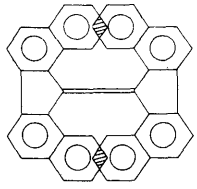
Oxidation of the double bond in α-methylstyrene obviously has the same mechanism:



(III)

It is interesting that the rate of oxidation of the double bond in bifluorenylidene exceeds that in *trans*-4-methylpent-2-ene—a compound from whose double bond torsional stress is completely absent—by a factor of 720. [13]

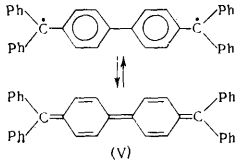
Homolytic reactions are still more characteristic of the double bond in bisdibenzo[*a*,*i*]fluorenylidene



(IV)

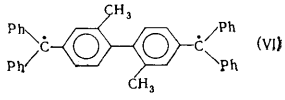
This hydrocarbon inhibits the autoxidation of certain organic compounds, in particular benzaldehyde, slows down the polymerisation of styrene, and in toluene solution readily reacts with oxygen when exposed to ultraviolet radiation [14].

Among compounds with torsionally stressed double bonds is Chichibabin's hydrocarbon [15]



(V)

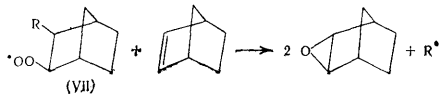
It adds oxygen fairly easily to form a peroxide, but if methyl groups are introduced into the *oo'*-positions of the biphenyl system the product



(VI)

is oxidised still more vigorously to a peroxide [16]. Interaction of the methyl groups results in complete uncoupling of the *p*-electrons of the central π-bond in biphenyl [17].

In cycloalkenes, especially in the bicyclic compounds, e.g. norbornene and its derivatives, serious angular deformations, leading to stress in the double bond, arise from the conditions of ring closure. Zefirov and Sokolov predicted that the study of strained cycloalkenes could lead to the discovery of fundamentally new reactions [6], a forecast which has recently been fulfilled. The oxidation of norbornene and its derivatives by oxygen has shown that the t-C–H bond in them is inert [18–20]. In the presence of azoisobutyronitrile, however, oxidation is fairly vigorous. The oxidation products are not hydroperoxides—as occurs in the oxidation of cycloalkenes whose double bond is unstressed—but cyclic oxides. This was explained [20] by a mechanism in which the epoxidising agent was a peroxy-radical formed by addition of a free radical R$^{\bullet}$ to one end of the double bond and of oxygen to the other end. Such a peroxy-radical (VII) reacts with the initial compound to form two molecules of the oxide:

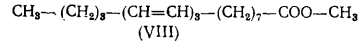


(VII)

Interaction of the radical with the strained double bond suggests that the stress makes the latter liable to radical dissociation (to become partly homolysed).

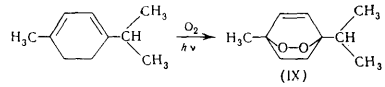
IV. EFFECT OF TENDENCY OF DOUBLE BONDS TO HOMOLYSIS ON THE REACTIVITY OF HYDROCARBONS TOWARDS OXYGEN

It will be extremely interesting to examine the oxidation of conjugated diene and polyene systems in terms of homolysis of the double bonds. These systems differ from monoalkenes and unconjugated polyenes in usually not forming hydroperoxides even when a methylene group appears at first glance to be in a position favourable for oxidation, e.g. in elaeostearic ester [21]



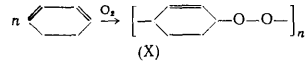
(VIII)

Instead, oxygen tends to add at the ends of a diene segment with formation of an oxygen bridge, as in transannular peroxides [22]:



(IX)

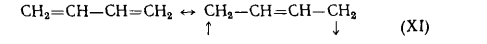
Polymeric peroxides



(X)

may also be formed [23,24]. All the above published information suggests that the interaction of alkenes and polyalkenes with oxygen is strongly dependent on the liability to homolysis of the bonds in the hydrocarbon.

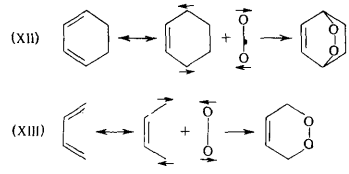
In conjugated diene systems, e.g. butadiene and cyclohexadiene, neighbouring π-bonds do not remain strictly localised, but interact with partial overlapping of the *p*-electrons of double bonds in positions 2 and 3. As a result of this interaction, the double bonds 1–2 and 3–4 become partly uncoupled (homolysed), which can be represented conventionally by



(XI)

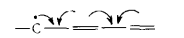
The arrows below the outer carbon atoms on the right-hand side denote single electrons, and their opposite directions indicate opposite spins [25,26]. Thus the uncoupling of the electrons at the ends of a diene system leads to weakening of the terminal bonds, which increases their activity in radical reactions. The right-hand formula obviously corresponds to an excited state of the butadiene molecule.

According to resonance theory, individual resonant structures do not correspond to physically real molecular states [27]. Recognition of the partial uncoupling of electrons in double bonds leads to the conviction that the symbols used by resonance theory can probably represent the excited (real) state of a molecule and—what is most important—predict the course of chemical (homolytic) reactions. This conclusion is confirmed by known oxidations of hydrocarbons, e.g. butadiene, cyclohexadiene, cyclohexene, and elaeostearic ester. Cyclohexadiene (XII) and butadiene (XIII) give with oxygen cyclic peroxides, which can be represented by the scheme



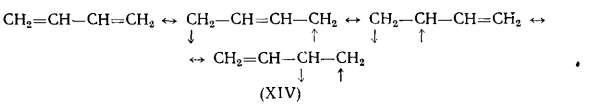
The right-hand formulae for the hydrocarbons have greater energy than the usual formulae on the left. With a planar arrangement of atoms in the molecule the two right-hand formulae have a different distribution of p-electrons and approach a triplet biradical state in which the ethylenic carbon atoms are no longer so double-bonded in character.

The concept of the uncoupling of electrons of a π-bond under the influence of a free electron in an allyl radical was put forward long ago in the early papers by Burton and Ingold [28]. In particular, they regarded stabilisation of a radical as involving interaction of an unpaired electron with the electron pair of a neighbouring π-bond, leading to partial uncoupling of the latter and a redistribution of electrons:



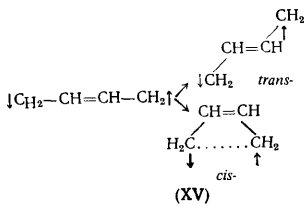
Ingold writes [29]: "In this paper, the main conclusions of which are partly applicable to the whole theory of organic chemistry, reference was first made to the relation between mesomerism and the uncertainty principle and to the fact that the motive force distributing electrons along a conjugated chain is of quantum origin".

The concept of partial uncoupling of electrons of a π-bond suggests that in an excited state butadiene may exist in the forms



(XIV)

The 2–3 bond obviously has one-third double-bond character, so that free rotation is unlikely about this bond. Separate existence of *cis*- and *trans*-forms of butadiene is therefore possible:

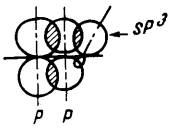


(XV)

Since the outer groups approach very closely in the *cis*-system, a homocomplex may be formed. The increased proportion of the *cis*-form of butadiene with rise in temperature (e.g. in diene synthesis) probably results not from rotational isomerism but from an increase in the statistical weight of the excited *cis*-form.

The above facts suggest that the liability of double bonds in a molecule to homolytic breakdown may well be as important in the oxidation of hydrocarbons as are the properties of the radical. Thus from a comparison of the interaction of peroxy-radicals of α-methylstyrene, styrene, and methyl methacrylate with monomers Mayo concluded [30] that the oxidation of vinyl monomers is governed mainly by the activity of their double bond.

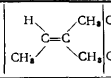
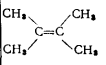
It follows from the above considerations that the hyperconjugation of α-CH bonds in alkenes and alkylated aromatic hydrocarbons can also be explained by their tendency to homolysis (partial uncoupling of the electrons of the α-CH bond). On certain postulates the interaction of an α-CH bond with the π-electrons of a double bond, e.g. in propene, is analogous to the interaction of π-electrons in a conjugated system. This can be represented [31]



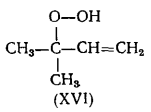
Here the hybrid sp^3 orbitals overlap the p_z orbitals of the double bond. Such interaction would probably result in partial uncoupling of the α-CH bond, its partial homolysis. The tendency to such homolysis will be most effective when the axis of the α-CH bond and the axes of the p-electrons are completely or nearly parallel, i.e. when the double bond is not weakened by steric factors. A partly uncoupled (homolysed) α-CH bond has far greater electron affinity for a peroxy-radical than has the unhomolysed bond. Attack by such a radical in the autoxidation of alkenes is therefore directed at an α-CH bond. In monoalkenes the double bond interacts with the α-CH bonds and homolyses them.

In the hyperconjugation effect the interaction of alkyl group and double bond is a reciprocal process. For example, a consequence of replacing an ethyl group in propane by vinyl is that the methyl group in propene reacts considerably more readily with oxygen than does a methyl group in propane. Replacing a hydrogen atom in ethylene by a methyl group makes the double bond in propene more susceptible to epoxidation than is the double bond in ethylene. Thus the relative rates of epoxidation of ethylene, propene, isobutene, trimethylethylene [2-methylbut-2-ene], and tetramethylethylene [2,3-dimethylbut-2-ene] are respectively 1, 21, 30, 5600, and 6000. [32] This is paralleled by a fall in the ionisation potential (Table 3): increase in the number of methyl groups in a molecule leads to a fall in the ionisation potential and an increase in the rate of epoxidation.

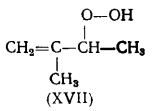
Table 3. Ionisation potentials of alkenes [33].

Alkene	$CH_2=CH_2$	$CH_2=CH-CH_3$	$CH_2=C(CH_3)_2$		
Ionisation potential, eV	10.62	9.84	9.35	8.85	8.45

The low-temperature autoxidation of hydrocarbons such as tri- and tetra-methylethylenes involves intermediate formation of an allyl radical. Examination by proton magnetic resonance spectroscopy of the products of the low-temperature oxidation of trimethylethylene has established the formation of two hydroperoxides—tertiary and secondary [34]

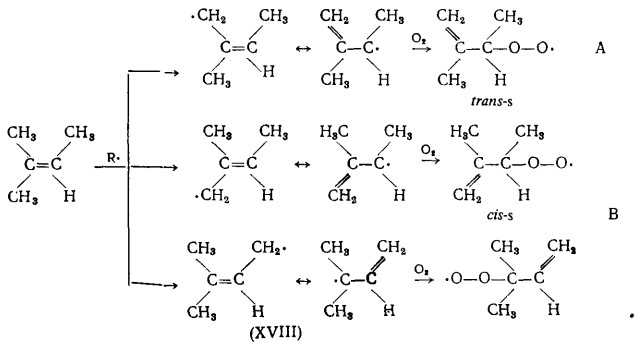


(XVI)



(XVII)

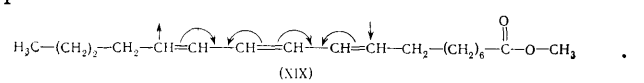
This can be explained in terms of resonance in the hydrocarbon free radicals of the isoalkene in the forms (XVIII) A and B



(XVIII)

All the free radicals indicated are equally likely to react with oxygen, but the probability of forming primary hydroperoxides is small because of the short lifetime of a primary allyl hydrocarbon radical. The more stable tertiary and secondary radicals are formed from the primary radicals. Since the rate of radical abstraction of the hydrogen atom is the same from all three methyl groups in trimethylethylene, the number of resonance structures formed under otherwise similar conditions is twice as great for a secondary radical (*cis*-s, *trans*-s) as for a tertiary radical. Therefore the statistical probability of involvement in reaction with oxygen is considerably greater for a secondary radical (form A) than for a tertiary radical (form B). This evidently explains why the quantity of secondary hydroperoxide formed is double the quantity of the tertiary hydroperoxide. Thus in this example the structure and the proportions of the hydroperoxides are governed solely by the number of resonance structures of the hydrocarbon free radicals.

If a system of conjugated double bonds is present, interaction of the π-electrons will evidently be stronger than that between double and α-CH bonds. In diene systems, therefore, the π-bonds—not the α-CH bonds—are homolysed (uncoupled) first. An example is the oxidation of cyclohexadiene. Elaeostearic esters are oxidised similarly, when uncoupling of the electrons may be represented



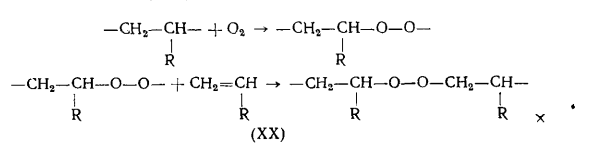
(XIX)

Radical unsaturation appears predominantly at the ends of the diene system, at which the action of oxygen is directed.

It is interesting that the addition of phenyl rings at the ends of a double bond increases the tendency to homolysis and accelerates oxidation of the double bond. For example, the rates of oxidation of the double bond by oxygen with formation of polyperoxides increase in the sequence [35]

styrene < α-methylstyrene < 1,1-diphenylethylene.

The mechanism of polymerisation is



(XX)

Table 4 lists kinetic data on the radical polymerisation of vinyl acetate with the above monomers [36]. This process is interesting because the same radical is interacting with the double bond in monomers having different structures.

The difference in reactivity of the above monomers therefore represents primarily a difference in the electronic nature of their double bond. Weakening of the double bond is greater in 1,1-diphenylethylene than in styrene, probably an effect of the two phenyl rings, which exert a stronger homolysing action on the π-bond. 1,1-Diphenylethylene is a structural analogue of benzophenone, in which the carbonyl π-bond passes considerably more readily into the triplet (biradical) state than does the corresponding bond in benzaldehyde [37]. Thus homolysis of the π-bond in hydrocarbons is promoted by steric factors (torsional or angular stress) and electronic factors (effect of non-polar substituents adjacent to double bonds capable of $\sigma-\pi$ or $\pi-\pi$ conjugation).

Table 4. Stoichiometric coefficient* of vinyl monomers in the polymerisation of vinyl acetate at 50°C. [36]

Monomer	μ_{theor}	μ_{exp}	$\frac{\mu_{exp}}{\mu_{theor}}$
Styrene	2.0	0.065	0.032
α-Methylstyrene	2.0	0.65	0.32
1,1-Diphenylethylene	2.0	1.77	0.88

*μ = stoichiometric coefficient in the equation $t_i = \mu z_0/w_1$, where t_i is the duration of the induction period, z_0 the initial inhibitor concentration, and w_1 the rate of initiation.

The increase in the polarity of the ethylenic bond may even produce an ambipolar ion $\overset{+}{\text{C}}-\overline{\text{C}}$, in which rotation about the central bond does not result in a decrease in the overlap integral between the p-electrons, since they are concentrated in the region of a single carbon atom. This situation diminishes the effect of the double bond on the α-CH bonds. It now becomes clear why, for example, the rate of autoxidation of 2-methylpent-1-ene is one-tenth of that of 2-methylpent-2-ene [38]: the double bond is polarised only in the former hydrocarbon.

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