HYPERCONJUGATION

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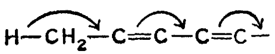
Since the review by C. L. Deasy [1] the concept of hyperconjugation has become well established, and, furthermore, has been extended and widely applied ; consequently, the present more extensive review was undertaken.

Historical Introduction and Definition of the Term.—If electron displacement in alkyl groups resulted solely from the operation of the inductive effect, then the order $Bu^t > Pr^i > Et > Me$ should always be obtained for those reactions which require accession of electrons to the reaction region.

Experimental evidence that this order is not universally applicable was first provided by J. W. Baker and W. S. Nathan,[2] who studied the rate of reaction of various alkyl-substituted benzyl bromides with pyridine. It was found that all alkyl substituents increased the reaction rate, while with a single *p*-alkyl substituent the rate decreased in the order

$$Me > Et > Pr^i \simeq Bu^t \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Since the reaction studied is one facilitated by electron accession towards the side chain, it follows that the accelerating effects of alkyl groups must be related to their capacity for electron release, and, furthermore, that the relative magnitude of this electron release diminishes in the order indicated in (*a*), which order is exactly the reverse of that expected on the basis of the inductive effect of alkyl groups. The methyl group, it would seem, is therefore capable of permitting additional electron release, by some mechanism which is either greatly reduced or inoperative in the more highly alkylated groups. Since an anomaly of this kind is not found in every type of system containing alkyl groups, Baker and Nathan pointed out that the additional mechanism of electron release by the methyl group in *p*-methylbenzyl bromide is to be associated with the presence of the attached conjugated system of the aromatic nucleus. It was therefore suggested that when a methyl group is attached to a conjugated system, the pair of electrons forming the C–H bond in the methyl group, are appreciably less localised than are those in a similarly situated carbon–carbon bond. Hence a methyl group attached to the requisite system permits electron release by what is essentially a type of electromeric effect :



$$H-CH_2-C=C-C=C-$$

This new effect acts in addition to, and in the same direction as, the inductive effect, but, since it depends on the number of C–H bonds, its magnitude clearly will diminish in the order $Me > Et > Pr^i > Bu^t$. Hence

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[1] *Chem. Reviews*, 1945, **36**, 145.

[2] *J.*, 1935, 1844.

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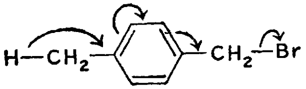
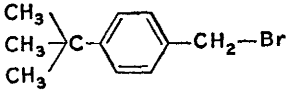
in *p*-methylbenzyl bromide, the methyl group by this new mechanism permits additional electron release at the C–Br bond :



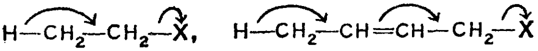
and therefore further facilitates the anionisation of the bromine atom.

On the other hand, in *p-tert.*-butylbenzyl bromide



although the inductive effect of Bu^t is greater than that of methyl, the postulated electron-release mechanism is no longer possible, for the intercalation of the tertiary carbon atom prevents the additional methyl groups from forming part of the necessary conjugated system.

Although the presence of a conjugated system was emphasised, it was assumed that the effect could also function in those systems where electron-pair displacements are rendered possible by fission of a group with its bond electrons, as, for example,



If, however, it requires separation as an anion, of a group, or atom, which normally ionises as a cation, the effect is assumed not to occur.

The mobility ($k_1 + k_2$) of the prototropic change in the azomethine system

$$p\text{-}RC_6H_4\cdot CH{:}N\cdot CH_2Ph \underset{k_2}{\overset{k_1}{\rightleftharpoons}} p\text{-}RC_6H_4\cdot CH_2\cdot N{:}CHPh$$

which is known to be facilitated by electron withdrawal from the triad system,[3] was found [4] to decrease in the order $Bu^t > Pr^i > Me$, indicating that the retarding effect of a *p*-methyl group is much greater than that of more highly alkylated groups. This result provides good evidence that the Baker–Nathan effect is of a mesomeric character, for it is well established that a mesomeric effect is capable of retarding a reaction which is facilitated by electron recession from the region of reaction.

This result was confirmed [5] by an investigation of the equilibrium $p\text{-}RC_6H_4\cdot CHO + HCN \rightleftharpoons p\text{-}RC_6H_4\cdot CH(OH)\cdot CN$, for the stabilities of the aldehydes, relative to the cyanohydrins, diminished in the order $Me > Et > Pr^i > Bu^t > H$. This is an observation to be expected if the Baker–Nathan effect predominates over the inductive effect, for in the free aldehyde conjugation extends to the side-chain carbonyl group, so that the new effect stabilises the free aldehyde to a greater extent than it would the cyanohydrin.

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[3] C. W. Shoppee, *J.*, 1933, 1117.

[4] J. W. Baker, W. S. Nathan, and C. W. Shoppee, *J.*, 1935, 1847.

[5] J. W. Baker and M. L. Hemming, *J.*, 1942, 191.

This power of alkyl groups to conjugate with multiple bonds (either double or triple) is known as hyperconjugation, *i.e.*, an additional conjugation beyond that ordinarily recognised.

Since groups which conjugate with unsaturated systems act as electron donors, single and multiple bonds are known as acceptor and donor bonds, respectively.

Some Theoretical Considerations.—The decrease of electron-repulsive character in ascending the homologous series of alkyl groups had been deduced by N. G. Burkhardt and M. G. Evans,[6] on the basis of Mulliken's theory of united atoms.

As a united atom group the methyl substituent has the electronic configuration ($1s^2 2s^2 2p^5$), which is the same as that of fluorine (except that all the orbitals are more or less deformed) and falls into line with other *o,p*-directing groups, all the electrons (except the carbon $1s$) making up the electronic shell of the group. Replacement of the hydrogen atoms of the CH_3 by other alkyl substituents results in (1) destruction of the united atom system with consequent reduction of the nuclear charge, and (2) removal to some extent of electrons which were available and taking part in the bond when the electronic configuration of the group resembled that of fluorine. This decrease in the availability of electrons, it was suggested, might contribute to the apparent decrease in *o,p*-directing power of substituted methyl groups.

More recently, R. S. Mulliken, C. A. Rieke, and W. G. Brown [7] studied the phenomenon quantitatively, using the method of molecular orbitals. In this method of treatment it is natural to write the methyl group as $—C\equiv H_3$, and to compare it with such groups as $—C\equiv N$, and $—C\equiv CH$. In general a quasi-triple bond is defined as one consisting of three ordinary single bonds from a carbon atom to any three other atoms, whenever there is opportunity for conjugation across an intervening carbon–carbon single bond, with a second, quasi- or ordinary multiple linkage. Since the quasi-triple bond $C\equiv H_3$ is much more saturated than the $C\equiv C$ triple bond, its conjugating power is smaller, but that it is still considerable is shown by certain physical data.

Second-order conjugation or first-order hyperconjugation involves one quasi- and one true multiple bond, whereas third-order conjugation or second-order hyperconjugation involves two quasi-multiple bonds ; ordinary conjugation fits into the scheme as first-order conjugation. The following molecules provide examples of conjugated systems in this generalised sense :

$$\left.\begin{array}{c} HC\equiv C—C\equiv CH \\ N\equiv C—C\equiv N \end{array}\right\}\text{Ordinary or first-order conjugation.}$$

$$\left.\begin{array}{l} H_3\equiv C—C\equiv CH \\ H_3\equiv C—C\equiv N \end{array}\right\}\begin{array}{l}\text{Second-order conjugation, or} \\ \text{first-order hyperconjugation.}\end{array}$$

$$H_3\equiv C—C\equiv H_3 \; \begin{array}{l}\text{Third-order conjugation, or} \\ \text{second-order hyperconjugation.}\end{array}$$

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[6] *Mem. Proc. Manchester Lit. Phil. Soc.*, 1933, **77**, 37.

[7] *J. Amer. Chem. Soc.*, 1941, **63**, 41.

On this basis nearly all saturated organic molecules are stabilised by third-order conjugation of rather a complicated character. Thus, propane may be written as either

$$H_3{\equiv}C{-}C{\equiv}H_2Me \quad \text{or} \quad MeH_2{\equiv}C{-}C{\equiv}H_3$$

the two ways of writing the formula indicating two different possibilities for hyperconjugation, both of which contribute to the stability of the molecule.

The three hydrogen atoms of CH_3 have three valency electrons just like the nitrogen atom in the $C{\equiv}N$ group. If therefore the three hydrogen atoms of the methyl group can be treated like a pseudo-atom, and suitable H_3 group molecular orbitals be formulated, the procedure for studying $N{\equiv}C{-}C{\equiv}N$ theoretically may likewise be applied to $H_3{\equiv}C{-}C{\equiv}H_3$.

In this connection it is recalled that a single bond is always formed by a pair of electrons each in a σ orbital, and in the molecular orbital (M.O.) approximation, both electrons occupy a single, bonding, σ M.O., which is symmetrical with respect to rotation about the axis of the molecule. A multiple linkage consists of a σ bond and one or more π bonds. Thus the triple bond in acetylene is composed of a σ bond, together with two pairs of electrons in π A.O. or M.O. If axes x, y, and z are taken, with the z axis along the symmetry axis of the molecule, then each π M.O. occurs in two forms, which may be called π_x and π_y, and these will hereafter be denoted simply by x and y.

If the three hydrogen atom 1*s* atomic orbitals of the H_3 group are denoted by a, b, and c and located at the vertices of an equilateral triangle, group orbitals of two types may be constructed, as follows.

(i) The linear combination $(a + b + c)$ may be formed, and this has approximate symmetry around an axis passing perpendicularly through the centre of the triangle. This group orbital may therefore be described as a quasi-σ M.O. and can be expected to interact with other σ orbitals. Delocalisation of this type is known as σ-hyperconjugation, and since σ electrons are relatively tightly bound, the resulting energy of delocalisation is likely to be very small. Consequently, σ-hyperconjugation is generally ignored.

(ii) There may also be constructed the linear combination $a - \frac{1}{2}(b + c)$ and $b - \frac{1}{2}(c + a)$, and these have the same type of symmetry as the dumb-bell orbital of an isolated carbon atom. Pictorial representations of these two types of group orbital are given by C. A. Coulson.[8]

The three hydrogen atoms of the methyl group can therefore function as a pseudo-atom with a π-type orbital, which can interact with other orbitals of the same symmetry, such interaction being known as π-hyperconjugation. Since the C–H bonding orbital is not of the right symmetry, the electrons of a single C–H bond clearly cannot be involved in π-hyperconjugation.

If CH_3 is attached to a benzene ring, there will be overlapping between the π orbitals of the ring and that of the H_3 group (*via* the C atom of CH_3)

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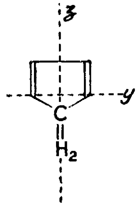
[8] *Quart. Reviews*, 1947, **1**, 144.

resulting in a M.O. in which electrons from the methyl group can migrate into and out of the ring. The resulting delocalisation energy in toluene is small, and stabilises the molecule by approximately 1·5 kcals. It might be noted that the hyperconjugation here is analogous to the ordinary conjugation which occurs in styrenes, where the group $-CH{=}CH_2$ instead of CH_3 is substituted in the ring.

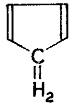
Hyperconjugation in Molecules containing Double Bonds.—Butadiene is the simplest example of ordinary or first-order x conjugation, the x axis being taken perpendicular to the plane of the nuclear framework.

In propylene, $H_3{\equiv}C{-}CH{=}CH_2$, the C–C single bond can act as an acceptor bond for second-order x conjugation between the x electrons of the $C{=}C$ double bond and the x electrons of the $C{\equiv}H_3$ quasi-triple bond. The y electrons of the $C{\equiv}H_3$ bond are inactive in second-order conjugation ; hence for this purpose the $C{\equiv}H_3$ bond acts like a double bond.

In *cyclo*pentadiene (I) there is a combination of first-order x conjugation, as in butadiene, and second-order x conjugation, as in propylene, the molecule having two second-order, and one first-order acceptor bonds.



(I.)



(II.)

Taking axes as shown, with the x axis perpendicular to the plane of the ring, the two hydrogen atoms of the CH_2 group are located one above, and the other below the plane of the ring. The quasi-double bond between the carbon atom and the pseudo-atom H_2, involves one σ bond, and one x bond with M.O. formed by combination of a σ and x carbon A.O. respectively with the following quasi-A.O. of the H_2 group :

$$[\sigma] = (a + b)/\sqrt{2} \, ; \quad [x] = (a - b)/\sqrt{2}$$

The quasi $[x]$ orbital, it will be noticed, is antisymmetrical with respect to the plane of the ring, and consequently two of the four C–H bonding electrons in the CH_2 group must be allocated in M.O. approximation to a quasi-unsaturation M.O., *i.e.*, to a M.O. whose symmetry permits it to interact with the unsaturation M.O. of the ring carbon atoms.

The nature of the hyperconjugation here is made clearer by comparing *cyclo*pentadiene with fulvene (II). The quasi-double bond, like the $C{=}CH_2$ ordinary double bond in fulvene, contains one pair of electrons which can enter into conjugation with the two pairs of unsaturation electrons associated with the two double bonds in the ring. However, since the conjugation in *cyclo*pentadiene involves ordinary double bonds and one quasi-double bond, the resonance here will be less intense than in fulvene, where ordinary double bonds only are involved.

Third-order Conjugation.—In ethylene only third-order conjugation is present. For each H_2 group there are quasi-A.O. as follows

$$[\sigma] = (a + b)/\sqrt{2} \, ; \quad [y] = (a - b)/\sqrt{2}$$

a and b being located on opposite sides of the xz plane.

The *y* electrons of the two CH_2 groups of ethylene can give third-order conjugation across the C═C bond, which here acts as acceptor in the same way that the [*x*] and the [*y*] electrons of the two CH_3 groups conjugate across the single bond of ethane. In both cases the acceptor bond takes on triple-bond character.

Bond Orders.—With regard to the analysis of bond lengths and the character of bonds, W. G. Penney [9] and C. A. Coulson[10] introduced the term bond order, taking values of 1, 2, and 3 respectively for the orders of the central bonds in ethane, ethylene, and acetylene, and drew curves relating bond length to bond order. Since there is no conjugation in acetylene, the value for the C≡C bond in this molecule is correct, but in ethylene and ethane, however, there is third-order conjugation and when allowance is made for this the orders of the central bonds in these molecules become 2·12 and 1·12, respectively.

The excess bond order above the usually assumed values of 1 and 2 for normal C–C and C═C may be expressed by saying that normal C–C and C═C bonds contain a certain % of triple-bond character the values being 6% and 12% respectively.

As a result of the inclusion of hyperconjugation, the curve relating bond order to length does not reach bond order 1 at 1·54 A. but at about 1·58 A. Although this value was interpreted as being the normal bond length for an isolated or ideal C–C single bond, the analysis does not in general definitely indicate that ethane should have a greater C–C bond length than the normal value of 1·54 A. found in saturated molecules.

Effects to be expected if Hyperconjugation occurs.—Hyperconjugation might be expected to reveal its occurrence in any molecule by its effects on the following properties, first-order hyperconjugation being anticipated to produce larger effects than second-order hyperconjugation.

(i) *Bond length.* The electron-diffraction studies by L. Pauling, L. O. Brockway, and J. Y. Beach [11, 12] have shown that first-order or ordinary conjugation causes considerable shortening of single bonds. Hyperconjugation, it might be expected, would produce similar changes, but since it is weaker in its effects than ordinary conjugation, appreciable changes are not likely to be produced.

(ii) *Dipole moments.* Conjugation alters the electron distribution in a molecule and so affects its dipole moment. Whether the moment, because of conjugation, is increased or diminished, depends on whether the conjugation or resonance moment is in the same or the opposite direction to the normal moment.

(iii) *Heats of hydrogenation.* Delocalisation whenever it occurs stabilises the system and therefore less heat will be evolved in the hydrogenation process than in the corresponding system not stabilised by hyperconjugation. Furthermore, progressive alkylation of a double bond may be expected to result in its progressive stabilisation, and this should be reflected in a progressive diminution in the heat of hydrogenation.

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[9] *Proc. Roy. Soc.*, 1937, *A*, **158**, 318.

[10] *Ibid.*, 1939, *A*, **169**, 419.

[11] *J. Amer. Chem. Soc.*, 1935, **57**, 2705.

[12] *Ibid.*, 1937, **59**, 1223.

(iv) *Spectroscopy.* It is found empirically that a compound with conjugated double bonds absorbs light of longer wave-lengths than an analogous compound with isolated double bonds. Moreover, as the number of double bonds in the conjugated system increases, the absorption is progressively shifted to longer wave-lengths. Conjugation causes (*a*) the unoccupied antibonding M.O. to become less strongly antibonding, and (*b*) a raising of the occupied bonding M.O., and hence absorption occurs at longer wave-lengths, an effect which increases with progressive conjugation.

Since hyperconjugation is generically similar to ordinary conjugation, it too might be expected in general to result in displacement of absorption bands towards longer wave-lengths when alkyl substituents are attached to unsaturated atoms.

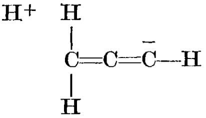
(v) *Kinetic studies.* Highly unsaturated substituents may be expected to exert pronounced effects, but with alkyl groups where the unsaturation is small the system itself may be expected to play a controlling part. This it will accomplish by enhancing the unsaturation in the substituent by means of its own unsaturation either as this exists permanently or as it is developed during the transition state of the reaction.[13] The electromeric effect therefore becomes of importance in those transition states which require an enhanced alkyl conjugation and in such reactions the phenomenon will manifest itself.

The remainder of this review will be devoted to the presentation of experimental evidence confirming these expectations and also to such other experimental work in which the concept of hyperconjugation has been applied.

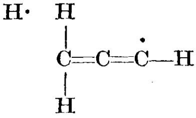
Bond Length.—It has been pointed out that hyperconjugation should produce detectable changes in the lengths of acceptor bonds. The results of electron-diffraction studies by L. Pauling, H. D. Springall, and K. J. Palmer [14] are shown below (in A.).

	Single bond adjacent to triple bond.	Single bond between two triple bonds.
$H_3{\equiv}C{-}C{\equiv}CH$	1·46	
$H_3{\equiv}C{-}C{\equiv}C{-}C{\equiv}H_3$	1·47	
$H_3{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{\cdot}CH_3$	1·47	1·38
$HC{\equiv}C{-}C{\equiv}CH$		1·36

It is seen that in those compounds in which the C–C single bond is adjacent to the C≡C triple bond its value is appreciably less than the normal value of 1·54 A., and this has been regarded as being due partly to contributions to the normal state from hyperconjugated structures.



$$\begin{array}{l} H^{+}\ \ H \\ \qquad | \\ \qquad C{=}C{=}\overset{-}{C}{-}H \\ \qquad | \\ \qquad H \end{array}$$



$$\begin{array}{l} H\cdot\ \ H \\ \qquad | \\ \qquad C{=}C{=}\dot{C}{-}H \\ \qquad | \\ \qquad H \end{array}$$

The carbon–carbon distance in acetaldehyde is approximately 0·04 A.

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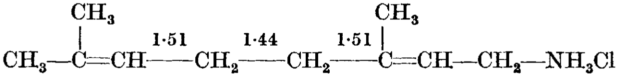
[13] M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw, and L. I. Woolf, *J.*, 1948, 2095.

[14] *J. Amer. Chem. Soc.*, 1939, **61**, 927.

less than the normal value,[15] and here again the shortening has been attributed to hyperconjugated structures.

The shortened bond length in methylacetylene has been confirmed by the spectroscopic studies of R. M. Badger and S. H. Bauer [16] and also of G. Herzberg, F. Patat, and H. Verleger,[17] and according to R. S. Mulliken,[18] when the formula is written as $H_3\equiv C-C\equiv CH$, it would indicate hyperconjugation almost as strong as the conjugation in $N\equiv C-C\equiv N$ where the C–C length is 1·43 A. It has also led to the conclusion that the methyl group conjugates more with $C\equiv C$ than with $C=C$. Indeed, two conjugated triple bonds can interact through either their x or their y orbitals so that for this system conjugation twice as great as for two conjugated double bonds might be expected. However, in the molecules C_2H_6, C_2H_4, and C_2H_2 in which there is no conjugation (ignoring third-order conjugation in C_2H_6 and C_2H_4) there is an abrupt shortening on passing from $C-C$ to $C=C$ to $C\equiv C$. Thus part of the observed shortening is no doubt due to changes of hybridisation.[18a]

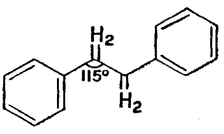
Recently, *X*-ray analysis [19] of the di-isoprene derivative geranylamine hydrochloride (III) has revealed a shortening of the central bond accompanied by the planar arrangement of the adjacent groups, and L. Bateman and G. A. Jeffrey [20] have suggested that this unique bond character which simulates ordinary conjugation is the result of hyperconjugation.



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH\overset{1\cdot51}{-\!\!-\!\!-}CH_2\overset{1\cdot44}{-\!\!-\!\!-}CH_2\overset{1\cdot51}{-\!\!-\!\!-}\overset{\overset{CH_3}{|}}{C}=CH-CH_2-NH_3Cl$$

(III.)

Hyperconjugation has also been invoked to account for the partial double-bond character of the C–C bond in dibenzyl [21] which is a similar system. In this molecule (IV) the three formally single carbon–carbon bonds have lengths of 1·523, 1·510, and 1·523 A.,[21a] and make angles of 115° with each other.[22]



(IV.)

Amongst other causes, the observed shortening in these two molecules may be due to third-order conjugation between the two quasi-double bonds, but this is hardly likely to produce decreases in bond length of the observed magnitude. Furthermore, just such third-order conjugation occurs in paraffin hydrocarbons, and in these molecules no such decrease in bond length has been obtained.

The angle *abc* is 115° and this is intermediate between 109° 28′ and 120°, the values required by sp^3 and sp^2 hybridisation, respectively. The

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[15] P. Stevenson, H. D. Burnham, and V. Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 2922.

[16] *J. Chem. Physics*, 1937, **5**, 599.

[17] *J. Physical Chem.*, 1937, **41**, 123.

[18] *J. Chem. Physics*, 1939, **7**, 339.

[18a] C. A. Coulson, Victor Henri Memorial Vol., Desoer, Liége, 1948, 15.

[19] G. A. Jeffrey, *Proc. Roy. Soc.*, 1945, *A*, **183**, 388.

[20] *Nature*, 1943, **152**, 446.

[21] M. Szwarc, Faraday Soc. Discussions, 1947, No. 2, 39.

[21a] E. G. Cox and D. W. J. Cruickshank, *Acta Cryst.*, 1948, **1**, 921.

[22] G. A. Jeffrey, *Proc. Roy. Soc.*, 1947, *A*, **188**, 222.

bond *bc* therefore has more *s* character and is consequently stronger than the normal C–C single bond.[23] This is a sufficient and probably the sole explanation of the observed shortening in these two molecules.

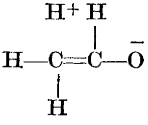
Application of the concept of hyperconjugation with caution is therefore indicated.

Dipole Moment.—Dipole-moment measurements have yielded significant evidence as to hyperconjugation in unsaturated molecules. Some pertinent values for the vapour state [24, 25] are shown in Table I.

TABLE I

Substance.	Dipole moment, D.	Substance.	Dipole moment, D.
Formaldehyde . . .	2·27	Crotonaldehyde . . .	3·67
Acetaldehyde . . .	2·72	1-Methylbutadiene . .	0·68
Propaldehyde . . .	2·73	2-Methylbutadiene . .	0·38
n-Butaldehyde . . .	2·72	2 : 3-Dimethylbutadiene	0·52

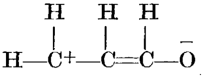
If the large increase in moment from formaldehyde to acetaldehyde is due solely to the inductive effect, it might be expected to have produced a further increase from acetaldehyde to propaldehyde. That this does not occur was regarded as indicating that resonance is partly responsible for the increase from formaldehyde to acetaldehyde. Thus structures of the type (V) among others would be expected to contribute to the observed increase in moment. The observed shortening of the C–C bond by 0·04 A. indicates that this bond contains about 8% of double-bond character.



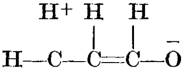
$\mathrm{H{-}\underset{H}{\overset{H^+}{C}}{=}\overset{H}{C}{-}\bar{O}}$

(V.)

The solution value of acraldehyde is 0·4 D. greater than that of acetaldehyde, an increase due to the transfer of charge to the oxygen atom facilitated by the conjugation of the molecule :

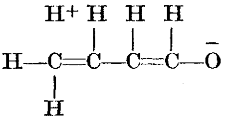


$\mathrm{H{-}\overset{H}{C}{}^{+}{-}\overset{H}{C}{=}\overset{H}{C}{-}\bar{O}}$



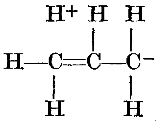
$\mathrm{H{-}\overset{H^+}{C}{-}\overset{H}{C}{=}\overset{H}{C}{-}\bar{O}}$

The effect of hyperconjugation is more strikingly shown in the large rise in moment of nearly 0·6 D. in *trans*-crotonaldehyde. In addition to polar structures analogous to those which have been written for acraldehyde, three further highly polar ones (as in VI) can be written for crotonaldehyde.



$\mathrm{H{-}\underset{H}{\overset{H^+}{C}}{=}\overset{H}{C}{-}\overset{H}{C}{=}\overset{H}{C}{-}\bar{O}}$

(VI.)



$\mathrm{H{-}\underset{H}{\overset{H^+}{C}}{=}\overset{H}{C}{-}\underset{H}{\overset{H}{C}}{}^{-}}$

(VII.)

In like manner the moments of propylene and but-1-ene are accounted

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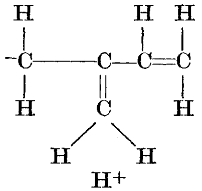
[23] A. D. Walsh, Faraday Soc. Discussions, 1947, No. 2, 18.

[24] E. C. Hurdis and C. P. Smyth, *J. Amer. Chem. Soc.*, 1943, **65**, 89.

[25] N. B. Hannay and C. P. Smyth, *ibid.*, p. 1931.

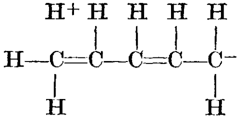
for by polar structures of the kind written for aldehydes. Thus for propylene may be written three structures of the type (VII).

The moments of the methylbutadienes provide further evidence of the polarity resulting from hyperconjugation. Thus the moment of 2-methylbutadiene is experimentally indistinguishable from that of propylene, suggesting participation in the resonance hybrid of structures of the type (VIII). However, the extent to which structures of this type contribute should be rather less than in the case of propylene, for the amount of double-bond character of the central butadiene bond should reduce that of the bond to the methyl carbon.



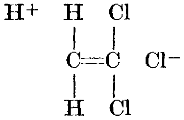
(VIII.)

In 1-methylbutadiene (penta-1 : 3-diene) polarity should arise from polar structures analogous to those proposed for propylene and 2-methylbutadiene, but here the negative charge, instead of being displaced three carbon atoms away from the methyl hydrogens, is displaced five carbons away to give (IX).



$$\mathrm{H{-}\underset{H}{\overset{H^+}{C}}{=}\overset{H}{C}{-}\overset{H}{C}{=}\overset{H}{C}{-}\underset{H}{\overset{H}{C}}{}^{-}}$$

(IX.)



$$\mathrm{H^+\quad \underset{H}{\overset{H}{C}}{=}\underset{Cl}{\overset{Cl}{C}}\quad Cl^-}$$

(X.)

Since three such structures are the principal source of the moment of the molecule as in 2-methylbutadiene, the moment of the molecule should be to that of 2-methylbutadiene approximately as the charge separation in the 1-methyl is to that in the 2-methyl. Measurement of the molecular models shows that the ratio of these distances is approximately 1·5 if 1-methylbutadiene is *cis* with respect to the central single bond and 1·8 if it has the more probable *trans*-structure. The fact that the ratio of the two moment values is 1·8 is considered by Smyth to give striking evidence in support of the validity of hyperconjugation as applied to unsaturated compounds. The argument, however, is of rather doubtful validity because in 2-methylbutadiene the conjugation is crossed, whereas in 1-methylbutadiene it is not ; hence the 2-methyl isomer should have a lower moment.

Hyperconjugation has also been invoked to account for the large increase in moment obtained on passing from chloroform to methylchloroform [26] for which there are possible nine resonance structures of the type (X). Similar considerations have been applied to account for the moments of acrylonitrile,

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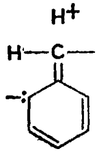
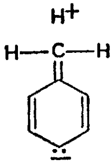
[26] E. C. Hurdis and C. P. Smyth, *J. Amer. Chem. Soc.*, 1942, **64**, 2829.

and *iso*crotyl chloride,[25] some unsaturated aldehydes, ethers, and halogen compounds.[27]

The observed zero moments of all *cyclo*hexanes combined with the known absence of a moment in benzene itself show that the moments of the corresponding alkylbenzenes must arise from electron displacement in the aromatic electronic system stimulated by the polar effect of the alkyl substituent. Thus hyperconjugated structures (XI) and (XII) contribute to the small moment of toluene.[24] However, the observed sequence of moment values relating to the vapour state [28] increases from toluene to *tert.*-butylbenzene, which is the order of the inductive effect—a result explained by J. W. Baker [29] on the basis of the simultaneous operation of both electron mechanisms.



(XI.)



(XII.)

Heats of Hydrogenation.—In Table II are recorded the heats of hydrogenation of certain relevant unsaturated molecules.[30] That the heat of hydrogenation of *cyclo*pentadiene is 50·9 kcals. per mole as compared with 57·1 for butadiene is regarded by Mulliken [18] as evidence suggesting an added stabilisation of *cyclo*pentadiene by hyperconjugation. However, it was also pointed out that the low heat of hydrogenation may be due equally well to instability of the saturated alicyclic five-membered ring as to the stability of the unsaturated compound. For 1 : 3-*cyclo*hexadiene, where the aliphatic six-membered ring would be expected to have normal stability, the value 55·4 kcals. would indicate that hyperconjugation has a smaller though appreciable stabilising effect.

TABLE II

Substance.	Heat at 355° K. in kcals.	Substance.	Heat at 355° K. in kcals.
Ethylene	32·8	Tetramethylethylene	26·6
Propylene	30·1	*cyclo*Hexa-1 : 3-diene	55·4
*iso*Propylethylene	30·3	*cyclo*Penta-1 : 3-diene	50·9
tert.-Butylethylene	30·3	Benzene	49·8
But-2-ene (*trans*)	27·6	Ethylbenzene	48·9
„ (*cis*)	28·6	Mesitylene	47·6
Trimethylethylene	26·9	*o*-Xylene	47·3

The progressive substitution by methyl groups of the hydrogen atoms of ethylene diminishes the heat of hydrogenation of the resultant compounds, the diminution being greatest for tetramethylethylene, for here 6·2 kcals. less heat is evolved than in the case of ethylene. However, the diminution from ethylene to propylene is 2·7 kcals. whereas that from trimethyl to tetramethylethylene is only 0·3 kcal., thus indicating that the

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[27] M. T. Rogers, *J. Amer. Chem. Soc.*, 1947, **69**, 1243.

[28] J. W. Baker and L. G. Groves, *J.*, 1939, 1144.

[29] *Ibid.*, p. 1150.

[30] J. B. Conant and G. B. Kistiakowsky, *Chem. Reviews*, 1937, **20**, 181.

effect of progressive substitution of hydrogen atoms of ethylene by methyl groups is not additive.

In the alkylbenzenes substitution likewise results in diminished heats of hydrogenation although here the stabilisation produced is lower than in ethylene. This is probably due to the large resonance stabilisation already present in the aromatic ring.[31]

Thermal data show, therefore, that double bonds are considerably affected by the nature of the groups attached to them. Since the π electrons are the ones involved in the hydrogenation process it follows that such substitutions affect their energy states and hence it might be expected that such changes will be reflected in the spectra and ionisation potentials of these electrons.

Absorption Spectra and Ionisation Potentials.—(A) *Alkylethylenes.* The work of E. P. Carr and her collaborators [32, 33] clearly shows that progressive substitution in ethylene by methyl groups results in progressive shift to longer wave-lengths of the bands in the Schumann region. Some of their results are shown in Fig. 1, where the wave-number of the first band is plotted against the number of alkyl groups.

The diminution in heat of hydrogenation and the long wave-length shift show parallel effects. Thus the largest fall in heat of hydrogenation (2·7 kcals.) occurs in passing from ethylene to propylene and this also corresponds to the greatest long wave-length shift (3500 cm.$^{-1}$), while the smallest diminution in heat of hydrogenation (0·3 kcal.) occurs in passing from trimethyl- to tetramethyl-ethylene, corresponding to the smallest shift (2000 cm.$^{-1}$).

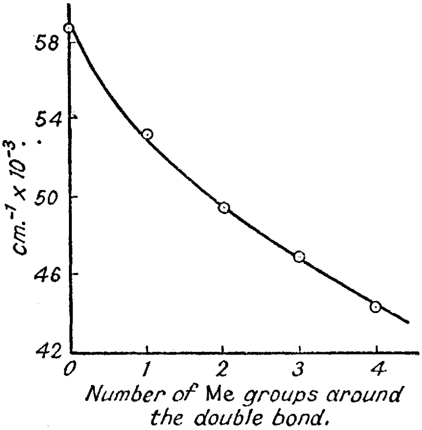

FIG. 1.

Table III shows the experimentally observed term values of methyl-substituted ethylenes for both the ground and the excited state.[34] It will be noticed that the term values of both states decrease with progressive methylation.

TABLE III

	0	1	2	3	4
No. of Me groups	0	1	2	3	4
Term values, ev. Ground state	10·45	9·6	9·2	8·75	8·3
Term values, ev. Excited state	3·04	2·66	2·38	2·04	1·72

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[31] W. C. Price, *Chem. Reviews*, 1947, **41**, 258.
[32] E. P. Carr and M. K. Walker, *J. Chem. Physics*, 1936, **4**, 751.
[33] E. P. Carr and H. Stücklen, *ibid.*, p. 760.
[34] R. S. Mulliken, *Rev. Mod. Physics*, 1942, **14**, 265.

These results are explained as being due to (i) charge transfer or inductive effect of the methyl group, and (ii) hyperconjugation of the CH_3 group and the double bond.

(i) Since the inductive effect is short-ranged it is likely to be of greater importance in small molecules and in terms of hybridisation may be described in the following way.[35] When the less electronegative CH_3 group replaces a hydrogen atom in ethylene, the bond linking the carbon atom of CH_3 contains more *s* character and therefore the σ bond of the C═C double bond contains more *p* character. The σ electrons of the C═C double bond therefore become less tightly bound and consequently the repulsion between them and the π electrons is increased, whence removal of the latter is more easily effected, *i.e.*, the inductive effect results in a raising of the ground-state orbital. However, the excited state must also be considered, for the wave-length at which an absorption band appears depends upon the energy difference between the ground and the excited state. Computation shows that the inductive effect results in a decrease in the excited term value, the change in the excited, however, being smaller than that brought about in the ground state.

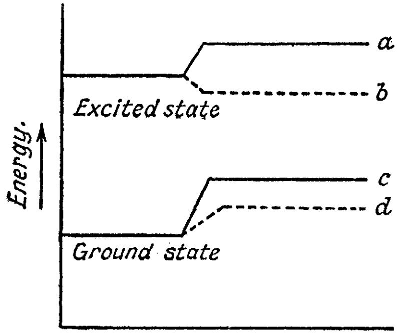

FIG. 2

Result on excited state of (a) *inductive effect and* (b) *hyperconjugation effect.*
Result on ground state of (c) *inductive effect and* (d) *hyperconjugation effect.*

(ii) Hyperconjugation of the CH_3 group with the ethylene double bond not only raises the ground state but also causes an increase in the excited-state term value.

The hyperconjugation and inductive effects are therefore opposed in the excited state, and when allowance is made for the greater effect of charge transfer the observed net decreases in excited-state term values are accounted for.

Since hyperconjugation raises the ground state, 0·14 ev.[34] of the total drop in ionisation potential (0·80 ev.) on passing from ethylene to propylene is regarded as being due to this cause.

Fig. 2 shows the influence of the two effects (acting independently) on the ground and the excited state.

(B) *Alkylbenzenes.* F. A. Matsen, W. W. Robertson, and R. L. Chuoke [36] have compared the near ultra-violet spectra of toluene, ethylbenzene, *iso*-propylbenzene, and *tert.*-butylbenzene and found that the bands representing transitions allowed by the lowered symmetry, relatively to benzene, due to migration of charge into the ring become stronger and shift to longer wave-lengths on passing from *tert.*-butylbenzene to toluene. This result was ascribed to increase of hyperconjugation between the ring and the side chain as the latter changes from *tert.*-butyl to methyl.

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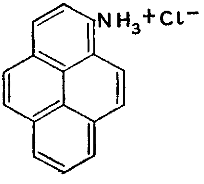
[35] A. D. Walsh, *Ann. Reports*, 1947, **44**, 32.

[36] *Chem. Reviews*, 1947, **41**, 273.

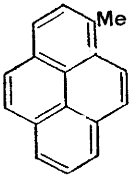
In Table IV are recorded the ionisation potentials of some alkylbenzenes. That hyperconjugation is more important here than in the ethylene system would seem to be indicated by the smaller lowering in ionisation potential on passing from benzene to toluene (0·32 ev.) compared with (0·80 ev.) on passing from ethylene to propylene. Indeed, if the inductive effect were equally important in larger molecules then, as R. N. Jones [37] points out, it is difficult to understand why the absorption spectra of the ions of aromatic amines should resemble those of the parent hydrocarbon so closely. The polar effect of the positive charge on the nitrogen atom must produce a greater electron displacement in the $—C—\overset{+}{N}H_3$ linkage than the relatively weak dipole displacement in $—C—CH_3$, yet in several cases the $\overset{+}{N}H_3$ substituent has been observed to produce shifts in aromatic hydrocarbons no larger than those produced by the introduction of a methyl substituent at the same position; *e.g.*, the wave-length and intensities of the maxima of 3-aminopyrene hydrochloride (XIII) and 3-methylpyrene (XIV).

TABLE IV

Substance.	Ionisation potential, ev.	Substance.	Ionisation potential, ev.
Benzene . . .	9·24	*tert.*-Butylbenzene .	8·5
Toluene . . .	8·92	*o*-Xylene . . .	8·3
Ethylbenzene . .	8·75	*m*- ,, . . .	8·3
*iso*Propylbenzene .	8·6	*p*- ,, . . .	8·3



(XIII.)



(XIV.)

(C) *Cyclic dienes. cyclo*Pentadiene and *cyclo*hexadiene show markedly lower first ionisation potentials (8·62 and 8·4 ev., respectively) and absorb at relatively long wave-lengths compared with open-chain dienes, and it was to explain this characteristic that Mulliken independently invoked the concept of hyperconjugation. However, T. M. Sugden and A. D. Walsh [38] obtained values of 8·71 and 9·02 ev. respectively for the ionisation potentials of *s-cis-* and *s-trans*-forms of butadiene and pointed out that the problem arose mainly because of the comparison of cyclic dienes with the spectra of predominantly *s-trans*-butadiene. Walsh maintains that when the more satisfactory comparison of cyclic dienes with *s-cis*-open-chain dienes is made, the changes in the ground states of the cyclic dienes may be explained as being due entirely to strain and charge-transfer effects.

Further applications of the concept of hyperconjugation to spectra are discussed by E. A. Fehnel and M. Carmack [39] and by I. M. Klotz.[40]

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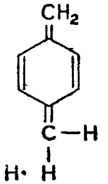
[37] *Chem. Reviews*, 1943, **32,** 1.

[38] *Trans. Faraday Soc.*, 1945, **41,** 76.

[39] *J. Amer. Chem. Soc.*, 1949, **71,** 84.

[40] *Ibid.*, 1944, **66,** 88.

M. Szwarc [41] determined the C–H bond energy in toluene and the xylenes from pyrolysis experiments and found the weakest bond to be the C–H bond in the methyl group. The energy of that bond was found to be 77·5 kcals. for toluene and *m*-xylene, 75 for *p*-xylene, and 74 for *o*-xylene. The data were taken to indicate that hyperconjugation in *p*-xylene decreases the C–H bond energy in the CH_3 group by 2·5—3 kcals., the weakening of the C–H bond in the methyl group of *p*-xylene as compared with that in toluene being expected on the basis of hyperconjugation occurring, for example, in the *p*-xylyl radical as in (XV).



(XV.)

The pyrolysis of the three fluorotoluenes gave a value for the C–H bond energy very nearly equal to that obtained for toluene.[42] Since, therefore, the field effect has very little influence on the bond energy, this result was regarded as supporting the suggestion that hyperconjugation is responsible for the weakening of the C–H bond of the CH_3 in *p*-xylene.

Recent kinetic studies have indicated that hyperconjugation might be of some significance in the oxidation of hydrocarbons.[43]

R. S. Mulliken and C. C. J. Roothaan [44, 45] have given a theoretical discussion of the twisting frequency and barrier height for free rotation in ethylene and find that a 90° rotation of the two parts of the molecule does not entirely destroy the π bond.

When the two CH_2 groups have been twisted through 90° relatively to each other, a kind of hyperconjugation must exist between the x unsaturation electron of each CH_2 group and a pair of quasi-unsaturation electrons y involved in C–H binding in the other CH_2 group. The unsaturation electrons which would have no bonding power in " perpendicular " ethylene contribute somewhat to the bonding because of this hyperconjugation and the barrier to free rotation must be lowered thereby.

As far as the methylethylenes are concerned, it might be thought that hyperconjugation would tend to stabilise certain orientations of the CH_3 group, but this is probably not so ; for, only the four conjugating electrons in propylene $H_3{\equiv}C{-}C{=}C$, being considered, and other electrons and also the other hydrogen atoms being neglected, the energy of the system is unchanged for successive rotations of the CH_3 group by 60° around its axis, and is probably very little if at all changed for rotations through intermediate angles.

In ethane also hyperconjugation has been shown to have little or no direct effect in restricting free rotation.[18]

Molecular Refractivities.—In the alkylbenzenes there is a progressive increase in exaltation with increase in the number of methyl groups, and furthermore, the exaltation increases with increasingly symmetrical distribution of the methyl groups. In aliphatic systems, *e.g.*, substituted

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[41] *J. Chem. Physics*, 1948, **16**, 128.
[42] M. Szwarc and J. S. Roberts, *ibid.*, p. 609
[43] C. F. Cullis, C. N. Hinshelwood, and M. F. R. Mulcahy, *Proc. Roy. Soc.*, 1949, *A*, **196**, 160.
[44] *Chem. Reviews*, 1947, **41**, 219.
[45] R. S. Mulliken, *Physical Rev.*, 1932, **43**, 301.

butadienes, changes in exaltation may be due to changes in the shape of the molecule, but since this is hardly possible here, R. S. Mulliken [46] regards hyperconjugation as being the constitutional cause of the observed increasing exaltation.

It has been shown that equilibrium and kinetic studies provide chemical evidence for the tautomeric electron displacement in alkyl groups, and it was in the field of kinetics that the first unambiguous evidence such as a well-spaced and complete sequence of rate constants substantiated by corresponding activation energies was obtained by E. D. Hughes, C. K. Ingold, and N. A. Taher.[47] Furthermore, it was pointed out why the effect had not clearly been observed before in such studies. Thus, in reaction rate, for example, the initial and the transition state must be treated in a differential manner, and since each will be subject to both inductive and mesomeric displacement the net result depends upon a combination of four effects. In this way the electron displacement is classified as a polarisation, *i.e.*, a mesomeric effect, if the unsaturation permitting alkyl conjugation is present in the initial state, but as a polarisability, *i.e.*, an electromeric effect, when the conjugation is either only present or enhanced in the transition state. Because of these complications it becomes clear why the complete inversion of the inductive-effect order had not previously been obtained. Indeed, the extreme rate range H : Me was only 1 : 1·65 in Baker and Nathan's experiments and, moreover, since the reaction was a bimolecular nucleophilic substitution with only a small electron demand, because of mutually accommodating electron transfers, no clear result should have been obtained.

Hughes, Ingold, and Taher studied the unimolecular hydrolysis of *p*-alkylbenzhydryl chlorides, which is a strongly electron-demanding reaction involving only a single electron transfer. Thus the factor involving alkyl conjugation swamps the others and the following unequivocal results were obtained :

X =	H.	Me.	Et.	Pr^i.	Bu^t.
10^6k_1 . .	2·82	83·5	62·6	46·95	35·9
E, kcals. .	21·0	18·9	19·4	19·8	20·05

More recent rate data concern the competitive bromination of toluene and *tert.*-butylbenzene,[48] which yielded relative rates of 4 : 1, a result readily explicable on the basis of hyperconjugation.

The relative rates of chlorination of a series of alkylbenzenes also show the operation of hyperconjugation.[49] For *tert.*-butylbenzene and benzene [50] a relative rate of 115 : 1 was obtained, a result which cannot be accounted for by hyperconjugation involving hydrogen atoms, and therefore the

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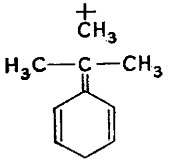
[46] *J. Chem. Physics*, 1939, **7**, 356. [47] *J.*, 1940, 949.

[48] E. Berliner and F. J. Bondhus, *J. Amer. Chem. Soc.*, 1946, **68**, 2355.

[49] P. B. de la Mare and P. W. Robertson, *J.*, 1943, 279.

[50] E. Berliner and F. J. Bondhus, *J. Amer. Chem. Soc.*, 1948, **70**, 854.

difference in rates was explained as being due to release of electrons from the *tert.*-butyl group through structures of the type (XVI) contributing to the resonance hybrid. The experimental data, however, are not sufficient to warrant such a postulate, for partial rate factors were not determined. Furthermore, the order of electron release by this mechanism is the same as that due to the inductive effect, and thus would be created the difficulty of two opposing orders based on the same effect.[50]


(XVI.)

Anionotropy.—The concept of hyperconjugation has also been used by A. G. Catchpole, E. D. Hughes, and C. K. Ingold [51] to account for equilibrium in anionotropic systems, that isomer being preferentially formed in which the methyl group is hyperconjugated with the double bond. The crude approximation being made that only the energy of hyperconjugation makes a direct contribution to the free energy of one of the isomerides, and this being taken to be 3 kcals. for the *gem*-dimethyl group, the system

$$(CH_3)_2C{:}CR{\cdot}CH_2Br \rightleftharpoons (CH_3)_2CBr{\cdot}CR{:}CH_2$$

at 300° K. should contain 1% of the $\alpha\alpha$-dimethylallylbromide. The amount present is known to be experimentally undetectable.

A similar calculation being made for the system

$$CH_3{\cdot}CH{:}CH{\cdot}CH_2Br \rightleftharpoons CH_3{\cdot}CHBr{\cdot}CH{:}CH_2$$

which has been experimentally investigated, the following results were obtained :

Predicted, %.		Observed, %.		Temp., °K.
γ.	α.	γ.	α.	
93	7	87	13	273
88	12	85	15	373

In this table γ and α refer to γ- and α-methylallyl bromide, respectively.

the agreement being fortuitously better than could have been expected.

Prototropy.—With regard to three-carbon prototropy, hyperconjugation has been used to account for the following facts.[52]

A single activating group in three-carbon systems does not much influence the equilibrium between $\alpha\beta$- and $\beta\gamma$-unsaturated forms, whereas alkyl substituents in certain positions do quite markedly influence the ratio in which the isomers are formed. For instance, in the case of an unsubstituted γ-position the $\alpha\beta$-unsaturated form is the one present at equilibrium. As a result of introducing a methyl group in the γ-position, the equilibrium is shifted to the side of the $\beta\gamma$-isomer which is now the important form and

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[51] *J.*, 1948, 8.

[52] P. B. de la Mare, E. D. Hughes, and C. K. Ingold, *ibid.*, p. 17.

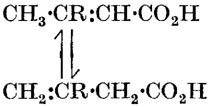
indeed frequently preponderates. Furthermore, higher alkyl groups are less effective, as is shown in the following table :

γ-Substituent.	H.	CH_3.	Et.	$CHMe_2$.
βγ-Form present at equilibrium, %	0	93	67	51

Also, pentenoic acids and their methyl derivatives show that an α-methyl substituent does not favour the production of βγ-forms, which is the opposite effect to that produced by a γ-methyl substituent. This is well illustrated in the following table :

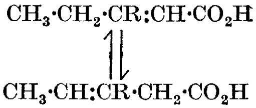
Acid.	Pentenoic.	γ-Methylpentenoic.	α-Methylpentenoic.
βγ-Form at equilibrium, % .	24·6	94·4	19·3

The above facts may be explained as follows. The αβ-form preponderates in the non-γ-substituted compounds such as (XVII) for, in that isomer there is conjugation between the olefinic bond and the activating group, whereas there is no such conjugation in the βγ-form. Consequently, hyperconjugation between the β-substituent and the double bond produces only second-order effects.



$$\begin{array}{c} CH_3{\cdot}CR{:}CH{\cdot}CO_2H \\ \rightleftharpoons \\ CH_2{:}CR{\cdot}CH_2{\cdot}CO_2H \end{array}$$

(XVII.)



$$\begin{array}{c} CH_3{\cdot}CH_2{\cdot}CR{:}CH{\cdot}CO_2H \\ \rightleftharpoons \\ CH_3{\cdot}CH{:}CR{\cdot}CH_2{\cdot}CO_2H \end{array}$$

(XVIII.)

In the γ-methyl compounds (XVIII) the hyperconjugation energy of the γ-methyl group with the double bond in the βγ-form compensates quite appreciably the conjugation energy in the αβ-form. That the methyl group should be more effective is characteristic of alkyl conjugation.

The data relating to pentenoic acid and its methyl derivatives are readily explained, for there is hyperconjugation between the γ-methyl and the βγ-double bond, whereas the hyperconjugation between the αβ-double bond is offset by conjugation between that bond and the activating group.

Ingold has also explained, on the basis of hyperconjugation, data relating to the proportions in which αβ- and αδ-dihydro-compounds are formed by reduction of vinylacrylic acid and certain methylated derivatives.

Halogen Addition.—Recently, halogen additions to conjugated unsaturated systems have been explained on the basis of hyperconjugation as exemplified by the systems

For instance, the equilibrium mixture obtained when bromine is added to butadiene contains 80% of the αδ-dibromide, a result regarded as a manifestation of the doubled bromine hyperconjugation in this compound, whereas in the αβ-isomeride there is only a single halogen hyperconjugation:

$$\underset{(80\%)}{CH_2Br{\cdot}CH{:}CH{\cdot}CH_2Br} \rightleftharpoons \underset{(20\%)}{CH_2Br{\cdot}CHBr{\cdot}CH{:}CH_2}$$

In β- and γ-alkylated butadienes, alkyl hyperconjugation is also of importance, and so in β-methylbutadiene, since γδ-addition is excluded by C_a initiation, only the αδ-compound, $CH_2X{\cdot}CMe{:}CH{\cdot}CH_2X$, of remaining possible addition compounds maintains the hyperconjugation of the methyl group. Since halogen hyperconjugation reinforces alkyl hyperconjugation, the αδ-dihalide may be expected to preponderate at equilibrium, a conclusion verified by experiment.[53]

Elimination.—The Saytzeff rule, namely, that in elimination reactions of *sec.*- or *tert.*-alkyl halides with alkali the most alkylated ethylene is formed, is readily explained as being governed by electromeric electron displacement. In the transition state the quasi-unsaturation electrons of the alkyl group hyperconjugate with the unsaturation electrons of the developing double bond. Since such conjugation creates a system of lower energy, the elimination is facilitated by the development of the latent hyperconjugation.[13]

Experimental investigations in which alkyl groups are conjugated with unsaturated olefinic bonds have normally been confined to cases where there is conjugation between C–H bonds and an aromatic nucleus. No such restriction is applicable theoretically, and so conjugation of a methyl group with a double bond should result in increased reactivity of α-methylenic hydrogen atoms. Recently, J. W. Baker [54] carried out the Prins reaction with propylene and obtained as products: (i) the diacetate of *n*-butane-1 : 3-diol (64%), (ii) the cyclic formal of this diol (14%), (iii) 4-acetoxytetrahydro-γ-pyran (22%). Acid-catalysed addition to the double bond resulted in the first two compounds being formed, whereas the third involves the direct reaction of the hydrogen of the methyl group activated by its conjugation with the olefinic linkage.

Further evidence for such α-methylenic activity in olefinic and polyolefinic systems will be found in references 55, 56, and 57.

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