

HYPERCONJUGATION

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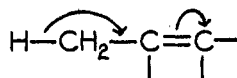
I. INTRODUCTION

During the past decade the concept of hyperconjugation has been employed in organic chemistry and in closely related fields to explain and to correlate a variety of experimental data. Although some of the ideas regarding specific detail are still in a state of flux, a review to indicate the wide applicability of the subject seems warranted at the present time.

II. THE CONCEPT OF HYPERCONJUGATION

The manner of definition of the term *hyperconjugation* depends primarily upon the particular method of approach to the problem. There are now in use three essentially different presentations of the concept, with resulting differences in terminology and, to some extent, in detail.

In England, Baker and Nathan (10) were the first explicitly¹ to put forth the concept of hyperconjugation in order to explain the abnormal behavior of certain series of alkyl-substituted compounds; hence in the English literature hyperconjugation is often referred to as the *Baker-Nathan effect*. In a paper in 1935 they suggested that the duplet of electrons forming the carbon-hydrogen bond of an alkyl group which is attached to an unsaturated carbon atom is less localized than that in a similar carbon-carbon bond; hence electron release is permitted by a mechanism which is essentially a type of tautomeric effect:



¹For earlier work pointing in the same direction, however, see references 13, 14, and 39.

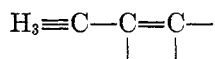
It should be noted that the postulated effect acts in addition to, and in the same direction as, the inductive effect of alkyl groups. The latter effect, however, increases in strength in the sequence methyl < ethyl < isopropyl < tertiary butyl; but the hyperconjugation effect would be expected to decrease in the order methyl > ethyl > isopropyl > tertiary butyl, if one assumes with Baker and Nathan that only the α -hydrogen atoms of the group are effective.

From the viewpoint of quantum mechanics two methods of approach which are less restricted in application have been used. According to one, hyperconjugation is considered to result from the contribution to the resonance hybrid of structures closely related to those occurring in conjugated systems:



Such structures are believed to make small but definite contributions to the ground state of the molecule² (38, 43).

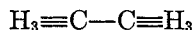
The second point of view, supported by quantum-mechanical calculations using the molecular orbital method, assumes that systems such as the following, which contain an unsaturated center, exhibit a kind of conjugation:



The quasi-triple bond, $\text{H}_3\equiv\text{C}$, is considered to be analogous to an ordinary triple bond, and therefore a conjugation will be present over and above that ordinarily recognized: hence the term *hyperconjugation* (36).

In this method of presentation, a quasi-triple bond is considered to be present whenever there are three ordinary single bonds from a carbon atom to *any* other three atoms, provided that there is an opportunity for conjugation with another multiple bond.

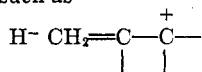
In addition to the above-mentioned *first-order hyperconjugation*, a weaker type of hyperconjugation, *second-order hyperconjugation*, is also assumed to occur whenever two quasi-multiple bonds are conjugated, as, for example, in ethane:



This type of hyperconjugation, however, presumably functions in all but the simplest molecules, and its effects therefore cannot be evaluated separately (44, 48). The term *hyperconjugation* is usually restricted to first-order hyperconjugation.

While each of the above methods of presentation of first-order hyperconjugation differs in terminology and in specific detail, it should be noted that in es-

² Contributions from structures such as



are, of course, also possible, but these are generally neglected as being of less importance (45, 46).

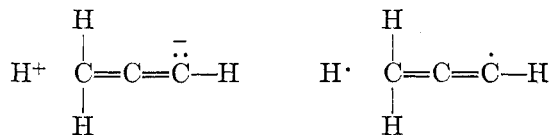
entials the same concept is involved: the tendency of the electrons to concentrate in the direction of the unsaturated atom in a system which contains a saturated atom joined to an unsaturated atom of identical nuclear charge (25).

III. APPLICATIONS OF THE CONCEPT OF HYPERCONJUGATION

The concept of hyperconjugation has been used to explain and to correlate phenomena in two fairly distinct fields—physical-organic and organic chemistry.

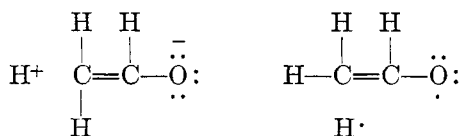
A. Applications in physical-organic chemistry

(1) *Bond lengths:* From electron-diffraction studies of methylacetylene, dimethylacetylene, dimethyldiacetylene, diacetylene, cyanogen, and methyl cyanide, it has been found that the length of the carbon-carbon single bond adjacent to the carbon-carbon triple bond is approximately 0.08 Å. less than the normal carbon-carbon single bond length of 1.54 Å. (38). For methylacetylene this shortened bond length has been confirmed spectroscopically (1, 23). The decrease in length of the carbon-carbon bond has been attributed (38) to the partial double-bond character of the bond, which is due in the main to hyperconjugation resulting from contributions to the normal state of structures such as:



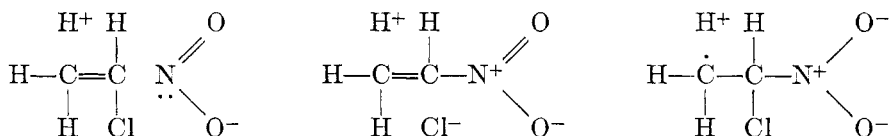
The bond length of a carbon-carbon single bond adjacent to a carbon-carbon double bond has been found by electron-diffraction studies to be normal to within the experimental error in "isobutene" (2-methylpropene), tetramethylethylene, mesitylene, and hexamethylbenzene (37). This is not unexpected. Since, owing to steric effects, a double bond can conjugate with only one carbon-hydrogen bond of a methyl group rather than with all three, the calculated decrease in length of the carbon-carbon single bond is only 0.03 Å., a value which is close to the limit of experimental error in electron-diffraction methods (38).

The carbon-carbon distance in acetaldehyde has been found to be approximately 0.04 Å. less than the normal value (42). This shortening has likewise been attributed partly to hyperconjugation, resulting from resonance with structures such as³:



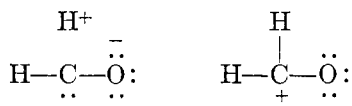
³ The structures given in reference 42 obviously contain typographical errors and have therefore been corrected here.

For 1-chloro-1-nitroethane, on the other hand, additional structures involving hyperconjugation, such as

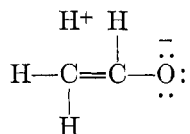


can be written; and the contributions of these structures were assumed to account for the observed increase in moment. Similar considerations can be applied to 1-chloro-1-nitropropane.

The moment of acetaldehyde has been found to be 0.45 D higher than that of formaldehyde. Hurdis and Smyth (28) attribute this increase in moment in acetaldehyde partly to the moment induced in the methyl group by the dipole of the carbon-oxygen bond and partly to hyperconjugation. In the case of formaldehyde, contributions of resonance structures of the following type would be expected to increase the moment:

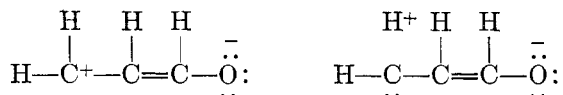


Structures similar to these can be written for acetaldehyde, as well as three structures of the type:

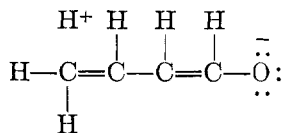


It will be recalled that results of electron-diffraction studies also indicate the influence of hyperconjugation in acetaldehyde (42).

The effect of hyperconjugation on the dipole moment is also shown by the large rise in moment of *trans*-crotonaldehyde as compared with acrolein (28). In addition to polar structures analogous to those which can be written for acrolein, such as



three further structures involving hyperconjugation are possible for *trans*-crotonaldehyde:



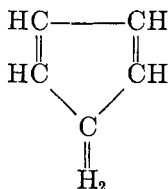
Similar considerations have been used to account for the moments of propylene, *p*-tolualdehyde, methyl cyanide, acrylonitrile, crotononitrile, and isocrotyl chloride (28).

The values of the dipole moments of toluene, ethylbenzene, isopropylbenzene, and *tert*-butylbenzene have been interpreted on the basis of the combined inductive and hyperconjugative effects (2, 7). The latter effect, however, seems to be of relatively minor importance in these compounds (2, 28, 45).

(3) *Molecular refractivities*: Mulliken (35) has attributed to hyperconjugation the increase in the exaltation of refractivity in methyl-substituted benzenes with increase in the number of methyl groups substituted. The lower refractivities of centrally substituted butadienes as compared with butadiene, and the increasingly large exaltations found with increasing end-substitution, are also postulated to be in part hyperconjugation effects.

(4) *Absorption spectra*: 1,3-Cyclopentadiene and 1,3-cyclohexadiene have their first absorption region at considerably longer wave lengths, and the bands are somewhat weaker than expected. These effects have been given a theoretical explanation on the basis of hyperconjugation by Mulliken (33, 34). The observed displacements of the spectra toward longer wave lengths when alkyl groups are substituted for hydrogen atoms in ethylene, butadiene, benzene, and other unsaturated compounds have similarly been attributed to hyperconjugation (34).

(5) *Heats of hydrogenation*: Conant and Kistiakowsky (15) found that the heat of hydrogenation of 1,3-cyclopentadiene is 50.9 kcal. per mole, as compared with 57.1 kcal. for 1,3-butadiene. Mulliken (34) noted that the data suggest an added effect of hyperconjugation in stabilizing 1,3-cyclopentadiene, as indicated in the following formula:



However, Mulliken considered that the low heat of hydrogenation of the compound may be due as much to the instability of the aliphatic five-membered ring as to the stability of the unsaturated compound. From the value 55.4 kcal. for 1,3-cyclohexadiene, where the aliphatic six-membered ring would be expected to have normal stability, it appears that hyperconjugation has a smaller, though appreciable, stabilizing effect.

The heats of hydrogenation of methylated ethylenes indicate an increased stability of the double bond with increase in the number of substituted methyl groups (15), an effect which might be attributed to hyperconjugation. The heats of bromination (16), however, show a trend opposite to that of the heats of hydrogenation, and Mulliken (34) has suggested that the heat effects may be due, in part at least, to causes other than hyperconjugation.

(6) *Depolarization potentials*: The depolarization potentials of a series of phenyl alkyl ketones (18) and of a series of *p*-alkylbenzaldehydes (5), as measured

polarographically, have been explained on the basis of the relative importance of the inductive and hyperconjugative effects of the alkyl groups.

(7) *Dissociation constants*: Baker, Dippy, and Page (6) have determined the thermodynamic dissociation constants for a series of *p*-alkyl-substituted benzoic acids. If hyperconjugation is of importance, a complete or partial inversion in the relative values of the dissociation constants anticipated on the basis of the inductive effect would be expected. Such an inversion was established experimentally, as it was found that the ethyl and isopropyl derivatives were stronger acids than the methyl and *tert*-butyl compounds. Baker, however, postulated that heat capacity and entropy effects might be at least partly responsible for the observed order.

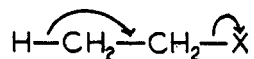
Davies (17) determined the basic dissociation constants of a series of *p*-alkyl-dimethylanilines. Since the basic strengths were found to decrease in the sequence methyl > isopropyl > tertiary butyl, Davies postulated that the hyperconjugative effect predominated over the inductive effect.

(8) *Phosphorescence*: Lewis and Kasha (31) were able to obtain phosphorescence from diisopropyl ketone, but not from acetone. On the basis of their theory of phosphorescence, they attributed the effect to hyperconjugation in the diisopropyl compound, which allowed a wider separation of the odd electrons.

B. Applications in organic chemistry

The influence of hyperconjugation on the reactivity of organic compounds was first explicitly recognized by Baker and Nathan (3, 9, 10) as a result of the study of the reaction velocities of a series of *p*-alkylbenzyl bromides with pyridine. The velocity of formation of the quaternary salt was assumed to be facilitated by an increase in the ease of anionization of the bromine atom, due to the electron release of the alkyl group. Since the velocities decreased in the sequence methyl > ethyl > isopropyl > tertiary butyl, which is the reverse of the order expected on the basis of the inductive effect, Baker and Nathan postulated an additional effect due to hyperconjugation.

They assumed that the effect diminished with a decrease in the number of hydrogen atoms bonded to the α -carbon atom, becoming zero in the tertiary butyl group. They also emphasized the importance of the presence of a conjugated system; but they assumed that hyperconjugation could also function in those systems in which the displacement of the pair of electrons is rendered possible by the fission of a group with its bond electrons, as, for example:

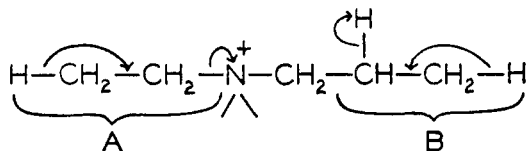


If the completion of the system should require the separation as a negative ion of a group which normally ionizes as a positive ion, as, for example, hydrogen, they assumed that hyperconjugation could not occur.

With the aid of the concept of hyperconjugation, Baker and Nathan (10) also were able to explain the course of the following chemical reactions.

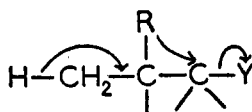
Ethylene, rather than higher olefins, is eliminated in the decomposition of

quaternary ammonium salts (22). Hyperconjugation, which can function as indicated at A, but cannot function at B because the elimination of a negative ion cannot occur, was assumed to be the decisive factor:

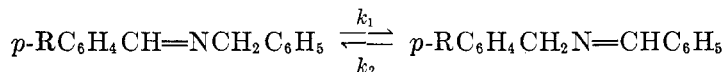


The substitution of *p*-alkyltoluenes by electrophilic reagents, which usually occurs ortho to the methyl group (12, 21), contrary to the known inductive effects, was explained by the greater capacity for electron release of the methyl group, due to hyperconjugation.

The lack of reactivity of isobutyl compounds in reactions of alkyl halides which involve the anionization of the halogen atom, as, for example, the reaction with sodium phenoxide (40), was also explained on the basis of the weak hyperconjugation of the isobutyl group. Similarly, the ionization of hydrogen from methyl and methylene groups in the Wagner-Meerwein reaction (4) was assumed to be a hyperconjugation effect, as indicated in the formula:

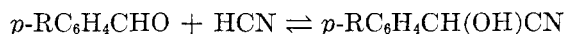


Baker and Nathan's original work had not given any indication as to whether hyperconjugation was a mesomeric or an electromeric effect, since the reaction studied was one facilitated by electron accession to the point of attack. It is known that a mesomeric effect is able to retard a reaction facilitated by electron recession from the point of attack, whereas an electromeric effect cannot retard such a reaction; therefore, Baker, Nathan, and Shoppee (11) studied the prototropic change in the azomethine system, which is known to be facilitated by electron recession from the triad system (41):



The velocity of interconversion of the system ($k_1 + k_2$) was found to decrease in the order tertiary butyl > isopropyl > methyl; hence hyperconjugation is a mesomeric effect.

It was thought, however, that evidence from the previous kinetic studies was not completely free from the possibility of electromeric influence. Baker and Hemming (8), therefore, studied the influence of hyperconjugation on the following equilibrium, as the equilibrium state is known to be unaffected by polarizability effects:



It was postulated that hyperconjugation would increase the stability of the free aldehyde to a greater extent than it would that of the cyanohydrin, because the conjugation can extend to the side-chain carbonyl in the aldehyde. If the hyperconjugative effect predominates over the inductive effect, the stabilities of the aldehydes relative to the cyanohydrins should decrease in the order: methyl > ethyl > isopropyl > tertiary butyl > hydrogen. This sequence was observed experimentally. Results of Lapworth and Manske (30) for a series of phenyl alkyl ketones were explained similarly.

The first completely satisfactory evidence for hyperconjugation from kinetic studies was not obtained until 1940. Hughes, Ingold, and Taher (26) pointed out that previous data had given either only incomplete inversion of series, or differences in reaction rates which were so small as to be difficult to interpret. They studied the effects of the alkyl groups on the rates of hydrolysis and alcoholysis of a series of *p*-alkylbenzylhydriyl chlorides. On the basis of the inductive effect, the sequence of reaction velocities would be expected to be hydrogen < methyl < ethyl < isopropyl < tertiary butyl; but if hyperconjugation predominates, the sequence should be hydrogen < {methyl > ethyl > isopropyl > tertiary butyl}. The latter sequence was obtained for the hydrolysis. The quantitative data were unequivocal, as the rate range from hydrogen to methyl was 1:30, and the increase in rates throughout the series was regular. Robinson's suggestion (39) that actual ionization of the hydrogen of the methyl group might have occurred in the reaction was shown by deuterium-exchange experiments to be untenable.

Another application of the concept of hyperconjugation was made by Evans (20) to explain the results of his study of the rates of bromination of a series of phenyl *n*-alkyl ketones and of isobutyrophenone. He attributed to hyperconjugation the large increase in the activation energy in going from acetophenone to propiophenone, and the approximate constancy of the activation energies of propiophenone, butyrophenone, and valerophenone. However, the equivalence of the activation energies of propiophenone and isobutyrophenone could not be explained on this basis.

Hughes, Ingold, Masterman, and McNulty (25) have applied the Baker-Nathan effect in an explanation of the accelerating action of α -alkyl substituents on first-order and second-order elimination reactions. They emphasize, however, that they prefer to use the concept of hyperconjugation in its broader aspect, as a tendency of electrons to concentrate in the direction of unsaturated atoms. This latter view they use to account for the results of Linstead and Kon (29), which show that, in the tautomerism of unsaturated acids and ketones, the introduction of alkyl groups at either end of the three-carbon system shifts the equilibrium in such a direction as to place the unsaturation next to the alkyl group.

A further application of the concept of hyperconjugation was made by Davies (17), who studied the velocity of the reaction of *p*-alkyldimethylanilines with methyl iodide. The sequence obtained for the velocity constants (methyl > isopropyl > tertiary butyl) is not expected on the basis of the inductive effect,

and, since a steric effect cannot be present, Davies explained the results on the basis of hyperconjugation.

The fact that the rate of hydrolysis of potassium *p*-ethylphenylsulfate is greater than that of potassium *p*-tolylsulfate was interpreted by Burkhardt, Horrex, and Jenkins (14) as a hyperconjugation effect. They assumed that hyperconjugation also accounts for the rapidity of hydrolysis of *o*-isopropylphenylsulfate as compared with the *o*-ethyl compound, although steric factors are generally of predominant importance when the substituent is in the ortho position.

Davies and Hammick (19), in a study of the complexes of tetranitromethane and alkylbenzenes in carbon tetrachloride solution, found that the stability of the complexes increased from benzene through toluene and ethylbenzene, fell in isopropylbenzene, and then rose in the tertiary butyl compound. Since the stability of the complex presumably increases with an increase in the anionoid character of the aromatic nucleus, Davies and Hammick attributed to hyperconjugation the drop in stability from the ethyl to the isopropyl derivative.

Wheland has applied the concept of hyperconjugation in an explanation of the normal addition of acids to carbon-carbon double bonds (46), and also to account for meta substitution of toluene by free radicals (47).

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