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# THE THERMOCHEMICAL EVIDENCE FOR HYPERCONJUGATION

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**Abstract**—Thermochemical evidence pertinent to the question of hyperconjugation is reviewed with the following conclusions. The data indicate that alkyl substitution at an unsaturated linkage results in stabilization of appreciable magnitude which is essentially independent of the nature of the alkyl group and which cannot, in the general case, be accounted for in terms of steric effects. Beyond these facts the calorimetric results do not provide significant information on the nature of the stabilization process and hence cannot distinguish among various interpretations that have been advanced in explanation of this phenomenon.

IN a series of investigations commencing in 1935, Kistiakowsky and his associates obtained by direct measurement the heats of hydrogenation of several substituted olefins in the vapor phase at 82°.[*] An experimental precision of the order of 0·1 per cent was achieved in this work, the results of which are recorded in Table 1. Although slightly less precise values for heats of hydrogenation are obtainable by difference from the heats of formation of various olefins and those of the corresponding paraffins,[1] the quantities derived in this way in general serve only to confirm and extend the original observations of Kistiakowsky without adding anything fundamentally new to his results.

Inspection of the data of Table 1 reveals three points of major interest. First, it will be noted that the heats of hydrogenation decrease in successively smaller increments with increasing substitution of the double bond, the difference in the values for ethylene and for tetramethylethylene being 6·2 kcal/mole. A similar trend is observed in the series benzene (−49·8 kcal/mole), ethylbenzene (−48·9 kcal/mole) and mesitylene (−47·6 kcal/mole),[2] and in the heats calculated for the reactions acetylene → ethylene (−42·2 kcal/mole), propyne → propylene (−39·6 kcal/mole) and 2-butyne → *trans*-butene (−38·0 kcal/mole).[3] Secondly, the heats of hydrogenation of propylene, 1-butene, *iso*propylethylene and *tert.*-butylethylene are found to be virtually identical. It follows that, whatever the origins of the substitution effect, the net result is essentially independent of the nature of the alkyl substituent, although the *neo*pentyl group may consitute an exception deserving special consideration.

The Kistiakowsky work finally emphasizes the fact that steric interactions, which

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[*] For a summary of a large portion of this work, see J. B. Conant and G. B. Kistiakowsky *Chem. Rev.* **20**, 187 (1937).

[1] *Selected Values of Properties of Hydrocarbons.* Circular C461 of the National Bureau of Standards, U.S. Printing Office, Washington, D.C. (1952).

[2] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Amer. Chem. Soc.* **58**, 146 (1936), and Reference 7. *o*-Xylene shows a slightly lower heat of hydrogenation (−47·3 kcal/mole) than does mesitylene. The origin of this discrepancy has not been established, although conformational factors in the reduction products may be involved.

[3] J. B. Conn, G. B. Kistiakowsky and H. A. Smith. *J. Amer. Chem. Soc.* **61**, 1868 (1939).

TABLE 1. VAPOR-PHASE HEATS OF HYDROGENATION (82°)

| Compound | $\Delta H$ (kcal/mole) | Reference |
|---|---|---|
| Ethylene | −32·8 | 4 |
| Propylene | −30·1 | 5 |
| 1-Butene | −30·3 | 5 |
| 1-Heptene | −30·1 | 6 |
| *neo*Pentylethylene | 29·5 | 7 |
| *iso*Propylethylene | −30·3 | 7 |
| *tert.*-Butylethylene | −30·3 | 7 |
| *cis*-Butene | −28·6 | 5 |
| *trans*-Butene | −27·6 | 5 |
| *iso*Butene | −28·4 | 5 |
| 2-Methyl-1-butene | 28·5 | 6 |
| 2,3-Dimethyl-1-butene | 28·0 | 6 |
| 2,4,4-Trimethyl-1-pentene | 27·2 | 7 |
| Trimethylethylene | −26·9 | 6 |
| 2,4,4-Trimethyl-2-pentene | −28·4 | 7 |
| Tetramethylethylene | −26·6 | 6 |

are undoubtedly the major source of the 1 kcal difference between the heats of hydrogenation of *cis*- and of *trans*-butene, cannot be disregarded, and that such factors may seriously compromise the investigation of other phenomena by the hydrogenation method. Since steric strain in the reactant will result in an increased heat of hydrogenation, whereas steric interactions in the product lower the enthalpy change for the hydrogenation process, a reduced heat of hydrogenation can be interpreted alternately on the basis of reactant stabilization or of product destabilization. A well-known example of the latter effect is the *cyclo*pentene–*cyclo*pentane case, in which eclipsing of hydrogens in the saturated product serves to depress the heat of hydrogenation of the five-ring olefin below the *cyclo*hexene value, despite the presence of greater strain in the *cyclo*pentene than in the *cyclo*hexene double bond.[3]

The effects of methyl substitution in the series ethylene, propylene, *trans*-butene, trimethylethylene and tetramethylethylene have in the past been uniformly interpreted in terms of olefin stabilization, questions of steric influence, particularly in the cases of the last two members of the group, having been neglected. Since trimethylethylene and tetramethylethylene possess, in order, one and two *cis*-butene interactions not found in the other compounds under consideration, the heats of hydrogenation

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[4] G. B. Kistiakowsky, H. Romeyn, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Amer. Chem. Soc.* **57**, 65 (1935).

[5] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Amer. Chem. Soc.* **57**, 876 (1935).

[6] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Amer. Chem. Soc.* **58**, 137 (1936).

[7] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, *J. Amer. Chem. Soc.* **59**, 831 (1937).

of these substances, corrected for olefin strain, should be lower than the values actually observed by at least 1·0 and 2·0 kcal/mole, respectively. Although it seems reasonable to suppose that repulsive interactions in paraffins will also increase with branching, the fact that within a group of isomers the more highly branched members possess the greater stability (cf. Table 2) makes the estimation of steric strains in saturated systems a matter of considerable difficulty. Some efforts in this direction have nevertheless been made, notably by Spitzer and Pitzer.[8] As applied to the case of 2,3-dimethylbutane the Pitzer method is as follows. It is observed that 2-methylpentane possessing one *iso* branch is 1·7 kcal/mole more stable than *n*-hexane, the corresponding straight-chain isomer. Assuming that the effects of branching are normally additive,[*] 2,3-dimethylbutane with two *iso* groupings should differ from *n*-hexane by −3·4 kcal/mole and from 2-methylpentane by − 1·7 kcal/mole. The latter difference is in fact only − 0·8 kcal/mole, and the discrepancy of 0·9 kcal/mole is assigned in this treatment to the steric energy difference between 2-methylpentane and 2,3-dimethylbutane. The method does not, of course, given any information on the strain energies of the *iso* compounds which are employed as reference substances. A possible approach to this problem may be given along the following lines.

TABLE 2. HEATS OF FORMATION OF VARIOUS PARAFFINS[1]
(VAPOR PHASE, 25°)

| Compound | $\Delta H_f$ | Difference from normal paraffin |
|---|---|---|
| *n*-Butane | −30·2 | 0 |
| *iso*Butane | −32·2 | −2·0 |
| *n*-Pentane | −35·0 | 0 |
| *iso*Pentane | 36·9 | −1·9 |
| *neo*Pentane | −39·7 | −4·7 |
| *n*-Hexane | −40·0 | 0 |
| 2-Methylpentane | 41·7 | −1·7 |
| 2,3-Dimethylbutane | −42·5 | −2·5 |
| 2,2-Dimethylbutane | −44·4 | −4·4 |

Structures (I), (II) and (III) are taken as the most stable arrangements of *n*-butane, 2-methylbutane and 2,3-dimethylbutane, respectively. Assuming that strain energy in (I) is negligible and disregarding "B-strain" in (II) and (III),[8] the differences in steric energy between (I) and (II) and between (II) and (III) may each be equated to the strain in a single skew *n*-butane structure. Since Pitzer[9] has assigned a value of 0·8 kcal

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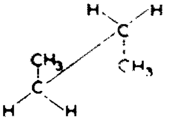
[*] A test of this assumption is provided by a comparison of the heats of formation of 2,5-dimethylhexane ( 53·2 kcal mole), in which the *iso* structures are widely separated, with those of 2-methylheptane (−51·5 kcal mole) and of *n*-octane (−49·8 kcal/mole), the differences being, respectively, −1·7 and − 3·4 kcal mole (ref. 8).

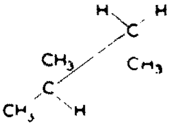
[8] R. Spitzer and K. S. Pitzer, *J. Amer. Chem. Soc.* **70**, 1261 (1948); see also H. C. Brown and W. H. Bonner, *Ibid.* **75**, 14 (1953), and ref. 12.

[9] K. S. Pitzer *Chem. Rev.* **27**, 39 (1940); C. W. Beckett, K. S. Pitzer and R. Spitzer *J. Amer. Chem. Soc.* **69**, 2488 (1947).

for the energy difference between the skew and staggered arrangements of *n*-butane, the above argument suggests that repulsive energy increases in increments of approximately 0·8 kcal/mole in the sequence (I) to (II) to (III). On this basis the heats of hydrogenation of trimethylethylene and of tetramethylethylene, corrected both for olefine and for paraffin strain, are 26·7 and 26·2 kcal/mole, respectively. It would therefore appear that the decrease in heat of hydrogenation that accompanies methyl substitution in this series is not of steric origin. That the effect resides specifically in an intrinsic stabilization of the olefines is most clearly demonstrated in cases where isomeric olefins differing in degree of substitution, and hence also in the nature of the alkyl substituents, yield the same reduction product. Thus the heat of hydrogenation of 1-butene (−30·3 kcal/mole) exceeds that of *trans*-butene ( 27·6 kcal/mole) by 2·7 kcal/mole, a value that represents the heat of isomerization of the mono- into the di-substituted derivative. Similarly, the heats of isomerization of 2-methyl-1-butene (disubstituted) into trimethylethylene (trisubstituted) and of 2,3-dimethyl-1-butene (disubstituted) into tetramethylethylene (tetrasubstituted) are −1·6 and −1·1 kcal/mole, respectively, while the heat of isomerization of *iso*propylethylene into trimethylethylene is −3·4 kcal/mole. The pair 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene constitutes a special exception, which is considered in a later section of this paper.



(I)



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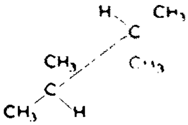

(III)

In 1939 Mulliken suggested that the stabilizing influence of methyl substituents on ethylenic and acetylenic linkages could be explained by hyperconjugation involving α C–H bonds.[10] If the entire effect is thus assigned, hyperconjugation would involve energies of the same order of magnitude as those associated with the conjugation of two double bonds.

Numerous objections to the original Mulliken proposal have been raised in recent years. Baker[11] has noted that if branching in paraffin hydrocarbons can result in stabilization amounting to some few kcal/mole, the same factors may be responsible for stabilization of compounds possessing branches at olefinic carbon atoms.*[10] Furthermore, the fact that methyl, ethyl, *iso*propyl and *tert*.-butyl groups appear to produce equivalent effects requires an explanation beyond that provided by the C–H hyperconjugation theory. Dewar and Pettit[12] have attempted to explain stabilization both in branched paraffins and in alkyl substituted olefins in terms of second-order perturbations in adjacent bonds (H–C–H, C–C–H, C–C–C, C–C–H, C–C–C). It is noted, however, that if C–H and C–C hyperconjugation play roles of comparable importance, the adjacent bond interaction theory for olefins would be unnecessary.

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* It may be noted in this connection that *iso*butene is more stable than *trans*-butene by 1·2 kcal/mole (from free energies of formation given in reference 1).

[10] R. S. Mulliken, *J. Chem. Phys.* 7, 339 (1939); R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* 63, 41 (1941).

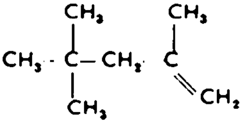
[11] J. W. Baker, *Hyperconjugation* p. 40. Oxford University Press (1952).

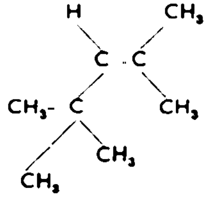
[12] M. J. S. Dewar and R. Pettit, *J. Chem. Soc.* 1625 (1954).

More recently, Dewar[13] has suggested that the effects conventionally ascribed to hyperconjugation in alkyl-substituted olefins, and to electronic delocalization (resonance) in systems of the butadiene type, can be interpreted on the basis of energy variations resulting from changes in hybridization. The greater stability of propylene as compared to ethylene is thus attributed to the fact that on hydrogenation the propylene C–C single bond, formed by $sp^3$–$sp^2$ overlap, is converted into an $sp^3$–$sp^3$ bond whereas in ethylene the analogous change is $s$–$sp^2$ to $s$–$sp^3$. This suggestion possesses considerable merit, although certain of Dewar's deductions regarding conjugated systems will require careful scrutiny.*

Taft and Kreevoy[14] have analyzed the Kistiakowsky data with the aid of an empirical relationship of the general Hammett form and have concluded that in cases where steric factors are unimportant the heats of hydrogenation can be correlated with a reaction parameter ($\rho^*$), an inductive substituent constant ($\sigma^*$), and a hyperconjugation factor ($h$) amounting to about 0·5 kcal for each α C–H bond. An additional parameter for C–C hyperconjugation has been employed by Taft and Lewis[15] in a discussion of hyperconjugative and inductive effects in various reactions of *m*- and *p*-alkylphenyl derivatives, but C–C hyperconjugation has not been specifically considered in the Taft treatment of the Kistiakowsky data.

In connection with a study of elimination accompanying the solvolysis of 2-halo-2,4,4-trimethylpentenes it has been noted that 2,4,4-trimethyl-1-pentene (IV) predominates over 2,4,4-trimethyl-2-pentene (V) in the olefinic portion of the reaction product.[16] Equilibration experiments[17] carried out on (IV) and (V) in 80 per cent aqueous ethanol at 25° furnish an equilibrium constant of the order of 5·7, favoring the $\Delta^1$-product (IV). The free-energy difference between (IV) and (V) is therefore approximately 1 kcal/mole, a result that is consistent with the gas-phase data of Table 1 and with measurements of the heats of hydrogenation of (IV) and (V) carried out in acetic acid solution at 25° (Table 3).[18] The fact that in this case the disubstituted olefin is more stable than the trisubstituted isomer constitutes an important exception to the general rule. Conversion of the *tert*.-butyl groups of (IV) and (V) into *iso*propyl groups gives 2,4-dimethyl-1-pentene and 2,4-dimethyl-2-pentene in


(IV)


(V)

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* The fact that butadiene, which can adopt a planar arrangement, and *cyclo*octatetraene, which cannot, show closely comparable experimental stabilization energies cf. [ref.2 and R. B. Turner, W. R. Meador, W. von E. Doering, J. R. Mayer and D. W. Wiley, *J. Amer. Chem. Soc.* **79**, 4127 (1957)] appears to constitute a discrepancy in the Dewar argument, since butadiene possesses only one $sp^2$-$sp^2$ bond, whereas four such bonds are present in *cyclo*octatetraene.

[13] M. J. S. Dewar and A. N. Schmeising, *Tetrahedron* **5**, 166 (1958).

[14] R. W. Taft and M. M. Kreevoy, *J. Amer. Chem. Soc.* **79**, 4011 (1957).

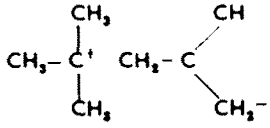
[15] R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.* **80**, in press (1958).

[16] Cf. H. C. Brown and H. L. Berneis, *J. Amer. Chem. Soc.* **75**, 10 (1953).

[17] E. D. Hughes, C. K. Ingold and V. J. Shiner, *J. Chem. Soc.* 3827 (1953).

[18] R. B. Turner, D. E. Nettleton and M. Perelman, *J. Amer. Chem. Soc.* **80**, 1430 (1958).

which the normal stability relationship is restored. In attempting to account for the anomalous behavior of (IV) and (V), Hughes *et al.*[17] noted that, although only five hydrogen atoms are available for hyperconjugation in (IV) as compared to six in (V), important contributions from form (VI) might serve to stabilize the $\Delta^1$-olefin.



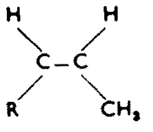
(VI)

Brown and his associates,[16,19] however, have emphasized the fact that the stability of (V) is adversely affected by the presence of a *cis*-methyl-*tert.*-butyl interaction, and that predominance of steric over hyperconjugative effects in this olefin provides a reasonable basis for interpretation of the observed stability order. Calorimetric evidence[18] on the magnitudes of interactions of this type supports the latter view.

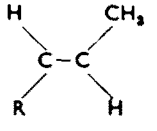
TABLE 3. HEATS OF HYDROGENATION IN ACETIC ACID SOLUTION (25°)*

| Compound | $\Delta H$ (kcal/mole) | $\Delta(\Delta H)$ |
|---|---|---|
| 2,4-Dimethyl-1-pentene | −26·7 | |
| 2,4-Dimethyl-2-pentene | −25·2 | −1·5 |
| 2,4,4-Trimethyl-1-pentene (IV) | −25·5 | |
| 2,4,4-Trimethyl-2-pentene (V) | −26·8 | 1·3 |
| 4-Methyl-*cis*-2-pentene (VIIa) | −27·3 | |
| 4-Methyl-*trans*-2-pentene (VIIIa) | −26·4 | −0·9 |
| 4,4-Dimethyl-*cis*-2-pentene (VIIb) | −30·8 | |
| 4,4-Dimethyl-*trans*-2-pentene (VIIIb) | −26·5 | −4·3 |

* Precision of the data is approximately ±0·5 per cent.



(VIIa. R = $Pr^i$)
(VIIb. R = $Bu^t$)



(VIIIa. R = $Pr^i$)
(VIIIb. R = $Bu^t$)

Whereas the difference between the heats of hydrogenation of the *cis*- and *trans*-4-methyl-2-pentenes (VIIa and VIIIa), in which hyperconjugative and inductive factors, hybridization effects and the like should cancel, is essentially the same as that for the *cis*- and *trans*-butenes (−1·0 kcal/mole), a considerably larger difference (−4·3 kcal/mole) is observed for the *cis*- and *trans*-4,4-dimethyl-2-pentenes (VIIb and VIIIb).*

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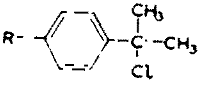
* The fact that the heats of hydrogenation of (VIIIa) (−26·4 kcal/mole), (VIIIb) (−26·5 kcal/mole), *trans*-di*iso*propylethylene (−26·8 kcal/mole, unpublished result) and of *trans*-di-*tert.*-butylethylene (−26·9 kcal/mole, reference 18) are all in close agreement lends further support to the conclusion that in the absence of strain, the effects of alkyl substitution are independent of the nature of the alkyl group.

[19] H. C. Brown and M. Nakagawa, *J. Amer. Chem. Soc.* 77, 3610 (1955); H. C. Brown and I. Moritani, *Ibid.* 77, 3623 (1955).

The strain in (V) resulting from the opposition of *cis*-methyl and *tert.*-butyl groups is therefore sufficient to account for the relative stabilities of (IV) and (V) without recourse to the suggestion of Hughes *et al.*

In 1957 Brown *et al.*[20] reported the results of an investigation of the rates of solvolysis of phenyldimethylcarbinyl chlorides carrying alkyl substituents in the *ortho*, *meta* and *para* positions (cf. (IX)). The *para*-substituted derivatives show marked acceleration in rate of solvolysis over that observed for the parent compound (IX; R = H), despite the presence of an intervening phenyl group and of two methyl groups attached directly to the center of developing electron deficiency. The ratios of rates for the substituted products to that of the unsubstituted derivative are: for *p*-methyl, 26·0; *p*-ethyl, 22·0; *p*-*iso*propyl, 18·8; and for *p*-*tert.*-butyl, 14·4. Since *meta* substitution by the same groups produces only about a two-fold acceleration, it is concluded that the *para* effect is predominantly of hyperconjugative rather than of inductive origin and further that C–C hyperconjugation is nearly as effective as C–H hyperconjugation in stabilizing an incipient carbonium ion. Comparison of the free energies of activation for the various reactions leads to values of about 0·5 kcal and 0·4 kcal for the respective contributions of hyperconjugated C–H and C–C bonds to the stability of the transition state.



(IX)

In this connection thermodynamic information on related neutral molecules would be of considerable interest. The only pertinent data that appear to be available relate to the heats of combustion of *m*-methylstyrene and of *p*-methylstyrene, which are reported[1] as −1163·06 and −1162·86 kcal/mole (vapor phase, 25°), respectively. Calculation of the heat of combustion of a hypothetical methylstyrene, devoid of possible interaction between the methyl and vinyl groups, from the heat of combustion of styrene (−1018·83 kcal/mole) and the difference between the heats of combustion of toluene (−901·50 kcal/mole) and of benzene (−757·52 kcal/mole)[1] gives a comparison value of −1162·8 kcal/mole. Assuming a calorimetric precision of the order of 0·01 per cent, it follows that, within the limits of experimental error, interaction between the methyl and vinyl groups in this system is absent. The result suggests that hyperconjugation is much less important in neutral molecules than it is in electron-deficient states. The rather large stabilization observed in propylene and the lack of such in *p*-methylstyrene may, of course, be attributable to dissipation of the interaction in the benzene ring in the latter compound. The evidence is, however, not inconsistent with Dewar's hypothesis.[13] *m*-Methylstyrene and *p*-methylstyrene possess equal numbers of equivalent bonds, and the hybridization change necessary for construction of the hypothetical model ($s$–$sp^2 \rightarrow sp^3$–$sp^2$) is accounted for in the toluene–benzene difference.

The thermochemical data discussed in this paper provide strong evidence for the stabilizing influence of alkyl substituents in many unsaturated systems. That the cumulative effect is large is indicated by the difference of 6·2 kcal/mole between the

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[20] H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *J. Amer. Chem. Soc.* **79**, 1897 (1957).

heats of hydrogenation of ethylene and tetramethylethylene. This value is comparable in magnitude to the enthalpy differences between *cis*- and *trans*-*cyclo*octene (9·2 kcal/mole),[21] and between *cis*- and *trans*-di-*tert*.-butylethylene ( −9·3 kcal/mole),[18] which result from the involvement of severe steric strains. It is clear, however, that the calorimetric results furnish little information on the origins of the stabilization phenomenon, the nature of which must hence be sought in evidence derived from other sources.

[21] R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.* **79**, 4133 (1957).