294. *Some Observations concerning the Interpretation of Heats of Hydrogenation of Olefinic Substances.*

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The theoretical implications of a recent analysis of tautomeric equilibria governed by the hyperconjugative power of alkyl groups on the one hand, and the conjugative power of phenyl, carboxylate ion, carbethoxy-, and cyano-groups on the other, as well as of the heats of hydrogenation of substituted ethylenes (*J.*, 1951, 2283), are scrutinised. The same experimental results are treated to an equally good approximation, empirical data rather than theoretically deduced resonance energies being used as far as possible. It is concluded that alkyl groups probably affect heats of hydrogenation of substituted ethylenes by their inductive, as well as by their hyperconjugative, effect.

Bateman and Cunneen (*J.*, 1951, 2283) have presented experimental data on the substituted phenylpropenes, in which the position of prototropic equilibrium is governed by the relative energies of conjugation, with an ethylenic double bond, of a phenyl group on the one hand, and of one or more alkyl groups on the other. The influence of different alkyl groups is regarded by these authors as correlated with (*a*) the extent of C–H bond first-order hyperconjugation and (*b*) the operation of a specific effect on replacement of a CH_2 group by CHR. These values, together with a selection of heats of hydrogenation of substituted ethylenes (from the work of Kistiakowsky and his co-workers, *J. Amer. Chem. Soc.*, 1935, **57**, 65, 876; 1936, **58**, 137, 146; 1938, **60**, 440), and values for the positions of equilibrium in systems involving αβ- and βγ-unsaturated acids, esters, and nitriles (from the data of Linstead, Kon, and their collaborators, summarised in Gilman's "Organic Chemistry," Wiley and Sons, N.Y., 2nd edn., 1944, p. 1042), are analysed in terms of a number of postulates (Treatment 1), namely:

(1*a*) That energy differences determined from the heats of hydrogenation (ΔH) of ethylene (32·6 kcal.) and substituted ethylenes may be used to calculate resonance energies, *e.g.*, of benzene (39 kcal.), butadiene (5·1 kcal.), and phenyl-to-vinyl conjugation (2·6 or 3·4 kcal.), which operate additively, and may be applied to the calculation of free-energy differences in prototropic systems.

(1*b*) That the energies of conjugation between an ethylenic link and a carboxylate ion, carbethoxy-, and cyano-group are respectively 1·5, 2·0, and 2·0 kcal.

(1*c*) That the hyperconjugative energy (i) of each single C–H bond with an ethylenic, butadienoid, or phenyl system is 0·3 kcal., (ii) of a C–H bond with a carboxylate ion, carbethoxy-, or cyano-group, is 0·2 kcal., (iii) of a C–C bond with an ethylenic system is negligible except in the absence of C–H bonds, and then is 0·03 kcal. per C–C bond.

(1*d*) That substitution at a CH_2 group in ethylene, irrespective of its nature, introduces a stabilising factor (*S*), which reduces the heat of hydrogenation by 1·5 kcal., while further substitution, whether by one, two, or three groups, introduces a further stabilisation of 1·5 kcal.

The Appendix shows the observed and calculated values. The fit is better for heats of hydrogenation and prototropic equilibria in the substituted phenylpropenes than for the remainder of the data.

In the author's view, this analysis suffers from at least one important unsatisfactory feature, namely, the introduction and the interpretation of the structural factor *S*, on which special emphasis is laid. It is stated that its origin is uncertain, but that it may arise from some interaction between the π-electrons of the methine carbon atom and the sp^3 orbitals of an adjacent saturated carbon atom. Yet this is not considered to be a form of hyperconjugation (not even CC-hyperconjugation), since CC- and CH-hyperconjugative effects are considered separately, and since *S* is held to be largely responsible for certain effects previously attributable to hyperconjugation. It appears to be regarded as related to the strength of the single bond in the system C=C–C; consistently, it is doubled in dialkylethylenes, whether these are 1 : 1- or 1 : 2-substituted; but, inconsistently, further substitution to give tri- or tetra-substituted olefins is regarded as contributing no further to the stabilisation of the molecule.

These difficulties suggest a reconsideration of the data, and it is submitted that the following postulates (Treatment 2) give an equally good account of the determined values:

(2*a*) That energy differences determined from the heats of hydrogenation of ethylene 312·6 kcal.), benzene (49·8 kcal.), butadiene (57·1 kcal.), and styrene (77·5 kcal.) may be applied to the correlation of heats of hydrogenation and free-energy differences in prototropic systems, with the following additional postulates.

(2*b*) That the system $CH_2{:}CH{\cdot}CH_2X \rightleftharpoons CH_3{\cdot}CH{:}CHX$, where X is CO_2^-, CO_2Et, or CN, lies to the right by virtue of a free-energy difference of 2·5 kcal.

(2*c*) That substitution for hydrogen of any alkyl or substituted-alkyl group reduces the heat of hydrogenation of (i) an ethylenic or butadienoid system by 2·3 kcal., (ii) a benzene nucleus by 0·9 kcal., (iii) the system $CH_2{:}CHX$, where $X = CO_2^-$, CO_2Et, or CN, by 1·0 kcal.

(2*d*) That the effectiveness of any alkyl group in the above situations is reduced by 0·5 kcal. for each cross- or opposed-hyperconjugation involving another alkyl group or a butadiene system.

The Appendix shows that Treatment 2 gives an account of the data which is at least as good as that of Treatment 1; it involves adoption of fewer particular numerical values, and is considered preferable as it uses fewer hypotheses. Let us now consider its theoretical implications.

In hypotheses (2*a*) and (2*b*) the argument depends on actual experimental figures, rather than on the derived resonance energies, used in the corresponding postulates (1*a*) and (1*b*) of Treatment 1. The value for the resonance energy of benzene obtained from these data is likely to be inexact; for although the heat of hydrogenation, *e.g.*, of *cyclo*hexene (28·6 kcal.) is similar to that of other 1 : 2-dialkylethylenes, the corresponding values for *cyclo*pentene (26·9 kcal.), *cyclo*heptene (26·5 kcal.), and particularly *cyclo*octene (23·5 kcal.) show discrepancies which are not properly understood (cf. Wheland, "Theory of Resonance," John Wiley and Sons, N.Y., 1944, p. 54; Dewar, *Trans. Faraday Soc.*, 1946, **42**, 767). It seems, therefore, that the properties of ethylenic links, when these are included in rigid or distorted ring structures, may be altered by factors other than those generally included in the category of resonance. Deductions in a conventional way of the resonance energies of butadiene conjugation (8·1 kcal.) and of phenyl-to-vinyl conjugation (4·0 kcal.) are larger in the present than in the earlier treatment, since in the latter the structural factor S is introduced (unnecessarily, in our view) into the calculations. It is preferred not to attempt to differentiate between the relative conjugative power with a double bond of the groups CO_2^-, CO_2Et, and CN (which may be calculated, on the present assumptions, to be worth 3·8 kcal. in stability), since it is considered that the data on the relevant systems are not sufficiently self-consistent to allow such differentiation. The present preference in regard to these first two assumptions is not, however, regarded as fundamental, but rather as a matter of formal convenience.

Hypothesis (2*c*) reveals the first major divergence between the two treatments. In Treatment 1 it is assumed that, in conjugation with the double link, each C–H bond has a hyperconjugative effect, which is some ten times greater than that of a C–C bond, and contributes 0·3 kcal. to the stability. In the present treatment, it is taken that the attachment of any tetrahedral carbon atom to the ethylene system has approximately the same effect on the heat of hydrogenation. The following comparisons from the work of Kistiakowsky and his co-workers (*locc. cit.*) illustrate the experimental justification for this view :

Compound	$CH_2{:}CHMe$	$CH_2{:}CHEt$	$CH_2{:}CHPr^i$	$CH_2{:}CHBu^t$
ΔH	30·1	30·3	30·3	30·3
Compound	$CH_2{:}CMe_2$	$CH_2{:}CMeEt$	$CH_2{:}CMePr^i$	
ΔH	28·3	28·5	28·0	

In these examples, the mean change in ΔH, on replacement, in the position α- to the ethylenic link, of a C–H bond by a C–C bond, is effectively zero. The groups $-CH_3$, $-CH_2Me$, $-CHMe_2$, and $-CMe_3$ have, therefore, approximately equal effect on the heat of hydrogenation. A conventional interpretation might be that these groups in this system have approximately equal conjugative power.

The existence of hyperconjugation from C–C bonds has been theoretically considered by many workers (cf. Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41; Hughes, Ingold, Masterman, and McNulty, *J.*, 1940, 899; Dhar, Hughes, Ingold, Mandour, Maw, and Woolf, *J.*, 1948, 2103; Berliner and Berliner, *J. Amer. Chem. Soc.*, 1948, **70**, 854). Its effect on the properties of chemical systems has, however, proved difficult to demonstrate, since it produces electronic movement qualitatively similar to that usually attributed to the inductive effect. Thus, in the bromination of *tert.*-butylbenzene, which is considerably more rapid than that of benzene (de la Mare and Robertson, *J.*, 1943, 279), it is uncertain whether the difference in reactivity is to be ascribed to an inductive effect or to CC-hyperconjugation, the latter view having been favoured by Berliner and Berliner (*loc. cit.*). In a similar way, the large effect of the *tert.*-butyl group, relative to hydrogen, in the comparison below (Hughes, Ingold, and Taher, *J.*, 1940, 949) may result from the inductive effect of the substituent, and the magnitude of any contribution from CC-hyperconjugation cannot at present be determined.

Solvolysis of $R{\cdot}C_6H_4{\cdot}CHPhCl$ in 80% acetone at 0°	R = H	Me	Et	Pr^i	Bu^t
Relative free energy of activation ($RT \log k_R/k_H$, kcal.)	0·0	1·8	1·7	1·5	1·4

No such difficulty arises, however, in attributing the smaller difference between the methyl and *tert.*-butyl compounds to the effect of CH-hyperconjugation. A similar argument applies to consideration of the prototropic systems :

(*a*) $Ph{\cdot}CH_2{\cdot}CH{:}CH_2 \rightleftharpoons Ph{\cdot}CH{:}CH{\cdot}CH_2{\cdot}H$ .... $\Delta F^* = >4$ kcal.
(*b*) $Ph{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CMe_3 \rightleftharpoons Ph{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CMe_3$ .... $\Delta F = 2{\cdot}0$ kcal.
(*c*) $Ph{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_3 \rightleftharpoons Ph{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_3$ .... $\Delta F = 1{\cdot}3$ kcal.

* The decrease in free energy on transferring 1 g.-mol. from left to right.

The introduction, in (*b*) or (*c*), of either a methyl or a *tert.*-butyl group results in a considerable displacement of the position of equilibrium. As in the similar cases discussed by de la Mare, Hughes, and Ingold (*J.*, 1948, 17), it is clear that CH-hyperconjugation controls the difference between the methyl- and *tert.*-butyl-substituted compounds, in which comparison any contribution from CC-hyperconjugation or from the inductive effect is obscured. The shift in the position of equilibrium on replacing a hydrogen atom by a *tert.*-butyl group [(*a*) $\longrightarrow$ (*b*)], however, could be entirely attributable to CC-hyperconjugation, or could be explained by maintaining that the inductive effect of the *tert.*-butyl substituent resists the tendency to allow a proton to attach itself to an adjacent carbon atom. Any combination of these two explanations is allowed, and the use of the "stabilising factor" (*S*) in Treatment 1 does not aid understanding of the results.

The changes in rate coefficients and in equilibrium constants, upon which depend the various demonstrations that CH-hyperconjugation is energetically more important than CC-hyperconjugation (see Crawford, *Quart. Reviews*, 1949, **3**, 226), are usually quite small, the relative rates of the methyl- and *tert.*-butyl-substituted compounds only rarely being equivalent to a difference in free energy of activation of even as much as 0·5 kcal. It is to be expected that inductive and hyperconjugative influences should have different relative importance in different chemical situations: from this arise, for example, the different spheres of influence of the Hofmann and the Saytzeff rule in elimination reactions (Dhar, Hughes, Ingold, Mandour, Maw, and Woolf, *loc. cit.*), and, in the author's opinion, certain of the differences between the effects of substituents on the rates of halogenation and nitration (cf. de la Mare and Robertson, *J.*, 1948, 100). To a first approximation, however, one would expect to find that CH- and CC-hyperconjugations were evoked to the same proportional extent in different situations. It is a real difficulty, then, that, though there is evidence of the preponderating effect of CH-hyperconjugation in, for example, the tautomeric equilibria of the alkylated phenylpropenes, yet no such clear difference is apparent in the studies of the heats of hydrogenation of alkylethylenes.

It seems probable, therefore, that, contrary to conventional interpretations, these heats of hydrogenation are partly subject to inductive influences. For this reason, hypothesis (2*c*) has been expressed in terms of the experimental results, rather than in a derived form depending on a particular theoretical interpretation. At the same time, a further improvement on the earlier treatment is achieved by assuming, in agreement with experiment, that an alkyl group has a smaller effect on the heat of hydrogenation when attached to a phenyl than to a vinyl group. It is assumed also that alkyl groups affect the heat of hydrogenation of systems containing CO_2Et and similar groups by only 1·0 kcal. Kistiakowsky and his co-workers (*locc. cit.*) discussed the following heats of hydrogenation (ΔH, for $X = CO_2R$):

Compound	Me·CH:CHX	Et·CH:CHX	$Me{\cdot}CH{:}CH{\cdot}CH_2X$	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2X$
ΔH	28·0	27·5	29·6	31·1

They concluded that the extent of conjugation between a double link and a carbethoxy-group is small, but equally methyl-to-vinyl hyperconjugation may have become reduced, when the vinyl group was also conjugated with a carbethoxy-group. That such compounds as $CH_3{\cdot}CH_2{\cdot}CH{:}CHX$ ($X = CO_2Me$, CO_2^-) are the predominant forms in their equilibria with prototropic isomers $CH_3{\cdot}CH{:}CH{\cdot}CH_2X$ supports the latter view. Bateman and Cunneen's treatment (*loc. cit.*), by stressing the stabilising factor *S*, gives calculated values for the heats of hydrogenation of these compounds which are consistently lower than the experimental values. Better agreement is secured by the present treatment.

A hypothesis such as (2*d*) is necessary because the reduction in the heat of hydrogenation of polymethylethylenes is not proportional to the number of methyl groups introduced. Two methyl groups appear to be about twice as effective as one, but the effect of further methyl groups becomes progressively less. The earlier treatment introduces an analogous, entirely empirical, assumption by using the stabilising factor *S* only twice, whether in 1 : 1-, 1 : 2-, 1 : 1 : 2-, or 1 : 1 : 2 : 2-substituted compounds. In the present treatment, a correction is applied by adding 0·5 kcal. to the calculated heat of hydrogenation (*a*) once for each pair of opposed alkyl groups (*i.e.*, once in 1 : 2-dialkylethylenes, twice in trialkylethylenes, and four times in tetra-alkylethylenes); (*b*) once when the hyperconjugation is crossed with a butadienoid conjugation (*i.e.*, when the alkyl group is placed in the 2- or the 3-position of a conjugated system –C:C·C:C–); (*c*) twice, in systems $C{:}C{\cdot}CH_2{\cdot}C{:}C$ or C:C·CHR·C:C.

In attempting to assess the success of the two treatments, we consider the experimental results in three sections. First, adequate treatment of the heats of hydrogenation requires independent knowledge of at least as many experimental values as are assumed in the present treatment. This makes fewer assumptions than the previous analysis, and gives a better fit (as measured by the mean square of the discrepancies between observed and calculated values), both for the compounds considered in the earlier treatment, and for those additional examples quoted in the Appendix.

APPENDIX

*Observed and Calculated * Energy Differences (kcal.).*

A. *Heats of hydrogenation* (ΔH) *of substituted ethylenes.*

	Found	Calc. (i)	Calc. (ii)
$CH_2{:}CH_2$	32·6	32·6	32·6
$CH_2{:}CHMe$	30·1	30·3	30·2
$CH_2{:}CH{\cdot}CH_2Me$	30·3	30·3	30·5
$CH_2{:}CH{\cdot}CHMe_2$	30·3	30·3	30·8
$CH_2{:}CMe_2$	28·3	28·0	27·8
$CH_2{:}CMe{\cdot}CH_2Me$	28·5	28·0	28·1
$CH_2{:}CMe{\cdot}CHMe_2$	28·0	28·0	28·4
$CH_2Me{\cdot}CH{:}CHMe$	28·0	28·5	28·1
$CMe_2{:}CHMe$	26·9	26·7	26·9
$CMe_2{:}CMe_2$	26·6	25·4	26·0
$CH_2{:}CH{\cdot}CH{:}CH_2$	57·1	57·1	57·1
$CH_2{:}CH{\cdot}CH{:}CHMe$	54·1	54·8	54·7
$CH_2{:}CMe{\cdot}CMe{:}CH_2$	53·9	53·5	52·3
$CH_2{:}CH{\cdot}CH_2{\cdot}CH{:}CH_2$	60·8	61·6	61·0
$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$	60·5	60·6	61·0
$Ph{\cdot}H$	49·8	49·8	49·8
$Ph{\cdot}CH_2Me$	48·9	48·9	49·2
$Ph{\cdot}CH{:}CH_2$	77·5	77·5	77·5

Addenda. Additional compounds relevant to the discussion.

	Found	Calc. (i)	Calc. (ii)
$CH_2{:}CH{\cdot}CMe_3$	30·3	30·3	(31·1)
$Me{\cdot}CH{:}CH{\cdot}CO_2Et$	28·0	27·8	(26·7)
$Et{\cdot}CH{:}CH{\cdot}CO_2Et$	27·5	27·8	(27·0)
$Me{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2Et$	29·6	29·0	(28·1)
$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$	31·1	30·3	(30·5)
$Me{\cdot}CH{:}CHMe$ (*cis*)	28·5	28·5	(27·8)
$Me{\cdot}CH{:}CHMe$ (*trans*)	27·5	28·5	(27·8)

B. *Free-energy differences* (ΔF) *from the position of equilibrium in the system* $R_1R_2C{:}CR_3{\cdot}CHR_4X \rightleftharpoons R_1R_2CH{\cdot}CR_3{:}CR_4X$.

R_1	R_2	R_3	R_4	X	ΔF (found)	ΔF (i)	ΔF (ii)
H	H	H	H	Ph	>4	4·0	(3·8)
H	CMe_3	H	H	Ph	2·0	2·2	2·0
H	$CHMe_2$	H	H	Ph	1·8	2·2	1·8
H	Me	H	H	Ph	1·3	2·2	1·3
Me	Me	H	H	Ph	0·2	0·4	0·2
H	H	H	H	CO_2^-	2·9	2·5	2·9
H	Me	H	H	CO_2^-	0·6	0·7	0·2
H	Et	H	H	CO_2^-	0·8	0·7	0·5
H	Me	H	Me	CO_2^-	1·1	1·2	1·6
H	Et	H	Me	CO_2^-	1·6	1·2	1·9
H	Me	Me	H	CO_2^-	−0·4	−0·1	0·2
Me	Me	H	H	CO_2^-	−1·0	−1·1	−1·0
H	Me	Et	H	CO_2^-	−1·0	−0·1	0·2
Me	Et	H	H	CO_2^-	−1·0	−1·1	−0·7
H	Me	Me	Me	CO_2^-	0·7	−0·1	1·6
H	Me	Et	Me	CO_2^-	0·0	−0·1	1·6
H	Et	H	H	CO_2Et	1·4	0·7	1·0
H	Et	H	Me	CO_2Et	1·8	1·2	2·4
H	Me	Me	H	CO_2Et	0·7	−0·1	0·7
Me	Me	H	H	CO_2Et	−1·4	−1·1	−0·5
H	Me	Me	Me	CO_2Et	1·6	−0·1	2·1
H	H	H	H	CN	2·3	2·5	3·4
H	Et	H	H	CN	1·1	0·7	1·0
H	Me	Me	H	CN	*2·7*	*−0·1*	*0·7*
Me	Me	H	H	CN	−0·8	−1·1	−0·5

* (i) = This paper; (ii) = Bateman and Cunneen, *J.*, 1951, 2283; values in parentheses have been calculated analogously.

In the second place, the results for the alkyl-phenylpropenes are fitted slightly better by the earlier than by the present treatment in two of the four examples available. This slightly better fit arises partly from the assumption of a different value for the effect of phenyl-to-vinyl conjugation in treating this section of the data, and partly as the result of a subsidiary hypothesis, which assumes a difference between the effectiveness of CC- and CH-hyperconjugation. Since this difference does not appear in the heats of hydrogenation, it must be impossible to interpret in a consistent manner the two sets of data without introducing some further subsidiary hypothesis. To take account of the difference between the observed effects of alkyl substituents in the two systems, therefore, a further degree of approximation than that of the treatment now preferred would be required.†

In the third place, the present treatment fits the data for acids, esters, and nitriles slightly better, if the italicised value for $CH_2Me{\cdot}CMe{:}CH{\cdot}CN$ is neglected, but slightly worse if this value is included. The error of estimate in each treatment is larger for this than for any other compound, and Bateman and Cunneen (*loc. cit.*) give a special explanation in terms of the mutual inductive influences of the methyl and cyano-substituents. In the author's view, a similar discrepancy would then have been expected in the analogous compound containing, in place of CN, the CO_2Et group which must also exert a very

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† For a similar reason, we have neglected, among other factors which may sometimes be important: (i) steric requirements of hyperconjugation (cf. Baddeley, Chadwick, and Rawlinson, *Nature*, 1949, **164**, 833); (ii) the effect of polar groupings in changing the hyperconjugative power of the C–H bonds in CH_2X (cf. Robertson, Heyes, and Swedlund, *J.*, 1952, in the press); (iii) hyperconjugation of the type $\overset{\curvearrowright}{CH_2{=}CH}{-}CH_2\overset{\curvearrowright}{-}X$ (cf. de la Mare, Hughes, and Ingold, *loc. cit.*).

strong inductive effect. Such a discrepancy is not observed, however, and therefore there seems to be no satisfactory explanation of the anomaly in terms of either treatment. Extension of the data relating to esters and cyanides to include further examples would seem to be required to solve this difficulty.

The position of equilibrium in the system $CH_3{\cdot}CHBr{\cdot}CH{:}CH_2 \rightleftharpoons CH_3{\cdot}CH{:}CH{\cdot}CH_2Br$ (ΔF : Found, 1·3. Calc., 1·8) is reasonably well explained on the scheme now preferred; there is no evidence to allow assessment of the effect which Bateman and Cunneen (*loc. cit.*) propose in this case. The bond energies of propane and propylene, compared with those of ethane and ethylene, are also understandable; in dissociating the C–Me bond in propylene, the energy of methyl-to-vinyl hyperconjugation (about 2·3 kcal., in the present estimate) is lost, whereas hyperconjugation of this type is not found in the other compounds.

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