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SUBSTITUENT EFFECTS ON HYPERCONJUGATION: EVALUATION OF HYPERCONJUGATION ENERGY FOR GROUPS OF THE TYPE $\cdot CH_2X$

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QUALITATIVE assessment of the relative magnitudes of the mesomeric hyperconjugation of groups of the type $\cdot CH_2X$, when X is varied, was attempted[1] by a study of the equilibria:

$$p\text{-}XCH_2\cdot C_6H_4\cdot CH{:}O + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} p\text{-}XCH_2\cdot C_6H_4\cdot CH(OH)\cdot CN$$

whence, from the value of $K = k_2/k_1$, the values of $\Delta F = -RT \ln K$ were determined. As defined, ΔF is the increase in free energy for the dissociation of the cyanohydrin into aldehyde and hydrogen cyanide. This free-energy change will include contributions from both polar (inductive) and mesomeric ($+M$) hyperconjugative effects of the substituent group CH_2X towards the stabilisation of the free aldehyde relative to its cyanohydrin. The difficulty in the interpretation of the results arose from the inability to separate the magnitudes of the inductive and hyperconjugative components. The inductive effect of a group R is essentially a measure of the ground-state change in polarity of a C–R bond relative to that of a C–H bond as standard and, as a first approximation, this should vary little from system to system. The hyperconjugative effect may, like any conjugative effect, vary in magnitude from system to system and it depends on the degree of electron-orbital overlap and so on the extent of the conjugated system involved, i.e., on the degree of possible electron delocalisation.

Separate evaluation of the inductive and conjugative contributions would thus give more reliable information regarding the hyperconjugative effects of a single H–C bond for various groups in a given system, or of any one group in different systems. A basis for such quantitative separation has recently been provided by the treatment developed by Taft,[2] who has shown the wide application of the relationships ΔF (for equilibria) or $\log (k_R/k_H)$ (for reaction velocities) $= \sigma^*_R\rho^* + nh$, where σ^*_R is the polar constant for the substituent R (determined from a wide range of data on ester hydrolysis), ρ^* is a reaction constant which measures the susceptibility of the reaction to polar effects, n is the number of hyperconjugated C–H bonds and h is the energy associated with a single H–C bond hyperconjugation.

Application of this treatment to the earlier results for the cyanohydrin reaction makes possible some degree of quantitative evaluation of h for different groups CH_2X.

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[1] J. W. Baker, J. A. L. Brieux and D. G. Saunders, *J. Chem. Soc.* 404 (1956).

[2] For a summary see R. W. Taft, Jr., *Separation of Polar, Steric, and Resonance Effects in Reactivity* in *Steric Effects in Organic Chemistry* (Edited by M. S. Newman) p. 556 *et seq.* Wiley, New York (1956).

Its application to certain reaction velocities also provides some indication of the effective hyperconjugation of alkyl groups in reactions of different polar requirements.†

In the evaluation of σ^*_{R} values Taft used the methyl compound as the reference standard, assigning to it the value $\sigma^*_{\mathrm{CH_3}} = 0{\cdot}000$. On this scale hydrogen, which is less electron repelling than methyl, has $\sigma^*_{\mathrm{H}} = +0{\cdot}490$. Since, in the systems here considered, the parent unsubstituted compound has been taken as the reference standard, the value of σ^*_{H} has been taken as 0·000, and Taft's values have been adjusted accordingly, e.g., $\sigma^*_{\mathrm{CH_3}} = -0{\cdot}490$. *All* σ^* *values used in this paper refer to* $\sigma^*_{\mathrm{H}} = 0{\cdot}000$. The treatment is first applied to cyanohydrin equilibria with *para*-alkyl-substituted benzaldehydes.

Equilibria

(a) *Alkyl groups*. The relevant data[3] for the equilibria between *p*-alkylbenzaldehydes and their cyanohydrins are in Table 1.

TABLE 1. EQUILIBRIUM CONSTANTS $K = k_2/k_1$ AND ΔF FOR THE EQUILIBRIA $p\text{-R}\cdot\mathrm{C_6H_4}\cdot\mathrm{CH{:}O} + \mathrm{HCN} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} p\text{-R}\cdot\mathrm{C_6H_4}\cdot\mathrm{CH(OH)}\cdot\mathrm{CN}$ IN CONSTANT-BOILING ALCOHOL AT 20°

R	σ^*_{R}‡	10^3K (mole/l.)	ΔF observed (kcal)	ΔF calculated (kcal)	h (kcal)
H	0·000	4·47	3·15	(3·15)	--
$\mathrm{CH_3}$	−0·490	8·98	2·75	2·75	0·07
$\mathrm{C_2H_5}$	−0·590	8·18	2·80	2·78	0·062
iso-$\mathrm{C_3H_7}$	−0·680	8·04	2·81	2·82	0·082
tert.-$\mathrm{C_4H_9}$	−0·790	7·49	2·85	(2·85)	—

‡ Ref. 2, p. 619.

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† After this treatment was completed later work by Taft suggested that σ^* values are valid indications of the magnitudes of the inductive effects of groups *only* in the aliphatic series, and he developed a treatment of equilibria and reaction velocities in aromatic systems on the basis of σ_I values, defined by the relationship $\sigma_I = 0{\cdot}45\sigma^*_{\mathrm{CH_2R}}$, for the substituent group R. Use of σ_I values, with the corresponding reaction constants ρ_I, evaluate the inductive polar effects of *ortho*-, *meta*- or *para*-substituent groups in aromatic systems, using the relationship $1/(1-\alpha)[\log(K_m/K_0) - \alpha\log(K_p/K_0)] = \sigma_I\rho_I$, where α is the (constant) fraction of the resonance effect of the substituent in the *para* position which operates as a second-order effect from the *meta* position. The values of the ratio of σ^*/σ_I differ widely for different groups, and it is evident that there is, at present, no consistent relationship between σ^* and σ_I values. Moreover, the present writer finds it difficult to accept that the magnitude of the inductive effect of a group R in the system $\mathrm{R{-}C_{arom}}$ should be only approximately 45 per cent of that of the group $\mathrm{R\cdot CH_2}$ in $\mathrm{R\cdot CH_2{-}C_{alip}}$. If a damping effect to about one-third is assumed for the intercalation of the saturated methylene group, this would imply that the magnitude of the inductive effect in $\mathrm{R{-}C_{arom}}$ is only approximately 15 per cent of that in $\mathrm{R{-}C_{alip}}$. In spite of the wide correlation effected by Taft using the $\sigma_I\rho_I$ relationship, it was decided to use σ^* values (which are available for all but one of the groups studied in the cyanohydrin reaction) derived from aliphatic reactions, as probably valid empirical assessments of the relative inductive contributions to the cyanohydrin equilibria. Almost the only other *variable* polar factor in the substituted benzaldehyde system studied is the degree of hyperconjugation, and the main purpose in this paper is to obtain some relative, empirical numerical values for this contribution. Any C–C hyperconjugation has been neglected, but there is some evidence (see below) that it is not significant in the equilibria studied. The writer understands from Professor Taft (personal communication) that his alternative treatment, using the $\sigma_I\rho_I$ relationship, applied to the cyanohydrin data, does not alter any of the conclusions reached in this paper, although it gives somewhat higher numerical values for *h*.

[3] J. W. Baker and M. L. Hemming, *J. Chem. Soc.* 191 (1942).

The reaction proportionality constant may be evaluated by elimination of h between the various equations $\Delta F_{\mathrm{R}} - \Delta F_{\mathrm{H}} = (\sigma^*_{\mathrm{R}} - \sigma^*_{\mathrm{H}})\rho^* - nh$. The value so obtained (+ 0·372) is almost identical with that obtained by assuming that C–C hyperconjugation of the *tert.*-butyl group is insignificant in these equilibria, whence, since C–H hyperconjugation is absent in both the unsubstituted and *tert.*-butylbenzaldehydes, $\Delta F_{\mathrm{Bu^t}} - \Delta F_{\mathrm{H}} = 0{\cdot}30 = 0{\cdot}790\rho^*$, i.e., $\rho^* = +0{\cdot}380$. The positive value of ρ^* is in harmony with the experimental finding that the equilibrium is displaced in the direction of the cyanohydrin by unequivocal electron attraction (e.g., $10^3K_{m\text{-}\mathrm{NO_2}} = 2{\cdot}1$; $\Delta F = 3{\cdot}31$ kcal) and towards the free aldehyde by electron release (e.g. $10^3K_{m\text{-}\mathrm{CH_3}} = 5{\cdot}5$; $\Delta F = 3{\cdot}03$ kcal). The values of h in the last column of Table 1 are determined from the relationships $\Delta F_{\mathrm{R}} - \Delta F_{\mathrm{H}} = +0{\cdot}380\,(\sigma^*_{\mathrm{R}} - \sigma^*_{\mathrm{H}}) - nh$†, the mean value being $h = 0{\cdot}072$. Use of this mean value assumes (with Taft) that, in this *alkyl* series of substituents, the hyperconjugation energy per H–C bond is approximately constant, an assumption which, as is shown below, is not correct when X in $\cdot\mathrm{CH_2X}$ is not alkyl.

In order to apply the correlation not to differences in ΔF but to the individual ΔF values themselves, it is necessary to evaluate the contribution (x) due to polar and conjugative interaction of the phenyl and aldehyde groups, present in all cases. This can be done by using the unsubstituted compound in which hyperconjugation is absent and the polar effect of R = H is, by definition, zero, i.e., $3{\cdot}15 = 0{\cdot}380x$, whence $x = 8{\cdot}29$ kcal. Taft's σ^* values (polar electron attraction) for $\mathrm{C_6H_5}$ and CH:O, corrected to the standard $\sigma^*_{\mathrm{H}} = 0{\cdot}000$ are, respectively $+0{\cdot}11$ and $+0{\cdot}86$, and the extra resonance energy associated with benzaldehyde is 7·1 kcal;[4] the combined polar and resonance effects of $\mathrm{C_6H_5\cdot CH{:}O}$ in the parent system would thus be of the order $7{\cdot}1 + 0{\cdot}97 = 8{\cdot}07$, a value in fair agreement with that determined by the above treatment. The ΔF values for the various cyanohydrin equilibria are then accurately represented by the equation $\Delta F = 0{\cdot}380\,(\sigma^*_{\mathrm{R}} + 8{\cdot}29) - 0{\cdot}072n$, or its alternative form, $\Delta F = 0{\cdot}380\,\sigma^*_{\mathrm{R}} + 3{\cdot}15 - 0{\cdot}072n$, whence the calculated values of ΔF in the fifth column of Table 1 are derived. In the former expression the total polar effects of the phenyl and the aldehyde groups are regarded as subject to the reaction constant $\rho^* = 0{\cdot}380$, whilst in the latter their constant contribution, assessed from the experimental data for the unsubstituted benzaldehyde, $\Delta F = 3{\cdot}15$ kcal/mole, is separately enumerated.

Although too much significance should not be attached to the actual numerical value of h, its small value indicates the order of magnitude of the + *M* effect of hyperconjugation per H–C bond in the equilibria studies. Thus in *p*-tolualdehyde the extra stabilisation of the free aldehyde relative to its cyanohydrin due to methyl-group hyperconjugation is only of the order of a few hundred cal/mole.

(b) *Groups of the type* $\cdot\mathrm{CH_2X}$. The apparent validity of the above-deduced relationship for ΔF for all alkyl substituents studied suggests that it may be used to evaluate the relative values of h in the various substituent groups $\cdot\mathrm{CH_2X}$, derived from similar data which were obtained by Baker *et al.*,[1] n in all cases (except X = H) being 2. The necessary data and results are in Table 2.

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† The sign of nh is negative because, with ρ^* positive, hyperconjugation electron release will increase K, i.e., decrease ΔF. When ρ^* is negative, the sign of nh will be positive, the value of h always being assigned a positive value.

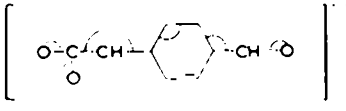
[4] M. M. Kreevoy and R. W. Taft, Jr., *J. Amer. Chem. Soc.* 79 4016 (1957).

TABLE 2. EVALUATION OF MESOMERIC h FOR GROUPS CH_2X IN THE EQUILIBRIA $p\text{-}XCH_2 \cdot C_6H_4CHO + HCN \rightleftharpoons p\text{-}XCH_2 \cdot C_6H_4 \cdot CH(OH) \cdot CN$ FROM THE RELATION $\Delta F = 0{\cdot}380\, \sigma^*_R + 3{\cdot}15 - nh$

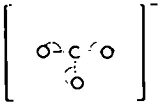
X	ΔF (kcal)	$\sigma^*_{CH_2X}$	h (kcal)
NEt_3^+	2·55	+1·41	0·57
Cl	2·79	+0·56	0·29
HO_2C	2·92	+0·56	0·22
$(O_2C$	2·74	?	?)
OH	2·84	+0·06	0·17
EtO_2C	3·06	+0·22	0·09
H	2·75	0·490	0·07
CH_3	2·80	0·590	0·06
$(OCH_3\text{-}p$	3·24	−0·03	0·04)
$(OCH_3\text{-}m$	3·26	+0·03	0·05)

+ σ^*_R Value for $CH_2 \cdot \overset{+}{N}Me_3$ used.

With the exceptions of X = OH and OMe (discussed below) the groups CH_2X are arranged, in Table 2, in order of decreasing values of σ^*, i.e., of decreasing −I effects (or increasing +I) and the effective hyperconjugation per H–C bond in these groups decreases from the top to the bottom of the table, in agreement with the qualitative order previously postulated.[1] This semi-quantitative treatment of the equilibria thus confirms the earlier suggestion[1] that hyperconjugation of CH_2X is increased by the capacity of the group X to stabilise the negative charge in the canonical structure $X \cdot \overset{\overset{+}{H}}{\bar{C}H} \cdot C_6H_4 \cdot CH{:}O$, involved in hyperconjugation, and thus to increase the importance of such structures in the mesomeric structure of the aldehyde. Such stabilisation may be by either inductive or conjugative effects of X. Stabilisation by the inductive effect (−I) is illustrated by the observation that the value of h for CH_2X decreases in the order X = $\overset{+}{N}Et_3$ > Cl > OH, which is the order of decreasing −I effects of X. Stabilisation by the conjugative effect of X is illustrated by the cases where X = CO_2Et, CO_2H and $CO \cdot \bar{O}$, all of which show a greater degree of hyperconjugation, per H–C bond, than when X = H. It is unfortunate the σ^* values are not available for the group $CH_2 \cdot \bar{CO_2}$, and hence it is not possible to get any quantitative assessment of the contribution of inductive electron release towards the relative stabilisation of the free aldehyde, but it may be noticed that the structure $\bar{O} \cdot CO \cdot \overset{\overset{+}{H}}{\bar{C}H} \cdot C_6H_4 \cdot CH{:}O$, in which the two negative charges may be distributed between two oxygen atoms and the formylbenzyl group (A), simulates very closely the resonance stabilisation in the symmetrical carbonate anion (B).



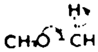
(A)



(B)

One other factor may possibly make a small contribution when X is strongly electron attracting. Before the experimental results were obtained Coulson (personal communication) made a very tentative guess that increase in the electron-attracting power of X would cause a flow of charge in the C–X bond, leading to increased electronegative character of the carbon atom. This should make the CH_2 group a little more coplanar with the phenyl ring and so facilitate hyperconjugation, but the effect, if present, would be very small. The conformity of the experimental results with this conclusion may indicate that it is a factor which makes a small contribution towards the increased hyperconjugation observed when X is a strongly electron-attracting group like $\overset{+}{N}R_3$.

The group $CH_3O \cdot CH_2$ is anomalous, since the values of ΔF for the *meta*- and *para*-substituted derivatives are almost identical, indicating the absence of any significant conjugative effect. The meaningless very small negative values for *h* found with this group confirm this conclusion. One possible explanation might be found in competing *anionic* hyperconjugation,[6]



but the different behaviour of the groups $HO \cdot CH_2$– and $CH_3O \cdot CH_2$– is difficult to explain on this basis.

Velocity data

In reaction velocities, all polarizability effects, favourable to the reaction, will be called into play. These may include inductomeric and electromeric effects and all such effects will be included, indiscriminately, in any conjugative or hyperconjugative effect derived from the application of the $\sigma^*\rho^*$ type of analysis. For this reason alone, similar analysis of velocity data may not be quite as satisfactory as a means of evaluating the hyperconjugation contribution, but such analyses do, nevertheless, provide some interesting results.

(a) *In the cyanohydrin reaction.* Baker and Hemming[3] also determined the separate values of k_1 and k_2 in the benzaldehyde-cyanohydrin reaction. Their results are in Table 3. These are less accurate than are those for the equilibrium constants *K*, especially those for k_2, which were determined from the relation k_2 k_1K and so involve the product of the separate experimental errors in both *K* and k_1. These k_2

TABLE 3. VELOCITY DATA FOR THE REACTION $p\text{-R} \cdot C_6H_4 \cdot CHO + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} p\text{-R} \cdot C_6H_4 \cdot CH(OH) \cdot CN$ IN EtOH OF CONSTANT BOILING POINT AT 20°

R =	H	CH_3	C_2H_5	*iso*-C_3H_7	*tert*.-C_4H_9
10^4k_1 (mole $^{-1}$l. sec $^{-1}$)	1·96	0·98	1·01	0·85	0·91
log $(k_1{}^R/k^H)$	0	0·301	0·288	0·363	0·333
$10^{10}k_2$ (sec $^{-1}$)	0·87	0·88	0·82	0·68	0·68
σ^*_R	0·00	0·490	0·590	0·680	0·790

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[6] F. H. Seubold, Jr., *J. Org. Chem.* **21**, 156 (1956).

values do not conform to the above analytical treatment. An approximate treatment of the k_1 values is, however, possible, although even here the very small velocity differences do not readily lend themselves to such analysis.

Although the values of *h* vary slightly for the different alkyl substituents (0·03, 0·02, 0·07), these results are approximately represented by the relationship $\log (k_1^R/k_1^H) = +0{\cdot}43\sigma^*_R - 0{\cdot}03n$. The rather larger positive value for ρ^* for the forward reaction than for the equilibrium is in agreement with Lapworth's early finding[6] that, in cyanohydrin formation, attack is by the CN ion and hence the forward reaction is facilitated by electron attraction away from the carbonyl carbon atom. The small value of *h*, of the same order of magnitude as that in the equilibrium expression, suggests that only the mesomeric component (+*M*) of hyperconjugation is operative in the forward reaction, a conclusion to be expected since hyperconjugation is an electron-release mechanism which would retard the electrostriction of the cyanide ion.

(b) *In unimolecular* (S_N1) *and bimolecular* (S_N2) *nucleophilic substitution.* In the unimolecular nucleophilic substitution, the solvolysis of benzhydryl chlorides,[7] the rate-determining stage $p\text{-R}\cdot C_6H_4\cdot CHPh\cdot Cl \rightarrow p\text{-R}\cdot C_6H_4\cdot \overset{+}{C}HPh + Cl^-$, is unequivocably facilitated by electron release by the group R = alkyl and hence the mesomeric hyperconjugation (+*M*) will here be greatly increased by the operation of a strong electromeric component (+*E*). Application of the above method of analysis should thus reveal the magnitude of this total H–C hyperconjugative effect. The relevant data, including some later results of Shiner and Verbanic,[8] are in Table 4.

TABLE 4. VALUES OF k_1 FOR THE SOLVOLYSIS OF $p\text{-R}\cdot C_6H_4\cdot CHPhCl$ IN 80 PER CENT AQUEOUS ACETONE AT 0°

R	σ^*_R	10^6k_1	$\log k_1^R/k_1^{H}$*	*h*
H	0·000	2·82[7]; 2·618[8]	0	–
CH_3	0·490	83·5	+1·4715[7]	0·26
C_2H_5	0·590	62·6	+1·3464[7]	0·26
iso-C_3H_7	0·680	47·0	+1·2219[7]	0·27
tert.-C_4H_9	−0·790	35·9	+1·1049[7]	– –
n-C_3H_7	−0·620	56·92	+1·3374[8]	0·23
$(CH_3)_2CH\cdot CH_2$	0·615	50·2	+1·2828[8]	0·21
$(CH_3)_3C\cdot CH_2$	0·655	40·06	+1·1848[8]	0·13

* With reference to value of log k^H observed by the particular investigator.

Solution of the various equations $\log (k_1^R/k_1^H) = \sigma^*_R\rho^* + nh$ gives $\rho^* = -1{\cdot}40$, whence the various values of *h* in the last column of Table 4 are determined. For the results of Hughes *et al.*[7] this unimolecular solvolysis is accurately represented by the relation $\log (k_1^R/k_1^H) = -1{\cdot}40\sigma^*_R + 0{\cdot}26n$; those of Shiner and Verbanic require a slightly smaller value for *h*. The large negative value of ρ^* indicates the expected strong *facilitation* of this reaction by electron release from R and the much larger

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[6] A. Lapworth, *J. Chem. Soc.* **83**, 995 (1903).

[7] E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.* 949 (1940).

[8] V. J. Shiner, Jr. and Verbanic, *J. Amer. Chem. Soc.* **79**, 369 (1957).

value of *h* (approximately 0·26) indicates that the total (+*M*, +*E*) hyperconjugative effect per H–C bond now operative is at least four times as great as the mesomeric component alone. The significantly lower value of *h* for the *neo*pentyl group may well indicate some steric inhibition of the hyperconjugation[9] in addition to the +*I* effect of the substituent CMe_3 group on the effective hyperconjugation of the attached CH_2 group.

The bimolecular nucleophilic substitution:

$$p\text{-R}\cdot C_6H_4\cdot CH_2Br + C_5H_5N \rightarrow p\text{-R}\cdot C_6H_4\cdot CH_2\cdot \overset{+}{N}C_5H_5\}\overset{-}{Br},$$

from the results of which the concept of H–C hyperconjugation was originally formulated,[10] will be much less electron demanding, since, in the transition state, electron release, although facilitating the separation of bromine with its bonding electrons, will hinder the electrostriction of the pyridine molecule. Hyperconjugative electron release should thus be much smaller. Analysis of the experimental results, given in Table 5, completely confirms both these conclusions.

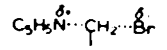
TABLE 5. VALUES OF k_2 FOR THE REACTION

$$p\text{-R}\cdot C_6H_4\cdot CH_2Br + C_5H_5N \rightarrow p\text{-R}\cdot C_6H_4\cdot CH_2\cdot \overset{+}{N}C_5H_5 \,:\, \overset{-}{Br}$$

IN DRY ACETONE AT 20°

R	σ^*_R	$10^4 k_2$ (mole^{-1}l. sec^{-1})	$\log (k_2^R/k_2^H)$	*h*
H	0·000	1·22	0	—
CH_3	0·490	2·02	+0·2190	0·049
C_2H_5	−0·590	1·81	+0·1693	0·040
iso-C_3H_7	−0·680	1·63	+0·1258	0·024
tert.-C_4H_9	0·790	1·65	−0·1311	

The relative velocity data are represented by the equation $\log (k_2^R/k_2^H$ − $0{\cdot}15\sigma^*_R$ + $0{\cdot}04n$ to an accuracy of 0·01 – 0·02 log units. The much smaller negative value of ρ^* reflects the smaller electron demand of this S_N2 reaction. The low value of *h*, of the same order of magnitude as that for the mesomeric component, suggests that the polarisation of the C–Br bond in the transition state



does not invoke appreciable unsaturation at the methylenic carbon atom to stimulate any electromeric hyperconjugative effect.

Too much significance must not be attached to the absolute numerical values of *h*, but these analyses, based on free-energy calculations, suggest that the energy associated with the mesomeric hyperconjugation of a single H–C bond in *alkyl* groups attached to an aromatic system is small and only about 40–70 cal/mole, whereas when the

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[9] G. Baddeley, J. Chadwick and S. B. Rawlinson, *Nature, Lond.* **164**, 833 (1949); cf. G. Baddeley and M. Gordon, *J. Chem. Soc.* 2190 (1952).

[10] J. W. Baker and W. S. Nathan, *J. Chem. Soc.* 1844 (1935); J. W. Baker, *J. Chem. Soc.* 1150 (1939).

electromeric effect is stimulated by a strongly electron-demanding reaction this value is increased about four-fold to approximately 260 cal/mole. These values of *h* are appreciably lower than the average value (approximately 0·5 kcal) found by Taft and Kreevoy for the enthalpies of hydrogenation of various substituted ethylenes and the free energies of hydrogenation of carbonyl compounds $R^1R^2C{:}O$. They suggest that the conclusion of these authors that hyperconjugation stabilisation is less susceptible to electron demand at the reaction centre and may be assigned an approximately constant value (approximately 0·5) is possibly a somewhat oversimplified generalisation. The value and usefulness of Taft's method of analysis for the evaluation of the approximate magnitudes of hyperconjugation effects is, however, further illustrated by the analyses described in this paper.