dures now available should make the radioiodine detection method more generally useful. Since it has been shown recently that carrier-free mixtures of the organic bromides can be separated on partition columns,[20] use of this technique may avoid difficulties due to failure to add proper carrier components. It is hoped that extension of these studies may reveal much more in the way of the fine structure of the radical spectrum produced by radiation.

Acknowledgment.—We wish to express our thanks to Mr. Paul R. Geissler for assistance in making some of the measurements reported here.

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[20] J. B. Evans and J. E. Willard, THIS JOURNAL, **78**, 2908 (1956).

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

The Evaluation of Inductive and Resonance Effects in Reactivity. II. Thermodynamic Properties of Hydrogenation of Non-conjugated Olefins, Aldehydes and Ketones[1]

BY ROBERT W. TAFT, JR., AND M. M. KREEVOY

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The effect of unconjugated (α,β-saturated) substituents on the enthalpies of hydrogenation of mono- and *trans*-disubstituted ethylenes, $\Delta\Delta H°$, and on the free energies of hydrogenation of carbonyl compounds, $R_1R_2C{=}O$, $\Delta\Delta F°$, are found to follow with acceptable precision eq. 2: $\Delta\Delta H°$ (or $\Delta\Delta F°$) $= (\Sigma\sigma^*)\rho^* + (\Delta n)h$. This empirical relationship is suggested by and is correlated with the hypothesis that polar and hyperconjugative effects of the substituents contribute approximately additively to give the observed effect on the thermodynamic property. This hypothesis unifies diverse observed effects of substituents with theory. An important polar contribution to the thermodynamic properties for these reactions is expected in view of the change from the sp^2 to the sp^3 valence state of carbon which accompanies the hydrogenation. Evidence is obtained that hyperconjugation stabilization is much less susceptible to electron demand at the reaction center than is stabilization by inductive electron-release. The hyperconjugation stabilization per α-hydrogen atom in an open chain olefin or carbonyl compound is found to be about 0.5 kcal./mole.

The effect of alkyl substituents on the enthalpies of hydrogenation of olefins has been commonly attributed to hyperconjugation of the group with the C–C double bond.[2,3] If the entire effect of the substituent on the enthalpy of hydrogenation is attributed to hyperconjugation or conjugation in the olefin, the resulting hyperconjugation energies obtained for alkyl groups appear to be unreasonably large compared to the conjugation energies obtained for α,β-unsaturated substituents.[4]

Adkins and students have determined the free energies of hydrogenation of numerous aldehydes and ketones in dilute toluene solutions at 60°.[5] Hyperconjugation of alkyl substituents with the carbonyl group is reasonably expected to make at least as important contribution to these hydrogenation equilibria as those for olefin hydrogenation. However, the effects of alkyl groups on the free energies of hydrogenation of aldehyde and ketones do not show a distinct hyperconjugation order. In fact, conjugation effects of unsaturated groups on the free energies of hydrogenation are frequently not (or only slightly) discernible.

The hydrogenation of double bonded compounds is accompanied by a marked decrease in the intrinsic electronegativity of the atoms at the double bond.[6] This results from the fact that the sp^2 valence state of a given atom is appreciably more electronegative than the sp^3 state. Rates and equilibria for reactions which involve a substantial change in the electron demand at the reaction center show large susceptibilities to the electron attracting and releasing powers of substituent groups. That is, polar effects of substituents are large for reactions of this kind.

Important inductive, as well as hyperconjugation, effects are therefore expected to contribute to the observed effects of substituents on the enthalpies and free energies of hydrogenation of olefins, aldehydes and ketones.

In paper I it was shown that the very large effects of substituents on the rates of hydrolysis of diethyl acetals and ketals (of non-conjugated aldehydes and ketones) are correlated in an approximately quantitative manner by an equation which attributes the total effect of the substituent on the free energy of activation to the sum of independent inductive and hyperconjugation effects.[7] The acid-catalyzed rate constants in this reaction series follow with acceptable precision the equation

$$\log (k/k_0) = (\Sigma\sigma^*)\rho^* + (\Delta n)h \qquad (1)$$

where $\Sigma\sigma^*$ is the sum of the polar substituent constants, σ^*, for the substituents, R_1 and R_2, of the acetal or ketal of the general formula $R_1R_2C(OC_2H_5)_2$. These polar substituent constants were ob-

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[1] The work herein reported was carried out on Project NR055-328 between the Office of Naval Research and The Pennsylvania State University. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] (a) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 149; (b) R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).

[3] J. W. Baker, "Hyperconjugation," Oxford at the Clarendon Press, 1952, p. 40, has pointed out that while the enthalpy data are consistent with hyperconjugation theory, it cannot be regarded as evidence for the validity of the concept.

[4] K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953, p. 184.

[5] H. Adkins, R. M. Elofson, A. G. Rossow and C. C. Robinson, THIS JOURNAL, **71**, 3622 (1949).

[6] (a) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934); **3**, 573 (1935); *cf.* also comments on the importance of the electronegativity of the valence state in reactivity considerations, R. W. Taft, Jr., *J. Chem. Phys.*, **26**, 93 (1957).

[7] M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **77**, 5590 (1955).

tained by Taft from data on the acid-catalyzed hydrolysis and the alkaline saponification of esters, $RCO_2C_2H_5$.[8] n is the total number of hydrogen atoms in R_1 and R_2 of the general compound (for which k is the rate constant). Δn is the difference between n and n_0, where n_0 pertains to the standard of comparison (for which k_0 is the rate constant). The standard was chosen so that $R_1 = R_2 = CH_3$ ($\Delta n = n - 6$, $\Sigma\sigma^* = 0.000$). The empirical reaction constant, ρ^*, measures the susceptibility of the hydrolysis reaction to polar effects. The empirical constant h is interpreted as a measure of the hyperconjugative stabilization of the reaction transition state by a single α-hydrogen atom.

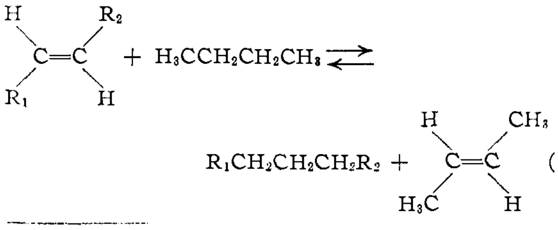
In this paper we report the correlation of the effect of substituents on the enthalpies of hydrogenation of *trans*-substituted, unconjugated olefins, $\Delta\Delta H°$, and of free energies of hydrogenation of unconjugated aldehydes and ketones, $\Delta\Delta F°$, by the equation

$$\Delta\Delta H° \text{ (or } \Delta\Delta F°) = (\Sigma\sigma^*)\rho^* + (\Delta n)h \qquad (2)$$

The empirical correlation eqs. 1 and 2 provide a simple, self-consistent theory of the effects of substituents on these rates and equilibria. In paper III it is shown that the evaluation of hyperconjugation and inductive effects by eqs. 1 and 2 can be used to obtain approximately quantitative values of the conjugation effects of α,β-unsaturated substituents.[9] The relative magnitudes of the hyperconjugation and conjugation effects obtained in this manner are quite reasonable.

Enthalpies of Hydrogenation of Gaseous Olefins.—Kistiakowsky and co-workers[10] have determined calorimetrically the vapor phase enthalpies of hydrogenation for a number of olefins. In addition a number of enthalpies of hydrogenation can be derived from accurate data on heats of formation.[11-13] The largest body of reliable data is available at 355°K.

The effect of structure on the enthalpy of hydrogenation of mono- and *trans*-disubstituted ethylenes is given by the enthalpy change, $\Delta\Delta H°_{355}$, of the following reaction, using *trans*-2-butene ($\Delta n = n - 6$) as the standard of comparison


(I)

where R_1 or R_2 is any substituent which is not conjugated with the functional group (hereafter referred to as an α,β-saturated substituent). The 21 available enthalpies of hydrogenation, $\Delta\Delta H°_{355}$, of this class cover a range of 5.2 kcal./mole, and are correlated by eq. 2 with a mean difference between calculated and observed values of 0.1 kcal. The latter figure is approximately the same as the estimated experimental uncertainty.[10-12]

The values of ρ^* and h which give the best fit of the data to equation 2 are: $\rho^* = -2.409 \pm 0.151$ and $h = 0.437 \pm 0.51$ (with a residual of $+0.1$ kcal./mole). Table I also lists the corresponding enthalpies at absolute zero, $\Delta\Delta H°_0$. It is important to note that corresponding values of $\Delta\Delta H°_{355}$ and $\Delta\Delta H°_0$ are nearly the same, and that eq. 2 therefore holds for the enthalpies at absolute zero.

The enthalpies of hydrogenation of *cis*- and vicinally disubstituted ethylenes and cyclic olefins are not generally fitted with precision by eq. 2. Deviations from eq. 2 for a number of typical olefins of this kind are given in Table II.

For the *cis*- and vicinally disubstituted olefins the deviations are reasonably attributed to steric effects which result from the shorter bond lengths and greater rigidity of the olefins as compared with the saturated hydrocarbons. For the cyclic olefins the deviations can be attributed to changes in the number of eclipsed carbon–hydrogen bonds on going from the unsaturated to the saturated compound.[14]

The enthalpies of hydrogenation of conjugated olefins also do not follow eq. 2. In this case the positive differences between the calculated and the observed enthalpies are thought to be close measures of the increase in resonance stabilization resulting from conjugation (*cf.* paper III).[9]

Free Energies of Hydrogenation of Aldehydes and Ketones.—Adkins and co-workers[5] made an extensive study of the equilibrium constants (which we shall denote by K/K_0) for the general reaction

$$R_1R_2C{-}O + (CH_3)_2CHOH \rightleftarrows R_1R_2CHOH + (CH_3)_2CO \qquad (II)$$

The reactions were carried out in dilute toluene solution, and were catalyzed by aluminum *t*-butoxide. Most of the data were obtained at 60° but a few data at other temperatures are included since the position of equilibrium does not appear to be appreciably temperature dependent. Seventeen available free energies, $\Delta\Delta F^0 = -2.303RT \log (K/K_0)$, for unconjugated aldehydes and ketones have a total spread of nearly 6 kcal./mole. These free energies are correlated by eq. 2 with an average deviation between observed and calculated values of 0.4 kcal., a figure of the same magnitude as the experimental uncertainty.[2,3] The standard of comparison is acetone ($\Delta n = n - 6$; $\Sigma\sigma^* = 0.000$) and the values of ρ^* and h which give the best fit of the data to eq. 2 are: $\rho^* = -6.39 \pm 0.26$, and $h = 0.54 \pm 0.06$ (with a residual of $+0.6$ kcal./mole).

Table III illustrates the fit of these free energies to eq. 2. The values given by Adkins, *et al.*, for dimethoxyacetone, formaldehyde and chloral have

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[8] R. W. Taft, Jr., THIS JOURNAL, **74**, 3120 (1952); **75**, 4231 (1953). For a recent compilation of σ^* values, *cf.* M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

[9] M. M. Kreevoy and R. W. Taft, Jr., *ibid.*, **79**, 4016 (1957).

[10] (a) J. B. Conant and G. B. Kistiakowsky, *Chem. Revs.*, **20**, 182 (1937); (b) M. A. Dolliver, J. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, THIS JOURNAL, **60**, 440 (1938); (c) earlier references given in (a) and (b).

[11] E. Schjanberg, *Z. physik. Chem.*, **179A**, 39 (1937).

[12] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimental, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pennslyvania, 1953, pp. 704–746.

[13] The fact that heats of hydrogenation derived from several types of measurements are all correlated by eq. 2 lends additional support to the validity of the treatment.

[14] H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

TABLE I

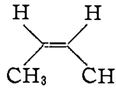
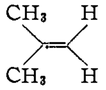
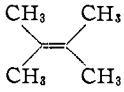
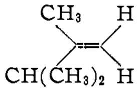
CORRELATION OF ENTHALPIES OF HYDROGENATION OF GASEOUS MONO- AND *trans*-DISUBSTITUTED ETHYLENES BY EQ. 2

Substituents R_1		$\Sigma\sigma^*$	n	$\Delta\Delta H°_{355}$, kcal./mole Calcd. eq. 2	Exp l.	$\Delta\Delta H°_0$[b] exptl. kcal./mole	$\Delta\Delta F°_{355}$,[b] kcal./mole Exptl.	"Cor.[f]"
CH_2OH	H	1.045	2	−4.3	−3.9[a]	...	...	...
H	H	0.980	0	−4.9	−5.2[a]	−5.1	−5.0	−4.9
$RO_2C(CH_2)_2$[e]	H	.750	2	−3.5	−3.5[c]	...	...	...
$H_2C{-}CH{-}CH_2$	H	.620[d]	2	−3.1	−3.0[a]	−2.6	−2.3	−1.8
$H_2C{-}CH{-}(CH_2)_2$	H	.535	2	−2.9	−2.7[a]	...	...	...
CH_3	H	.490	3	−2.4	−2.5[a]	−2.1	−1.4	−1.9
C_2H_5	H	.390	2	−2.6	−2.7[a]	−2.7	−2.0	−2.5
n-C_3H_7	H	.375	2	−2.6	−2.6[a]	−2.5	−1.8	−2.3
n-C_4H_9	H	.360	2	−2.5	−2.6[b]	−2.5	−1.9	−2.4
n-C_5H_{11}	H	.360	2	−2.5	−2.5[a]	−2.5	−1.8	−2.3
i-C_4H_9	H	.365	2	−2.5	−2.5[b]	−2.7	−2.7	−2.7
neo-C_5H_{11}	H	.325	2	−2.4	−1.9[a]	...	...	...
i-C_3H_7	H	.300	1	−2.8	−2.7[a]	−2.2	−2.1	−2.1
s-C_4H_9	H	.280	1	−2.8	−2.8[b]	−2.6	−1.8	−1.8
t-C_4H_9	H	.190	0	−3.0	−2.7[a]	−2.9	−2.7	−2.7
RO_2CCH_2[e]	CH_3	.710	5	−2.1	−2.0[c]	...	...	...
CH_3	CH_3	.000	6	+0.1	(0.0)[a]	(0.0)	(0.0)	(0.0)
C_2H_5	CH_3	− .100	5	−0.1	0.0[b]	−0.1	+1.3	+0.8
n-C_3H_7	CH_3	− .115	5	−0.1	0.0[b]	+0.1	+0.4	+0.4
i-C_3H_7	CH_3	− .190	4	−0.3	−0.2[b]	+0.5	0.0	0.0
C_2H_5	C_3H_5	− .200	4	−0.3	0.0[b]	−0.1	−0.1	−0.1

[a] Ref. 1; $\Delta H°_{355}$ for *trans*-butene-2 is −27.6 kcal. [b] Ref. 12. [c] Ref. 11. [d] The σ^* value for $CH_3CH{=}CHCH_2$ was used. [e] Average value for seven different esters; mean deviation ±0.8 kcal./mole. [f] The values of $\Delta\Delta H°_{355}$ and $\Delta\Delta F°_{355}$ differ by terms involving partition functions for translational, rotational and vibrational motions. (*Cf.* ref. 18, pp. 563-564): $\Delta\Delta H° - \Delta\Delta F° = RT^2\,[d(\ln \pi Q)/dt] + RT \ln (\pi Q)$; $(\pi Q) = \frac{q_P q_{R_0Y}}{q_{P_0} q_{RY}}$, where q's are partition functions for the substances involved in reactions I and II and generalized by the notation: $RY + P_0 \rightleftarrows R_0Y + P$. The similarity of products and reactants in reaction I or II suggests that the partition functions will be nearly the same for products and reactants, *i.e.* $(\pi Q) \cong 1$, except that in a number of cases the "symmetry numbers" which enter into rotational partition functions (*cf.* ref. 23, p. 296) will be different. These "symmetry numbers" have no effect on $\Delta\Delta H°$ but they may alter $\Delta\Delta F°$ appreciably. The effect is calculated readily and can be subtracted from the observed values of $\Delta\Delta F°$. For olefin hydrogenation the resulting "corrected" values of $\Delta\Delta F°_{355}$ are generally more nearly equal to corresponding $\Delta\Delta H°$ values than the uncorrected $\Delta\Delta F°_{355}$ values.

TABLE II

DEVIATIONS FROM EQ. 2 FOR *cis*- AND VICINALLY SUBSTITUTED ETHYLENES AND CYCLIC OLEFINS

Olefin	$\Delta\Delta H°_{355}$,[a] kcal./mole	$\Delta\Delta H°_{355}$ calcd. eq. 2 kcal./mole
	−1.0	+0.1
	−0.8	+0.1
	+1.0	+5.2
	−0.4	−0.3
	+0.7	−0.1[b]
	−1.0	−0.3[c]

[a] Data of ref. 10. [b] Calculated value is based on σ^* for methylethylethylene. [c] Calculated value is based on $\sigma°$ for diethylethylene.

been omitted from the correlation. The data for these compounds appear to be unreliable. The original authors report doubt as to whether equilibrium was established in these cases. It was also suspected that side reactions, *e.g.*, polymerization and acetal formation, may have been involved.[15]

TABLE III

CORRELATION OF FREE ENERGIES OF HYDROGENATION OF ALDEHYDES AND KETONES ($R_1R_2C{-}O$) BY EQ. 2[a]

Substituents R_1	R_2	$\Sigma\sigma^*$	n	$\Delta\Delta F°_{333}$, kcal./mole Calcd. eq. 2	Exptl.
CH_3	H	+0.490	3	−4.2	−4.4
i-C_4H_9	H	+ .365	2	−3.9	−4.2
t-C_4H_9	H	+ .190	0	−3.9	−3.8
CH_3OCH_2	CH_3	+ .520	5	−3.3	−2.8
$(C_6H_5)_2CH$	CH_3	+ .405	4	−3.2	−2.4
$C_6H_5CH_2$	CH_3	+ .205	5	−1.3	−0.5
CH_3	CH_3	.000	6	+0.6	(0.0)
C_2H_5	CH_3	− .100	5	+0.7	+0.3
Cyclo-C_6H_{11}	CH_3	− .150	4	+0.5	+0.6
i-C_3H_7	CH_3	− .190	4	+0.7	+0.3
t-C_4H_9	CH_3	− .300	3	+0.9	+0.4
$C_6H_5CH_2$	$C_6H_5CH_2$	+ .430	4	−3.2	−4.0
C_2H_5	C_2H_5	− .200	4	+0.8	+0.9
n-C_3H_7	n-C_3H_7	− .230	4	+1.0	+1.4
n-C_4H_9	n-C_4H_9	− .260	4	+1.2	+1.4
i-C_4H_9	i-C_4H_9	− .250	4	+1.1	+1.3
i-C_3H_7	i-C_3H_7	− .380	2	+0.9	+1.4

[a] "Symmetry numbers" corrections of $\Delta\Delta F°_{333}$ (*e.g.*, those given in Table I) are small (on the order of experimental uncertainty), and therefore "corrected" $\Delta\Delta F_{333}$ values are not included in Table III.

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(15) R. M. Elofson, Ph.D. Thesis, University of Wisconsin, 1944.

α,β-Unsaturated substituents are not included in the correlation because of expected conjugation effects. The difference between the free energies calculated by eq. 2 and the observed values for such system are taken as measures of the energies of conjugation stabilization in the aldehyde or ketone (*cf.* paper III[9]).

Discussion and Conclusions

In accord with expectations based upon the greater electron demand made by the sp^2 than the sp^3 valence state, the correlation of the enthalpies and free energies of hydrogenation by eq. 2 provides evidence of an appreciable polar contribution to these thermodynamic properties.

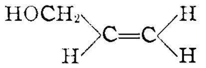
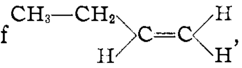
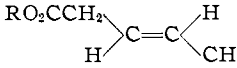
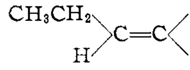
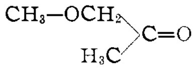
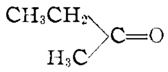
The hydrogenation of aldehydes and ketones is much more favored by electron-withdrawing substituents ($\rho^* = -6.39$) than is the hydrogenation of olefins ($\rho^* = -2.41$). This result is reasonably attributed to a significant contribution from the form $>C^+—O^-$ which makes a carbonyl carbon atom more electron deficient than those of the olefin C–C double bond. The magnitude of the ρ^* values as well as that of the difference between them is perhaps larger than expected but since a quantitative theory for prediction of ρ^* values has not been developed further comment is unwarranted.

In contrast to the marked difference in susceptibilities (ρ^*) of the thermodynamic properties of hydrogenation to inductive electron-releasing power of substituent groups, the hyperconjugation parameter, h, is the same within the combined uncertainties for olefins ($h = 0.44 \pm 0.05$) as for aldehydes and ketones ($h = 0.54 \pm 0.06$). This result is in line with other evidence (*cf.* paper III) which indicates that the resonance stabilization in these systems is much less susceptible to electron demand at the reaction center than is stabilization by inductive electron-release.[9] The availability of an open orbital for conjugation or hyperconjugation appears to be the important variable contributing to resonance stabilization.

The empirical parameter, h, measures the hyperconjugation stabilization due to a single α-H atom in an olefin, aldehyde or ketone in kcal./mole since the effect on the hydrogenation equilibrium is assumed to be associated entirely with the unsaturated state.

Kreevoy and Eyring have recently adopted a model for theoretical consideration of hyperconjugation. Their results are in approximate accord with the values of the h parameter and the linear dependence of hyperconjugation energy on the number of α-hydrogen atoms.[16]

While the correlations of eq. 1 and 2 provide no apparent evidence of C–C hyperconjugation, it is quite probable that such interactions exist. Evaluation of the effects due to such interaction requires more critical data than are presently available.

Dewar and Pettit have recently suggested that enthalpies of hydrogenation of olefins (and several similar reactions) can be explained without involving the concept of hyperconjugation.[17] From certain simplified theoretical considerations, these authors conclude that all olefins having the general formula $H_2C{=}CH(CR_1R_2R_3)$ should have a characteristic enthalpy of hydrogenation, as should olefins of the given general formula $(R_1R_2R_3C)CH{=}CH(CR_4R_5R_6)$, etc. However, this conclusion is not in accord with available data, unless the R groups are confined to alkyl groups. Thus, the hydrogenation of  is 1.2 kcal. more exothermic than that of , and the hydrogenation of  is 2.0 kcal. more exothermic than that of . The free energy of hydrogenation of  is 3.1 kcal. more negative than that of .

According to eq. 2 these differences are due to polar contributions to the thermodynamic properties.

The near constancy of the enthalpies of hydrogenation for a given structural type with substitution of only *alkyl groups* is typical of a number of similar observations. In terms of eq. 1 and 2, which consistently describe the behavior of other types of substituents, this constancy results from an approximate cancellation of opposed polar and hyperconjugation effects of the *alkyl groups*.

An interesting feature of the correlation of the free energies of hydrogenation of the carbonyl compounds by eq. 2 is that the classical distinction between aldehydes and ketones is not required. In terms of eq. 2, the more positive free energy of reduction displayed by a ketone than the corresponding aldehyde results from the greater electron-releasing power of alkyl groups (than a hydrogen atom) through both inductive and hyperconjugative interactions with the carbonyl group.

The effects of α,β-saturated substituents on rates and equilibria for a number of other reactions are correlated by eqs. 1 and 2. These reactions are of such character that hyperconjugation effects are expected and it is reasonable that steric effects should be nearly constant within the reaction series. Unfortunately, the available data do not cover either a wide enough range in the polarities of the substituent groups or in hyperconjugation effects to provide a convincing test of eq. 1 or 2. Examples are summarized in Table IV. Reaction series 1 and 2 of Table IV have been previously correlated (less precisely) with σ^* values alone.[18,19]

It was noted earlier that the effects of substituents on the enthalpies of hydrogenation of olefins at 0°K are also correlated satisfactorily by eq. 2. Evidence is thus provided that the thermodynamic

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[16] M. M. Kreevoy and H. Eyring, THIS JOURNAL, **79**, in press (1957).

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TABLE IV

REACTION SERIES CORRELATED BY EQ. 1 OR 2

Reaction	Equation	Ref.
1. Ionization of carboxylic acids, RCO_2H, H_2O, 25°	$\log (K/K_0) = (1.72)\sigma^* + (n - 3)(-0.08)^a$: K_0, ionization constant for acetic acid	*Cf.* ref. 18
2. Rate of solvolysis of *t*-carbinyl chlorides $R(CH_3)_2CCl$, aq. ethanol. 25°	$\log (k/k_0) = (-3.40)\sigma^* + (n - 3)(0.25)^b$: k_0, rate constant for *t*-butyl chloride	*Cf.* ref. 19
3. Rate of solvolysis of 3-substituted 1,1-dimethylprop-2-ynyl chlorides, $RC{\equiv}C(CH_3)_2CCl$, aq. ethanol. 25°	$\log (k/k_0) = (-3.79)\sigma^* + (n - 3)(0.45)^c$: k_0, rate constant for $CH_3C{\equiv}C(CH_3)_2CCl$	20
4. Vapor phase hydrogenation of substituted acetylenes, $R_1C{\equiv}CR_2$, 355°K.	$\Delta\Delta H^\circ_{335} = (-5.53)(\sigma^*) + (n - 6)(0.59)^d$: ΔH°_0, enthalpy of hydrogenation of dimethylacetylene	12. 21

[a] Mean deviation of calcd and observed values ± 0.05 log units for 18 acids covering a range of 3.75 log units. [b] Mean deviation of calcd. and observed values ± 0.18 log units for 12 compounds covering a range of 3.8 log units. [c] Mean deviation between calcd. and observed values ± 0.05 log units for 5 compounds covering a range of 3.3 log units. [d] Mean deviation been calculated and observed values ± 0.2 kcal./mole for 8 compounds covering a range of 9.5 kcal./mole.

properties are good estimators of potential energy terms.[22]

For hydrogenation of aldehydes and ketones, $\Delta\Delta H^\circ$ values are not generally available. However, $\Delta\Delta F^\circ_{333}$ values for acetaldehyde and methyl ethyl ketone, −4.4 and +0.3 kcal./mole, respectively, may be compared with corresponding $\Delta\Delta H^\circ_{355}$ values determined directly in the vapor phase,[10] −3.4 and +0.2 kcal./mole, respectively. The nature of the agreement lends support to the conclusion that the $\Delta\Delta F^\circ_{333}$ values are significant measures of potential energies.

Equations 1 and 2 provide evidence that polar and hyperconjugation effects contribute independently (at least approximately) to the free energies. This conclusion bears an analogy to first order perturbation theory, which gives the following relationship.[23]

$$E = E_0 + \lambda_n \int \psi_0{}^* H_n \psi_0 d\tau$$

In this equation E_0 is the energy of the unperturbed system, λ_n is a parameter characteristic of the perturbation n, ψ_0 is the eigenfunction of the unperturbed system, and H_n is an operator characteristic of perturbation n. E is the energy of the slightly perturbed system. If more than one kind of perturbation is made, E is obtained from the sum of independent small perturbation energies. Since the effects with which eq. 1 and 2 deal are in the order of 0–10 kcal./mole, while bond energies are of the order of 50–100 kcal./mole, the assumption of the independent character of polar and hyperconjugation terms is apparently equivalent to the use of first order perturbation theory.

Calculation of Parameters Giving Best Fit of Data to Eq. 2.—The values of ρ^* and h giving best fit of the experimental data to eq. 2 have been obtained from the generalized equations of Anderson and Bancroft.[24] Pavelich has set these equation into a form convenient for determining best fit of data to an equation (*e.g.*, eq. 2) in two variables.[25]

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