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

The Evaluation of Inductive and Resonance Effects in Reactivity. III. Extra Resonance Energies of Conjugation[1]

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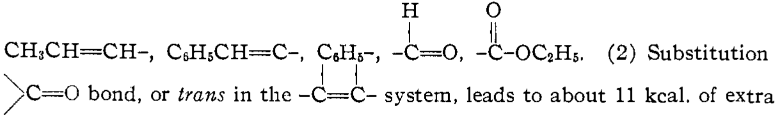
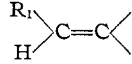
The extra resonance energies of conjugation of α,β-unsaturated substituents in aldehydes, ketones and mono- or *trans*-disubstituted ethylenes have been evaluated by correcting the observed free energies and enthalpies of hydrogenation for polar and hyperconjugation effects. The results show the following systematic relationships to structure: (1) substitution of an α,β-unsaturated substituent at a C–C or C–O double bond leads to about 6 kcal. of extra resonance energy. This figure has been found to hold for a wide variety of α,β-unsaturated substituents within which resonance varies markedly, *e.g.*,



$CH_3CH{=}CH-$, $C_6H_5CH{=}C-$, C_6H_5-, $-\overset{H}{\overset{|}{C}}{=}O$, $-\overset{O}{\overset{\|}{C}}-OC_2H_5$. (2) Substitution of two α,β-unsaturated substituents at the $>C{=}O$ bond, or *trans* in the $-\underset{|}{C}{=}\underset{|}{C}-$ system, leads to about 11 kcal. of extra resonance energy. (3) The extra resonance energy of mono-conjugation of an α,β-unsaturated substituent is approximately ten times greater than that of hyperconjugation by an α-hydrogen atom. All of these structural relationships are correlated by theoretical calculations based upon the LCAO–MO method. The extra resonance energies of conjugation for the transition states for the acid-catalyzed hydrolysis of diethylacetals and ketals are evaluated and discussed. Some applications to rates of addition of carbonyl compounds are discussed.

In papers I and II, the effects of unconjugated (α,β-saturated) substituents, R, on (1) the acid-catalyzed rates of hydrolysis of diethyl acetals and ketals, $R_1R_2C(OC_2H_5)_2$; (2) the enthalpies of hydrogenation of gaseous *trans*-substituted ethylenes,  $R_1HC{=}CHR_2$, and (3) the free energies of hydrogenation of aldehydes and ketones $R_1R_2C{=}O$, were shown to follow the equation[2]

$$\Delta\Delta F^\circ \text{ (or } \Delta\Delta H^\circ\text{, or } \Delta\Delta F^{\ddagger}) = (\Sigma\sigma^*)\rho^* + (\Delta n)h \quad (1)$$

The effects of α,β-unsaturated substituents on the thermodynamic properties deviate from eq. 1 in the direction expected for extra resonance stabilization in the conjugated system.[2] In the present paper these deviations are considered in detail.

We define a thermodynamic property conjugation effect parameter ($\Delta\Delta F_\psi$, for example) by the relationship

$$\Delta\Delta F_\psi = \Delta\Delta F^\circ - (\Sigma\sigma^*)\rho^* - (\Delta n)h \quad (2)$$

The utility of this definition depends upon the degree of approximation attending the following assumptions: (1) the substituent effect on the thermodynamic property ($\Delta\Delta F^\circ$, for example) is equal to the sum of independent polar, hyperconjugation and conjugation ($\Delta\Delta F_\psi^\circ$) effects[3]; (2) the polar and hyperconjugation effects are evaluated by the terms $(\Sigma\sigma^*)\rho^*$ and $(\Delta n)h$, respectively; and (3) the steric effects of substituents are constant within the reaction series.

The polar effect susceptibility parameter, ρ^*, and the hyperconjugation parameter, h, are determined for each reaction series by the substituents which do not have α,β-unsaturation (*cf.* papers I and II). The fact that the effects of α,β-saturated substituents of markedly varying steric requirements are successfully correlated by eq. 1—without the inclusion of a steric effect term—strongly suggests that steric effects specific to α,β-unsaturated substituents are small.

Polar effects are implied to make important contributions to the thermodynamic properties for α,β-unsaturated substituents since σ^* values are appreciably more positive (electron-withdrawing) for this type of substituent than for the methyl group (for example, $\sigma^* = 0.600$ for C_6H_5 and 0.360 for $CH_3CH{=}CH-$), and ρ^* values of large magnitude have been established.[2]

The quantity $[(\Sigma\sigma^*)\rho^* + (\Delta n)h]$ may be regarded by the present treatment as the effect on the thermodynamic property expected for the hypothetical α,β-unsaturated substituent without conjugation stabilization. It is apparent from eq. 2 that the conjugation effect parameter is obtained as the difference between the observed and this hypothetical value of the substituent effect on the thermodynamic property.

Each of the reaction series treated in papers I and II (and in this paper) involves a state for which the reaction center is saturated. In accord with the usual convention that conjugation and hyperconjugation interactions are considered to be negligible at saturated centers,[4] the conjugation effect parameter obtained from eq. 2 may be taken as a measure of the extra resonance energy of conjugation between substituent and unsaturated center involved in each reaction.

Although the conjugation energies derived by eq. 2 are rough because of the approximations listed above, the results (given in Tables I, II and III) are obtained from a reasonable extension suggested by earlier correlations and interpretations of reactivity. It will be shown in this paper that the results are uniquely more systematic and self-consistent than earlier estimates. The results are also reasonably correlated by calculations from simple molecular orbital theory.

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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) M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **77**, 5570 (1955); (b) R. W. Taft, Jr., and M. M. Kreevoy, *ibid.*, **79**, 4011 (1957).

[3] This same model has been employed earlier by P. B. D. De la Mare (*J. Chem. Soc.*, 1602 (1952)) and also L. Bateman and J. I. Cunneen (*ibid.*, 2283 (1951)), in procedures for empirically calculating enthalpies of hydrogenation. However, these authors were unable to deal adequately with polar effects and, as a result, their resonance parameters are unrelated to those reported in this paper.

[4] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 152.

TABLE I

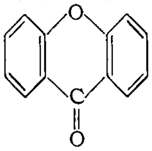
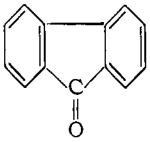
EXTRA RESONANCE ENERGY OF CONJUGATION FROM ENTHALPIES OF HYDROGENATION OF GASEOUS OLEFINS[l]

Compound	$\Delta\Delta H°_{355}$,[g] kcal./mole	$(\Sigma\sigma^*)\rho^* + (\Delta n)h$	$\Delta\Delta H_\psi$, kcal.	ΔE_ψ, kcal.
		Monoconjugated		
$CH_3CH{=}CHCHO$[h]	+2.4	−4.9[a]	7.3	6.6 (0.49 β)
$C_6H_5CH{=}CH_2$[h]	−1.0[b]	−5.3	4.3	5.8 (.43 β)
$CH_2{=}CHCH{=}CH_2$[h]	+0.8[c]	−4.3[d]	5.1	6.3 (.47 β)
$CH_3CH{=}CHCH{=}CH_2$[h]	+3.7[e]	−1.8	5.5	6.3 (.47 β)
$CH_3CH{=}CHCO_2R$[i]	−0.4	−6.1[f]	5.7	6.6 (.49 β)
$C_2H_5CH{=}CHCO_2R$[i]	+0.1	−6.3[f]	6.4	6.6 (.49 β)
		Diconjugated		
$C_6H_5CH{=}CHCO_2CH_3$[j]	+2.9	−8.9	11.8	12.8 (.95 β)
$C_6H_5CH{=}CHC_6H_5$[j]	+7.0	−5.5	12.5	12.6 (.93 β)
$C_2H_5O_2CCH{=}CHCO_2C_2H_5$[j]	−2.2	−12.3[f]	10.1	13.4 (.99 β)
		Other		
$C_6H_5CH{=}CHCH{=}CHC_6H_5$[j,k]	+10.8	−8.3	19.1	19.4 (1.40 β)

[a] σ* value of +1.65 used for –CH=O group. [b] $\Delta\Delta H°_{355}$ value obtained by subtracting value for hydrogenation of ethylbenzene from that for complete hydrogenation of styrene. [c] $\Delta\Delta H°_{355}$ value obtained by subtracting the value for hydrogenation of 1-butene from that for complete hydrogenation of 1,3-butadiene. [d] σ* value of +0.360 used for $\mathrm{H}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}{=}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}-$ group. [e] $\Delta\Delta H°_{355}$ value obtained by subtracting the value for hydrogenation of 1-pentene from that for complete hydrogenation of 1,3-pentadiene. [f] σ* value of +2.000 used for $-CO_2C_2H_5$ group. [g] $\Delta H°_{355} = -27.6$ kcal./mole for standard of comparison, *trans*-butene-2. [h] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, THIS JOURNAL, **59**, 831 (1937); **60**, 440 (1938); J. B. Conant and G. B. Kistiakowsky, *Chem. Revs.*, **20**, 181 (1937). [i] E. Schjånberg, *Z. physik. Chem.*, **179A**, 39 (1937). The values quoted are average values for six esters of the general formula $CH_3CH{=}CHCO_2R$ and for seven esters of the general formula $C_2H_5CH{=}CHCO_2R$. The mean deviations from the average value are ±0.6 and ±0.7 kcal./mole, respectively. [j] Data of R. B. Williams, THIS JOURNAL, **64**, 1395 (1942), corrected to 355°K. and the vapor phase by G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 80. [k] The tabulated values pertain to the sum of successive hydrogenations of the two non-benzenoid double bonds. Effectively this compound provides a triconjugated system. [l] The conjugation effect parameters, $\Delta\Delta H_\psi$, are obtained from the equation, $\Delta\Delta H_\psi = \Delta\Delta H°_{355} - [(\Sigma\sigma^*)\rho^* - (\Delta n)h]$, using values of $\rho^* = -2.41$ and $h = 0.44$ given in paper II,[2b] and the available data[h–j] on the gas phase enthalpies of hydrogenation of conjugated *trans*-substituted ethylenes. The enthalpies of hydrogenation of α,β-saturated cyclic and *cis*-substituted ethylenes do not follow eq. 1.[2b] Therefore, no *cis* or cyclic conjugated olefins have been included in Table I since eq. 2 is of questionable applicability.

TABLE II

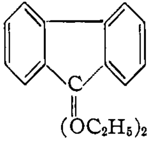
EXTRA RESONANCE ENERGY OF CONJUGATION FROM FREE ENERGIES OF HYDROGENATION OF ALDEHYDES AND KETONES[g]

Compound	$\Delta\Delta F°_{333}$,[a] kcal./mole	$(\Sigma\sigma^*)\cdot\rho^* + h(\Delta n)$, kcal./mole	$\Delta\Delta F_\psi$, kcal./mole	ΔE_ψ, kcal./mole
		Monoconjugated		
$CH_3CH{=}CHCHO$	−3.0	−8.1	5.1	6.6 (0.49 β)
$C_6H_5CH{=}CHCHO$	−2.6	−8.4	5.8	7.0 (.52 β)
C_6H_5CHO	−3.1	−10.2	7.1	5.9 (.44 β)
$C_6H_5COCH_3$	+0.6	−5.4	6.0	5.9 (.44 β)
$C_6H_5COC_2H_5$	+0.6	−5.3	5.9	5.9 (.44 β)
C_6H_5CO*n*-C_3H_7	+0.8	−5.2	6.0	5.9 (.44 β)
C_6H_5CO*i*-C_3H_7	+0.2	−5.3	5.5	5.9 (.44 β)
C_6H_5CO*n*-C_4H_9	+0.6	−5.1	5.7	5.9 (.44 β)
$C_6H_5CO(CH_2)_3C_6H_5$	+0.7	−6.1	6.8	5.9 (.44 β)
$C_6H_5CO(CH_2)_2C_6H_5$	+0.4	−6.5	6.9	5.9 (.44 β)
$C_6H_5COCH_2C_6H_5$	−0.3	−7.3	7.0	5.9 (.44 β)
$C_6H_5COCH_2OCH_3$	−3.8	−9.3	5.5	5.9 (.44 β)
$(CH_3)_3CCOCHO$	−5.3	−11.3[b,c]	6.0	5.9 (.44 β)
$CH_3COCO_2C_2H_5$	−7.8	−14.4[d]	6.6	5.9 (.44 β)
CH_3COCO_2*i*-C_3H_7	−7.8	−14.4[d]	6.6	5.9 (.44 β)
$C_6H_5COC(CH_3)_3$	−1.8	−5.1	3.3	5.9 (.44 β)
$C_6H_5COCH(OCH_3)C_6H_5$	−3.2	−11.2	8.0	5.9 (.44 β)
$C_6H_5COCH(OCH_3)_2$	−3.8	−12.9[e]	9.1	5.9 (.44 β)
		Diconjugated		
$C_6H_5COC_6H_5$	+0.1	−10.9	11.0	11.2 (.83 β)
	+0.3	−10.9[f]	11.2	12.6 (.93 β)
	+0.6	−10.9[f]	11.5	11.1 (.82 β)
$C_6H_5COCO_2$-*i*-C_3H_7	−7.0	−19.8[d]	12.8	11.2 (.83 β)

[a] From ref. 5; standard of comparison is $(CH_3)_2C{=}O$. [b] Calculated on the basis of reduction of the faster reacting ketone carbonyl group. [c] Value of σ* = +1.35 used for the –C=O group. [d] Value of σ* = +2.00 used for $CO_2C_2H_5$ and CO_2-*i*-C_3H_7 groups. [e] Value of σ* = 1.00 used for $CH(OCH_3)_2$ group. [f] Value of Σσ* = +1.200 used, as for two phenyl substituents. [g] The conjugation effect parameters, $\Delta\Delta F_\psi$, are obtained from the equation, $\Delta\Delta F_\psi = \Delta\Delta F°_{333} - [(\Sigma\sigma^*)\rho^* + (\Delta n)h]$, using the values of $\rho^* = -6.39$ and $h = 0.54$ in paper II,[2b] and the available data on the substituent effects on free energy taken from the work of Adkins, *et al.*[5] (which was carried out in dilute toluene solutions at 60°). Cyclic α,β-unsaturated substituents have not been treated (for the reason given in the previous section), except in the cases of fluorenone and xanthone. The latter compounds do not appear to involve much bond deformation, and the systems are planar for both the ketone and the alcohol.

TABLE III

EXTRA RESONANCE ENERGY OF CONJUGATION IN THE TRANSITION STATES FOR THE ACID-CATALYZED HYDROLYSIS OF DIETHYL ACETALS AND KETALS[e]

Compound	$k_1^{25°}$, l. mole sec.$^{-1}$	$\Delta\Delta F^{\ddagger}_{29}$, kcal./mole	$(\Sigma\sigma^*)(+4.91) + (\Delta n)(-0.73)$	$-\Delta\Delta F^{\ddagger}_{\psi}$, kcal./mole
		Monoconjugated		
$CH_3CH{=}CHCH(OC_2H_5)_2$[a]	2.98×10^2	0.55	7.85	7.3
$C_6H_5CH{=}CHCH(OC_2H_5)_2$[a]	1.52×10^2	0.95	8.10	7.1
$C_6H_5CH(OC_2H_5)_2$[a]	7.07	2.77	9.77	7.0
p-$NO_2C_6H_4CH(OC_2H_5)_2$[b]	1.12×10^{-2}	6.59	13.60[c]	7.0
$C_6H_5C(C_2H_5)(OC_2H_5)_2$[b]	7.40×10	1.38	5.40	4.0
		Diconjugated		
$(C_6H_5)_2C(OC_2H_5)_2$[b]	3.27×10^{-1}	4.58	10.31	5.7
	4.38	3.06	10.31[d]	7.3

[a] Data of paper I, ref. 2a. The standard of comparison is acetonal, $k_2 = 7.52 \times 10^2$. [b] New data, *cf.* Experimental. [c] The value of σ* for the *p*-$NO_2C_6H_4$ is taken as the sum of the σ* for C_6H_5 plus the Hammett σ value for *p*-NO_2, *i.e.*, σ* = +1.38. [d] The value of Σσ* taken as +1.200, that for two phenyl groups. [e] The conjugation effect parameters, $-\Delta\Delta F_\psi^{\ddagger}$, are obtained from the equation, $-\Delta\Delta F_\psi^{\ddagger} = \Delta\Delta F^{\ddagger}_{298} - [(\Sigma\sigma^*)(+4.91) - (\Delta n)(-0.73)]$, in accord with the results of paper I. The free energies of activation pertain to the second-order rate constants for the acid-catalyzed hydrolysis of diethyl acetals and ketals at 25.0° in 50% dioxane–water.

The essential difference in the conjugation energies derived from eq. 2 and those estimated by earlier methods (the difference in some instances is very substantial—*Cf.* Discussion) is that an explicit basis is proposed for evaluating expected polar and hyperconjugation contributions to the thermodynamic properties. In effect, the present method is more objective than earlier ones in providing an appropriate standard of comparison on which to base the extra resonance energy of the conjugated system.

Conjugation Energies Estimated from Molecular Orbital Theory.—The Hückel method of "Linear Combination of Atomic Orbitals–Molecular Orbital" (LCAO-MO) has been used.[6–8] Several of the values of resonance energies for conjugated olefins obtained by this method have been reported previously.[9]

The resonance energies are obtained in units of β, the resonance integral for p-orbitals on adjacent carbon atoms, *i.e.*, $\int \psi_1 H \psi_2 \, d\tau = \beta$. For compounds having oxygen as part of the conjugated system, the difference between the coulomb integral for a p-orbital on carbon, $E_0{}^c = \int \psi_c \psi_c \, dT$, and on oxygen, $E_0{}^\circ = \int \psi_c \psi_c \, dT$, must be evaluated, as well as the resonance integral for the carbon–oxygen π bond.

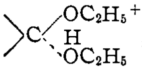
Although there is considerable disagreement as to the appropriate values of these coulomb integrals,[10] the present calculations are not very sensitive to the values chosen.[11] A value of 0.5 β has been used for $E_0{}^\circ - E_0{}^c$, a value similar to that used by Jaffé (0.51 β).[12] For the resonance integral for the carbon–oxygen π bond the same value (β) as for the carbon–carbon π bond has been used. For the resonance integral for p-orbitals on carbon and on a *saturated* oxygen atom, a value of 0.5 β has been used (Jaffé has used the value 0.56 β[12]).

Using these values it was found that the calculated resonance energy arising from the conjugation of a double bond with a carbonyl group (0.49 β) is essentially unchanged if a saturated oxygen atom is attached to the carbonyl carbon (the new value is 0.47 β). Accordingly, the calculations for all ester groups were simplified by treating the group as the corresponding aldehyde.

Resonance energies were calculated in the usual manner.[13] The extra resonance energy of the conjugated system was obtained from the difference between the resonance energy of this system and that of the appropriately saturated system. That is, if the product of hydrogenation of the double bond contains unsaturation (*e.g.*, $C_2H_5C_6H_5$), the extra resonance energy of the conjugated system ($C_6H_5CH{=}CH_2$) is obtained as the difference of the resonance energies for the two systems.

Tables I and II list in parentheses values of extra resonance energies in units of β which have been calculated in this manner. Also listed, as ΔE_ψ values, are figures obtained by arbitrarily assigning to β the value 13.5 kcal./mole.

Discussion

A number of striking regularities are apparent from the empirical conjugation energies given in Tables I and II. These regularities are well illustrated by "mean" values of the extra resonance energies of conjugation for systems which we shall refer to as mono- or diconjugated (*cf.* Table IV). The conjugation number is defined as the number of α,β-unsaturated substituents substituted at the unsaturated carbon reaction center ($-\overset{\diagdown}{C}{=}\overset{\diagup}{C}-$, for olefins: $\rangle C{=}O$, for aldehyde or ketone:  $\rangle C\langle^{OC_2H_5\,+}_{H\;\;OC_2H_5}$, for the hydrolysis transition state).

The use of "mean" values should not be taken as an implication that individual values should necessarily conform to the mean. Instead the mean values provide a "norm" from which individual values generally do not deviate by more than 1 kcal. (*cf.* average deviations from the mean listed in Table IV). Deviations of individual values from the mean which appear to be significant are discussed below.

TABLE IV

"MEAN" VALUES OF EXTRA RESONANCE ENERGIES FOR MONO- AND DICONJUGATED OLEFINS, ALDEHYDES AND KETONES

	Olefin $\Delta\Delta H^\circ_\psi$, kcal.	Aldehyde, ketone $\Delta\Delta F_\psi$, kcal.
Monoconjugated	5.7 ± 0.8	6.2 ± 0.5
Diconjugated	11.5 ± 0.9	11.6 ± 0.6

Monoconjugation of an aliphatic carbon–carbon double bond, a phenyl group, a cinnamyl group, an aldehyde carbonyl group, or ester carbonyl group with a carbonyl carbon all give rise to nearly the same value of $\Delta\Delta F_\psi$ (*cf.* Tables II and IV). In turn mono-conjugation of these same groups with a carbon–carbon double bond gives rise to nearly the same value of $\Delta\Delta H_\psi$ (*cf.* Tables I and IV). The mean value for the extra resonance energy resulting from monoconjugation with the $C{=}C$ group is essentially the same (perhaps only slightly less) than that for the $C{=}O$ group (in spite of the very large difference in the susceptibility to polar effects of the hydrogenation of olefins, $\rho^* = -2.41$ and of carbonyl compounds $\rho^* = -6.39$). *We may thus draw the important generalization that the extra resonance energy of conjugation of the two double bonds in these systems is approximately independent of the nature of these double bonds.*

Secondly, the extra resonance energy resulting from diconjugation is nearly the sum of the monoconjugation energies produced by the groups individually. For example, fluorenone, xanthone and benzophenone give essentially the same value for $\Delta\Delta F_\psi$,

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

(6) E. Hückel, *Z. Physik*, **70**, 204 (1931); **72**, 310 (1931); **76**, 628 (1932).

(7) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 254.

(8) C. A. Coulson, "Valence," Oxford at the Clarendon Press, 1953, p. 238.

(9) *Cf.* ref. 8, p. 235.

(10) *Cf.* ref. 8, p. 244, and ref. 12.

(11) The insensitivity of resonance energy calculations to the values of the various coulomb integrals has been noted previously by N. Muller, L. W. Rickett and R. S. Mulliken, THIS JOURNAL, **76**, 4770 (1954), and H. H. Jaffé, ref. 12.

(12) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952).

(13) *Cf.* ref. 8, p. 239.

and this is only slightly less than twice the mean $\Delta\Delta F_\psi$ value for monoconjugation (*cf.* Tables II and IV).

A third striking regularity is revealed by a comparison of the extra resonance energies of monoconjugation with the corresponding monohyperconjugation parameters, *h*, obtained in papers I and II.[2] The ratio of these two parameters, as may be seen in Table V, is essentially constant (approximately 10 to 1) for each reaction series. Thus the polar correction of observed substituent effects, which is the essence of the treatment in the papers of this series, has removed the objection noted earlier that hyperconjugation energies based upon observed substituent effects are unreasonably large compared to the conjugation energies.[14] We conclude from the above figures that hyperconjugation is truly second order compared to conjugation.

TABLE V

COMPARISON OF MEAN ENERGIES OF MONOHYPERCONJUGATION AND MONOCONJUGATION

	Hydrolysis transition state	Olefin	Aldehyde, ketone
Hyperconjugation parameter, *h*, kcal./mole	0.73 ± 0.08	0.44 ± 0.05	0.54 ± 0.06
Monoconjugation parameter, kcal./mole	7.0 ± 0.1	5.5 ± 0.9	6.6 ± 0.6

The constancy of the ratio of conjugation to hyperconjugation parameters constitutes a limited linear resonance energy relationship. The assumption used in papers I and II that the total hyperconjugation effect is obtained approximately as the product of the number of α-hydrogen atoms times a fixed hyperconjugation parameter, *h*, for a single α-H atom finds support in the present results, namely, in the fact that the much larger extra resonance energies for monoconjugation also contribute approximately additively to give the extra resonance energy of diconjugation.

The values of the extra resonance energy of conjugation given in Tables I, II and III in general support the basis of eq. 2, *i. e.*, that these resonance energies are independent (within approximately 1 kcal.) of the polarity and the number of α-hydrogen atoms in the substituent groups. The few apparent exceptions are discussed individually in later sections of the discussion. For the acetal hydrolysis transition states, the $-\Delta\Delta F_\psi^{\ddagger}$ values are essentially the same (7.1 kcal.) for benzacetal, cinnamacetal, crotonacetal and *p*-nitrobenzacetal, in spite of the fact that the σ^* values for the substituent groups involved vary from +0.850 to +1.870, and reaction rates vary by more than four powers of ten.

The importance of the polar and hyperconjugation contributions to the enthalpies of hydrogenation of olefins is illustrated by comparing some typical values of the extra resonance energy of conjugation obtained from eq. 2 with corresponding values obtained by Wheland by earlier methods[15] (Table VI).

ADDED IN PROOF.—Compare, however, with "obsd. conjugation Energies" calculated by A. Lofthus, THIS JOURNAL, **79,** 24 (1957), based upon the method of R. S. Mulliken and R. G. Patt, *J. Chem. Phys.*, **19,** 1271 (1951).

TABLE VI

COMPARISON OF EXTRA RESONANCE ENERGIES OF CONJUGATION (KCAL./MOLE) OBTAINED BY THE PRESENT AND EARLIER METHODS

Substance	From eq. 2	From Wheland
1,3-Butadiene	5.1	3.5
Styrene	4.3	0.9
Crotonaldehyde	7.3	2.4
trans-Methylcinnamate	11.8	2.9
trans-Ethyl fumarate	10.1	−2.2

It is apparent from Table VI that none of the generalizations given above may be derived from the earlier values of conjugation energies.

The importance of polar and hyperconjugation contributions to the effects of α,β-unsaturated substituents on the free energies of hydrogenation of aldehydes and ketones is even more dramatic (*cf.* Table II). Thus, for example, the free energy of hydrogenation of benzophenone is within 0.1 kcal. of that of acetone, and the value for benzaldehyde is actually 3.1 kcal. more negative than that of acetone. In themselves, these values provide no evidence of resonance stabilization (a positive value is required) in the conjugated system. Yet the values of $\Delta\Delta F_\psi$ derived from eq. 2 using these values of $\Delta\Delta F^\circ$ are in accord with the generalizations concerning the relationship of extra resonance energies of conjugation to structure.

The simple molecular orbital calculations predict each of the three generalizations established from the empirical values of the extra resonance energy of conjugation obtained from eq. 2. Arbitrarily assigning β the value of 13.5 kcal./mole (a figure somewhat lower than that used to correlate resonance energies of aromatic hydrocarbons) the extra resonance energies of 28 conjugated olefins, aldehydes and ketones, with values varying from 4 to 19 kcal./mole, are obtained with an average difference of less than 1 kcal. between the theoretical and the empirical values. The agreement is considered satisfactory in light of the simplicity of both the theoretical model and of eq. 2.

The accord between the empirical and theoretical values of resonance energies of conjugation establishes a consistency between resonance theory and a theory of structural effects on reactivity which unifies diverse effects of structure on reactivity (compare corresponding values of $\Delta\Delta H^\circ$, $\Delta\Delta F^\circ$ and $\Delta\Delta F_\psi^{\ddagger}$ of Tables I, II and III). These results provide further evidence that steric effects in the thermodynamic properties of olefin, aldehyde and ketone hydrogenations are small, as well as in the formation of the hydrolysis transition state from the acetal or ketal.[2]

Although direct steric effects appear to be absent or small, an indirect one, steric inhibition to resonance in the conjugated systems, apparently is definitely present. "Compression energies," of course, always reduce "observed" values of resonance energies.[16] The value of $\Delta\Delta F_\psi$ for pivalo-

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

[15] Ref. 4, p. 80, 85.

[16] *Cf.* ref. 8, p. 236.

phenone (3.3 kcal.) is significantly less than the mean value for monoconjugated aldehydes or ketones (6.2 kcal.) indicating (in accord with molecular models) an appreciable steric inhibition of phenylcarbonyl conjugation by the adjacent *t*-butyl group. Judging from the generalizations reached above steric inhibition appears to be small or at least roughly constant in other olefins and carbonyl compounds of Tables I and II.

Steric inhibition of resonance in the transition state also apparently accounts for the lower value of $-\Delta\Delta F_{\psi}^{\ddagger}$ for the diethyl ketal of propiophenone (4.0 kcal.) than the mean value (7.1 kcal.) for monoconjugated acetal transition states. The values of $\Delta\Delta F_{\psi}^{\ddagger}$ for fluorenone and benzophenone diethyl ketals (7.2 and 5.7 kcal., respectively) are markedly less than that estimated by the additivity rule (14 kcal.). The additivity rule appears applicable since the L.C.A.O.-M.O. calculated extra resonance energy for the $(C_6H_5)_2CH^+$ ion is, for example, nearly twice that for the $C_6H_5CH_2^+$ ion. Two explanations may be invoked to account for the exceptional behavior. First, steric inhibition of resonance in the transition state may reduce the value. Second, there is a probable breakdown in the implied parallelism between corresponding free energies of the hydrolysis transition state and that of the intermediate oxocarbonium ion.[2a] With increased resonance stabilization of the carbonium ion, the transition state is reasonably expected to resemble the carbonium ion less and become more like the conjugated acid of the ketal, which is insensitive to resonance stabilization by conjugation.

The $\Delta\Delta F_{\psi}$ values obtained from eq. 2 for the hydrogenation of three carbonyl compounds (in addition to pivalophenone) do not fit the general picture: (the values for these compounds were not used in obtaining the "mean" values given in Table IV) dimethoxyacetophenone, phenylmethoxyacetophenone and diethyloxomalonate. The value obtained for the latter (23 kcal.) is appreciably greater than for comparable compounds (and is not listed in Table II). Elofson has noted that these compounds are very slow to equilibrate, and has suggested that the equilibrium value reported for the oxomalonic acid ester may be in error for this reason or because of an interfering side reaction.[17] The marked deviation of these compounds from normal behavior suggests that the reported $\Delta\Delta F^{\circ}$ values may be in considerable error.

Applications.—The figure of five to seven kcal./mole for the extra resonance energy of monoconjugation has useful application to the effect of structure on reactivity in a number of carbonyl addition reactions. The polar and steric effects of a phenyl group or a hydrogen atom substituted at the carbonyl carbon atom have been found to be very similar in the rates of esterification or hydrolysis of esters.[18] It may be proposed that this close similarity in polar and steric effects holds for other carbonyl addition reactions. Further, it is reasonable that the transition states for most such reactions are nearly saturated at the carbonyl reaction center. It is expected then that the free energy of activation for the conjugated reactant will be increased by an amount nearly equal to its extra resonance energy of conjugation.[18]

Making these assumptions, the difference in the free energy of activation for the corresponding phenyl and hydrogen substituted carbonyl compound, $\Delta F_{C_6H_5}^{\ddagger} - \Delta F_{H}^{\ddagger}$ $(= -2.303RT \log (k_{C_6H_5}/k_H))$, should be approximately 6 kcal./mole. Values of the relative rates $k_{C_6H_5}/k_H$ predicted in this manner and corresponding observed values are listed in Table VII for several reactions. The agreement is considered to support satisfactorily the assumptions made.

Apparently, the extra resonance energy of conjugation of ethyl benzoate (or benzoic acid) is perhaps only slightly less than that of acetophenone (or benzaldehyde, etc.) in spite of the substantial resonance within the ester group itself. This is a result in accord with the M.O. calculation cited earlier, which indicates that the extra resonance energy of conjugation of an α,β-unsaturated carboxylic acid or ester is 0.02 β (0.3 kcal./mole) lower than that of the corresponding unsaturated aldehyde.

In this connection it is also of interest that the extra resonance energy of conjugation of an α,β-unsaturated carboxylate ion is calculated by the M.O. method to be 0.06 β (0.8 kcal./mole) lower than that of the α,β-unsaturated acid. Branch and Calvin,[19] and Taft,[20] by methods which parallel those described in this paper, have estimated from relative ionization constants in water at 25° that the extra resonance energy of conjugation is about one kcal. less in the carboxylate ion than in the acid. The fact that the reduction is small indicates that the energies of the various resonances are roughly independent of one another (only a small saturation effect is shown), in accord with the approximate additivity generalization given earlier. Further, the linear resonance energy relationship, namely, that the hyperconjugation effect of a single α-hydrogen atom is about one-tenth that of the conjugation effect of an α,β-unsaturated substituent is followed, for in paper II the hyperconjugation effect on the free energy of ionization is given as 0.1 kcal. per α-hydrogen atom.[2b]

Applying to a carboxylic ester the linear resonance energy relationship, the hyperconjugation parameter, *h*, for the free energy of activation for the hydrolysis of the ester may be estimated to be about 0.5 kcal. On this basis, and the model applied above to conjugation effects on rate, the rate of hydrolysis of an acetate ester ($n = 3$) at 25° is expected to be retarded by about 1.1 powers of ten compared to the corresponding formate ($n = 0$). This figure is very close to the factor usually observed for the relative rates of acid-catalyzed hydrolysis or esterification (of the corresponding acids).[21] Taft has ascribed this factor to a steric effect and included it within the steric

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

(18) R. W. Taft, Jr., in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 670.

(19) G. E. K. Branch and M. Calvin, "Theory of Organic Chemistry," Prentice-Hall Book Co., Inc., New York, N. Y., 1941, p. 243.

(20) *Cf.* ref. 18, p. 656.

(21) *Cf.* R. W. Taft, Jr., THIS JOURNAL, **74**, 2729 (1952).

TABLE VII

PREDICTED AND OBSERVED RELATIVE RATES

Reaction	Conditions	Ref.	$k_{C_6H_5}/k_H$	
			Obsd.	Predicted
$RCO_2C_2H_5 + H_2O \rightarrow RCO_2H + C_2H_5OH$	Acid cat. hydrolysis, 60% (vol.) aq. acetone, 25°	[a]	8.3×10^3	2.5×10^4
$RCO_2C_{10}H_{19} + CH_3OH \rightarrow$ $RCO_2CH_3 + C_{10}H_{19}OH$	Methoxide ion catalysis CH_3OH, 30°	[b,c]	7.6×10^3	2.0×10^4
$R(CH_3)C{=}O + H_2NNHCONH_2 \rightarrow$ $R(CH_3)C{=}NNHCONH_2 + H_2O$	Phosphate buffer *p*H 7, 25°	[d,e]	1.5×10^4	2.5×10^4

[a] W. B. S. Newling and C. N. Hinshelwood, *J. Chem. Soc.*, 1357 (1936). [b] R. W. Taft, Jr., M. S. Newman and F. H. Verhoek, THIS JOURNAL, **72**, 4511 (1950). [c] W. A. Pavelich and R. W. Taft, Jr., unpublished results. [d] J. B. Conant and P. D. Bartlett, THIS JOURNAL, **54**, 2881 (1932). [e] F. P. Price, Jr., and L. P. Hammett, *ibid.*, **63**, 2387 (1941).

substituent constant, E_s.[22] The present results suggest, therefore, that the steric substituent constants include small but significant contributions from hyperconjugation effects. However, in accord with the basic arguments of the method,[23] these effects are not expected to alter Taft's polar substituent constants, σ^*.

Experimental

The technique for measuring acetal and ketal hydrolysis rates and the preparation of the 50% dioxane–water mixture have been previously described.[24] Propiophenone diethyl ketal,[25] b.p. 104° (14 mm.), benzophenane diethyl ketal,[26] m.p. 49–50.5°, and fluorenone diethyl ketal,[27] m.p. 78–80°, are all previously known compounds.[28] The diethyl acetal of *p*-nitrobenzaldehyde, a slightly yellow liquid with b.p. 162–163° (14 mm.), is not a previously reported compound.

Anal. Calcd. for $C_{11}H_{15}O_4N$: C, 58.67; H, 6.67; N, 6.22. Found[29]: C, 58.31; H, 6.56; N, 6.47.

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[22] R. W. Taft, Jr., THIS JOURNAL, **74**, 3120 (1952).

[23] *Cf.*, ref. 18, p. 588.

[24] M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **77**, 3146 (1955).

[25] E. L. Beals and F. A. Gilfillan, *J. Am. Pharm. Assoc.*, **25**, 426 (1936).

[26] Mack, *J. Chem. Soc.*, **69**, 990 (1887).

[27] Smedley, *ibid.*, **87**, 4252 (1905).

[28] All boiling points are uncorrected, melting points are corrected.

[29] Microanalysis was performed by Clark Microanalytical Laboratory, Urbana, Illinois.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA]

The Temperature Dependence of Ion Pair Dissociation Constants. I. *o*-Dichlorobenzene[1]

BY H. L. CURRY AND W. R. GILKERSON

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The conductances of tetraethylammonium, tetra-*n*-propylammonium and tetra-*n*-butylammonium picrates in *o*-dichlorobenzene have been determined as a function of concentration at 25, 35, 45, 55 and 65°. The ion pair dissociation constants and limiting equivalent conductances have been calculated at each temperature. The variation of the dissociation constant with temperature is discussed with reference to Bjerrum's theory and also a recent one proposed by one of the authors.

As has been pointed out in a recent critical review of the ion pair concept,[2] Bjerrum's[3] theory of ion pair dissociation qualitatively but not quantitatively describes experimental results that have been obtained. His theory gives

$$K^{-1} = \frac{4\pi N}{1000} (\epsilon^2/DkT)^3 Q(b) \qquad (1)$$

where $b = \epsilon^2/aDkt$. Here, N is Avogadro's number, ϵ is the unit of charge and a is the distance of closest approach, being an empirical parameter. While a, as determined experimentally, is generally larger than the charge separation as determined from dipole moment measurements, it may also be much smaller.

The dependence of K upon the dielectric constant at constant temperature has been investigated in solvent mixtures and while the agreement is quite good for the water–dioxane system,[4] a discrepancy has been observed[5] in nitrobenzene–carbon tetrachloride mixtures. Further, specific solvent effects have been shown when results in ethylene chloride ($D = 10.23$), ethylidene chloride ($D = 9.90$) and *o*-dichlorobenzene ($D = 9.93$) are compared at 25°.[6] The ratio of the dissociation constant of Et_4NPi in ethylene chloride to that in *o*-dichlorobenzene is 13.9, far too large to be accounted for on the basis of the difference in dielectric constant alone. There are very few data available concerning K as a function of temperature. An early study in anisole,[7] while in qualitative agreement with Bjerrum's equation, is of doubtful validity due to approximations that were necessary to evaluate the K values. Studies in ethylene chloride, ethylidene chloride and propylene chloride have been reported.[8] It seemed, in view of the scarcity of information, of interest to extend such studies to other solvents, using salts which have been the subject of previous examina-

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[1] Presented at the Southwide Chemical Conference, Memphis, December 6, 1956.

[2] C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

[3] N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

[4] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933).

[5] H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5905 (1954).

[6] F. Accascina, E. L. Swarts, P. L. Mercier and C. A. Kraus, *Proc. Natl. Acad. Sci.*, **39**, 917 (1953).

[7] G. S. Bien, R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **56**, 1860 (1934).

[8] (a) K. H. Stern and A. E. Martell, *ibid.*, **77**, 1983 (1955); (b) J. T. Denison and J. B. Ramsey, *ibid.*, **77**, 2615 (1955).