Tetrahedron, 1959, Vol. 5, pp. 233-242. Pergamon Press Ltd. Printed in Great Britain.

EXPERIMENTAL AND THEORETICAL EVALUATIONS OF THE BAKER-NATHAN EFFECT

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FOR a number of reactions in which steric effects can be neglected and relative reactivity can be sorted out into inductive and resonance contributions equations (1) hold with reasonable precision[1, 2, 3] In equations (1) $\rho^*\Sigma\sigma^*$ represents an

$$\log(k/k_0) = \rho^*\Sigma\sigma^* + B - (\Delta F_\phi/2{\cdot}3RT)$$
$$\Delta F - \Delta F_0 = \rho^*\Sigma\sigma^* + B + \Delta F_\phi$$
$$\Delta H - \Delta H_0 = \rho^*\Sigma\sigma^* + B + \Delta H_\phi \qquad (1)$$

inductive effect on reactivity.[4] The effect of conjugation on reactivity is given by ΔF_ϕ or ΔH_ϕ, which can be calculated with reasonable accuracy by the LCAO-MO method.[3, 5] B represents the Baker–Nathan effect.[6, 7] In previous work[1, 2, 3] the Baker–Nathan effect has been defined by equation (2), in which n is the number of

$$B = h(n - n_0) \qquad (2)$$

α hydrogens in a given compound, n_0 is the number in a standard compound and h is an empirically determined constant. Equation (2) suggests that the Baker–Nathan effect is peculiar to hydrogen atoms. A possible alternative to equation (2) is equation (3), in which the same Baker–Nathan effect is attributed to all alkyl groups. In equation (3), n' is the number of alkyl groups directly attached to a functional group, n_0' is the

$$B = h'(n' - n_0') \qquad (3)$$

number attached in the standard compound and h' is an empirically determined constant. If the Baker–Nathan effect is something peculiar to hydrogen atoms, h will be, in fact, reasonably constant. If not, then h' will be more nearly constant than h. Table 1 compares h and h' for acid-catalyzed hydrolysis of acetals and ketals, while Table 2 does the same for heats of hydrogenation of monosubstituted and *trans*-disubstituted olefins.

Tables 1 and 2 clearly show that for these reactions at least h is a more nearly constant quantity than h'. Although data from other reaction series are less conclusive,

[1] M. M. Kreevoy and R. W. Taft, Jr., *J. Amer. Chem. Soc.* **77**, 5590 (1955).
[2] R. W. Taft, Jr. and M. M. Kreevoy, *J. Amer. Chem. Soc.* **79**, 4011 (1957).
[3] M. M. Kreevoy and R. W. Taft, Jr., *J. Amer. Chem. Soc.* **79**, 4016 (1957).
[4] R. W. Taft, Jr., *Steric Effects in Organic Chemistry* (Ed. M. S. Newman) p. 556. Wiley, New York (1956).
[5] C. A. Coulson, *Valence* p. 238. Clarendon Press, Oxford (1953).
[6] J. W. Baker and W. S. Nathan, *J. Chem. Soc.* 1844 (1935).
[7] M. M. Kreevoy and H. Eyring, *J. Amer. Chem. Soc.* **79** 5121 (1957).

TABLE 1. COMPARISON OF h AND h' FOR HYDROLYSIS OF ACETALS AND KETALS $R_1R_2C(OC_2H_5)_2$*

R_1	R_2	$\log(k/k_0) + 3{\cdot}60\Sigma\sigma^*$	h	h'
CH_3	H	1·72	0·57	1·7
iso-C_3H_7	H	2·62	0·52	2·6
tert.-C_4H_9	H	2·99	0·50	3·0
$(C_2H_5)_2CH$	H	2·43	0·49	2·4
H	H	3·73	0·62	1·9
XCH_2†	H	–	0·57	2·3
XCH_2‡	CH_3	–	0·3 : ·2	0·3/0

* Data taken from ref. 1. The standard compound, for which $k = k_0$, $\Sigma\sigma^* = 0$, $n = n_0 = 6$ and $n' = n_0' = 2$, is acetonal.
† Average of seven monosubstituted acetals in which $n = 2$ and $n' = 1$.
‡ Average of seven monosubstituted ketals in which $n = 5$ and $n' = 2$.

TABLE 2. COMPARISON OF h AND h' FOR HEATS OF HYDROGENATION OF OLEFINS $R_1CH=CHR_2$*

R_1	R_2	$\Delta H - \Delta H_0 + 2{\cdot}41\Sigma\sigma^*$	h	h'
H	H	2·8	0·47	1·4
CH_3	H	·1·3	0·43	1·3
iso-C_3H_7	H	2·0	0·40	2·0
sec.-C_4H_9	H	2·1	0·42	2·1
tert.-C_4H_9	H	2·2	0·37	2·2
XCH_2†	H	–	0·39	1·6
iso-C_3H_7	CH_3	0·5	0·25	·5/0
C_2H_5	C_2H_5	0·5	0·25	·5/0
tert.-C_4H_9	CH_3	-1·2‡	0·40	-1·2/0
tert.-C_4H_9	tC_4H_9	·2·3‡	0·39	2·3/0
XCH_2§	CH_3	—	0·27	·27/0

* These data were taken from ref. 2 except as otherwise noted. The standard compound is *trans*-2-butene, for which $\Delta H = \Delta H_0$, $\Sigma\sigma^* = 0$, $n = n_0 = 6$ and $n' = n_0' = 2$.
† Average of ten monosubstituted compounds in which $n = 2$ and $n' = 1$.
‡ Taken from the data of R. B. Turner, D. E. Nettleton and M. Perelman, *J. Amer. Chem. Soc.* 80, 1430 (1958); corrected from solution in acetic acid at 25° to the gas phase at 82°.
§ Average of three monosubstituted compounds in which $n = 5$ and $n' = 2$.

it seems quite likely that we are dealing with a phenomenon in which hydrogen plays a special role, quantitatively, if not qualitatively. This is in accord with the original ideas of Baker and Nathan,[6, 8] based on a qualitative comparison of reactivities.

Table 3 compares h, ρ^* and the average value of $\Delta H_{\ddagger}$ or $\Delta F_{\ddagger}$ to which a single $\alpha\beta$-unsaturated substituent gives rise. These values were empirically determined from equations (1) and (2).[3, 9] It seems quite plain that ρ^* is not related in any simple way to h or $\Delta F_{\ddagger}$ or $\Delta H_{\ddagger}$. If the Baker–Nathan effect is closely related to the resonance effects arising from conjugation and if the α-hydrogen bonding model is used, simple theory[7, 9] predicts that h should equal 0·07 times the resonance effect of a single $\alpha\beta$-unsaturated substituent for the first three reactions in Table 3, but should be 0·13 times this resonance effect for the hydrogenation of acetylenes to alkanes. Table 3 bears out this prediction. These facts strongly suggest that the Baker–Nathan effect is related to conjugation, a view which has been widely held since the effect was first recognized.[6, 8, 10]

TABLE 3. INDUCTIVE, CONJUGATION AND BAKER NATHAN EFFECTS*

Reaction	ρ^*	h	$\Delta F_{\ddagger}$ or $\Delta H_{\ddagger}$†
Acetal hydrolysis	+4·93‡	+0·73‡	7·0
Olefin hydrogenation	2·41	+0·44	5·5
Carbonyl hydrogenation §	6·39	+0·54	6·6
Acetylene hydrogenation	5·06	+0·61	4·7

* Taken from refs. 3 and 9.
† The average value of $\Delta F_{\ddagger}$ or $\Delta H_{\ddagger}$ to which a single $\alpha\beta$-unsaturated substituent gives rise.
‡ These values have been multiplied by 2·3 RT to make them comparable with others in this Table.
§ ΔF for the reaction $R_1R_2CH-O + H_2 \rightarrow R_1R_2CHOH$ at 60° in toluene solution, obtained as described in Ref. 2.

Table 4 shows that $\Delta F_{\ddagger}$ for hydrogenation of carbonyl compounds and $\Delta H_{\ddagger}$ for hydrogenation of olefins and acetylenes are closely approximated by the change in resonance energy, $\Delta E_{\ddagger}$, calculated for the reaction by the LCAO–MO method.[3, 5] Table 5 shows that these calculations are much less satisfactory for estimating the effect of conjugation on the acid-catalyzed hydrolysis rates of acetals and ketals. In these calculations the carbon–carbon π-bond resonance integral (β) was given the value 13·5 kcal/mole and it was assumed that the resonance integral for the carbon–oxygen bond was equal to that for the carbon–carbon π bond.[3] The Coulomb integral for oxygen was given a value larger by 0·5β than that for carbon, but the results are not too sensitive to the values of the Coulomb integrals.

In calculating the resonance energies of the acetal and ketal hydrolysis transition states the transition state was assumed to resemble the product of the rate-determining step, $(R_1R_2COC_2H_5)^{\oplus}$.

[8] J. W. Baker, *Hyperconjugation*. Oxford University Press (1952).
[9] M. M. Kreevoy, unpublished work.
[10] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.* 17, 1248 (1949).

TABLE 4. RESONANCE ENERGIES OF OLEFINS AND CARBONYL COMPOUNDS*

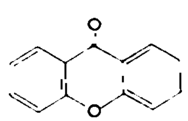
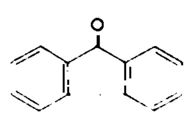
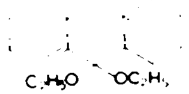
Compound	$\Delta H_{\ddagger}$ or $\Delta F_{\ddagger}$ (kcal/mole)	$\Delta E_{\ddagger}$ (kcal/mole)
Olefins:		
$-CH$ $CH{=}CO-$†	6·2 ± 0·6	6·6
$CH{=}CHCH$ $CH-$‡	5·3 ± 0·2	6·3
$C_6H_5CH{=}CH_2$	4·3	5·8
$C_6H_5CH{=}CHCO_2CH_3$	11·8	12·8
$C_6H_5CH-CHC_6H_5$	12·5	12·6
$C_2H_5O_2CCH$ $CHCO_2C_2H_5$	10·1	13·4
$C_6H_5CH-CHCH{=}CHC_6H_5$	19·1	19·4
Acetylenes:		
C_6H_5C CH	4	5·8
n-C_4H_9C $C-C$ CnC_4H_9	10	12·6
C_6H_5C C C_6H_5	11	12·6
HOOCC CCOOH	12	13·4
$C_6H_5C{\equiv}C-C$ CC_6H_5	19	19·9
Carbonyl compounds:		
CH_3CH $CHCHO$	5·1	6·6
C_6H_5CH $CHCHO$	5·8	7·0
C_6H_5CO-§	6·3 ± 0·6	5·9
$C_6H_5COC_6H_5$	11·0	11·2
	11·2	12·6
	11·5	11·1
$C_6H_5COCO_2$-*iso*-C_3H_7	12·8	11·2

TABLE 5. ACETAL AND KETAL HYDROLYSIS TRANSITION STATE RESONANCE ENERGIES*

Acetal or ketal	$\Delta F_{\ddagger}$† (kcal/mole)	$\Delta E_{\ddagger}$‡ (kcal/mole)
$CH_3CH=CHCH(OC_2H_5)_2$	7·3	11
$C_6H_5CH=CH(OC_2H_5)_2$	7·1	12
	7·3	15

* Data taken from ref. 3.
† Empirical value.
‡ Calculated resonance energy of the appropriate carbonium ion with $\beta = 13{\cdot}5$ kcal mole.

This will be a satisfactory approximation only as long as the product ion is much less stable than the protonated substrate, which is the starting point of the rate determining step.[11] The low empirical values of $\Delta F_{\ddagger}$ for the acetals and ketals leading to

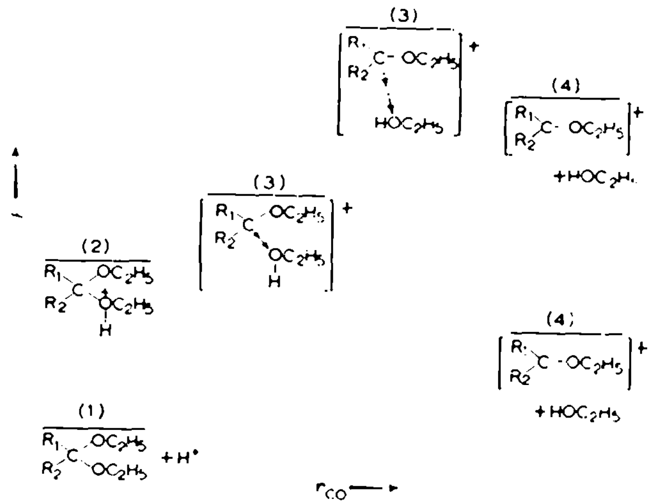


FIG. 1. The energy levels and structure of acetal and ketal hydrolysis transition states and intermediates. State (1) is the starting state. State (2) is the protonated starting state. State (3) is the transition state for a non-conjugated acetal or ketal. State (4) is the carbonium ion intermediate for a non-conjugated acetal or ketal and is the product of the rate-determining step. State (4′) corresponds to state (4) except that it is highly stabilized by resonance. State (3′) is the transition state leading to (4′). The ordinate is free energy per mole and the abscissa is the length of the carbon–oxygen bond which is breaking.

[11] G. S. Hammond, *J. Amer. Chem. Soc.* 77, 334 (1955).

* Data taken from refs. 3 and 9.
† Average of three compounds of the structure shown and all having $\Delta E_{\ddagger} = 6{\cdot}6$ kcal mole.
‡ Average of two compounds of the structure shown and all having $\Delta E_{\ddagger} = 6{\cdot}3$ kcal/mole.
§ Average of thirteen compounds of the structure shown and all having $\Delta E_{\ddagger} = 5{\cdot}9$ kcal mole.

more highly stabilized carbonium ions indicates that the transition state for the hydrolysis of these compounds in a resonance hybrid to which the protonated substrate is an important contributor. Conversely the moderately good fit for benzacetal suggests that the ion $(R_1R_2COC_2H_5)^{\oplus}$ is a fair model for the acid-catalyzed hydrolysis of non-conjugated acetals and ketals.[1, 3] The situation is illustrated in Fig. 1.

The good agreement of the empirical and calculated resonance energies of such compounds as diethyl fumarate and acetylenedicarboxylic acid lends strong support to the ρ^*'s calculated from unconjugated compounds. The carbethoxy group σ^* is 2·0 and that for COOH is 2·9 (the groups are strongly electron-withdrawing by an inductive mechanism) so that any serious error in ρ^* would lead to a grossly incorrect value of $\Delta H_{\ddagger}$. For example, Wheland[12] obtained a *negative* resonance energy for diethyl fumarate essentially by setting $\rho^* = 0·0$ for the hydrogenation of olefins.

These two examples demonstrate the usefulness of reliable estimates of $\Delta E_{\ddagger}$. Comparison of calculated and observed values of h could be just as useful if reliable calculations can be made.

In the naive LCAO–MO method of calculating resonance energies[5] the π energy levels, E, of a hypothetical non-resonating allyl cation, $C_1 = C_2 - C_3^{\oplus}$, can be calculated from equation (4). The interactions which give rise to the π bond are represented by the non-zero 1,2-resonance integral, β. If interactions between the empty π orbital

$$\begin{vmatrix} -E & \beta & 0 \\ \beta & -E & 0 \\ 0 & 0 & -E \end{vmatrix} = 0 \qquad (4)$$

on C_3 and the π orbital on C_2 are recognized, the 2,3-resonance integral also becomes β, since the ion is symmetrical. Equation (4) then becomes equation (5). The roots of equation (4) are $E = 0 \pm \beta$. Since β is a negative quantity, the total π-electron

$$\begin{vmatrix} -E & \beta & 0 \\ \beta & -E & \beta \\ 0 & \beta & -E \end{vmatrix} = 0 \qquad (5)$$

delocalization energy of the non-resonating allyl cation is 2β. (Putting the two electrons into the lowest possible energy level.) The roots of equation 5 are $E = 0 \pm 1·41\beta$ and the calculated total delocalization energy of the resonating allyl cation is $2·82\beta$. Subtracting $2·00\beta$ from $2·82\beta$, the resonance energy of the allyl cation is $0·82\beta$.

The facts cited above strongly suggest that a carbon-hydrogen bond adjacent to a π orbital should also be linked to that orbital through a non-zero resonance integral. Since this system is not symmetrical, the resonance integral binding the π orbital to the carbon–hydrogen bond will not be the same as that binding carbon to hydrogen. If H_{12} represents the resonance integral for the carbon-hydrogen bond and H_{23} represents the resonance integral binding the π orbital to the carbon–hydrogen bond, the energy levels of a carbonium ion $H_1{-}C_2{-}C_3{+}$ will be given by equation (6a) in which:

$$\begin{vmatrix} -E & H_{12} & 0 \\ H_{12} & -E & H_{23} \\ 0 & H_{23} & -E \end{vmatrix} = 0 \qquad (6a)$$

[12] G. W. Wheland, *Resonance in Organic Chemistry* pp. 80 and 85. Wiley, New York (1955).

differences in Coulomb integrals have been neglected. The resonance energy given by equation (6a) is $[(H_{23}^2 + H_{12}^2)^{\frac{1}{2}} - H_{12}]$ and represents the stabilizing influence of a single carbon–hydrogen bond on an adjacent cation. The secular determination shown in equation (6a) can be enlarged in a straight forward manner to give the energy levels and resonance energy if more than one carbon–hydrogen bond is involved. Compounds other than carbonium ions can be dealt with similarly. The resonance energy to which α-carbon hydrogen bonds give rise is thought to be the cause of the Baker–Nathan effect.

Equation (6) assumes that there is a non-zero resonance integral for the π orbital on C_3 with the sp^3 orbital on C_2 which is holding the hydrogen atom. A particular formulation of this assumption has been called "hyperconjugation" and its consequences extensively explored.[13] Another alternative is to consider a non-zero resonance integral for the π orbital on C_3 with the hydrogen $1s$ orbital. This has been called "α-hydrogen bonding" and produces a secular determinant which is formally equivalent to that in equation (6a).[7]

Hyperconjugation explains most of the features of the Baker–Nathan effect. It has the advantage that, when estimated by equation (7), the resonance integral for the carbon sp^3 orbital with a π orbital on an adjacent carbon atom is substantially larger than that for the π orbital with the hydrogen $1s$ orbital.

$$H_{ab} = \beta \frac{A_{ab} I_{ab} S_{ab}/(1 + S_{ab})^{13}}{AIS/(1 + S)} \qquad (7)$$

Equation (7) is based on the assumption that the exchange integral is a nearly constant fraction of the bond energy.[14] The parameters A are those of Mulliken.[14] Parameters I are the mean of the ionization potentials of the orbitals making up a bond. The overlap integrals, S, used in this paper are for Slater atomic orbitals and are taken from the tables of Mulliken *et al.*[10] Quantities marked with the subscript ab pertain to the bond in question. Others pertain to the aromatic π bond.

Hyperconjugation, however, has the disadvantage that one is hard pressed to explain the particular effectiveness of *hydrogen* atoms, which is clearly shown in Tables 1 and 2.

As an alternative to hyperconjugation we may consider α-hydrogen bonding. α-Hydrogen bonding leads to equation (6b), which differs from equation (6a) only in that the numerical value of H_{13} is not necessarily the same as that of H_{23}.

$$\begin{vmatrix} -E & H_{12} & H_{13} \\ H_{12} & E & 0 \\ H_{13} & 0 & -E \end{vmatrix} = 0 \qquad (6b)$$

α-Hydrogen bonding would represent the Baker–Nathan effect as a sort of minor neighboring group participation,[15, 16] not important enough to lead to major alterations of molecular geometry. It would explain the unique effectiveness of hydrogen,

[13] O. Lofthus, *J. Amer. Chem. Soc.* **79**, 24 (1957). Reference to voluminous work by Mulliken and his co-workers can be found in this paper.
[14] R. S. Mulliken, *J. Phys. Chem.* **56**, 295 (1952).
[15] M. Simonetta and S. Winstein, *J. Amer. Chem. Soc.* **76**, 18 (1954).
[16] S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.* **70**, 828 (1948).

since both theory[7] and experiment[17] indicate that a hydrogen atom interacts more effectively than a saturated carbon atom with a π orbital on a neighboring carbon atom.

Equation (7) gives $H_{13} = 0{\cdot}3\beta$, where β is the aromatic carbon–carbon bond, if the 2,3-interactions are assumed to be those of the π orbital with the hydrogen 1s orbital. The Morse function and the spectroscopic properties of C–H indicate that this molecule would retain about 1/4 of its bond energy if stretched to the distance separating C_3 from H_1. It seems plausible, at least, to set $H_{23} = 1/4\beta$ in calculations of α-hydrogen bonding.[7]

The empirical data suggest that the Baker–Nathan effect should be a fairly linear function of the number of carbon–hydrogen bonds adjacent to the π orbital. The calculated resonance stabilization provided by α-hydrogen bonding will be such a function provided that two conditions are satisfied: (1) that H_{23} is small by comparison with H_{12}, and (2) that H_{23} is the same for all of the carbon–hydrogen bonds. For example, if $H_{23} = 1/4H_{12}$, the resonance stabilization of a carbonium ion by a single α-carbon–hydrogen bond is $0{\cdot}062\ H_{23}$. With the same assignment of integrals the stabilization of a carbonium ion by six adjacent carbon–hydrogen bonds is $6 \times 0{\cdot}055\ H_{23}$.

The Baker–Nathan effect can be calculated from equations like (6) by calculating the resonance energy of the general starting material (I), the general product (II), the standard starting material (III) and the standard product (IV).

$$\left.\begin{aligned} B &= (\mathrm{II}) - (\mathrm{I}) - (\mathrm{IV}) + (\mathrm{III}) \\ h &= \frac{(\mathrm{II}) - (\mathrm{I}) - (\mathrm{IV}) + (\mathrm{III})}{n - n_0} \end{aligned}\right\} \tag{8}$$

Using $H_{12} = \beta = 14$ kcal/mole and $H_{23} = 1/4\ H_{12}$, a number of average h values have been computed from equation (8) by varying n from 0 to n_0.[7] Those for the reactions

$$R_1R_2C{=}O + H_2 \longrightarrow R_1R_2CHOH \tag{9}$$

$$R_1CH{=}CHR_2 + H_2 \longrightarrow R_1CH_2CH_2R_2 \tag{10}$$

$$R_1C{\equiv}CR_2 + 2H_2 \longrightarrow R_1CH_2CH_2R_2 \tag{11}$$

are compared with empirical values in Table 6.

TABLE 6. CALCULATED AND EMPIRICAL VALUES OF h

Reaction	Calcd.	Empirical
9	0·43	0·56 ± 0·06
10	0·43	0·44 ± 0·05
11	0·85	0·61 ± 0·05

[17] G. W. Wheland, *Advanced Organic Chemistry* p. 513. Wiley, New York (1949). The experimental evidence referred to is the high "migratory aptitude" of a hydrogen atom on a carbon atom adjacent to a carbonium ion.

[18] E. Berliner and F. Berliner, *J. Amer. Chem. Soc.* **71**, 1195 (1949); *Ibid.* **72**, 222 (1950).

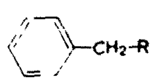
The calculated h for the formation of a carbonium ion from a saturated compound is $-0{\cdot}80$ kcal/mole. The empirical h for acid catalyzed hydrolysis of acetals and ketals is $-0{\cdot}73$ kcal/mole. The agreement supports the conclusion, previously suggested on other grounds, that for most acetals and ketals the hydrolysis transition state closely resembles the carbonium ion. On the other hand, the empirical h for solvolysis of *tert.*-carbinyl chlorides in aqueous ethanol at 25° is only $-0{\cdot}34$ kcal/mole, which suggests that the solvolysis transition state has substantial resonance contributions involving a covalent bond from a solvent oxygen to the central carbon atom. The calculated h for reaction (12):

$$H^{\oplus} + (R_1)(R_2)C=CH_2 \rightleftharpoons (R_1)(R_2)\overset{\oplus}{C}-CH_3 \qquad (12)$$

is $-(0{\cdot}80 - 0{\cdot}43) = -0{\cdot}37$ kcal/mole. It has recently been shown that this is approximately the value of h for the hydration of monosubstituted *iso*butylenes,* $XCH_2C(CH_3)=CH_2$, supporting the conclusion that the transition state for this reaction in some ways resembles the carbonium ion. These examples illustrate the usefulness of equation (6) and the integrals given for the estimation of h.

It is recognized that H_{23} is actually not independent of n. The first α-carbon–hydrogen bond can exert the greatest stabilizing influence because it can assume the ideal position in space, as nearly as possible parallel to the π orbital. A carbon–hydrogen bond lying in the nodal plane of the π orbital will exert no stabilizing influence at all. These effects, however, are probably considerably leveled by rotation about the C_2–C_3 σ bond, so that something of an average effect is actually observed. Much the same thing is true of open-chain conjugated systems. It is thought to be responsible for the lowering of the resonance integral from 18–20 kcal/mole in systems having fixed, ideal, geometry, to 13–14 kcal/mole in open-chain conjugated systems. The use of the latter value for β undoubtedly results in a partial compensation for the non-ideal geometry in α-hydrogen bonding.

A "Baker-Nathan order" has been observed for rates of bromination of compounds



in which R was varied from methyl to *tert.*-butyl. This might very well be due to "β-hydrogen bonding",[7] in which the overlap integral for a π orbital with a β-hydrogen atom is considered to be non-zero.

The most realistic approach to the problem of resonance stabilization due to a carbon–hydrogen bond α to a π orbital is to assume that *both* the resonance integrals mentioned above are non-zero. Such an assumption leads to equation (12)

$$\begin{vmatrix} -E & H_{12} & H_{13} \\ H_{12} & -E & H_{23} \\ H_{13} & H_{23} & -E \end{vmatrix} = 0 \qquad (12)$$

from the ion H_1–C_2–$C_3^{\oplus}$. Since none of the resonance integrals, H_{ab}, in equation (12)

* Unpublished results kindly communicated by Professor R. W. Taft, Jr.

can be reliably evaluated, it is plain that this model can accommodate a wide variety of Baker–Nathan effects for any particular reaction series, so that no single value can be used to test it. If H_{13} is of about the same order of magnitude as H_{23}, this model does make the unique prediction that the Baker–Nathan effect will be far larger for carbonium ion reactions than for carbanion reactions. This prediction can be seen in Table 8, which compares the calculated resonance energies of H_1–C_2–$C_3^{\oplus}$, H_1–C_2–$C_3^{\ominus}$ and H_1–C_2–C_3 C_4. In these calculations it was assumed that $H_{12} = \beta$ and, where needed, $H_{34} = \beta$. All differences in Coulomb integrals were neglected.

TABLE 8. CALCULATED RESONANCE ENERGIES FOR A VARIETY OF H_{13} AND H_{23}

H_{13}	H_{23}	Resonance energy		
		$H_1C_2C_3^{\oplus}$	$H_1C_2C_3^{\ominus}$	$H_1C_2C_3-C_4$
0	0	0·000	0·000	0·000
1/4β	0	0·062β	0·062β	0·031β
1/8β	0	0·016β	0·016β	0·008β
1/4β	1/4β	0·225β	0·000	0·062β
1/8β	1/8β	0·060β	0·000	0·016β
1/4β	1/8β	0·132β	0·016β	0·040β

It can be seen from Table 8 that the predicted resonance energies of carbanions are identical with those of carbonium ions as long as either H_{13} or H_{23} is zero. If the smaller of these is even half of the larger, however, the resonance energy of the carbanion is only a little more than 1/10 of the resonance energy of the carbonium ion. As the difference between the two becomes less, the resonance energy of the carbanion becomes smaller still, while that of the carbonium ion becomes larger. These general conclusions are *independent* of the absolute values of any of the resonance integrals, and also independent of which resonance integral is the larger.

If the magnitude of the Baker–Nathan effect on some carbanion or carbanion-like reactions could be compared with some carbonium ion reactions, an estimate of H_{13}/H_{23} (or H_{23}/H_{13}) could be made. Unfortunately (or fortunately, depending on one's point of view) the required data do not seem to be available for carbanion-type reactions.