Charge Distribution and Chemical Effects in Saturated Hydrocarbons

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Abstract: The charge distributions calculated by several MO methods for a variety of alkanes reproduce (i) the inductive effects of the alkyl groups in Taft's order and (ii) an additional effect, by which a positive site is best favored by a negative surrounding (and conversely). This effect enables an approximate "chemical" estimate of the charge distributions in selected alkanes. Its relevance to chemistry is illustrated by its ability of rationalizing in a simple manner both the inductive order $CH_3 < \cdots <$ *tert*-C_4H_9 of electron donation and the "hyperconjugative" order $CH_3 > \cdots >$ *tert*-C_4H_9 of stabilization of positive sites.

Much of the versatile arrow pushing which is used to represent electron displacements in reacting molecules is difficult, if not impossible at present, to be rationalized in a quantitative manner. In special cases, however, the electron-withdrawing or -releasing ability of groups can be evaluated and described by numbers. Typical examples are the Hammett substituent constants[1] and Taft's polar σ^* constants,[2] which are widely used in reactivity problems. In Taft's scale, the electron-releasing ability of the methyl group is assigned the value $\sigma^*(CH_3) = 0$. The ethyl group, which is a better electron donor than methyl, is described by $\sigma^*(C_2H_5) = -0.100$. These two values (for methyl and ethyl) define the origin and the scale for the evaluation of the electron-releasing ability of the alkyl groups. In this scale, σ^*(isopropyl) $= -0.195$ and σ^*(*tert*-butyl) $= -0.300$. Hence, the net electron loss of the *tert*-butyl group is more important than that of a methyl group under similar circumstances, *i.e.*, if both groups are attached to a same atom or group of atoms. This is typically a case which, in principle, can be studied on the basis of electron distributions.

Neopentane, for example, can be considered as a *tert*-butyl group attached to a methyl group. Since the *tert*-butyl group is a better electron donor than methyl, a net positive charge should be carried by the *tert*-butyl group and an equal negative charge by the CH_3 group. The net negative charge on the CH_3 group in isobutane is expected to be lower than in the case of neopentane, because isobutane is isopropylmethyl and the isopropyl group is less electron donating than *tert*-butyl. For similar reasons, in terms of Taft relationships, the primary H atom in isobutane is expected to carry more electrons than any H atom in ethane because the *tert*-butyl group is a better electron donor than the ethyl group.

The object of the present study is twofold. First it is examined whether these electronic effects are reflected by population analyses calculated by different LCAO methods. Secondly, the converse problem is studied: electron populations in saturated hydrocarbons are calculated on the assumption that in these molecules the general properties of the alkyl groups are preserved.

Basic Assumptions and Their Verification

The basic assumptions which are made are represented by eq 1–4. In these equations, q always represents a net charge with its sign; hence $q > 0$ represents a positive (electron-deficient) site, and $q < 0$ an excess negative charge.

$$\sum q = 0 \tag{1}$$

$$q_H = a\sigma^* + b \tag{2}$$

$$q(R) = a'\sigma^* \tag{3}$$

$$q_{C_i} = \alpha\left(\sum q_{C_j} + \sum q_{H_j}/k\right) + \beta \tag{4}$$

Equation 1 expresses the fact that the molecules are neutral, *i.e.*, that the sum of the net charges over the whole molecule is 0.

Equations 2 and 3 are Taft's equations for inductive effects, in which σ^* are the Taft polar constants of the alkyl substituents. It should be noted that important conclusions can be drawn *without* the actual knowledge of the σ^* constants for the isopropyl and the *tert*-butyl groups. The reference scale is that defined by Taft, *i.e.*, $\sigma^*(CH_3) = 0$ and $\sigma^*(C_2H_5) = -0.100$, but any other arbitrary reference scale would be equally suitable. In eq 2, q_H is the net charge on H attached to a group whose electron-releasing ability is characterized by the constant σ^*; b is the q_H value in methane (methyl H), because $\sigma^*(CH_3) = 0$. Figure 1 indicates that the q_H values which are calculated by (i) the Hoffmann extended Hückel (EHMO),[3] (ii) Hoyland's[4] *ab initio* BO, and (iii) by the Sándorfy–Katagiri[5] Pariser–Parr type methods correlate satisfactorily with eq 2, as do the q_H values calculated by Del Re's method.[6]

In eq 3, $q(R)$ is the charge released by the group R toward a methyl group; hence, $q(R)$ is also the net positive charge carried by R. In ethane, $q(R)$ is necessarily 0 because both methyl groups are equivalent. The results in Figure 2 indicate that the inductive effects (eq 3) are reproduced by the LCAO calculations of electron distributions. This is satisfactory in connections with the discussion of the effects of alkyl groups, but the fact should be remembered that already in the Hückel method a feedback effect opposing large charge sep-

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[1] L. P. Hammett, *J. Amer. Chem. Soc.*, **59**, 96 (1937); "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940.

[2] R. W. Taft, *J. Amer. Chem. Soc.*, **75**, 4231 (1953).

[3] (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962); (b) R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962); (c) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

[4] J. R. Hoyland, *ibid.*, **50**, 473 (1969).

[5] S. Katagiri and C. Sándorfy, *Theor. Chim. Acta*, **4**, 203 (1966).

[6] G. Del Re, *J. Chem. Soc.*, 4031 (1958).

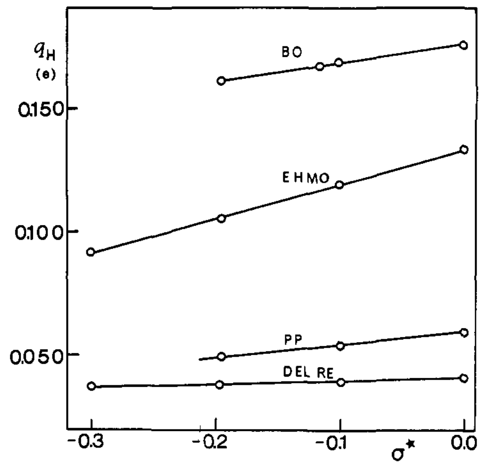

Figure 1. Verification of eq 2. Comparison of q_H values *vs.* Taft's polar σ^* constants. A similar correlation is also obtained with the CNDO/2 results.

arations was introduced by means of "inductive parameters."

Equation 4 is an expression of the verbal argument that "electroneutrality is a good thing." A consideration of this argument at different degrees of refinement could result in the following approaches. The first approach would be to suppose that all the centers are neutral. This is not the case for obvious reasons. The second approach would be to suppose that each center with its immediate neighbors is an electroneutral ensemble. Although this is necessarily the case in methane, this approach is dismissed in favor of the next, less restrictive approach according to which the net charge q_{C_i} on a center C_i (carbon atom *i*) is related to the net charge/q_{C_j} of the neighboring C atoms C_j and to the net charges q_{H_j} of the H atoms H_j neighboring C_i. According to this concept, a positive net charge on the central atom C_i is more likely when its neighbors carry negative charges and, conversly, a negative charge on C_i is favored by neighbors carrying positive charges. This concept agrees, in spirit, with what Pople and Beveridge[7] have discussed in terms of charge alternation. Crudely it may also be expressed as follows: "Avoid, as much as possible, building up charges of same sign on neighboring atoms" or "a positive site is best favored when inbedded in a negative surrounding, and conversly."

Equation 4 is a description of these views in form of a linear relationship. Although it seems reasonable to say that the charge on a center C_i is related to the sum of charges on its neighbors, there is no *a priori* reason for stipulating that this relationship is linear and should not include higher terms in Σq_{C_j} and $\Sigma q_{H_j}/k$. Hence, eq 4 can only be considered as a first approximation. The term *k* in eq 4 is a weighting factor which differentiates an H neighbor to C_i from a C neighbor. The quantities α and β are parameters necessary for writing the linear relationship and shall be discussed later in detail.

Figure 3 indicates that eq 4 is satisfactorily obeyed by the different LCAO calculations, hence, that this first approximation seems adequate. This agreement will result in conclusions relevant to chemistry; at

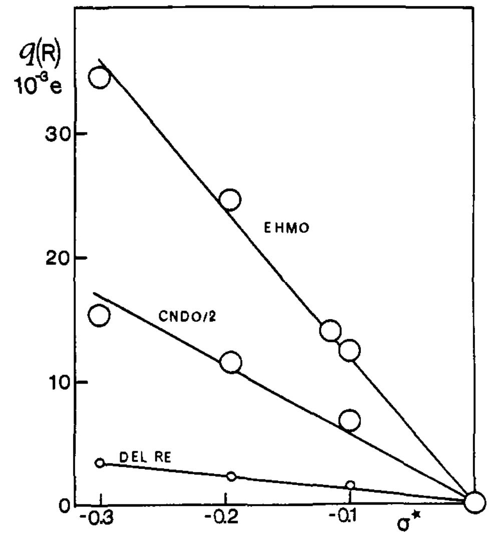

Figure 2. Verification of eq 3, by means of EHMO, CNDO/2, and Del Re's results.

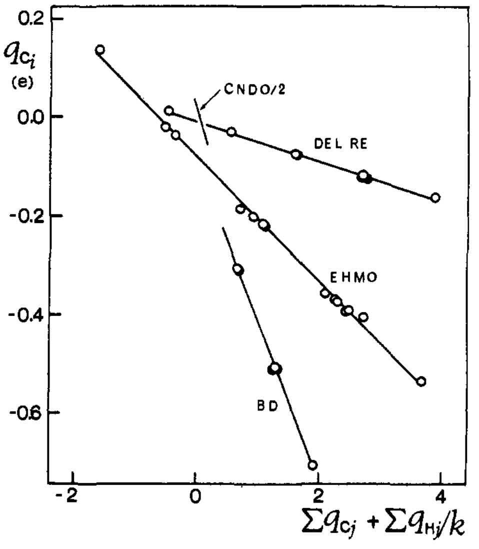

Figure 3. Verification of eq 4. The EHMO results include the alkanes reported in Table I and the results[8c] for isopentane, cyclopropane, methylcyclohexane, and *n*-nonane. The EHMO, Del Re, and CNDO/2 results are drawn in the scale indicated. The only change in scale is for the BO results, where 2 stands for 10 eu.

present only the fact is retained that eq 4 is in satisfactory agreement with quantum chemical information.[8]

It is noted that eq 4 is identical with Del Re's formulation for the δ parameters,[6] *i.e.*, $\delta_\mu = \delta_\mu{}^0 + \Sigma\gamma_{\mu(\lambda)}\delta_\lambda$ (λ adjacent to μ). Here δ_μ is a parameter influenced only by atoms directly bound to μ, which is introduced in equations of the type $H_{\mu\mu} = \alpha + \delta_\mu\beta$. A possible theoretical interpretation of the assumptions related to this treatment had been offered.[6,10] The point is that in Del Re's treatment the charges are linear to first order in the parameters δ; the latter are connected to one

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[7] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

[8] The correlations with CNDO/2[9] charge densities are somewhat less satisfactory than those obtained by the other methods of calculation. It is stressed that no attempt has been made to improve the quality of the correlations with eq 2–4, although this could be achieved by an adequate choice of parameters.

[9] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43,** S129, S136 (1965).

[10] The sequence of inductive effects of the alkyl groups, in conjunction with charge densities, has also been discussed by Del Re.[6]

Table I. Net Charges and Parameters (Electron Units)

Molecule	Atom (parameter)	EHMO[a]	PP[b]	BO[c]	Del Re[d]	CNDO/2[e]
	α	−0.1255	−0.1504	−0.0643	−0.0404	−0.5136
	k	0.1456	0.2011	0.0743	0.0418	0.4217
	β	−0.0822	−0.0607	−0.0956	−0.0077	0.0079
	a	0.132	0.057	0.069	0.011	0.089
	b	0.133	0.059	0.175	0.041	0.0126
	a'	−0.120	−0.081	−0.086	−0.012	−0.0555
Methane	C	−0.532	−0.236	−0.699	−0.162	−0.0503
Ethane	C	−0.356	−0.160	−0.504	−0.117	−0.0076
Propane	C_{prim}	−0.373	−0.167	−0.508	−0.118	−0.0088
	C_{sec}	−0.185	−0.083	−0.303	−0.073	0.0236
	H_{sec}	0.105	0.050	0.160	0.038	−0.0050
n-Butane	C_{prim}	−0.372		−0.504	−0.118	
	C_{sec}	−0.202		−0.309	−0.074	
	H_{sec}	0.108		0.159	0.037	
Isobutane	C_{prim}	−0.388			−0.118	−0.0091
	C_{tert}	−0.019			−0.030	0.0461
	H_{tert}	0.092			0.037	−0.0110
Neopentane	C_{prim}	−0.403			−0.119	−0.0087
	C_{quat}	0.137			0.014	0.0615

[a] Reference 3c. [b] Reference 5. [c] Reference 4. [d] Calculated with the parameters of ref 6. [e] Parameters as in ref 9. Eq 4: Correlation coefficient $r = 0.9989$, standard deviation $s = 0.0098$, number of points $n = 14$ (EHMO); $r = 0.9992$, $s = 0.004$, $n = 4$ (PP); $r = 0.9998$, $s = 0.0041$, $n = 6$ (BO); $r = 0.9996$, $s = 0.0017$, $n = 10$ (Del Re); $r = 0.9742$, $s = 0.0096$, $n = 6$ (CNDO/2, excluding neopentane).

another by "inductive effects" which are but a way of introducing a tendency to restore electroneutrality. In this sense, it may be considered that eq 4 ressembles to a certain extent to Del Re's approach. Though similar in spirit, the present approach appears, however, to be more direct since eq 4 involves the charges instead of the quantities δ related to charges.

The satisfactory comparison of eq 2–4 with the MO charge distributions now enables the problem to be defined more precisely. Since eq 2–4 are found to agree *individually*, it is now requested that these equations also hold *simultaneously*. This demand imposes severe restrictions since the parameters in eq 2–4 are found not to be independent. All of them can be calculated, except β, which appears to be a unity parameter. The internal consistency of the corresponding parameters, as calculated from the LCAO results (Figures 1–3, Table I), can thus be evaluated, as well as the internal consistency of the LCAO charge distributions.

Charge Distributions

For *methane*, the net charge on C is calculated from eq 1 and 4, and b is deduced from eq 2 and 5.

$$q_C = \beta/(1 + \alpha/k) \tag{5}$$

$$b = -\beta/4(1 + \alpha/k) \tag{6}$$

In *ethane*, $q_C + 3q_H = 0$ and $q_{C_i} = q_{C_j}$. Hence, from eq 4

$$q_C = \beta/(1 + \alpha/k - \alpha) \tag{7}$$

and, from eq 2, 6, and 7, it follows that

$$a = -\frac{\beta(1 + \alpha/k + 3\alpha)}{12\sigma^*(\text{Et})(1 + \alpha/k)(1 + \alpha/k - \alpha)} \tag{8}$$

Neopentane is suitable for calculating the coefficient a' of eq 3. First, the charges $q_{C_{quat}}$ and $q_{C_{prim}}$ of the quaternary and primary carbon atoms are calculated by means of eq 4 and 1.

$$q_{C_{quat}} = \frac{\beta(1 + \alpha/k + 4\alpha)}{1 + \alpha/k - 4\alpha^2 + \alpha^2/k} \tag{9}$$

$$q_{C_{prim}} = \frac{\beta[1 + \alpha + 0.75\alpha/k + \alpha^2/k - 0.25(\alpha/k)^2]}{(1 + \alpha/k)(1 + \alpha/k - 4\alpha^2 + \alpha^2/k)} \tag{10}$$

The four methyl groups are equivalent in neopentane and carry the net charge $q(CH_3) = -q_{C_{quat}}/4$. Hence (eq 3 and 9)

$$a' = \frac{\beta(1 + \alpha/k + 4\alpha)}{4\sigma^*(\textit{tert}\text{-Bu})(1 + \alpha/k - 4\alpha^2 + \alpha^2/k)} \tag{11}$$

In the case of *propane*, eq 1, 2, and 4 give the following results.

$$q_{H_{sec}} = -\beta\left[\frac{\sigma^*(i\text{-Pr})(1 + \alpha/k + 3\alpha)}{12\sigma^*(\text{Et})(1 + \alpha/k)(1 + \alpha/k - \alpha)} + \frac{1}{4(1 + \alpha/k)}\right] \tag{12}$$

$$q_{C_{sec}} = \frac{2(\alpha/k)(1 + \alpha/k - \alpha)}{1 + \alpha/k - 2\alpha^2 + \alpha^2/k}q_{H_{sec}} + \beta\frac{1 + \alpha/k + 2\alpha}{1 + \alpha/k - 2\alpha^2 + \alpha^2/k} \tag{13}$$

$$q_{C_{prim}} = \frac{\alpha(1 - 1/2k)}{1 + \alpha/k}q_{C_{sec}} - \frac{\alpha/k}{1 + \alpha/k}q_{H_{sec}} + \beta/(1 + \alpha/k) \tag{14}$$

An alternative calculation, involving eq 3 instead of eq 4, also enables the net charge on the secondary carbon atom to be calculated.

$$q_{C_{sec}} = \frac{\beta\sigma^*(\text{Et})(1 + \alpha/k + 4\alpha)}{2\sigma^*(\textit{tert}\text{-Bu})(1 + \alpha/k - 4\alpha^2 + \alpha^2/k)} - 2q_{H_{sec}} \tag{15}$$

From a comparison of the two solutions for $q_{C_{sec}}$, *i.e.*, eq 13 and 15, the following equation is deduced for propane

$$\Delta q/\beta = \frac{1 + \alpha/k + 2\alpha}{1 + \alpha/k - 2\alpha^2 + \alpha^2/k} - \frac{\sigma^*(\mathrm{Et})(1 + \alpha/k + 4\alpha)}{2\sigma^*(\mathit{tert}\text{-}\mathrm{Bu})(1 + \alpha/k - 4\alpha^2 + \alpha^2/k)} - \frac{1}{2}\left[\frac{\sigma^*(i\text{-}\mathrm{Pr})(1 + \alpha/k + 3\alpha)}{3\sigma^*(\mathrm{Et})(1 + \alpha/k)(1 + \alpha/k - \alpha)} + \frac{1}{(1 + \alpha/k)}\right] \times \left[\frac{(1 + \alpha/k)^2 - 2\alpha^2}{1 + \alpha/k - 2\alpha^2 + \alpha^2/k}\right] \quad (16)$$

This equation shall be discussed later, in conjunction with the solution of an equation similar to (16) which can be derived for isobutane.

In the case of *isobutane*, eq 1, 2, and 4 gives the following results.

$$q_{\mathrm{H_{tert}}} = -\frac{\beta}{4}\left[\frac{\sigma^*(\mathit{tert}\text{-}\mathrm{Bu})(1 + \alpha/k + 3\alpha)}{3\sigma^*(\mathrm{Et})(1 + \alpha/k)(1 + \alpha/k - \alpha)} + \frac{1}{(1 + \alpha/k)}\right] \quad (17)$$

$$q_{\mathrm{C_{tert}}} = \frac{(\alpha/k)(1 + \alpha/k - \alpha)}{1 + \alpha/k - 3\alpha^2 + \alpha^2/k} q_{\mathrm{H_{tert}}} + \beta\frac{1 + \alpha/k + 3\alpha}{1 + \alpha/k - 3\alpha^2 + \alpha^2/k} \quad (18)$$

The following alternative calculation of $q_{\mathrm{C_{tert}}}$ in isobutane involves the use of eq 3 instead of eq 4.

$$q_{\mathrm{C_{tert}}} = 3a'\sigma^*(i\text{-}\mathrm{Pr}) - q_{\mathrm{H_{tert}}} \quad (19)$$

Substitution of eq 11 and 17 in eq 19 yields an expression for $q_{\mathrm{C_{tert}}}$ in terms of α, β, and k. A comparison of this solution for $q_{\mathrm{C_{tert}}}$ with the previous one (eq 18) leads to eq 20, where Δq is the difference between the two solutions for $q_{\mathrm{C_{tert}}}$.

$$\Delta q/\beta = \frac{1 + \alpha/k + 3\alpha}{1 + \alpha/k - 3\alpha^2 + \alpha^2/k} - \frac{3\sigma^*(i\text{-}\mathrm{Pr})(1 + \alpha/k + 4\alpha)}{4\sigma^*(\mathit{tert}\text{-}\mathrm{Bu})(1 + \alpha/k - 4\alpha^2 + \alpha^2/k)} - \frac{1}{4}\left[\frac{\sigma^*(\mathit{tert}\text{-}\mathrm{Bu})(1 + \alpha/k + 3\alpha)}{3\sigma^*(\mathrm{Et})(1 + \alpha/k)(1 + \alpha/k - \alpha)} + \frac{1}{1 + \alpha/k}\right] \times \left[\frac{(1 + \alpha/k)^2 - 3\alpha^2}{(1 + \alpha/k) - 3\alpha^2 + \alpha^2/k}\right] \quad (20)$$

This terminates the "chemical" population analysis for the alkanes. The charge densities, as well as the parameters a, b, and a' are all expressed in terms of α, β, and k. Two equations (16 and 20) relate the quantities α and k which, therefore, can be calculated by using appropriate values for the Taft σ^* constants $\sigma^*(i\text{-}\mathrm{Pr})$ and $\sigma^*(\mathit{tert}\text{-}\mathrm{Bu})$. More general conclusions can, however, be obtained without the precise knowledge of these σ^* constants; they are discussed below.

Discussion

The present discussion is restricted to what may be regarded "reasonable" solutions. Hence, unnatural situations, such as those which would arise by letting $\alpha = 0$, are not considered, since they can be deduced easily from the results of the preceding section. It is assumed that the carbon atoms in methane and ethane carry net negative charges, as indicated by the LCAO results,[11] and that $\alpha < 0$. The parameter a is positive to account for the fact that the net positive charge q_{H} decreases as the group attached to H is a better electron donor.

Sign of β. If β were positive, both $1 + \alpha/k$ and $1 + \alpha/k - \alpha$ should be negative, because (eq 5, 7) the charges on C in methane and ethane are assumed to be negative. Since a (eq 8) is positive, $1 + \alpha/k + 3\alpha$ should also be positive. Because $1 + \alpha/k + 3\alpha > 0$ is incompatible with $1 + \alpha/k - \alpha < 0$, it is concluded that β can only be negative.

Acceptable Values for α and k. Since $\beta < 0$, it is deduced from eq 5 and 7 that

$$1 + \alpha/k > 0 \quad (21)$$

$$1 + \alpha/k - \alpha > 0 \quad (22)$$

A consideration of the conditions 21, 22, and of eq 8, indicates that

$$\alpha < -1/(3 + 1/k) \quad (23)$$

Finally, a consideration of eq 9 indicates that

$$1 + \alpha/k - 4\alpha^2 + \alpha^2/k > 0 \quad (24)$$

because $1 + \alpha/k + 4\alpha < 0$ and $q_{\mathrm{C_{quat}}} > 0$.

It is now possible to calculate, from 21, 23, and 24, the range of α values which are acceptable for assigned k values (Table II) and to compare the present results with those of LCAO calculations. It is noted that, so far, no use has been made of equations which imply the knowledge of the σ^* values for the isopropyl and the *tert*-butyl groups.

Table II. Permissible and "Best" α Values

	α		
k	Lower limit	Upper limit	Best
0.04	−0.04	−0.0357	−0.0357
0.10	−0.10	−0.0769	−0.0773
0.12	−0.12	−0.0882	−0.089
0.15	−0.15	−0.1034	−0.106
0.20	−0.20	−0.1250	−0.132
0.25	−0.2500	−0.1429	−0.157
0.28	−0.2712	−0.1522	−0.170

The "best" α value can be estimated by means of eq 16 and 20. In each case, Δq represents the difference between solutions which have been obtained by different means for the charge q, *i.e.*, $q_{\mathrm{C_{sec}}}$ of propane (eq 16) and $q_{\mathrm{C_{tert}}}$ of isobutane (eq 20). The quantities Δq would be 0 if rigorous equations had been used for their derivation and if the σ^* values for the isopropyl and *tert*-butyl groups were known with absolute precision, which is not the case. It appears, therefore, reasonable to allow for some uncertainty and to accept solutions which are compatible with small Δq values. In practice it appears that a reasonable range of possible solutions can be covered by allowing an error less than 3×10^{-3} β units on q. The simplest, not necessarily the best, way for estimating α consists in inserting the k value in eq 16 and 20 and to retain the α value correspond-

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[11] In a recent study on localized orbitals, Rothenberg[12] offers an interesting argument indicating that the C–H bond has a net sign of $\mathrm{C^{-}}$–$\mathrm{H^{+}}$.

[12] S. Rothenberg, *J. Amer. Chem. Soc.*, **93**, 68 (1971).

Table III. Net Charges and Parameters in the Arbitrary Unit Scale: $q_C(C_2H_6) = -1.00$

Molecule	Atom (parameter)	Present calculation			EHMO	PP	BO	Del Re	CNDO/2
	k	0.12	0.20	0.28					
	α	−0.089	−0.132	−0.17					
	a	0.028	0.137	0.248	0.370	0.356	0.137	0.094	11.7
	b	0.336	0.347	0.358	0.370	0.369	0.347	0.347	1.62
	a'	−0.097	−0.205	−0.354	−0.336	−0.506	−0.170	−0.100	−7.3
Methane	C	−1.34	−1.39	−1.43	−1.49	−1.47	−1.39	−1.39	−6.5
Ethane	C	−1.00	−1.00	−1.00	−1.00	−1.00	−1.00	−1.00	−1.00
Propane	C_{prim}	−1.09	−1.11	−1.14	−1.05	−1.05	−1.01	−1.01	−1.14
	C_{sec}	−0.64	−0.60	−0.55	−0.52	−0.52	−0.60	−0.62	3.06
	H_{sec}	0.331	0.32	0.31	0.29	0.31	0.32	0.324	−0.65
Isobutane	C_{prim}	−1.20	−1.24	−1.29	−1.09			−1.01	−1.18
	C_{tert}	−0.27	−0.18	−0.076	−0.053			−0.26	6.0
	H_{tert}	0.328	0.31	0.28	0.26			0.32	−1.43
Neopentane	C_{prim}	−1.30	−1.36	−1.45	−1.13			−1.02	−1.13
	C_{quat}	0.12	0.25	0.42	0.38			0.12	8.0
Cyclic[a]	C_{sec}	−0.79	−0.78	−0.77	−0.61			−0.64	

[a] For unsubstituted cyclic hydrocarbons, it follows from eq 4 that $q_C = \beta/(1 + \alpha/k - 2\alpha)$ because $q_C + 2q_H = 0$.

ing to the smallest error. In the present calculations, the usual Taft constants were used for the isopropyl (−0.195) and the *tert*-butyl group (−0.300).

Table III indicates the charge distributions which were calculated for selected k values, using the "best" α values, together with LCAO results.

It is difficult to define any sharp range of possible k values. It may be considered that $k = 0.12$ is close to a reasonable lower limit; almost no inductive effect is experienced by the H atoms, which is indicated by their very similar charges and by the small a value. For $a \rightarrow 0$, *i.e.*, $1 + \alpha/k + 3\alpha \rightarrow 0$, insertion of this limit in eq 5 and 7 indicates that $q_C(CH_4)/q_C(C_2H_6) \rightarrow {}^4/_3$. Indeed, in the absence of any inductive effect, q_H would be the same in CH_4 and in C_2H_6; the C atom in CH_4 carries the charge released by 4 H atoms and is, hence, ${}^4/_3$ of the net charge on the ethane C atom, which carries the charge contributed by 3 H atoms. Consequently, unless one is willing to accept the idea that the ethyl group is more electron withdrawing than the methyl group, it is

$$q_C(CH_4)/q_C(C_2H_6) > 4/3 \qquad (25)$$

This condition is met by most LCAO results.[13] The choice of a "reasonable" upper limit for k appears to be a matter of deciding how far the conspiracy of good will is to be pushed. It is felt, however, that charge separations significantly greater than those corresponding to $k = 0.28$ are not likely; at this limit, the present results are similar to Hoffmann's EHMO charge distributions.

Table III indicates that most LCAO results are roughly within the limits required for the simultaneous validity of eq 2–4. The CNDO/2 results, on the other hand, satisfy individually eq 2–4. It is concluded that the chemical effects described by eq 2–4 provide a reasonable description of the electronic effects in the molecules which have been studied.

Conclusions

The population analyses calculated for a series of alkanes by means of different LCAO methods reflect the electron-releasing ability of the alkyl groups in Taft's order. In addition, the concept of charge alternation (eq 4) is correctly reproduced: "Avoid, as much as possible, building up charges of some sign on neighboring atoms." The calculations indicate that "a positive site is favored in a situation in which it is best inbedded in a negative surrounding (shell), and conversely." For convenience this effect is referred to as "shell-effect."

The equations describing the inductive and the shell effect are *individually* verified. From their *simultaneous* application in the back calculation of charge densities, criteria for their internal consistency are developed, which are met by a number of LCAO results.

The shell effect can be used for unifying the electronic effects exhibited by alkyl groups. To begin with, the effect of replacing an H atom in methane by a methyl group is considered; a slightly positive H neighbor to the C atom is replaced by a center carrying a negative charge. Hence, the charge on C in ethane is less negative than in methane. Consequently, some negative charge is repelled toward the H atoms and, finally, it is observed that the ethyl group is a better electron donor than methyl. This electron-repelling shell effect is more pronounced by further replacements of H atoms by negative centers; hence the tertiary H atom in isobutane is electron richer than the secondary H in propane or the H atoms in ethane or methane. A consideration of the net electron loss by the different alkyl groups toward the methyl group to which they are attached also illustrates the interrelationship of shell and inductive effects. In propane, for example, the two primary negative C atoms which belong to the shell of the secondary carbon atom further deplete its electron density; part of the hereby repelled electrons are directed toward the methyl groups and some toward the secondary H atoms. The charge accepted by the methyl groups is readily accepted by the primary C

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[13] SCF calculation by Palke and Lipscomb[14] indicate $q_C(CH_4) = -0.532$ e and $q_C(C_2H_6) = -0.372$ e, *i.e.*, a ratio of 1.43:1; a similar ratio is also deduced from Hoyland's[4] SCF calculations. Duke's[15] iterative EH calculations, which indicated $q_C(CH_4) = -0.100$ e and $q_C(C_2H_6) = -0.076$ e (*i.e.*, a ratio of 1.31:1) are, according to this author, subject to caution. To this, it appears interesting to recall Harris's comments[16] on self-consistent Hückel methods, namely that "it is insufficient to solve conventional Hückel theory equations iteratively until the solution is consistent with the parameters, for such a solution will not necessarily correspond to a charge distribution of minimum energy."

[14] W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2384 1966).

[15] B. J. Duke, *Theor. Chim. Acta*, **9**, 260 (1968).

[16] F. E. Harris, *J. Chem. Phys.*, **48**, 4027 (1968).

atoms. This appears not to be an unhappy situation, in terms of shell effect, since its neighboring C atom does not carry anymore a large negative charge. This is exactly what is shown by the population analyses and what is expressed by eq 4. The consequence is that the CH_2 group in propane is electron deficient and, finally, that the ethyl group appears to be a better electron donor than methyl. Similar arguments can also be applied to isobutane and neopentane.

It follows, from these considerations, that methyl groups cannot simply be regarded as electron donors with the implication that the electron donation toward a center is increased as the number of methyl groups attached to this center is increased. Hence, the argument which is occasionally invoked that "a tertiary carbonium ion is more stable than the secondary or primary one since there are more methyl groups that can release electrons toward the positive center" should not be retained. Anyway, the charges are distributed so as to minimize their total energy and, consequently, any subsequent charge pushing is unnecessary. The order of stabilization of carbonium ions can be interpreted in terms of eq 4, which indicates that a positive center is favored by neighboring negatively charged atoms.

This interpretation has a further consequence. Since a positive site appears to be favored by negative neighbors, the methyl group is expected to be more effective in favoring a carbonium ion than, say, a *tert*-butyl group, whose central C atom is electron deficient with respect to the methyl C atom. Clearly, from a consideration of the shell effect, the alkyl groups are expected to favor a positive site in the order methyl > ethyl > isopropyl > *tert*-butyl, *i.e.*, in the so-called "hyperconjugative order." This is illustrated, both on experimental and theoretical grounds, by a detailed study of the formation of zwitterionic carbocations from the decomposition of 1,2,3-trioxolanes (primary ozonides), in terms similar to the arguments presented here.[17,18]

It is, hence, concluded that the shell effect (eq 4) is capable of explaining both the inductive order (*tert*-butyl > ··· > methyl) and the "hyperconjugative" order (methyl > ··· > *tert*-butyl) of reactivity exhibited by alkyl groups.

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(17) S. Fliszár, J. Renard, and D. Z. Simon, *J. Amer. Chem. Soc.*, **93**, 6953 (1971).

(18) Any over generalization of the present interpretation of the "hyperconjugative order" could, however, be misleading since, in a number of cases, solvolysis may be responsible for the ordering of effects exhibited by alkyl groups.

All-Electron Nonempirical Calculations of Potential Surfaces. I. Dissociation of Formaldehyde into Radical Products

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Abstract: *Ab initio* calculations on the lowest two singlet and triplet states of formaldehyde have been performed using excited-state SCF orbitals as an expansion set in a modest CI. The calculations were repeated for several molecular geometries representative of the dissociation path to radical products. The nature of the dissociation as examined in terms of the molecular orbital energies and coefficients as well as the weighting coefficients of electronic configurations is discussed. The calculated values for spectral excitations of formaldehyde and formyl radical and the H–HCO bond dissociation energy are compared with experiment and with previous calculations where available.

The success of recent efforts to perform SCF calculations for ground-state polyatomic molecules has stimulated a need for at least equally satisfactory methods for molecular excited states. The present work is an attempt to find a suitable compromise between accuracy and economy of application so that investigation of excited-state potential surfaces can be carried out with some degree of reliability. The difficulties of open shell SCF calculations are widely recognized and have been discussed by Berthier.[1] For carefully selected problems, primarily those involving a single electron outside a closed shell core, SCF calculations may be sufficient to yield good results for spectral excitation energies. However, for most molecular spectra the problem is more difficult and consideration must be taken of possible changes in correlation energy upon excitation. If one is interested in the change of molecular energy as a function of internuclear geometry, as in chemical reactions, the SCF result has the additional disadvantage that frequently the calculated energies misbehave at asymptotic values of the geometric parameters. The dissociation of molecular hydrogen in the MO approximation to a fictitious energy of equal weights of ($H^- + H^+$) and of (2H) is the simplest example of this misbehavior.

In the present work it was hoped to evolve a relatively economic scheme which would somewhat overcome

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(1) G. Berthier, "Molecular Orbitals in Physics, Biology, and Chemistry," P. Lowdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1965.