

A Simple Approach to the Chemistry of Alkyl Groups and to Their Study by Theoretical Methods

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Abstract: The concept "avoid, as much as possible, charges of same sign on neighboring atoms," represented by $Q_i = \sum(\alpha_j Q_j + \beta_j)$ (j adjacent to i), appears to be basic for explaining the chemical effects of alkyl groups. A Taft-like description of their inductive effects is adequate when, in the arbitrary scale $\sigma^*(\text{CH}_3) = 0$ and $\sigma^*(\text{C}_2\text{H}_5) = -0.100$, the electron-releasing abilities of the isopropyl and *tert*-butyl groups are described by $\sigma^*(i\text{-C}_3\text{H}_7) = -0.200$ and $\sigma^*(\text{tert-C}_4\text{H}_9) = -0.300$. The inductive effects, in terms of net electron release, as well as the above equation, are reflected by the charge distributions calculated by several theoretical methods, thus stressing their similarities in reproducing chemical effects. This may justify the approach of discussing inductive effects in terms of LCAO population analyses. It also results from the present treatment that the alkyl groups appear to promote adjacent positive sites in the "hyperconjugative order" $\text{CH}_3 > \dots > \text{tert-C}_4\text{H}_9$.

A recent attempt¹ to discuss chemical effects in terms of charge distributions indicated that the electron-releasing ability of alkyl groups in the inductive order $\text{CH}_3 < \dots < \text{tert-C}_4\text{H}_9$ and their ability in favoring adjacent positive sites in the order $\text{CH}_3 > \dots > \text{tert-C}_4\text{H}_9$ are linked in a simple manner to the concept "avoid, as much as possible, charges of same sign on neighboring atoms." This concept, which is similar in some aspects to what Pople and Beveridge² have discussed in terms of charge alternation, can also be expressed as follows, in familiar terms, "a positive site is best favored when embedded in negative neighbors."

Advantage was taken from the observation that several theoretical LCAO methods reproduce correctly the inductive effects of alkyl groups in Taft's order.^{1,3} Hence, Taft-like equations were used as input, and their coherence with an equation describing the above concept was examined.

The present treatment offers an improvement in that (i) no Taft-like equation need be assumed *a priori*, (ii) the degree of approximation can be evaluated to a certain extent, and (iii) the chemical understanding gains in clarity. The alkanes are chosen as model compounds.

The only basic assumption which is made is represented by eq 1, where Q_i represents the net charge on

$$Q_i = \sum(\alpha_j Q_j + \beta_j) \quad (1)$$

$$\sum Q = 0 \quad (2)$$

each j atom neighboring atom i , whose net charge is Q_j . The α_j are negative coefficients which define an appropriate weight for the contributions of the Q_j 's of different types of atoms and, hence, differentiate a C neighbor to atom i from an H neighbor. This equation indicates that the more negative the weighted sum of the charges on the neighbors j , the more positive is the charge on atom i , and conversely. The β_j are terms required for writing the linear relationship and shall be discussed below. Equation 2 expresses the fact that the molecules are neutral.

(1) S. Fliszár, *J. Amer. Chem. Soc.*, **94**, 1068 (1972).

(2) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

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

The meaning of the parameters can be deduced easily from the following examples. For methane, eq 1 is written

$$Q_C(\text{CH}_4) = 4\alpha_H Q_H + 4\beta_H$$

and, by means of eq 2

$$Q_C(\text{CH}_4) = 4\beta_H / (1 + \alpha_H)$$

Similarly, for ethane

$$Q_C(\text{C}_2\text{H}_6) = 3\alpha_H Q_H + \alpha_C Q_C + 3\beta_H + \beta_C$$

$$Q_C(\text{C}_2\text{H}_6) = (3\beta_H + \beta_C) / (1 + \alpha_H - \alpha_C)$$

The use of the parameters n and m considerably facilitates the calculations (eq 3 and 4). It is further

$$1 + \alpha_H = -n\alpha_C \quad (3)$$

$$m\beta_H = \beta_C \quad (4)$$

noted that the β_j have the dimension of charge. Since they cannot be calculated, it is convenient to refer all the quantities with the dimension of Q with respect to some unity. With the arbitrary choice

$$Q_C(\text{C}_2\text{H}_6) = -1.000 \quad (5)$$

the net charge on the methane C atom is given by eq 6, in relative units (ru).

$$Q_C(\text{CH}_4) = -4(n + 1) / n(3 + m) \text{ (ru)} \quad (6)$$

In order to avoid tedious subscript notation, eq 1 is written as follows for the H atoms

$$Q_H = A Q_C + B \quad (7)$$

where A and B are the appropriate α_i and β_j of eq 1.

Figure 1 represents a comparison of eq 7 with the charges calculated by Hoffmann⁴ for a series of alkanes. According to these extended Hückel (EHMO) results, $A = -0.078$ and $B = 0.091$ electron unit; *i.e.*, with $Q_C(\text{C}_2\text{H}_6) = -0.356$ eu, $B = 0.256$ ru.

It is noted that for ethane eq 7 becomes, in ru

$$B - A = 1/3 \quad (8)$$

(4) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

The Inductive Effect

In order to test in what manner eq 1 reproduces the inductive effects in terms of electron release, the following Taft-like equations are examined.

$$Q_H = a\sigma^* + b \quad (9)$$

$$Q(\text{CH}_3) = -a'\sigma^* \quad (10)$$

Equation 9 describes the dependence of Q_H on a parameter σ^* , which can be assimilated to Taft's polar constants.⁵ Equation 10 correlates the net charge of a methyl group in compounds R-CH₃ to the σ^* value corresponding to R. The reference scale chosen for the σ^* values is (i) the origin $\sigma^*(\text{CH}_3) = 0$ and (ii) the slope $\sigma^*(\text{C}_2\text{H}_5) = -0.100$, but any other reference scale would be equally suitable.

It is stressed that eq 9 and 10 are not to be considered as inputs but only as auxiliary equations as long as the σ^* values for the isopropyl and the *tert*-butyl groups are not fixed *a priori*. Here, these σ^* constants are treated as unknowns.

The parameters a and b can be calculated as follows. A consideration of methane, together with eq 9, indicates that $b = Q_H(\text{CH}_4)$, since $\sigma^* = 0$; hence, from eq 2 and 6, it is, in ru

$$b = (n + 1)/n(3 + m) \quad (11)$$

From a consideration of ethane ($Q_H = 1/3$ ru), it follows from eq 9 and 11 that

$$a = (3 - mn)/0.3n(3 + m) \text{ (ru)} \quad (12)$$

The calculation of Q_H for the primary H atoms in compounds R-CH₃ is facilitated by introducing eq 7 in eq 10 ($Q_C + 3Q_H = -a'\sigma^*_R$). Remembering eq 8, it results

$$Q_{H \text{ prim}} = -Aa'\sigma^*_R/(1 + 3A) + 1/3 \text{ (ru)} \quad (13)$$

$$Q_{H \text{ prim}} = a''\sigma^*_R + 1/3 \quad (14)$$

where $a'' = (Aa')/(1 + 3A)$.

It is now possible to calculate the appropriate σ^* values for the isopropyl and *tert*-butyl groups to be used in eq 9 and 10. These σ^* values clearly represent the electron-releasing ability of these groups in the arbitrary scale defined by $\sigma^*(\text{CH}_3) = 0$ and $\sigma^*(\text{C}_2\text{H}_5) = -0.100$.

The following point should be noted. In this calculation, eq 1 is applied only in situations where the neighbors to atom i are CH₃ carbon atoms; hence, whether the α_C values for secondary to quaternary C atoms differ from that of a methyl C atom is, at this stage, immaterial. Similarly, eq 7 is only applied to methyl H atoms. It is reasonable to assume that under these conditions any departure from eq 1 due to second-order perturbations may be kept to a minimum.

First, the parameter a' of eq 10 is calculated. This can be done in three different ways. From neopentane, by means of eq 1, 2, 10, and 14, it follows that

$$a' = [-3\alpha_C(a''\sigma^*_{t\text{-Bu}} + 1/3) + \beta_C]/(1 + \alpha_C)\sigma^*_{t\text{-Bu}} \quad (15)$$

In a similar way, using also eq 9, it results from pro-

(5) R. W. Taft, *J. Amer. Chem. Soc.*, **75**, 4231 (1953).

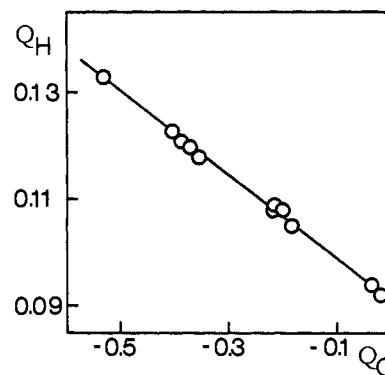


Figure 1. A verification of eq 7 by Hoffmann's results⁴ for alkanes, in electron units.

pane that

$$a' = \frac{-3\alpha_C(a''\sigma^*_{\text{Et}} + 1/3) - n\alpha_C(a\sigma^*_{t\text{-Pr}} + b) + (m + 1)\beta_C}{(1 + \alpha_C)\sigma^*_{\text{Et}}} \quad (16)$$

and, finally, from isobutane

$$a' = \frac{-9\alpha_C(a''\sigma^*_{t\text{-Pr}} + 1/3) - n\alpha_C(a\sigma^*_{t\text{-Bu}} + b) + (3 + m)\beta_C}{3(1 + \alpha_C)\sigma^*_{t\text{-Pr}}} \quad (17)$$

Equating the results for a' obtained from neopentane and propane, and those calculated from neopentane and isobutane, the following solutions are obtained

$$0.3(\sigma^*_{\text{Et}}/\sigma^*_{t\text{-Bu}} - 1) = \sigma^*_{t\text{-Pr}}$$

$$0.9(\sigma^*_{t\text{-Pr}}/\sigma^*_{t\text{-Bu}} - 1) = \sigma^*_{t\text{-Bu}}$$

i.e., with $\sigma^* = -0.100$ for the ethyl group

$$\sigma^*(i\text{-C}_3\text{H}_7) = -0.200$$

$$\sigma^*(\text{tert-C}_4\text{H}_9) = -0.300$$

This order of electron-releasing ability, which results as a direct consequence of the effect described by eq 1, is in agreement with the experimental Taft order.⁵ From this, it may be inferred that for the alkyl groups the usual interpretation of the inductive effects in terms of net electron release is adequate. Hence, any reasonable theoretical method should be expected to reproduce the inductive effects.

This has been found to occur.^{1,3} For a series of alkanes, eq 1 and the Taft-like eq 9 and 10 are satisfactorily obeyed by the Pariser-Parr-Pople,⁶ Hoffmann's EHMO,⁴ Hoyland's BO,⁸ Pople's CNDO/2,⁹ and Del Re's^{10,11} methods. Thus, it seems justified to use theoretical charge distributions for an evaluation of inductive effects in terms of electron release.

(6) Charges calculated by Sándorfy and Katagiri,⁷ using a Pariser-Parr type method, were used for this verification.

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

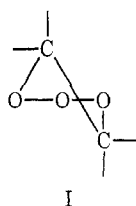
(8) J. R. Hoyland, *J. Chem. Phys.*, **50**, 473 (1969).

(9) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129, S136 (1965).

(10) G. Del Re, *J. Chem. Soc.*, 4031 (1958).

(11) The verification of inductive equations by Del Re's method is not further surprising. 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 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 1 resembles to a certain extent Del Re's approach, $\delta_\mu = \delta_\mu^0 + \sum \gamma_{\mu(\lambda)}\delta_\lambda$ (λ adjacent to μ). Though similar in spirit, the present approach appears, however, to be more direct in that eq 1 involves the charges instead of the quantities δ related to charges.

Indeed, it has been shown recently⁸ that the inductive effects expected for the alkyl groups are reproduced by the CNDO/2 and EHMO calculations of a variety of 1,2,3-trioxolanes, I.



Both methods indicate that the net electron release by equatorial alkyl groups correlates in a remarkably constant fashion with Taft's polar constants. The same holds for the axial substituents. In addition, both methods reproduce correctly the expectation that the electron loss by equatorial substituents should be more important than that for axial position. Furthermore, a consideration of the charge distributions indicates that a positive site is best favored as its immediate surroundings are the most negative, as stated by eq 1. This has been considered as the key explanation for the observed fact that, in the cleavage of selected trioxolanes, the alkyl groups promote the formation of zwitterionic carbonium ions in the order $\text{CH}_3 > \dots > \text{tert-C}_3\text{H}_9$, somewhat better when in axial than in equatorial position. It is felt that, because of the theoretical interpretation given above, the judicious evaluation of inductive effects in terms of charge distributions can be justified and prove useful in the discussion of reactivity problems.

The present approach can now be developed further. Insertion of the appropriate σ^* values in the expressions for a' shows that

$$a' = 10B\alpha_C(3 - mn)/(3B + \alpha_C)(3 + m) \quad (\text{ru}) \quad (18)$$

In principle, the charge distributions in alkanes can now be calculated. For example, the secondary and tertiary H atoms in propane and isobutane are given by eq 9.

$$Q_{\text{H sec}} = [3(n - 1) + 2mn]/3n(3 + m) \quad (19)$$

$$Q_{\text{H tert}} = (n - 2 + mn)/n(3 + m) \quad (20)$$

The charge of the quaternary C atom in neopentane is calculated from $Q_{\text{C quat}} = -4Q(\text{CH}_3)$, with $Q(\text{CH}_3) = -a'\sigma^*(\text{tert-C}_4\text{H}_9)$.

$$Q_{\text{C quat}} = -1.2a' \quad (21)$$

It is also noted that for any assigned value for $Q_{\text{C}}(\text{CH}_4) = -4b$, it is

$$m = (n + 1)/bn - 3 \quad (22)$$

However, any comparison with LCAO calculations would, at this stage, be of questionable interest. In the following, the present treatment is reduced to an approximate one-parameter theory.

A First Approximation

It seems reasonable to consider that, to a first approximation, it should be possible to assume that the parameters in eq 1 (hence, also those in eq 7) are the same for primary to quaternary atoms. There is no *a priori* reason why this should be so; only the final

results seem to justify this approximation to a certain extent.

In the case of methane, it follows from eq 7, 8, and 11 that

$$B = b/3(4b - 1) = (n + 1)/(4 + n - mn)3 \quad (23)$$

It is now possible to calculate α_C . For propane, the result for $Q_{\text{H sec}}$ (eq 19) is compared to that obtained by solving the eq $Q_{\text{H sec}} = A Q_{\text{C sec}} + B$ and $Q_{\text{C sec}} + 2Q_{\text{H sec}} = -2Q(\text{CH}_3) = 2a'\sigma^*(\text{C}_2\text{H}_5)$. Alternatively, for isobutane, the previous result for $Q_{\text{H tert}}$ (eq 20) is compared to that obtained from the eq $Q_{\text{H tert}} = A Q_{\text{C tert}} + B$, and $Q_{\text{H tert}} + Q_{\text{C tert}} = -3Q(\text{CH}_3) = 3a'\sigma^*(i\text{-C}_3\text{H}_7)$. In both cases the solution is

$$\alpha_C = -3B/(1 + 3Bn) \quad (24)$$

Inserting this result in eq 18, a comparison with eq 12 indicates that

$$a' = -a \quad (25)$$

Assuming equal α_C values for primary to quaternary C atoms, it is possible to calculate m . For neopentane, the eq $Q_{\text{C prim}} = 3\alpha_{\text{H}}Q_{\text{H prim}} + \alpha_{\text{C}}Q_{\text{C quat}} + 3\beta_{\text{H}} + \beta_{\text{C}}$, together with eq 10 and 14, and the comparison with $Q_{\text{C quat}}$ given by eq 21 show that $m = 0$.

The same result is obtained from similar calculations made for C_{sec} of propane and C_{tert} of isobutane. This, of course, considerably simplifies the calculations. The results obtained with $m = 0$ are summarized in Table I.

Table I. Parameters and Net Charges, with $m = 0$ (ru)

	$a = -a' = 10/3n$
	$b = (n + 1)/3n$
	$\alpha_C = -(n + 1)/(n^2 + 2n + 4)$
	$A = -1/(n + 4)$
	$B = (n + 1)/3(n + 4)$
Methane	$Q_{\text{C}} = -4(n + 1)/3n$
Propane	$Q_{\text{C prim}} = -[4(n + 1) + 3n^2]/3n(n + 1)$
	$Q_{\text{C sec}} = 2(2 - n)/3n$
	$Q_{\text{H prim}} = [1 + n(n + 1)]/3n(n + 1)$
	$Q_{\text{H sec}} = (n - 1)/3n$
Isobutane	$Q_{\text{C prim}} = -[1 + 2(n + 4)]/3n(n + 1)$
	$Q_{\text{C tert}} = (8 - n)/3n$
	$Q_{\text{H prim}} = 1/3 + 2/3n(n + 1)$
	$Q_{\text{H tert}} = (n - 2)/3n$
Neopentane	$Q_{\text{C prim}} = -[1 + (n + 4)]/n(n + 1)$
	$Q_{\text{C quat}} = 4/n$
	$Q_{\text{H}} = 1/3 + 1/n(n + 1)$
Cyclobutane	$Q_{\text{C}} = -2(n + 1)/3(n + 2)$

The numerical result obtained by means of the equations of Table I with $n = 34$ and $n = 9.5$ are presented in Table II, together with the corresponding figures calculated by Del Re's and Hoffmann's theories.

Table II indicates that the present method can generate almost equally well both Del Re's and Hoffmann's results by an appropriate choice of n . It must be stressed that also the Sándorfy-Katagiri⁷ results ($n \approx 9.5$) obtained by a Pariser-Parr-Pople method and Hoyland's⁸ results ($n \approx 30$) can be reproduced.¹² This may possibly suggest that the approx-

(12) The comparison with the CNDO/2 results calculated¹ by means of the original parameters⁹ is, however, not satisfactory, although the inductive effects and eq 1 are individually reproduced by this method.^{1,3} It is stressed that no attempt has been made to improve the quality of the correlations, although this could be probably achieved by an adequate choice of parameters.

Table II. Net Charges and Parameters in the Arbitrary Unit Scale $Q_C(C_2H_6) = -1.000$

Molecule	Atom (parameter)	$n = 34$	Del Re	$n = 9.5$	EHMO
Methane	C	-1.373	-1.385	-1.474	-1.494
Ethane	C	-1.000	-1.000	-1.000	-1.000
Propane	C_{prim}	-1.011	-1.009	-1.045	-1.048
	C_{sec}	-0.627	-0.624	-0.526	-0.520
	H_{prim}	0.334	0.332	0.337	0.338
	H_{sec}	0.324	0.325	0.298	0.295
Isobutane	C_{prim}	-1.021	-1.008	-1.090	-1.090
	C_{tert}	-0.255	-0.256	-0.053	-0.053
	H_{prim}	0.334	0.330	0.340	0.340
	H_{tert}	0.314	0.316	0.263	0.258
	H_{sec}	0.314	0.316	0.263	0.258
Neopentane	C_{prim}	-1.032	-1.017	-1.135	-1.132
	C_{quat}	0.118	0.120	0.421	0.385
	H	0.334	0.330	0.343	0.345
Cyclobutane	C	-0.648	-0.644	-0.609	-0.599
	a	0.098	0.094	0.351	0.370
	a'	-0.098	-0.100	-0.351	-0.336
	A	-0.026	-0.026	-0.074	-0.078
	B	0.307	0.309	0.259	0.256

imation of all equal α_C 's is acceptable to a certain degree; *i.e.*, that in the final analysis the effect to nearest neighbors is, in the present case, dominant with respect to the ultimate chemical effects.

In turn, the clear recognition of the "chemical consistency" of theoretical charge distributions hopefully discloses useful possibilities for the discussion of reactivity problems where inductive effects, as well as effects directly related to eq 1, are important.

It must be stressed, however, that the present approach should *not* be regarded as an alternative general means of calculating charge distributions. For the alkyl groups it appears that if charge distributions obey eq 1, the Taft-like equations (9, 10) should also be satisfied. This approach should, thus, be regarded simply as a description of the conditions for the *simultaneous* validity of eq 1, 9, and 10 which were already found¹ to agree *individually* with a number of LCAO charge distributions.

Conclusions

The chemical relevancy of the concept expressed by eq 1, *i.e.*, "a positive site is best favored when embedded in negative surroundings," is illustrated by its two major consequences. (i) Taft-like equations can be derived for the inductive effects, in terms of net electron release by the alkyl groups in the order $CH_3 < \dots < tert-C_4H_9$. The reduction to an approximate one-parameter theory, neglecting second-order perturbations, enables an evaluation of charge distributions in the alkanes in a relative scale. The remarkable agreement with selected theoretical methods stresses their chemical consistency and, in this sense, their similarity. This may justify the approach of discussing inductive effects in terms of LCAO population analyses.

(ii) An outcome of charge alternation (eq 1) is that electron-poorer sites are found in the neighborhood of electron-richer sites. Hence, a site is expected to be electron poorer when adjacent to a methyl than, say, to a *tert*-butyl group, whose central C atom is electron deficient with respect to the methyl C atom. Clearly, from a consideration of the effect expressed by eq 1, the alkyl groups promote adjacent electron-poorer

sites in the order $CH_3 > \dots > tert-C_4H_9$, *i.e.*, in the so-called "hyperconjugative order."¹³ An extension of these views to the primary carbonium ions RCH_2^+ leads to similar conclusions. The positive charge on the formal C^+ is expected to be more important with $R = CH_3$ than with $R = tert-C_4H_9$.¹⁴ Because of the interdependence of the inductive with the charge alternation effect demonstrated in this paper, this conclusion can also be reached as follows. Since, under similar circumstances, a *tert*-butyl group appears to be a better electron donor than a methyl group, the positive charge carried by $-CH_2^+$ in compounds RCH_2^+ is expected to be somewhat reduced when $R = tert-C_4H_9$, as compared to the situation with $R = CH_3$. It must be stressed that the present considerations concern only the more or less pronounced positive character on C^+ in the "hyperconjugative order" and *not* the order of stability of these primary carbonium ions. Indeed, both experimental¹⁵ and calculated¹⁶ heats of formation indicate increasing stability in the order $CH_3CH_2^+ < \dots < tert-C_4H_9CH_2^+$. Hence, in the primary carbonium ions, it appears that stability is increased as the positive charge on C^+ is reduced, which is in line with the familiar argument that "electroneutrality is a good thing."

The effect of α -methyl substitution on a carbonium ion can be visualized in terms of eq 1.¹⁷ In the series of primary to tertiary carbonium ions, eq 1 predicts that the tertiary C^+ ion carries the most important positive charge because $\sum \alpha_i Q_i$ is largest in this case. This expectation is supported by recent ¹³C nmr results by Olah and White¹⁸ which indicate that the positive charge on C^+ is more important in the tertiary than in the secondary carbonium ion. Moreover, this expectation is supported by recent *ab initio* calculations by Pople, *et al.*,¹⁶ which show that the positive charge on C^+ increases in the order: +0.225 (CH_3^+), +0.249 ($CH_3CH_2^+$), +0.283 [$(CH_3)_2CH^+$], and +0.328 [$(CH_3)_3C^+$].

In the preceding, the order $CH_3 > \dots > tert-C_4H_9$ was referred to as "hyperconjugative order," but hyperconjugation as such has not been discussed. To this, it appears most interesting to examine the recent detailed *ab initio* results by Pople, *et al.*^{16,19} The pronounced preference for C-C *vs.* C-H hyperconjugation in terms of overlap effects involving bonds β to a vacant orbital is capable of explaining the observed trends in stabilization energies of the carbonium ions. The calculated stabilizations,¹⁶ in terms of heats of formation, are in remarkable agreement with the observed ones. It appears, among other results, that both induc-

(13) Any overgeneralization 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.

(14) This trend is reflected by *ab initio* calculations on the RCH_2^+ carbonium ions in their most stable conformations: $Q_{C^+} = +0.249$ electron units ($R = CH_3$), +0.233 ($R = C_2H_5$), +0.225 ($R = i-C_3H_7$), and +0.223 ($R = tert-C_4H_9$) (Professor J. A. Pople, unpublished results, private communication).

(15) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

(16) L. Radom, J. A. Pople, and P. v. R. Schleyer, unpublished results.

(17) This effect is discussed in ref 16 in terms of stabilization energies.

(18) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(19) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **94**, 311 (1972); **93**, 1813 (1971); **92**, 6380 (1970).

tive and hyperconjugative stabilization energies are in the inductive, *not* in the Baker–Nathan, order.¹⁶ These energetic aspects are, however, not in contradiction with the concept of charge alternation (eq 1) which concerns total charge distributions, *i.e.*, in the present case, the preferential positions for the formation of positive sites.

The final conclusion is that the simple concept of charge alternation expressed by eq 1 is basic, despite its crudeness and its obvious limitations, in that it unifies the effects exhibited by alkyl groups, *i.e.*, (i)

the net electron release in the inductive order and (ii) the “hyperconjugative order” for promoting neighboring positive sites.

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The Meaning of the “Polar Effect” in Hydrogen Abstractions by Free Radicals. Reactions of the *tert*-Butoxy Radical¹

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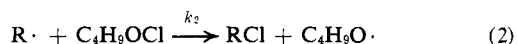
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Abstract: Abstractions from substituted toluenes by *tert*-butoxy radicals derived from *tert*-butyl hypochlorite exhibit a Hammett ρ of -0.41 ; it is confirmed that previously reported higher values were due to chlorine atom chains. A plot of ρ for abstractions from toluenes by various radicals *vs.* ΔH for each radical is linear. This is interpreted as proof that ρ reflects differences in the bond dissociation energies of substituted toluenes and that its magnitude is a measure of the sensitivity of the abstracting radical to these differences. In several cases which were thought to demonstrate the importance of the “polar effect,” the postulation of partial charge separation in the transition state is shown to be either unnecessary, inadequate, or inconsistent with experimental observations.

The “polar effect” in hydrogen abstractions by radicals is a widely used concept, but we have found inconsistencies in its applications. This led us to re-examine some reactions of the *tert*-butoxy radical, a typical selective hydrogen abstracting radical.

The “polar” character of the *tert*-butoxy radical has been investigated several times with the general conclusion that the radical is electrophilic. Relative reactivities of meta- and para-substituted toluenes give good Hammett $\sigma\rho$ plots. Using *tert*-butyl hypochlorite as a source of *tert*-butoxy radicals, Walling and Jacknow have reported that the reaction constant ρ for reaction 1



with substituted toluenes has the value of -0.82 at 40° in excess hydrocarbon solvent;² Gilliom and Ward found $\rho = -0.75$ at 40° in benzene,³ and Walling and Gibian -0.96 at 0° in acetonitrile.⁴ The extensive work of Kennedy and Ingold at 40° in CCl_4 gave $\rho = -0.86$; the correlation was better when \log (relative reactivity) was plotted *vs.* σ^+ values, with $\rho = -0.68$.^{5,6}

(1) (a) Presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972, ORGN 60; (b) taken in part from the M.S. Dissertation of J. A. P., The Brooklyn Center, Long Island University, 1971.

(2) C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, **82**, 6108, 6113 (1960).

(3) R. D. Gilliom and B. F. Ward, *ibid.*, **87**, 3944 (1965).

(4) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

(5) R. Kennedy and K. U. Ingold, *Can. J. Chem.*, **44**, 2381 (1966).

(6) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

More recent investigations employed di-*tert*-butyl peroxalate rather than the hypochlorite as a source of the oxy radical; Sakurai and Hosomi reported much lower values for the reaction constant in chlorobenzene, 1,1,2-trifluorotrchloroethane (Freon-113), and acetonitrile at 45° with ρ values between -0.36 and -0.43 .⁷ The correlation was better with σ^+ substituent constants and $\rho^+ = -0.32$ to -0.39 were reported. In that work, relative reactivities were obtained by the indirect method; the ratio of k_1/k_3 was determined



with a series of substituted toluenes and was compared to k_1/k_3 with toluene. It was suggested⁷ that the ρ values reported previously were near the value of -0.76 found for chlorinations of substituted toluenes by chlorine,⁸ and that chlorine atom chains may become involved in chlorinations with *tert*-butyl hypochlorite. Walling and McGuinness repeated the measurements using di-*tert*-butyl hyponitrite and di-*tert*-butyl peroxalate, again employing the indirect method of k_1/k_3 ratios.⁹ Their results in chlorobenzene solvent at 40° also indicated low values; $\rho = -0.39$ and $\rho^+ = -0.35$ with better statistics in the latter case.

Since direct competitions toward *tert*-butyl hypochlorite are suspect,^{7,9} and k_1/k_3 ratios are known to be solvent dependent¹⁰ and are inherently less accurate

(7) H. Sakurai and A. Hosomi, *ibid.*, **89**, 458 (1967).

(8) C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957).

(9) C. Walling and J. A. McGuinness, *ibid.*, **91**, 2053 (1969).

(10) C. Walling and P. J. Wagner, *ibid.*, **86**, 3368 (1964).