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EVALUATION OF RESONANCE EFFECTS ON REACTIVITY BY APPLICATION OF THE LINEAR INDUCTIVE ENERGY RELATIONSHIP–IV

HYPERCONJUGATION EFFECTS OF PARA-ALKYL GROUPS*

ROBERT W. TAFT, JR. and IRWIN C. LEWIS

College of Chemistry and Physics, Pennsylvania State University

Abstract—The σ^* (or σ_I) scale of inductive effects and the linear inductive energy relationship, inductive effect $= \sigma^* \rho^*$ (or $\sigma_I \rho_I$), enables an empirical but quantitative estimation of inductive effects on reaction rates and equilibria. In the present paper the inductive effects of *para*-alkyl groups (Me, Et, Pr^i, Bu^t) in diverse reactivities of benzene derivatives are evaluated in this manner by using the inductive reaction constants, ρ_I, obtained in previous work with groups such as NO_2, CN, OCH_3 and halogens.

The observed effects of the *para*-alkyl groups, i.e., log (k/k_0) values, upon correction for the inductive effects (equation (1)) give results (called *R* values) which are in accord with resonance theory. The Baker–Nathan order is obtained and the Berliner and the Bartlett theories of C–C hyperconjugation effects are confirmed. In most instances the *R* values follow satisfactorily Brown's empirical additive relationship (3): $R = n_H h_H + n_C h_C$, where n_H and n_C are the number of α-C–H and α-C–C bonds, respectively, in the alkyl group, and h_H and h_C are the corresponding hyperconjugation constants. The ratio h_H/h_C is found equal to $1{\cdot}3 \pm 0{\cdot}1$, totally independent (within these limits) of electron demand (ρ_I values range from -12 to $+6$), solvent, temperature and nature of the reaction process (rate or equilibrium). An independent method (equation (2)) of obtaining *R* values provides evidence of second-order solvation effects of alkyl groups in certain reactions.

The effects of alkyl groups on the transition energies of the O–O bands of the gaseous benzene ultraviolet spectra follow equation (3), providing independent evidence corroborating the above interpretation of *R* values.

The unequivocal evidence for C–C hyperconjugation in the aromatic reactivities has lead to a re-examination of the aliphatic series reactivities correlated previously by Kreevoy and Taft in terms of inductive and C–H hyperconjugation parameters. The *R* values obtained follow equation (3) with improved precision. However, $h_H/h_C = 2{\cdot}5$, in accord with the earlier conclusion that C–H hyperconjugation effects in these aliphatic series reactions are appreciably larger than C–C hyperconjugation effects.

EXTENSIVE evidence has been obtained for the concept of an approximately fixed quantitative order of inductive effects of substituent groups on reaction rates and equilibria.[1, 2, 3, 4, 5] Quantitative correlations of inductive effects by the relationship: inductive effect $= \sigma^*\rho^*$, have been made which are widely independent of reaction

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* This work was supported in part by the Office of Naval Research, Project NR055-38. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[1] G. E. K. Branch and M. Calvin, *The Theory of Organic Chemistry* pp. 193–200. Prentice-Hall, New York (1941).

[2] S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.* **70**, 828 (1948).

[3] R. W. Taft, Jr., *J. Amer. Chem. Soc.* **74**, 3120 (1952); *Ibid.* **75**, 4231 (1953).

[4] R. W. Taft, Jr., *Steric Effects in Organic Chemistry* (Ed. M. S. Newman) Chap. 13. Wiley, New York (1956).

[5] R. W. Taft, Jr. and I. C. Lewis, *J. Amer. Chem. Soc.* **80**, 2436 (1958).

type.[3, 4, 5] Reaction series following this relationship and values of the reaction constant, ρ^*, are given in reference 4 (additional reactions subsequently reported may be found in references 7, 14, 15, 16, 17, 19 and 22). These correlations have been termed linear inductive (or polar) energy relationships.[4] The inductive substituent constants, σ^*, for R groups have been obtained by the method of Ingold[6] and of Taft[3] from rates of normal saponification and acid-catalyzed hydrolysis of esters, $RCO_2C_2H_5$, and from the ionization constants[1, 4] for carboxylic acids, RCO_2H (wherein R = XCH_2).

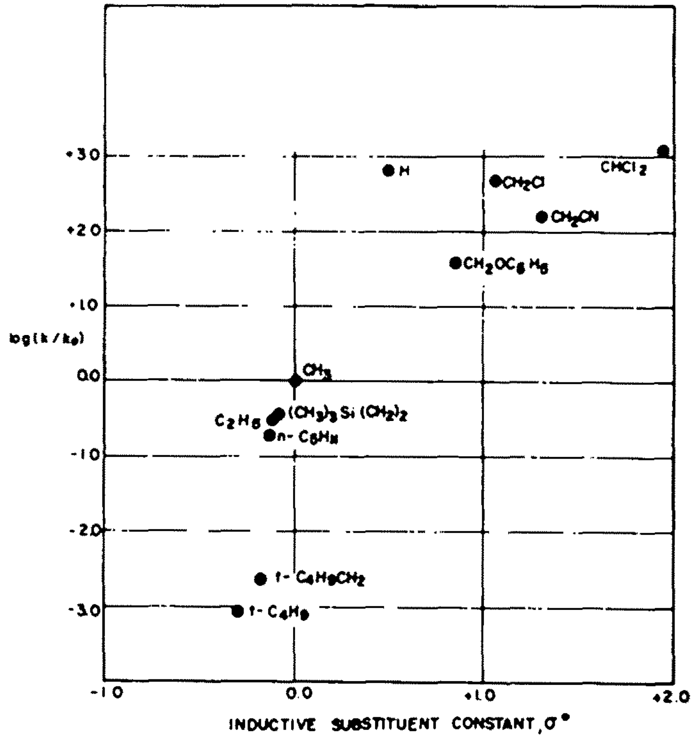

FIG. 1. Rates of sodium methoxide-catalyzed methanolysis of *l*-menthyl esters, R $CO_2C_{10}H_{19}$, in methanol at 30°.

Only when steric, resonance and other effects are very small (or negligible) in comparison to inductive effects do rates or equilibria for a reaction series follow the equation[3, 4]: $\log(k/k_0) = \sigma^*\rho^*$. In favorable cases, however, rates or equilibria which are complicated by steric effects may be corrected for these effects, and linear inductive energy relationships result. Figs. 1 and 2, taken from the work of Pavelich and Taft[7], provide an illustration of such a result.

Fig. 1 gives values of $\log(k/k_0)$ plotted vs. σ^* for the sodium methoxide catalyzed rates of methanolysis of a series of *l*-menthyl esters, $RCO_2C_{10}H_{19}$ (k_0 is the rate constant for the acetate ester). No direct relationship with σ^* values exists. In Fig. 2 the values of $\log(k/k_0)$ are corrected for steric effects, and, in contrast, a relatively precise

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[6] C. K. Ingold, *J. Chem. Soc.* 1032 (1930).

[7] W. A. Pavelich and R. W. Taft, Jr., *J. Amer. Chem. Soc.* 79, 4935 (1957); R. W. Taft, Jr. *Abstracts Fifteenth National Organic Chemistry Symposium* p. 53. Rochester, New York (June 1957).

correlation with σ^* values is obtained. The steric effect corrections are obtained by assuming a linear (steric energy) relationship[4, 8] between steric effects in the methanolysis rates and those in the rates of hydrolysis of corresponding esters.

A similar situation is found for rates or equilibria complicated by resonance effects.[4] An illustration is taken from the work of Taft and Lewis on application of the linear inductive energy relationship to the reactivities of *meta-* and *para-*substituted benzene derivatives.[5] In treating such reactivities it has proven convenient to "normalize" σ^* values so they are quantitative measures of the inductive contribution of Hammett's σ values.[9] It has been found that $0{\cdot}45\sigma^*_{XCH_2}$ gives the desired inductive constant for a *meta* or *para* substituent X relative to a hydrogen atom.[4] The inductive constants so obtained are given the symbol, σ_I.[10] Fig. 3 shows the wide scatter of points obtained in a plot of log (K/K_0) for the ionization of *meta-* and *para-*substituted benzoic acids in water at 25° vs. the inductive substituent constants, σ_I. This result is typical of the reactivities of *meta-* and *para-*substituted benzene derivatives in general.[5] Fig. 4 demonstrates the linear inductive energy relationship (inductive effect = $\sigma_I \rho_I$) which results upon correcting the log (K/K_0) values for resonance effects. This too is a

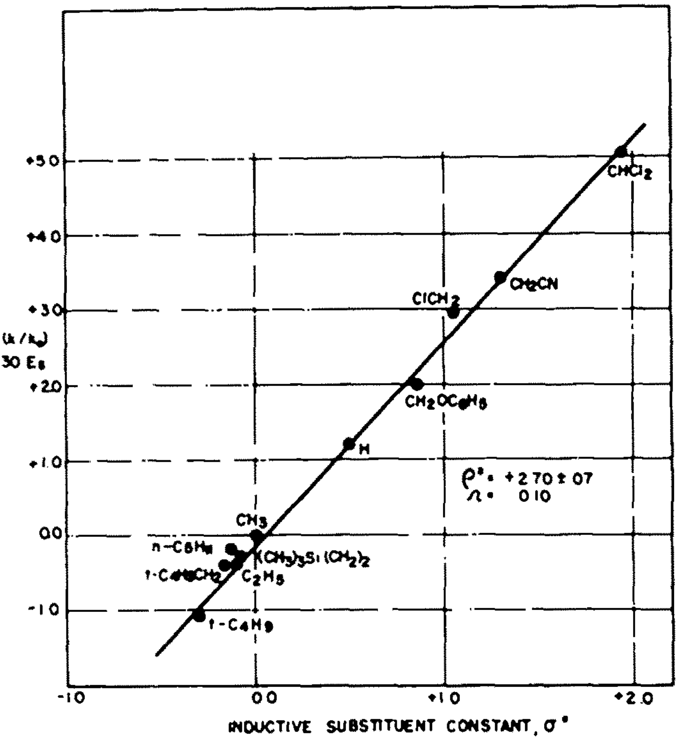

Fig. 2. Linear inductive energy relationship for rates of methanolysis of *l*-menthyl esters, R $CO_2C_{10}H_{19}$.

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[8] R. W. Taft, Jr., *J. Amer. Chem. Soc.* **75**, 4538 (1953).

[9] L. P. Hammett, *Physical Organic Chemistry* p. 404. McGraw-Hill, New York (1940); references to earlier work are given in this book.

[10] R. W. Taft, Jr., *J. Amer. Chem. Soc.* **79**, 1045 (1957).

result typical of all types of aromatic reactivities involving uncharged *meta*- and *para*-substituents. The method used by Taft and Lewis to separate inductive and resonance effects of *meta*- and *para*-substituted derivatives of benzene is discussed at length in the later sections of this paper.

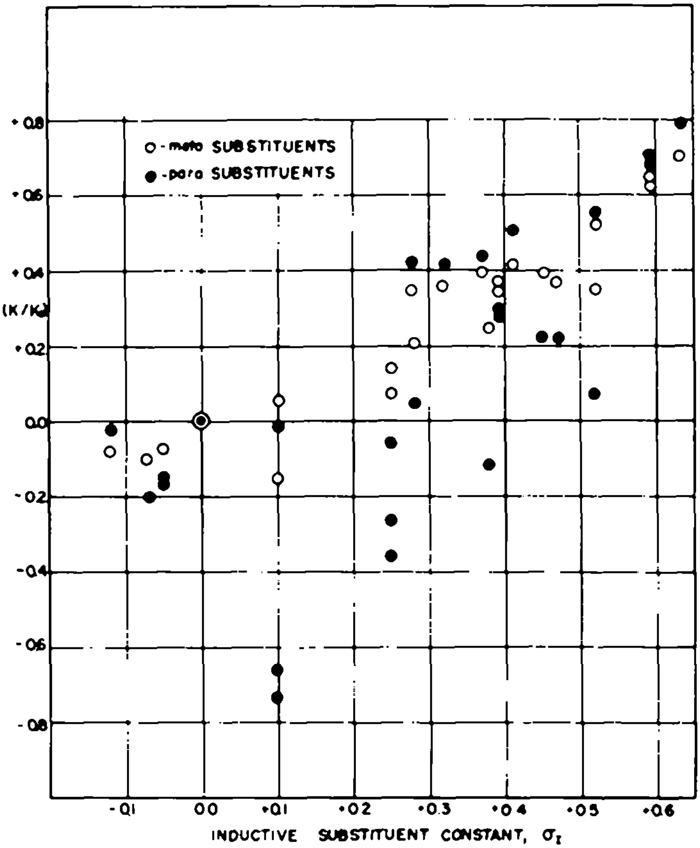

FIG. 3. Ionization of *meta*- and *para*-substituted benzoic acids in water at 25°.

A potentially valuable use which can be made of the linear inductive energy relationship is the approximately quantitative evaluation of the other effects (resonance, steric, etc.) of molecular structure on reactivity. This evaluation is obtained as the difference between the measured substituent effect and the calculated inductive effect.[4, 11] That is, $\log(k/k_0) - \sigma^*\rho^* =$ total effects other than inductive. In this way less ambiguous (perhaps in favorable cases unambiguous) studies of the other effects of molecular structure on reactivity are permitted via analysis of the relationship of these variables to structure. Interpretations reached on this basis may be further corroborated by additional generalized structure-reactivity relationships and by

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[11] G. E. K. Branch and M. Calvin, *The Theory of Organic Chemistry* pp. 203–245. Prentice-Hall, New York (1951).

correlations with theoretical calculations.[12, 13] In this manner, studies of a quantitative nature have been made of intramolecular steric effects,[4, 7, 14] resonance effects[4, 6, 15, 16] and resonance energies,[12] anchimeric assistance,[17, 18, 19] the determination of fractional steric inhibition of resonance,[20, 21] and hydrogen bonding and steric effects on solvation.[22]

A major difficulty in the study of hyperconjugation effects* on reaction rates and equilibria has been the relatively small magnitude of effects which might be attributed to this cause and the attending uncertainty of their contribution to the measured reactivity relative to that of other effects, such as the inductive effect. As a result no body of characteristic observations of great generality has been forthcoming and the existence of direct hyperconjugation effects on reactivity has remained open to question.[23]

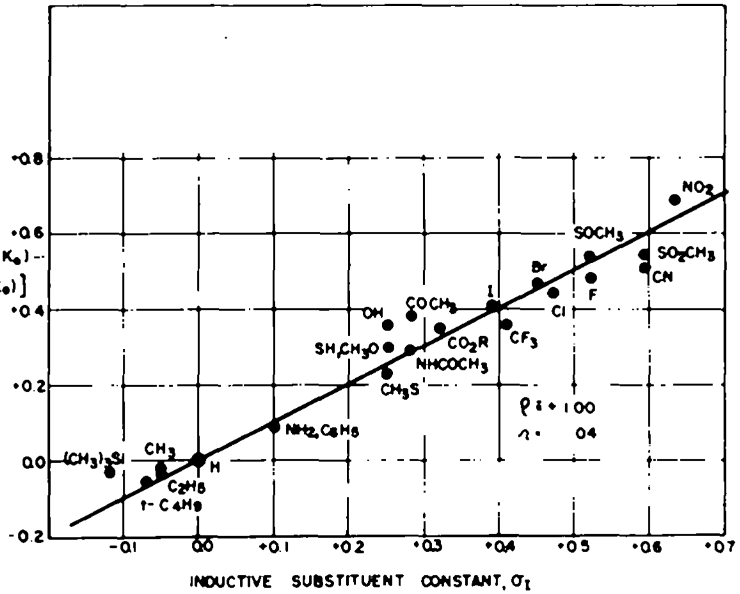

FIG. 4. Linear inductive energy relationship for the ionization of *meta*- and *para*-substituted benzoic acids.

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* The term hyperconjugation effect is used throughout the present paper in the general sense of denoting an effect on reactivity which results from a change during the reaction process in the total *potential energy of resonance interaction between an alkyl group and an adjacent atom with an open (unsaturated) stable orbital*—cf. further comments in the discussion section. The term hyperconjugation is not used as a connotation to distinguish between either of the two models which have been proposed to account for alkyl resonance interactions. Cf. references 13 and 61.

[12] M. M. Kreevoy and R. W. Taft, Jr., *J. Amer. Chem. Soc.* **79**, 4016 (1957).
[13] M. M. Kreevoy and H. Eyring, *J. Amer. Chem. Soc.* **79**, 5121 (1957).
[14] S. S. Biechler and R. W. Taft, Jr., *J. Amer. Chem. Soc.* **79**, 4927 (1957).
[15] M. M. Kreevoy and R. W. Taft, Jr., *J. Amer. Chem. Soc.* **77**, 5590 (1955).
[16] R. W. Taft, Jr. and M. M. Kreevoy, *J. Amer. Chem. Soc.* **79**, 4011 (1957).
[17] A. Streitwieser, Jr., *J. Amer. Chem. Soc.* **78**, 4935 (1956); *Chem. Rev.* **56**, 571 (1956).
[18] D. S. Noyce and B. R. Thomas, *J. Amer. Chem. Soc.* **79**, 755 (1957).
[19] S. Winstein, E. Alfred, R. Jeck and R. Glick, *J. Amer. Chem. Soc.* in preparation.
[20] B. M. Wepster, *Rec. Trav. Chim. Pays-Bas* **76**, 335, 357 (1957).
[21] R. W. Taft, Jr. and H. D. Evans, *J. Chem. Phys.* **27**, 1427 (1957).
[22] H. K. Hall, Jr., *J. Amer. Chem. Soc.* **79**, 5441, 5444 (1957).
[23] Cf., for example, W. A. Sweeney and W. M. Schubert, *J. Amer. Chem. Soc.* **76**, 4265 (1954).

The application of the linear inductive energy relationship to the quantitative estimation of the inductive contribution to widely diverse effects of alkyl groups on a variety of reactivities (in which hyperconjugation effects are expected in principle) leads to results which may be accounted for in terms of direct hyperconjugation effects.

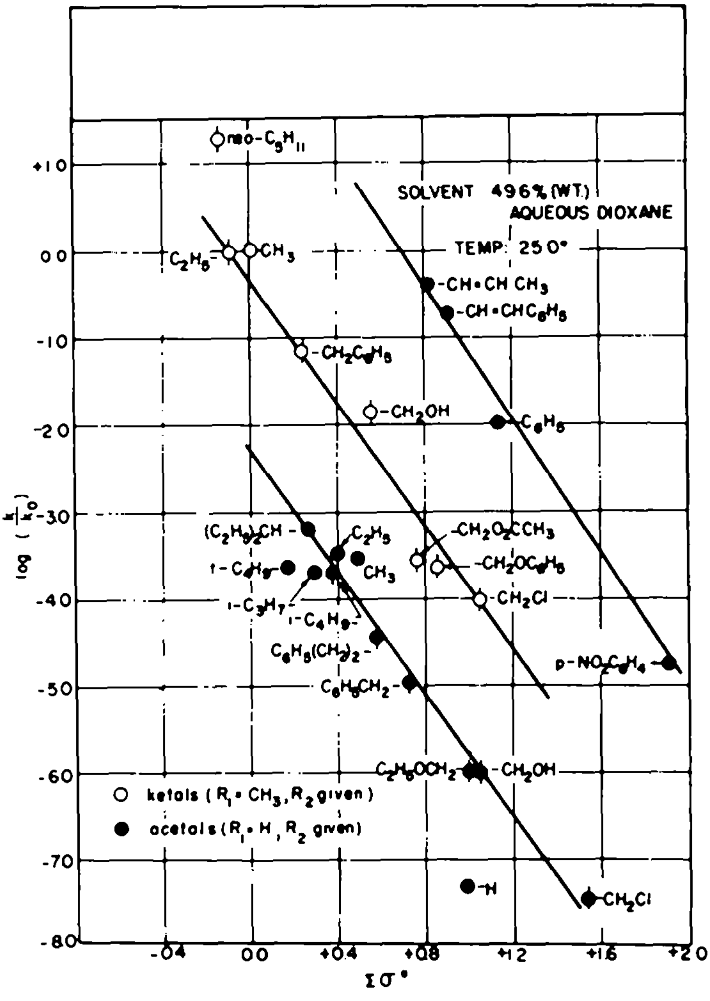

FIG. 5. Relationship between diethyl acetal and ketal, $R_1R_2C(OC_2H_5)_2$, hydrolysis rates and sum of polar substituent constants, σ^*, for R_1 and R_2.

Values of log (k/k_0) $\sigma^*\rho^*$ (or $\sigma_I\rho_I$) are related to alkyl structure in an approximately additive manner. Quantitative evidence is thereby provided that the measured reactivity effects are approximately the sum of inductive and hyperconjugation effects. The need to invoke more complex interpretations is frequently (but not always) lacking.

The method was first applied by Kreevoy and Taft[18] to the study of the effect of structure on the acid-catalyzed rates of hydrolysis of diethyl acetals and ketals,

$R_1R_2C(OC_2H_5)_2$, in 50 per cent aqueous dioxan at 25° with substituents of widely varying polar and steric requirements. A plot (Fig. 5) of log (k/k_0) vs. the sum of σ^* values of the substituents R_1 and R_2 leads to essentially parallel lines (slope ρ^* 3·60) defined by the points for three classes: mono-substituted acetals, mono-substituted ketals (except methyl *tert.*-butyl and methyl *neo*pentyl ketals—cf. later discussion) and $\alpha\beta$-unsaturated acetals (with increasing intercepts in the order given). The conclusion was drawn that within each class, inductive electron release determines the increase in rate with variation of structure. The order of the increasing intercepts indicates that resonance stabilization of the oxo-carbonium ion-like transition state also contributes to increase the reaction rates. The rate constants for twenty acetals and ketals of unconjugated aldehydes or ketones (with the two exceptions indicated above) covering a spread of nearly eight powers of ten were fitted relatively satisfactorily by the equation:

$$\log (k/k_0) = (\Sigma\sigma^*)(-3{\cdot}60) + (0{\cdot}54)(n_H \quad 6)$$

wherein k_0 refers to acetonal and n_H to the total number of α-hydrogen atoms in R_1 and R_2. The constant 0·54 was attributed to the average stabilization of the reaction transition (in log units of rate) produced by an α-hydrogen atom Equations of this form were also found applicable to the correlation of the effects of unconjugated substituents on the gas-phase enthalpies of hydrogenation of mono- and *trans*-disubstituted ethylenes, and on the free energies of hydrogenation of carbonyl compounds, R_1R_2C O, in toluene solution.[18] Steric effects are consequently implied to be nearly constant in each of these three reaction series.

In the present paper the results of the application of the linear inductive energy relationship to *para*(and *meta*)-alkyl groups in the reactivities of benzene derivatives are presented and considered in detail. These results, which are a part of the general evaluation of the resonance effects of *para* substituents by the method of Taft and Lewis,* provide evidence of both C–H and C–C hyperconjugation effects, and an approximately quantitative additive relationship of each to structure. A basis is also provided for modification of the earlier correlations of hyperconjugation effects in the aliphatic series.

PROCEDURE

The procedure of Taft and Lewis[6] is based upon the demonstration by Hammett and others[9] that the reactivities of *meta*- and *para*-substituted derivatives of benzene as a class are characterized as rarely if ever involving variable steric effects at the reaction center. The model equation used is: log (k^p/k_0) = inductive effect plus resonance effect. The further assumptions made are that (1) for unchanged substituents the inductive effect for all practical purposes is equivalent in the *meta* and *para* positions†

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* Paper V, forthcoming *J. Amer. Chem. Soc.* This paper should be consulted for a discussion of the sense in in which the separation of log (k/k_0) values to *I* and *R* parameters is proposed. It is of particular importance to the present discussion to note that *R* values represent the total effect on reactivity other than that due to inductive delocalization of charge through the σ and π bonds (and space) between the alkyl group and the benzene ring (including any inductive effects arising as a consequence of the mesomeric inter-action). *R* values represent the total of the effects distinguished as resonance effect and resonance polar effect in ref. 4.

† For supporting evidence, cf. refs. 4 and 10 and J. D. Roberts, R. A. Clement and J. J. Drysdale, *J. Amer. Chem. Soc.* 73, 2182 (1951), and J. D. Roberts and W. T. Moreland, Jr., *Ibid.* 75, 2167 (1953).

while the resonance effect is reduced by a constant factor α in the *meta* compared to the *para* position. That is:

$$\log (k^p/k_0) = I + R$$

$$\log (k^m/k_0) = I + \alpha R,$$

where I is the inductive effect (called the I value) and R is the resonance effect (called the R value) from the *para* position.

Combining these equations to eliminate R:

$$I = \left[\frac{1}{1-\alpha}\right] [\log (k^m/k_0) - \alpha \log (k^p/k_0)]$$

Using for the resonance effect fall-off factor, α, a value of 1/3 for those substituents which from the *para* position are conjugated only with the benzene ring and a value of 1/10 for those *para* substituents which undergo a change in conjugation with the first atom of the side-chain reaction center during the reaction process, I values have been obtained which follow the linear inductive energy relationship, $I = \sigma_I \rho_I$, for a wide variety of reaction types (Fig. 4 is an example). Included are reactivities which demand for correlation by the Hammett equation all of the proposed multiplicities of sigma values[9, 10, 24, 25] (σ, σ^-, σ^+), as well as some reactivities which do not satisfactorily fall into any of these schemes.[6]

The method leads to two independent (but equivalent, according to the model) means by which the resonance effects may be evaluated. First:

$$R = \log (k^p/k_0) - \sigma_I \rho_I \tag{1}$$

and second:

$$R = \left(\frac{1}{1-\alpha}\right) \log (k^p/k^m) \tag{2}$$

To obtain the R value by equation (1) requires the knowledge of the rate or equilibrium constant for the *para* substituent relative to the unsubstituted derivative and the value[*] of the inductive reaction constant, ρ_I, based upon the inductive effects of substituents such as NO_2, CN, OCH_3, halogen, and others.[6] By equation (2), one must have the rate or equilibrium constant for the substituent in both the *meta* and *para* positions (the inductive effect is assumed to cancel in the ratio, k^p/k^m), and the appropriate value of the resonance fall-off factor, α (cf. footnotes *m*, *n* and *o* of Table 2).

RESULTS AND DISCUSSION

R values for alkyl groups are potentially quantitative measures of the total hyperconjugation effects on rates and equilibria. This assignment can be substantiated by the demonstration of appropriate qualitative and quantitative relationships of R values to alkyl structure. For example, we may anticipate that these values will be

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[*] For reactions which follow the Hammett equation, ρ_I values are the same as Hammett ρ values—cf. ref. 5.

[24] H. H. Jaffe, *Chem. Rev.* **53**, 253 (1953).

[25] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.* **79**, 1913 (1957); N. C. Deno and W. L. Evans *Ibid.* **79**, 5804 (1957).

positive for processes which are facilitated by electron release and negative for the contrary. Further, according to the classical Baker–Nathan effect,[26] we expect the magnitude of the *R* values to lie in the order Me > Et > Pr^i > Bu^t. Finally, according to the theoretically derived conclusions of Mulliken[61] and experimentally derived conclusions of Berliner,[27] the value for the Bu^t group should not be zero because of C–C hyperconjugation.

Of particular importance are quantitative relationships between *R* values and structure. Bartlett from a well-reasoned analysis (differing in rather minor detail from our method) of the effects of methyl and *tert.*-butyl groups on the free energy of ionization of *meta-* and *para-*substituted triphenylmethyl chlorides in liquid sulfur dioxide has obtained the estimate that the resonance effect of the *p*-methyl group is −1·18 kcal and the *tert.*-butyl group is −0·96 kcal.[28] Thus the C–H hyperconjugation effect exceeds that of C–C hyperconjugation by about 25 per cent. Bartlett concludes that, since the inductive effect of the *tert.*-butyl group is larger than that of the methyl group, the resultants of the three factors—the experimentally observed effects of the methyl and *tert.*-butyl groups on reactivity—are likely to appear confusing not only in this reaction, but generally.

More recently Brown *et al.*, by a method which also differs in minor detail from ours, have shown that the C–H and C–C hyperconjugation effects of *p*-methyl, *p*-ethyl, *p*-*iso*propyl and *p*-*tert.*-butyl groups in the rates of solvolysis of phenyldimethylcarbinyl chlorides in 90 per cent aqueous acetone, at 0–25°, are approximately additive.[29] Brown also finds for this reaction the same ratio of the C–H to C–C hyperconjugation effect as given above by Bartlett. That this figure should be the same for the two reactions under discussion is perhaps not surprising for both involve a similar change in inductive electron demand at the reaction center (ρ_I for both reactions is on the order of −4). We shall want to examine *R* values generally both with respect to the additive relationships and the dependence on reaction type (electron demand, solvent, etc.) of the ratio of the C–H to the C–C hyperconjugation effects.

Table 1 summarizes typical *R* values for a number of reaction series obtained by both equations (1) and (2). It is immediately apparent that each of the qualitative criteria of hyperconjugation effects mentioned above is satisfied by the *R* values. Attention may therefore be focused upon the quantitative aspects of the results. It may be seen from Tables 1 and 2 that equations (1) and (2), which according to our procedure should in principle give identical results, do not do so precisely. Generally, however, the agreement is considered quite satisfactory. The differences in several instances are probably due at least in part to ρ_I and to α values which have not been very precisely determined by the available data. In other instances the differences are probably quite real and this result will be discussed further.

The agreement between *R* values obtained by equations (1) and (2) for the reactions numbered 1, 2, 4, 7, 10 and 16 in Table 2 is probably representative of the order of precision that one can expect from the model equation and the method of quantitative separation of resonance and inductive effects. The average of the *R* values obtained

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[26] J. W. Baker and W. S. Nathan, *J. Chem. Soc.* 1844 (1935).

[27] E. Berliner and F. J. Bondhus, *J. Amer. Chem. Soc.* **70**, 854 (1948).

[28] P. D. Bartlett, *J. Chem. Educ.* **30**, 29 (1953); N. N. Lichtin and P. D. Bartlett, *J. Amer. Chem. Soc.* **73**, 5530 (1951).

[29] H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *J. Amer. Chem. Soc.* **79**, 1897 (1957).

from the two equations for these reactions is also listed in Table 1. Finally Table 1 illustrates the quantitative additive relationship:

$$R = n_H h_H + n_C h_C \tag{3}$$

where n_H is the number of α-C–H bonds, n_C is the number of α-C–C bonds of the alkyl group, and h_H and h_C are C–H and C–C hyperconjugation constants, respectively (in log units of rate or equilibrium).

TABLE 1. *R* VALUES. CORRELATION BY EQUATION (3)*

Solvolysis of benzyhydryl chlorides, $Ar(C_6H_5)CHCl$

	7. 90% Aq. EtOH, 0° ($\rho_I \simeq$ 4·0)				4. 80% Aq. acetone, 25° ($\rho_I \simeq$ 4·0)			
	R(eqn. 1)	*R*(eqn. 2)	*R*(aver.)	*R*(calcd.) eqn. 3	*R*(eqn. 1)	*R*(eqn. 2)	*R*(aver.)	*R*(calcd.) eqn. 3
Me	1·31	1·33	1·32	1·32	1·15	1·22	1·19	1·20
Et	1·22	—	1·22	1·22	1·03	1·19	1·11	1·10
Pr^i	1·12		1·12	1·12	0·89	1·11	1·00	1·00
Bu^t	1·00	1·04	1·02	1·02	0·75	0·96	0·86	0·90
	h_H 0·44; h_C 0·34; h_H/h_C 1·3				h_H 0·40; h_C 0·30; h_H/h_C 1·3			

Solvolysis of *tert.*-cumyl chlorides, $Ar(CH_3)_2CCl$

	1. 90% Aq. acetone, 0° ($\rho_I \simeq$ 4·2)				2. 90% Aq. acetone, 25° ($\rho_I \simeq$ 4·2)			
	R(eqn. 1)	*R*(eqn. 2)	*R*(aver.)	*R*(calcd.) eqn. 3	*R*(eqn. 1)	*R*(eqn. 2)	*R*(aver.)	*R*(calcd.) eqn. 3
Me	1·34	1·34	1·34	1·35	1·22	1·23	1·23	1·23
Et	1·22	1·30	1·26	1·25	1·11	1·15	1·13	1·13
Pr^i	1·09	1·24	1·17	1·15	1·00	1·07	1·04	1·03
Bu^t	0·95	1·11	1·03	1·05	0·86	0·99	0·93	0·93
	h_H 0·45; h_C 0·35; h_H/h_C 1·3				h_H 0·41; h_C 0·31; h_H/h_C 1·3			

16. Ionization of pyridinium ions, $XC_5H_4NH^+$, H_2O, 25° ($\rho_I \simeq +5·7$)

	R(eqn. 1)	*R*(eqn. 2)	*R*(aver.)	*R*(calcd.) eqn. 3
Me	0·59	0·51	0·55	0·54
Et	0·54	0·48	0·51	0·49
Pr^i	0·49	0·45	0·47	0·44
Bu^t	0·40	0·26	0·33	0·39
	h_H = 0·18; h_C = 0·13; h_H/h_C = 1·4			

* Numbers refer to the reaction series as listed in Table 2.

10. Bromination of benzene with HOBr, 50% Aq. dioxan, 25° ($\rho_I \cong -5{\cdot}8$)

	R(eqn. 1)	R(eqn. 2)	R(aver.)
Me	+1·50	+1·52	+1·51
Bu^t	+1·16	+1·31	+1·24

$h_H = +0{\cdot}50$; $h_C = +0{\cdot}41$; $h_H/h_C = 1{\cdot}2$

22. Methoxide-ion catalyzed methanolysis of *l*-menthyl benzoates, MeOH, 30°($\rho_I \cong +2{\cdot}6$)

	R(eqn. 1)	R(eqn. 2)	R(calcd.) eqn. 3
Me	−0·26	−0·37	−0·36
Et	−0·17	−0·32	−0·33
Pr^i	−0·12	−0·32	−0·30
Bu^t	−0·06	−0·26	−0·27

$h_H = -0{\cdot}12$; $h_C = -0{\cdot}09$; $h_H/h_C = 1{\cdot}3$

20. Decomposition of phenyldiazonium fluoroborates, ArN_2^+, H_2O, 47°($\rho_I \cong -3{\cdot}9$)

	R(eqn. 1)	R(eqn. 2)	R(calcd.) eqn. 3
Me	−1·15	−0·93	−1·17
Pr^i	−1·06	—	−1·05
Bu^s	−1·04	—	−1·05
Bu^t	−1·00	−1·08	−0·99

$h_H = -0{\cdot}39$; $h_C = -0{\cdot}33$; $h_H/h_C = 1{\cdot}2$

Table 2 summarizes the values of h_H, h_C and h_H/h_C obtained for all of the reactions for which the required data have come to our attention. The item of first importance in these results is the fact that $h_H/h_C = 1{\cdot}3 \pm 0{\cdot}1$, a figure which undoubtedly represents the relative conjugative capacities of C–H and C–C bonds in *para*-alkyl groups. This figure is quite independent of reaction type (it holds, for example, for equilibria between stable species as well as for reaction rates) and encompasses reactions with such variable changes in electron demand at the reaction center that ρ_I covers the enormous range from +6 to −12. Also without effect (within the indicated limits) on h_H/h_C are marked variations in solvent (from liquid C_6H_5COCl to aqueous H_2SO_4, for example) and temperature (0° to 51°). One must therefore look to considerable lengths if he is to avoid the conclusion that the *primary* effects of *para*-alkyl groups on these reactivities are caused by a change during the reaction process in the inductive and resonance potential energy interactions of the alkyl groups.

TABLE 2. SUMMARY OF $h_{\rm H}$ AND $h_{\rm C}$ VALUES

Reaction	Eqn. (1)				Eqn. (2)			Reference
	$h_{\rm H}$	$h_{\rm C}$	$h_{\rm H}/h_{\rm C}$	ρ_I	$h_{\rm H}$	$h_{\rm C}$	$h_{\rm H}/h_{\rm C}$	
1. Solvolysis of $Ar(CH_3)_2CCl$, 90% aq. acetone, 0°	0·44^{a}	0·33	1·3	−4·2^{c}	0·45$^{a, m}$	0·38	1·2	29
2. Solvolysis of $Ar(CH_3)_2CCl$, 90% aq. acetone, 25°	0·41^{a}	0·29	1·4	−4·2^{a}	0·41$^{a, m}$	0·33	1·2	29
3. Solvolysis of $Ar(C_6H_5)CHCl$, 80% aq. acetone, 0°	0·43^{a}	0·28	1·5	−4·0^{f}	0·47$^{a, m}$	0·37	1·3	30, 31
4. Solvolysis of $Ar(C_6H_5)CHCl$, 80% aq. acetone, 25°	0·38^{a}	0·26	1·5	−4·0^{f}	0·41$^{a, m}$	0·32	1·3	30, 31
5. Solvolysis of $Ar(C_6H_5)CHCl$, 70% aq. acetone, 0°	0·44^{a}	0·29	1·5	−4·0^{f}	0·47$^{a, m}$	0·37	1·3	32
6. Solvolysis of $Ar(C_6H_5)CHCl$, EtOH, 25°	0·40^{a}	0·33	1·2	−4·0^{f}	—	—	—	31
7. Solvolysis of $Ar(C_6H_5)CHCl$, 90% aq. EtOH, 0°	0·44^{a}	0·34	1·3	−4·0^{f}	0·45$^{a, m}$	0·36	1·3	32
8. Ionization $Ar(C_6H_5)CHOH$, aq. H_2SO_4, 25°	0·48^{a}	0·36	1·3	−5·6^{e}	—	—	—	33
9. Ionization $Ar(C_6H_5)_2CCl$, liq. SO_2, 0°	0·37^{d}	0·32	1·2	−3·7^{e}	0·33$^{d, m}$	0·25	1·3	34
10. Bromination of benzenes with HOBr, 50% dioxan, 25°	0·50^{d}	0·39	1·3	−5·8^{e}	0·51$^{d, m}$	0·44	1·2	35
11. Bromination of benzenes with Br_2 in HOAc, 25°	0·91^{d}	0·63	1·4	12·1^{e}	—	—		36
12. Benzoylation of benzenes in C_6H_5COCl, catalyzed by $AlCl_3$, 25°	0·78^{d}	0·64	1·2	−9·6^{e}	—	—	—	37
13. Benzoylation of benzenes in $C_6H_5NO_2$, with C_6H_5COCl, $AlCl_3$, 25°	0·82^{a}	0·69	1·2	−10^{e}	—	—	—	38
14. Brominolysis of $ArSi(CH_3)_3$, HOAc, 25°	0·48^{a}	0·35	1·4	−5·7^{a}	—	—	—	39
15. Protonolysis of $ArSi(CH_3)_3$, $HClO_4$ in 72% aq. MeOH, 51°	0·37^{a}	0·29	1·3	−4·3^{e}	—		—	40
16. Ionization of pyridinium ions, H_2O, 25°	−0·19^{a}	−0·15	1·3	+5·7^{a}	0·17$^{a, n}$	−0·12	1·4	41
17. Reaction of 2-nitrobromobenzenes with piperidine, 25°	−0·20^{d}	−0·14	1·4	+5·0^{h}	—	—	—	42

TABLE 2 *continued.*

Reaction	Eqn. (1)			Eqn. (2)				Reference
	h_H	h_C	h_H/h_C	ρ_I	h_H	h_C	h_H/h_C	
18. Reaction of 2-nitrobromobenzenes with piperdine, 35°	−0·20[d]	−0·13	1·5	+4·9[h]	—	—	—	42
19. Nitration of benzenes, Ac_2O, 45°	0·49[d]	0·46	1·1	6·7[k, f]	+0·50[d, m]	+0·47	1·1	43
20. Decomposition of diazonium fluoroborates, H_2O, 47°	−0·39[d]	0·33	1·2	+3·9[l, g]	0·31[d, o]	0·36	0·9	44
21. Ionization anilinium ions, H_2O, 25°	−0·12[a]	−0·07	1·7	+2·8[e]	0·18[d, n]	0·11	1·6	45
22. Methanolysis of *l*-$ArCO_2C_{10}H_{19}$, MeOH, 30°	−0·08[a]	−0·03	2·7	+2·6[e]	−0·12[a, i]	0·09	1·3	46
23. Methanolysis of *l*-$ArCO_2C_{10}H_{19}$, MeOH, 40°	0·06[a]	0·02	3·0	+2·6[f]	0·11[a, i]	−0·10	1·1	46
24. Saponification of $ArCO_2Et$, 85% aq. EtOH, 25°	0·08[a]	−0·03	2·7	+2·3[e]	—	—	—	47
25. Hydrolysis of $(ArCO)_2O$, 75% aq. dioxan, 50°	0·10[d]	0·06	1·7	+3·3[f]	—	—	—	48
26. Hydrolysis of $(ArCO)_2O$, 75% aq. dioxan, 80°	0·10[d]	0·07	1·4	+1·8[f]	—	—	—	48
27. Ionization ArCOOH, H_2O, 25°	−0·04[a]	0·04	1·0	+1·0[e]	0·05[c, i]	0·05	1·0	49
28. Alkaline hydrolysis Et_3SiOAr, 51% aq. EtOH, 25°	−0·05[d]	0·04	1·3	+1·7[e]	—	—	—	50
29. Reaction of ArCHO with HCN, H_2O, 25°	−0·09[a]	−0·05	1·8	+0·9[f]	—	—	—	51

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[a] Based on Me, Et, Pr^i, Bu^t.

[b] Based on Me, Pr^i, Bu^s, Bu^t.

[c] Based on Me, Et, Bu^t.

[d] Based on Me, Bu^t.

[e] ρ_I values given in ref. 5.

[f] ρ_I values determined from available data by method of ref. 5.

[g] Insufficient data available for determining ρ_I. Value given is ρ^+, obtained by the method of Brown and Okamoto, ref. 25 and unpublished results.

[h] Insufficient data available for determining ρ_I. Value given is ρ, H. H. Jaffe, *Chem. Rev.* **53**, 191 (1953). For a discussion of the validity of equating ρ and $\rho_I$values see ref. 5.

[i] ρ_I value for reaction 1 taken the same as for reaction 2.

[j] ρ_I value assumed to be approximately the same as for reaction 6.

[k] Value of ρ_I obtained from data at 25°.

[l] Based upon the ρ_I value for decomposition of diazonium chlorides, H_2O, 29°.

[m] Obtained by using $\alpha = 1·10$.

[n] Obtained by using $\alpha = 1·3$.

[o] Obtained by using $\alpha = -0·65$, based upon the decomposition of benzenediazonium chlorides—cf. ref. 5.

Apparent exceptions to the rule, $h_H/h_C = 1{\cdot}3 \pm 0{\cdot}1$, are to be found infrequently in Table 2 and where they do exist generally occur for reactions in which h_H is of smaller magnitude than $\pm 0{\cdot}10$. It is therefore probable that these apparent exceptions are not the result of any significant dependence of the hyperconjugation ratio, h_H/h_C, on reaction type, but rather result either from the lack of high precision of the method of separation of inductive and resonance effect, or the interference of small additional effects not considered in the model equation. In several reactions (notably reactions 20 and 22 of Tables 1 and 2, and reactions 5 and 23 of Table 2), equations (1) and (2) give sufficiently different R values to lead to discordant h_H/h_C ratios. With only a single notable exception (the R value for the CH_3 group in reaction 20), equation (2) in each instance gives results corresponding more closely to our general rule. It thus appears that log (k/k_0) values contain in these reactions an additional variable (or variables) other than inductive and hyperconjugative effects, whereas in values of $1/(1 - \alpha)$ [log (k^p/k^m)] these variables (as well as the inductive effect) have essentially cancelled. The additional variables are probably to be associated with small but measureable specific alkyl solvation effects[32] (or possibly some other non-polar effects). It is possible that studies based upon the deviations of the results of equations (1) and (2) may be used to obtain a characterization of these secondary solvation (or other) effects.

The rates of decomposition of phenyldiazonium fluoroborates[44] (reaction 20) provide the exception noted above. While no explanation can be offered for the apparent anomalous R value for the methyl group obtained for this reaction by equation (2), it is important to note that this reaction is unique in that its rate is markedly *increased* by inductive electron-release ($\rho_I = -4{\cdot}2$) yet $-R$ *para* substituents (alkyl groups as in Table 1, or other such as OCH_3, Cl, etc.[5]) *retard* the rate. A reasonable explanation has been advanced by Bunnett and Zahler[52] and by Lewis[44] which accounts for the fact that resonance interaction of substituents of the latter class stabilize the reactant more than the transition state. This reaction therefore uniquely gives h and ρ_I values of the same sign.

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Sigma values

Reaction series which closely follow the Hammett equation,[9] $\log (k/k_0) = \sigma\rho$, give satisfactory linear relationships in plots of h_H or h_C values vs. ρ_I values. From the slopes of these plots, and the relationship[10] $R/\rho_I \equiv \sigma_R \equiv n_H h_H/\rho_I + n_C h_C/\rho_I$, one obtains the values of σ_R listed in Table 3. Included also in Table 3 are the values of σ_I and the Hammett σ values for *meta-* and *para*-alkyl groups which are consistent with the present general results. (The only σ value obtained in this manner which differs significantly from that obtained from the ionization of benzoic acid is the *p*-Bu^t value, given as −0·20 by the latter method[49]). The lack of a distinct ordering of the σ values for the alkyl groups is noteworthy and is in the line with Bartlett's earlier conclusion that composites of three contributing effects are not likely to bear distinct relationships to structure.[28] The inductive and C–C hyperconjugation effects generally lead to the same ordering of alkyl groups, i.e., Me < Et < Pr^i < Bu^t (the diazonium decomposition mentioned above is an exception), while the C–H hyperconjugation effects lead to the ordering Me > Et > Pr^i > Bu^t. Only the separation of σ values to these three contributing effects makes apparent the approximate additive relationships exhibited by each of these contributors.

The convincing feature of our results is that $\log (k/k_0)$ values for reaction series which show a distinct Baker–Nathan order, essentially no order (constant values for all alkyl groups), or as distinct "inductive" order all give essentially a fixed quantitative order of R values (i.e., $R_{Me} : R_{Et} : R_{Pr^i} : R_{Bu^t} = 1{\cdot}3 : 1{\cdot}2 : 1{\cdot}1 : 1{\cdot}0$). The cancellation of the order among inductive and hyperconjugation effects to give $\log (k/k_0)$ values which show no distinct order is apparently a common and sometimes confusing characteristic of alkyl groups.* This is illustrated by the constancy of the σ values for *para*-alkyl groups (Table 3) and by some further examples of $\log (k^p/k_0)$ values listed in Table 4. In the latter table, $\log (K^p/K_0)$ values for the diarylcarbinal - carbonium ion equilibria and for the pyridinium ion ionization equilibria conform to this pattern. By contrast, the $\log (k^p/k_0)$ values given for the benzhydryl chloride solvolysis in Table 4 show a distinct Baker–Nathan order, a result which becomes apparent for reaction series which have relatively large negative values for the ratio h_H/ρ_I.

TABLE 3. σ VALUES FOR ALKYL GROUPS

	σ_I	σ_R	σ_p	σ_m
Me	0·046	−0·102	−0·15	−0·08
Et	−0·055	−0·094	−0·15	−0·09
Pr^i	−0·064	−0·086	0·15	−0·09
Bu^t	0·074	−0·078	0·15	0·10

The $\log (k^p/k_0)$ values for the decomposition rates of diazonium ions (also given in Table 4) provide a rare example in which the inductive and C–H hyperconjugation effects reinforce one another and are in opposition to the more minor C–C hyper-

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* Cf. earlier discussion of this point by J. W. Baker, *Hyperconjugation* Chap. I. Oxford University Press (1952).

conjugation effect (h_H/ρ_I is positive), so that a distinct ordering of log (k/k_0) values is apparent.*

TABLE 4. EXAMPLES ILLUSTRATING CANCELLATION OF INDUCTIVE AND HYPERCONJUGATION EFFECTS IN LOG (k^p/k_0) VALUES FOR ALKYL GROUPS

Ionization $Ar(C_6H_5)CHOH$, aq. H_2SO_4, 25° ($\rho_I \cong -5{\cdot}6$; $h_H = 0{\cdot}48$)		Ionization pyridinium ions H_2O, 25° ($\rho_I \cong +5{\cdot}7$; $h_H = -0{\cdot}18$)	
	$\log(K^p/K_0)$		$\log(K^p/K_0)$
Me	+1·7	Me	−0·85
Et	+1·7	Et	−0·85
Pr^i	+1·7	Pr^i	−0·85
Bu^t	+1·5	Bu^t	−0·82
Solvolysis of $Ar(C_6H_5)CHCl$ 90% EtOH, O_0 ($\rho_I \cong -4{\cdot}0$; $h_H = 0{\cdot}44$)		Decomposition of diazonium fluoroborates, H_2O, 47° ($\rho_I \cong -3{\cdot}9$, $h_H = -0{\cdot}39$)	
	$\log(k^p/k_0)$		$\log(k^p/k_0)$
Me	+1·34	Me	−0·97
Et	+1·27	Et	—
Pr^i	+1·17	Pr^i	−0·81
Bu^t	+1·05	Bu^t	−0·71

Similar plots of h_H and h_C values vs. ρ^+ values for the electrophilic reactions, for which H. C. Brown has proposed[25] the equation $\log(k/k_0) = \sigma^+\rho^+$, give less precise linear plots than those referred to above. While this result may be indicative of an inadequacy in Brown's relationship, it may equally well be due to uncertainties in available values of ρ^+ (these uncertainties fortunately do not produce very appreciable errors in obtaining R values for alkyl groups by equation (1)).

It is quite significant that the two equilibria of Table 4 conform to the $h_H/h_C = 1{\cdot}3$ rule (cf. Table 2) since the alkyl resonance is of the isovalent category in the aryl carbonium ions and of the sacrificial type in the pyridinium ion ionizations. Apparently then the relative hyperconjugation capacities of the C–H and C–C bonds are the same for Muller and Mulliken's two classifications of hyperconjugation.†

Finally it is important to note that the R values for reactions 16, 17, 18, 21 and 22 indicate that sacrificial hyperconjugation is not necessarily trivial in magnitude in ground states or transition states. This conclusion is strongly supported by shielding effects of *m*- and *p*-methyl substituents in the F^{19} fluorobenzene nuclear magnetic resonance spectra (cf. reference 10).

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* Professor S. Winstein (in discussion) has pointed out that precise conformity to equations (1) and (3) demands that $\log(k^p/k_0)$ values for the series Me, Et, Pr^i and Bu^t must lie in a regular order (either increasing, decreasing or one in which the ordering is so slight that $\log(k/k_0)$ are essentially constant). Thus any reaction series for which $\log(k/k_0)$ values show an *inversion* among this series of alkyl groups does not conform precisely to these equations. Actually, all the reactions listed in Table 2 show a regular order of $\log(k^p/k_0)$ values, with the sole exception of reaction 27, which shows a very slight inversion order.

† N. Muller and R.S. Mulliken, *J. Amer. Chem. Soc.* **80**, 3489 (1958) cf. also R. S. Mulliken. this volume, p. 253.

Ultraviolet spectra of alkylbenzenes

Matsen and coworkers[53, 54] have made a thorough study of the effect of alkyl- and chlorine-substituted alkyl groups on the ultraviolet absorption spectra of benzene in the vapor phase. These spectra were determined under conditions of high resolution and detailed band assignments were made. Of particular interest are the positions of the so called O–O bands. This band is due to the transition between the zero point vibrational levels of the ground state and the first excited state. The position of this band provides the closest direct experimental measure of the difference in the electronic energies of the excited and the ground state. The position of the O–O bands of the alkylbenzenes generally differs quite appreciably from the position of the integrated maximum of all of the peaks for the 2600 Å ultraviolet bands.

There is much spectroscopic evidence that the transition from the ground to the first excited state of benzene is accompanied by enhanced resonance interaction of the substituent in the excited state but there is no appreciable inductive effect on the transition energy.[53] [55] Matsen's data not only verify this conclusion qualitatively[53] but also quantitatively. The effects of open-chain alkyl substituents on the O–O-band transition energies follow equation (3) quite precisely, i.e., $\Delta\Delta\epsilon \quad n_{\mathrm{H}}h_{\mathrm{H}} + h_{\mathrm{C}}h_{\mathrm{C}}$ with $h_{\mathrm{H}} \quad -0{\cdot}025$ eV, $h_{\mathrm{C}} \quad 0{\cdot}018$ eV and $h_{\mathrm{H}}/h_{\mathrm{C}} \quad 1{\cdot}4$. The experimental values of $\Delta\Delta\epsilon$ and those correlated by this equation are listed in Table 5. This correlation of spectral data appears to afford strong confirmation of the conclusions concerning hyperconjugation reached from the analysis of reactivity effects.

The agreement between calculated and observed $\Delta\Delta\epsilon$ values (Table 5) for n-C_3H_7, $ClCH_2CH_2$ and $ClCH_2CH_2CH_2$ substituents shows that the values of h_{H} and h_{C} are not appreciably affected (although perhaps slightly[*]) by the inductive effect of replacing a β-CH_3 group by a β-CH_2Cl group or a β-Cl atom. The possible effect of mass of the substituent on the transition energies is also indicated as being of minor importance.[54]

Robertson *et al.*[56] also investigated the cyclic substituents: *cyclo*propyl, *cyclo*pentyl and *cyclo*hexyl. A very substantial red shift is observed for the O–O band for the *cyclo*propyl group ($\Delta\Delta\epsilon \quad 0{\cdot}152$ eV) in accord with much other evidence of the unsaturated nature of this group. The *cyclo*hexyl group gives the same transition energy as expected for a secondary open-chain alkyl group (cf. Table 5). The *cyclo*pentyl group, however, gives a red shift ($\Delta\Delta\epsilon \quad 0{\cdot}081$ eV) larger even than that for the methyl group. The authors assume that this results from a certain unsaturated character in the *cyclo*pentyl ring. The lack of general evidence of such unsaturated character, however, suggests the alternate possibility that the α-hydrogen atoms in the *cyclo*pentyl ring are held in a position especially favorable to hyperconjugative interaction.[†]

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[*] For possible evidence of inductive effects on hyperconjugation which are in opposite direction to the slight apparent trend shown in Table 5. Cf. J. W. Baker, J. A. L. Brieux and D. G. Saunders, *J. Chem. Soc.* 404 (1956).

[†] Cf. in this connection the paper by W. R. Moore, Erich Marcus, S. E. Fenton and R. T. Arnold, p. 179 of this volume.

[53] F. A. Matsen, W. W. Robertson and R. L. Chuoke, *Chem. Rev.* **41**, 273 (1947).

[54] W. F. Hamner and F. A. Matsen, *J. Amer. Chem. Soc.* **70**, 2482 (1948).

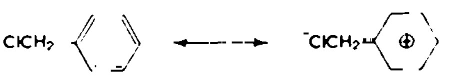
[55] L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.* **69**, 2714 (1947); J. R. Platt, *J. Chem. Phys.* **19**, 101 (1951); H. Sponer, *Ibid.* **22**, 234 (1954); L. Goodman and H. Shull, *Ibid.* **27**, 1388 (1957).

[56] W. W. Robertson, J. F. Music and F. A. Matsen, *J. Amer. Chem. Soc.* **72**, 5260 (1950).

TABLE 5. CORRELATION BY EQUATION (3) OF THE TRANSITION ENERGIES FOR THE 0–0 BANDS OF THE GAS-PHASE ULTRAVIOLET ABSORPTION SPECTRA OF ALKYL BENZENES

Substituent	$\Delta\Delta\epsilon$ exptl. (eV)	$\Delta\Delta\epsilon$ calcd. eqn. (3) (eV)
*cyclo*Pentyl	0·081	0·061
CH_3	0·076	0·075
C_2H_5	0·070	0·068
$ClCH_2CH_2CH_2$	0·069	0·068
$ClCH_2CH_2$	0·066	0·068
Pr^i	0·060	0·061
Bu^s	0·062	0·061
*cyclo*Hexyl	0·062	0·061
Bu^t	0·054	0·054

In a further study Hamner and Matsen have determined the effects of CH_2Cl, $CHCl_2$ and CCl_3 groups on the O–O band transition energies.[64] Substantial red shifts are observed and these are attributed to hyperconjugation of the type:



We note that the observed transition energies follow approximately the equation: $\Delta\Delta\epsilon = n_H h_H + n_{Cl} h_{Cl}$, wherein the h_H value is that obtained above and the h_{Cl} hyperconjugation parameter (0·056) is that obtained from the observed value of $\Delta\Delta\epsilon$ for the CCl_3 group. This correlation is summarized in Table 6.

TABLE 6. CORRELATION OF THE TRANSITION ENERGIES FOR THE 0–0 BANDS OF THE GAS-PHASE ULTRAVIOLET ABSORPTION SPECTRA OF CHLOROMETHYL-SUBSTITUTED BENZENES BY THE EQUATION: $\Delta\Delta\epsilon = n_H h_H + n_{Cl} h_{Cl}$

Substituent	$\Delta\Delta\epsilon$ exptl. (eV)	$\Delta\Delta\epsilon$ calcd. eqn. (4) (eV)
CH_3	0·076	0·075
$ClCH_2$	0·121	0·106
Cl_2CH	0·133	0·137
Cl_3C	0·167	0·168

The results of Brown[57] and of Schubert *et al.*[58] on the effects of *para*-alkyl groups on the ultraviolet absorption spectra of nitrobenzene differ appreciably from Matsen's results with benzene. A possible explanation may lie with the fact that the former spectra were not resolved to give the precise position of the O–O bands. Further, since the exact nature of the electronic transition is in question, the possibility exists that

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[57] W. G. Brown and H. Reagan, *J. Amer. Chem. Soc.* **69**, 1032 (1947).

[58] W. M. Schubert, J. Robins and J. L. Haun, *J. Amer. Chem. Soc.* **79**, 930 (1957); W. M. Schubert and J. Robins, *Ibid.* **80**, 559 (1958).

inductive effects make important contributions to the observed spectral shifts. As noted in the reactivity section of this paper, an experimentally observed quantity which is the appropriate composite of inductive, C–H and C–C hyperconjugation effects will show little distinct order among alkyl groups. This is the observed result for the *p*-alkyl nitrobenzene spectra.

Hyperconjugation effects in the aliphatic series

The unequivocal quantitative evidence for C–C hyperconjugation effects in the reactivities of *para*-substituted derivatives of benzene prompts a re-examination of the aliphatic series reactivities which Kreevoy and Taft[15, 16] have previously considered to be satisfactorily correlated by inductive and C–H hyperconjugation effects.

The inductive effects in the acid-catalyzed rates of hydrolysis of acetals and ketals, $R_1R_2C(OC_2H_5)_2$, have been well demonstrated (cf. Fig. 5 and earlier discussion) to follow the linear inductive energy relationship: inductive effect $= (\Sigma\sigma^*)(-3{\cdot}60)$, and, with the probable exception of methyl *neo*pentyl and *tert.*-butyl ketals, steric effects have been shown to be nearly constant. Consequently, resonance effects (R values) may be obtained for this reaction by the relationship:

$$\log(k/k_0) - (\Sigma\sigma_H^*)(-3{\cdot}60) = R \tag{5}$$

Column 2 of Table 7 lists R values so obtained from the $\log(k/k_0)$ values given in column 1.† The values listed are relative to the hydrogen atom as the standard of comparison, that is with k_0 corresponding to the rate constant for formal ($R_1 = R_2 =$ H) and σ^* values adjusted to H (instead of the methyl group) as the standard of comparison (designated accordingly as $\sigma_H)^*$.

With the exception of methyl *neo*pentyl and *tert.*-butyl ketals, R values for a variety of alkyl substituents follow quite precisely the relationship: $R = n_Hh_H + n_Ch_C$, with $h_H = 0{\cdot}62$ (log units), $h_C = 0{\cdot}24$ (log units) and $h_H/h_C = 2{\cdot}6$. This is demonstrated by the agreement between the values in columns 2 and 3 of Table 7. The latter column gives the R values calculated by this correlation. For comparison, values of R calculated by the earlier correlation, $R = (0{\cdot}54)n_H$, are shown in column 4. Both the evidence from the aromatic series reactivities and the improved precision of correlation of these R values appear to justify the C–C hyperconjugation terms for the acetal and ketal hydrolysis rates. The details of this modification in the interpretation of these reactivities are, however, in accord with the conclusion of Kreevoy and Taft that the principle conjugative effect for alkyl groups is a C–H hyperconjugation effect and the C–C hyperconjugation effect is by comparison sufficiently smaller to be approaching the limits of reliability of the method. Also unaffected is the earlier demonstration[12] that the acetal transition state is stabilized by conjugation with $\alpha\beta$-unsaturated substituents to an extent about one power of ten greater than that by hyperconjugation by an α-C–H bond (note that R values for the $\alpha\beta$-unsaturated groups listed at the bottom of Table 7 are on the order of $10\,h_H \cong 6$).

In one attributes the quantity, $\log(k/k_0) - (\Sigma\sigma_H^*)(-3{\cdot}60) - n_Hh_H - n_Ch_C$, to steric assistance to the hydrolysis rates for methyl *neo*pentyl and *tert.*-butyl ketals, driving forces amounting to $+1{\cdot}0$ and $+2{\cdot}0$ log units, respectively, are obtained.

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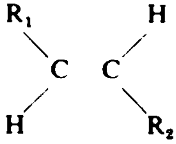
† Since the value of ρ^* is for all practical purposes determined by the substituents, R = $ClCH_2$, B_1CH_2, $ROCH_2$ and $C_6H_5CH_2$, the R values of Table 7 may be regarded as based upon independently determined inductive effects.

TABLE 7. *R* VALUES FOR THE RATES OF HYDROLYSIS OF ACETAL AND KETALS $R_1R_2C(OEt)_2$, 50% DIOXON-WATER, 25°

Substituents				Column 1	Column 2	Column 3	Column 4
R_1	R_2	n_H	n_C	$\log(k/k_0)$	R eqn. (5) (log units)	R calcd. eqn. (3)	$n_H(0{\cdot}54)$
H	H	0	0	0·0	0·0	0·0	0·0
H	Bu^t	0	3	+3·7	+0·7	+0·7	0·0
H	Pr^i	1	2	+3·6	+1·1	+1·1	+0·5
H	$(C_2H_5)_2CH$	1	2	+3·9	+1·3	+1·1	+0·5
H	C_2H_5	2	1	+3·8	+1·6	+1·4	+1·1
H	Bu^i	2	1	+3·6	+1·4	+1·4	+1·1
H	$CH_2CH_2C_6H_5$	2	1	+2·8	+1·4	+1·4	+1·1
H	CH_3	3	0	+3·8	+2·0	+1·9	+1·6
CH_3	C_2H_5	5	1	+7·2	+3·4	+3·3	+2·7
CH_3	CH_3	6	0	+7·3	+3·7	+3·7	+3·2
H	CH_3CH CH		—	+6·9	+5·2	—	—
H	C_6H_5CH CH	—	—	+6·6	+5·1	—	—
H	C_6H_5	—		+5·2	+5·0	—	
H	p-$NO_2C_6H_4$	—	—	+2·6	+5·0		

These figures are in reasonable accord with estimates by Streitwieser[17] for steric assistance driving forces in the solvolysis rates for similarly crowded tertiary carbinyl halides.

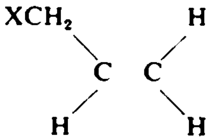
Table 8 gives the results of a similar re-examination of the effects of substituents on the enthalpies of hydrogenation of *trans*-disubstituted ethylenes



in the vapor phase at 355°K. *R* values are obtained from the relationship:

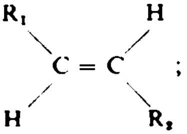
$$R = \Delta H_0 - \Delta H_0^\circ = (-2{\cdot}2)(\Sigma\sigma_H^*) \qquad (6)$$

The value of $\rho^* = -2{\cdot}2 \pm 0{\cdot}2$ is based upon the linear inductive energy relationship obtained with olefins of the general formula



which is illustrated in Table 9. Because of the much more limited range of polarities covered by the available data, this ρ^* value cannot be as confidently accepted as that for the acetal and ketal hydrolysis. Taft and Kreevoy[18] maintain that a decrease in enthalpy of hydrogenation with an increase in electron-withdrawing power of the substituent is expected because of the greater electronegativity of the unsaturated (sp^2) than the saturated (sp^3) central carbon atoms.

TABLE 8. *R* VALUES FOR THE ENTHALPIES OF HYDROGENATION OF TRANS-DISUBSTITUTED ETHYLENES, ; GAS PHASE, 355°K



Substituents				Column 1	Column 2	Column 3	Column 4
R_1	R_2	n_H	n_C	$\Delta\Delta H^\circ$ (kcal)	*R* eqn. (6) (kcal)	*R* calcd. eqn. (3)	$n_H(0{\cdot}44)$
H	H	0	0	0·0	0·0	0·0	0·0
H	Bu^t	0	3	+2·5	+0·7	+0·6	0·0
H	Bu^s	1	2	+2·4	+0·8	+0·9	+0·4
H	Pr^i	1	2	+2·5	+0·9	+0·9	+0·4
H	Et	2	1	+2·5	+1·2	+1·2	+0·9
H	Pr^n	2	1	+2·6	+1·2	+1·2	+0·9
H	Bu^i	2	1	+2·7	+1·3	+1·2	+0·9
H	Pe^{neo}	2	1	+3·3	+1·8	+1·2	+0·9
H	$CH_2CH_2CO_2R$	2	1	+1·7	+1·1	+1·2	+0·9
H	$CH_2CH{=}CH_2$	2	1	+2·2	+1·4	+1·2	+0·9
H	Me	3	0	+2·7	+1·6	+1·5	+1·3
Bu^t	Bu^t	0	6	+4·9[*]	+1·0	+1·2	0·0
Me	Bu^t	3	3	+4·5[*]	+2·0	+2·1	+1·3
Me	Pr^i	4	2	+5·0	+2·3	+2·4	+1·8
Et	Et	4	2	+5·2	+2·5	+2·4	+1·8
Me	Et	5	1	+5·2	+2·8	+2·7	+2·2
Me	Pr^n	5	1	+5·2	+2·8	+2·7	+2·2
Me	CH_2CO_2R	5	1	+3·2	+2·5	+2·7	+2·2
Me	Me	6	0	+5·2	+3·0	+3·0	+2·6
H	C_6H_5	—		+4·2	+4·4	—	
H	$CH{=}CH_2$	—		+6·0	+5·7	—	

Column 2 of Table 8 lists *R* values for the olefin hydrogenation obtained as indicated above (equation (6)). Column 1 gives the experimental values of the enthalpies of hydrogenation relative to ethylene. Column 3 of this Table lists values of *R* as correlated by the equation:

$$R = n_H h_H + n_C h_C \tag{3}$$

with $h_H = +0{\cdot}50$ kcal, $h_C = +0{\cdot}20$ kcal and $h_H/h_C = 2{\cdot}5$. Column 4 lists *R* values as calculated by the earlier correlation equation: $R = (0{\cdot}44)n_H$. Again the improved precision of the correlation equation which includes the C–C hyperconjugation term is distinctly noticeable. The mean deviation from equation (3) is of the order of experimental uncertainty (the deviation for the *neo*pentyl group suggests a steric effect).

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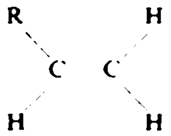
[*] Obtained from the data of R. B. Turner, D. E. Nettleton, Jr. and M. Perelman, *J. Amer. Chem. Soc.* **80**, 1430 (1958), assuming the same value of $\Delta\Delta H$ for acetic acid solution and the vapor phase.

TABLE 9. DETERMINATION OF ρ^* FOR THE HYDROGENATION OF SUBSTITUTED ETHYLENES, GAS PHASE, 355°K

Based upon $\Delta\Delta H^\circ = 2.2(\Delta\sigma^*)$ for



$RHC{=}CH_2$ with R = CH_2X

X	$\Delta\Delta H^\circ$ obs. (kcal)	$\Delta\Delta H^\circ$ calcd. (kcal)
OH	1·2	1·4
CH_2CO_2R	0·8	0·8
$CH=CH_2$	0·3	0·5
$CH_2CH=CH_2$	0·0	0·3
Me	(0·0)	(0·0)
Et	+0·1	+0·1
Pr^i	+0·2	+0·1
		aver. dev. = ±0·1

The fact that equation (3) is precisely followed for R groups of widely varying steric requirements (for example, $R_1 = R_2 = H$ to $R_1 = R_2 = Bu^t$) provides evidence of a constancy of steric effects, implying that the effect of σ bond expansion on the change between the sp^2 and sp^3 valence states[59] produces a contribution to the enthalpy of hydrogenation which is constant (with the possible exception of the *neo*pentyl group) for the compounds of Table 8. Deviations of *cis* and vicinally substituted ethylenes from equation (3), which may reasonably be associated with steric effects,[16] follow closely the empirical rules of Dewar and Pettit[60] dealing with the effects of such substitution on the enthalpies of hydrogenation.

Both Tables 7 and 8 provide examples which indicate that h_H and h_C are not appreciably affected by the inductive effects of polar substituents within the alkyl group. The approximate "10 to 1" rule of Kreevoy and Taft[12] for conjugative stabilization relative to C–H hyperconjugative stabilization of the olefin is illustrated by *R* values for two typical $\alpha\beta$-unsaturated substituents listed at the bottom of Table 8.

The free energies of hydrogenation of unconjugated carbonyl compounds, $R_1R_2C{=}O$, in dilute toluene solutions at 333°K are also correlated with slightly improved precision by the equation, $\Delta F^\circ - \Delta F_0^\circ = (-6{\cdot}0 \pm 0{\cdot}5)(\Sigma\sigma_H^*) - n_H h_H + n_H h_C$ (the standard of comparison is $R_1 = R_2 = H$, for which ΔF_0^0 is taken as 4·4 kcal more negative than that for acetaldehyde—the same as the difference between acetaldehyde and acetone). However, the data for this reaction are less accurate than the former two, and the ρ^* value has a substantial uncertainty. Consequently, a precise h_H/h_C value for this reaction is in question, but is probably also on the order of 2($h_H \cong 0{\cdot}5 \pm 0{\cdot}1$ kcal and $h_C \cong 0{\cdot}25 \pm 0{\cdot}1$ kcal). The uniquely systematic relationship of the extra resonance energies of conjugation and of hyperconjugation in carbonyl compounds and olefins found and discussed by Kreevoy and Taft[12] is

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[59] M. J. S. Dewar and H. N. Schmeising, This volume, p. 166.

[60] M. J. S. Dewar and R. Pettit, *J. Chem. Soc.* 1625 (1954).

essentially unaffected by this modification of including small C-C hyperconjugation effects.

Our interpretation of the enthalpies of hydrogenation of olefins and carbonyl compounds does not support the conclusion of Dewar and Schmeising[59] that resonance stabilization is of no importance in molecules such as butadiene or propene. Instead the relationships of R values to structure are those expected by resonance theory.[12] On the other hand, the possibility that effects associated with σ bond expansion make measureable contributions to these R values cannot be excluded.

The re-examination of these aliphatic series reactivities leads us to conclude that h_H/h_C is on the order of 2 to 3. The dependence of this value on electron demand is less certain than the demonstration of a constant h_H/h_C ratio for the aromatic series reactivities. However, ρ^* values (in log units) vary from -4 to $+4$ for the three reaction series with no indication of a pronounced change in h_H/h_C. The question of why h_H/h_C is materially larger for the aliphatic than the aromatic reactivities is one of interest and importance, but one for which we can give no satisfactory answer at present.

The Kreevoy and Eyring model[13], [61] for hyperconjugation (called α-hydrogen bonding by these authors) is attractive in accounting for the additive relationship (3). According to the naive model, Kreevoy and Eyring concluded that h_H/h_C should be of the order of 2 to 3. However, it is quite conceivable that h_H/h_C depends upon the unsaturated system to which the alkyl group is bonded. Thus the h_H/h_C ratio of 1·3 which holds so generally for the aromatic series reactivities may be associated with the common unsaturated system (phenyl) to which these alkyl groups are bonded. So few examples are available that it is by no means certain that h_H/h_C is a constant for aliphatic series reactivities. Definite answers to these questions awaits further experimental and theoretical investigations.

Acknowledgements—It is a pleasure to acknowledge correspondence with Dr. J. W. Baker concerning the subject of this paper. Helpful discussions with Professor R. S. Mulliken and Professor Lionel Goodman are also gratefully acknowledged.

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[61] Compare with the classical model: R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* 63, 41 (1941).