before.[4] Detailed structural configurations of the activated states responsible for the rates and the orientational effects in the two groups of reactions are still highly uncertain and no attempt will be made to discuss them here.

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[A CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Electronic Properties of Alkyl Groups. I. Dispersion and Induction Forces

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Electronic effects arising from the large variations in the polarizabilities of alkyl groups are considered. The magnitude of the dispersion energy existing between the alkyl group and the ring in alkyl benzenes is estimated, and it is concluded that this quantity in the series of alkyl groups, methyl, ethyl, isopropyl and *t*-butyl, varies over a range of about 4.5 kcal./mole. Polarizabilities play an important part in connection with the inductive effect ascribed to an alkyl group. The polar substituent constants, σ^*, for alkyl groups are evaluated in a system in which the purely inductive and polarizability effects are opposed. It is argued that these constants may not be generally applicable as measures of the electronic properties of alkyl groups in systems where, for example, the inductive and polarizability effects operate in the same direction. The behavior of the neo-pentyl group is explainable on the basis of its polarizability. It can be concluded that the dispersion and induction forces due to alkyl groups in molecules are at least in part responsible for variations in the apparent order of electron release by the alkyl groups.

It was observed by Baker and Nathan in 1935 that the inductive order of electron release (methyl < ethyl < isopropyl < *t*-butyl) of alkyl groups is apparently not followed in the kinetics of the reaction of *para*-substituted benzyl bromides with pyridine.[1] The inversion of the inductive order of electron release by alkyl groups has subsequently been observed in many other contexts and is termed the Baker–Nathan effect. The most popular explanation of the effect has for many years involved the concept of hyperconjugation.[2,3] Recently it has been pointed out that other factors may be of overriding importance, and various experimental evidence has been offered to show the importance of these other effects.[4–6] As evidence accumulates, however, particularly on the physical properties of alkyl-containing compounds, it appears that there is as yet no completely satisfactory picture of the properties of alkyl groups. In this series of papers some experimental results will be presented regarding the physical properties of alkyl-containing compounds which will, it is hoped, help to clear up certain questions which remain open at present. The purpose of the present paper is to point out that the dispersion force interactions and other effects arising from the polarizabilities of alkyl groups, factors which have been largely neglected, many be of considerable importance in determining their behavior as parts of larger molecules.

In considering the electronic energy of molecules, it is generally necessary to ignore the dispersion forces which operate between atoms in the same molecule, because the treatment of such forces would be too difficult. They are apparent, however, in determining the properties of the rare gases and of non-polar molecules.[7–9] Pitzer has applied the concept of dispersion forces to show that they may be of considerable importance when operating between atoms in the same molecule.[10,11] Schubert and Robins have considered polarizabilities in a qualitative sense in discussing the effect of the neo-pentyl group on spectral transition energies.[12]

The simple equation derived by London[7] to express the dispersion energy between two unlike atoms is

$$E = -\frac{3\alpha_1\alpha_2}{2r^6}\frac{I_1 I_2}{I_1 + I_2} \qquad (1)$$

where α_1 and α_2 are the polarizabilities in cm.^{3}, I_1 and I_2 are the ionization energies and r is the internuclear distance in cm. In applying this expression to polyatomic systems as we do below it is necessary to make some rather gross approximations. Nevertheless when it is applied to molecules containing alkyl groups it is possible to gain some insight into an important effect in determining their behavior.

The systems to be considered first are the alkylbenzenes; the molecules are assumed to be in the vapor state. The alkyl group and the ring are considered as two "pseudo-atoms," and we evaluate the dispersion energy between these two. The polarizabilities of the alkyl groups are estimated by summing the bond polarizabilities,[13] taking only the components which lie in the plane of the ring. One-half of the polarizability of the C–C bond joining the alkyl group to the ring is taken as belonging to the alkyl group. Since the polarizability of the C–H bond is not far from isotropic, this procedure is quite satisfactory; the values so

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

[2] R. S. Mulliken, C. A. Riecke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).

[3] J. W. Baker, "Hyperconjugation," Oxford Univ. Press, London, 1952.

[4] (a) A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954); (b) 2085 (1955); (c) 2557 (1955).

[5] (a) W. M. Schubert and W. A. Sweeney, THIS JOURNAL, **76**, 4625 (1954); (b) *J. Org. Chem.*, **21**, 119 (1956).

[6] W. M. Schubert, J. Robins and J. L. Haun, THIS JOURNAL, **79**, 910 (1957).

[7] F. London, *Trans. Faraday Soc.*, **33**, 8 (1937).

[8] H. Margenau, *Rev. Mod. Phys.*, **11**, 1 (1939).

[9] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Liquids and Gases," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 955.

[10] K. S. Pitzer, *J. Chem. Phys.*, **23**, 1735 (1955).

[11] K. S. Pitzer and E. Catalano, THIS JOURNAL, **78**, 4844 (1956).

[12] W. M. Schubert and J. Robins, *ibid.*, **80**, 559 (1958).

[13] K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

obtained are shown in the second row of Table I.[14] The polarizability of the ring is taken as 123 × 10^{-25}, the value given for the component normal to the sixfold axis in benzene.[16] The value to be used for *r* is critical, since it appears as the inverse sixth power. As a conservative figure 3.70 Å. has been chosen, 0.7 Å. greater than the distance from the center of the ring to the central carbon atom of the alkyl group. The terms which would correspond to the ionization energies of the two atoms are not easy to evaluate, but it seems reasonable to set both I_1 and I_2 equal to 225 kcal./mole, so that the term in parentheses in equation 1 has the value 112 kcal./mole. Using these figures the values of dispersion energy listed in the bottom row of Table I are obtained.

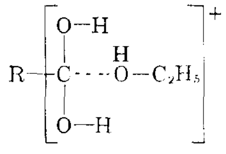
TABLE I

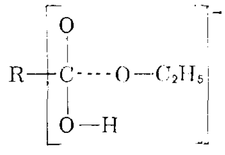
POLARIZABILITIES OF ALKYL GROUPS AND THEIR DISPERSION ENERGY WITH THE PHENYL RING IN ALKYL BENZENES

Group	Methyl	Ethyl	Isopropyl	*t*-Butyl
Polarizability (× 10^{-25}, cm.^{3})	27	46	65	84
Dispersion energy with phenyl ring (kcal./mole)	2.2	3.7	5.2	6.8

These values are a crude approximation to but a single part of the total dispersion energy of the molecules under consideration. At the same time, in view of the conservative estimates of the parameters, it is felt that the variation in the dispersion energies among the alkyl groups is at least as large as that calculated. The above considerations can be applied to explain the variation in the heat of hydrogenation of benzene, toluene and ethylbenzene to the respective cyclohexanes (the values at 25° are −49.25, −48.94, and −48.17 kcal./mole, respectively).[17] Cyclohexane is less polarizable than benzene,[16] so there is a loss of dispersion energy on hydrogenation which is greatest for the most polarizable group.

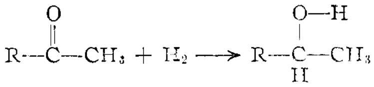
Polarizabilities play an important part in connection with the inductive effect of alkyl groups. In any experimental measure of "inductive effect" there may be a considerable contribution from polarizability effects. The inductive effect is distinguished by Ingold[18] from the so-called direct effects which include polarizability interactions but an experimental distinction is difficult to achieve. The variations in inductive effect among most groups are generally sufficiently large so that direct effects are unimportant, or at any rate do not cause confusion. Among alkyl groups, on the other hand, inductive effects vary only slightly, whereas polarizabilities are widely different. Therefore, the relative importance of inductive and direct effects may vary considerably from one situation to another. An example of this is to be found in connection with the polar substituent constants, σ^*, for alkyl groups.[19] These constants are determined from the relative rates of acid- and base-catalyzed hydrolysis of ethyl esters, for which the two transition states are


Acid


Base

In this case inductive electron release by the group R clearly stabilizes the acid-catalyzed transition state; dispersion force interaction between R and the remainder of the system will be greater, however, in the base-catalyzed system because of the greater polarizability of the negatively charged group. This is an instance, then, in which inductive electron release and the direct (polarizability) effect operate in opposite senses, and the importance of the direct effect (dispersion energy) is determined by the difference in polarizabilities of the two bracketed groups.

It has been pointed out a number of times[5,6,20] that the solvent may play an important role in determining the apparent relative electron-releasing abilities of alkyl groups. There is also much to indicate, however, that solvent effects cannot account for all of the cases in which the Baker–Nathan effect is operative. Taft and Kreevoy[21] have utilized the σ^*-values for alkyl groups to correlate the relative enthalpies of hydrogenation of gaseous olefins and the relative free energies of hydrogenation of aldehydes and ketones in toluene. These authors claim that hyperconjugation energies appear as a contribution to the thermodynamic quantities after the inductive effect, presumably measured by σ^*, has been accounted for. However, if the nature of the reactants and products in these systems is considered, it can be seen that the σ^*-values may not be correct measures of the electronic properties of the attached alkyl groups. For example, consider the hydrogenation of alkyl methyl ketones to the corresponding carbinols



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3} + \mathrm{H_2} \longrightarrow \mathrm{R{-}\overset{\overset{\displaystyle O{-}H}{|}}{\underset{\displaystyle H}{C}}{-}CH_3} \qquad (2)$$

Inductive electron release stabilizes the carbonyl compound relative to the carbinol.[21] Further, since the carbonyl group is more polarizable than the carbinol, the dispersion energy between the group R and carbonyl is greater than that between R and the carbinol. In this example the inductive electron release and polarizability effects operate in

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(14) Values of the polarizabilities of the methyl and *t*-butyl groups can be estimated from some observed polarizabilities. If the polarizability of the C–X bond is subtracted from the appropriate component of polarizability of the methyl and *t*-butyl halides,[15] and half the value of the C–C bond polarizability added to the remainder, average values of group polarizability of 25 and 86 cm.^{3} are obtained for the methyl and *t*-butyl groups, respectively.

(15) C. C. LeFevre and R. J. W. LeFevre, *Rev. Pure Appl. Chem.*, **5**, 261 (1955).

(16) Landolt–Börnstein, "Zahlenwerte und Functionen," Vol. 1, Pt. 3, J. Springer, Berlin, 1951, p. 510.

(17) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, 1953, pp. 473 and 482.

(18) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 60.

(19) R. J. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(20) V. J. Shiner, THIS JOURNAL, **76**, 1603 (1954).

(21) R. W. Taft, Jr., and M. M. Kreevoy, *ibid.*, **79**, 4011 (1957).

the same direction, whereas in the systems employed for determination of σ^*, they operate in opposite senses, as pointed out above.

A rough measure of the difference in dispersion energies of reactant and product molecules in equation 2 brought about by the presence of the group R can be obtained by application of equation 1. Taking the difference in polarizabilities of carbonyl and carbinol as 5×10^{-25} cm.[3] (carbonyl is the more polarizable), setting the term in parentheses in equation 1 equal to 100 kcal./mole, and choosing 2.5 Å. as the distance from the alkyl group to the other polarizable center, one obtains equation 3, which represents the loss in dispersion energy in going from the carbonyl to the carbinol which is due to the group R. Using the values of polarizability for the alkyl groups given in Table I, the values of ΔE for each group are, in kcal./mole

$$\Delta E = \frac{3 \times 5 \times 10^{-25}\alpha_R(100)}{2(2.5 \times 10^{-8})^6}$$

Methyl	Ethyl	Isopropyl	*t*-Butyl
0.8	1.4	2.0	2.6

The variation in these values among the alkyl groups is greater than the variations observed in the relative free energies of hydrogenation of the methyl ketones.[21] Arguments analogous to those applied to ketones also can be applied to alkyl substituted ethylenes and acetylenes. The values given above are of course not quantitatively very reliable, but they serve to show that dispersion energy differences among the alkyl groups are of a magnitude which requires their consideration.[22]

In a recent paper by Muller and Mulliken[25] the stabilization energies of alkyl radicals and ions are discussed and interpreted in terms of "isovalent hyperconjugation." It is also possible to understand these stabilization energies, at least in part, in terms of the electrostatic forces which must operate in such systems. In an alkyl ion such as $(CH_3)_3C^+$ there should be a charge-induced dipole energy term of considerably larger magnitude than in H_3C^+, in view of the greater polarizability of the three methyl groups as compared with three hydrogens. When a radical is formed by abstraction of hydrogen from a hydrocarbon, there is formed a substantial dipole consisting of the single electron occupying a hybrid orbital and the central carbon nucleus. This dipole can, in a simple view, be thought of as interacting with the polarizable groups attached to the central carbon. The potential energy of this dipole-induced dipole interaction is much smaller than the charge-induced dipole interaction present in the alkyl ions. The stabilization energies of the alkyl radicals are considerably smaller than those of the alkyl ions,[26] in agreement with this conclusion.

In systems in which the Baker–Nathan effect is apparent the behavior of the neopentyl group has always been considered more or less anomalous. The various explanations for the behavior of this group have been reviewed by Schubert and Robins,[12] who conclude that the polarizability of the group is probably of principal importance. It is rather difficult to make a calculation of the dispersion energy between the neopentyl group and phenyl as was done for the other alkyl groups, but a crude estimate can be had by considering the $-CH_2-$ and $-C(CH_3)_3$ parts of the group separately and summing the dispersion energies of each with the ring. The sum of these dispersion energies falls between isopropyl and *t*-butyl. Insofar as such a crude estimate can be trusted, the essential correctness of Schubert and Robin's proposal is indicated.

In conclusion a word on the role of the dispersion energies in solvent media is necessary. When a molecule such as an alkyl benzene is immersed in a solvent medium, it interacts quite strongly with the closely packed solvent molecules; the interactions are largely electrostatic in nature, of the dipole-induced dipole or dispersion force variety. It is quite likely that the interaction of the alkyl group and ring with one another is affected by the interaction of each with the solvent. Although dispersion energies are assumed to be additive,[8] the assumption is based on perturbation theory and is not likely to be good in condensed media where the number of interacting particles is large and distances are rather small. It seems reasonable to speculate that the interactions of the ring and of the alkyl group with the solvent will reduce the dispersion energy acting between them. The reduction should be greatest for the most polarizable alkyl group and should also be greatest when the interactions with the solvent are strongest. It is quite possible, then, that dispersion energies also play a role in affecting changes in the relative electron-releasing ability of alkyl groups in solvent media.

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(22) Professor R. W. Taft, Jr., has pointed out to the writer that there are at least two reaction series in which the alkyl groups follow a line with different slope in the σ^* correlations. These are in the pK_a's of RPO_2OH^- acids[23] and in the acid- and base-catalyzed hydrolyses of esters in which the alkoxide substituent is varied.[24]

(23) P. C. Crofts and G. M. Kosolapoff, THIS JOURNAL, **75**, 3379, 5739 (1953).

(24) Ref. 19, Table IX, footnote 35.

(25) N. Muller and R. S. Mulliken, THIS JOURNAL, **80**, 3489 (1958).

(26) J. E. Franklin and H. E. Lumpkin, *J. Chem. Phys.*, **20**, 745 (1952).