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The Effect of Substitution on the Ionization Potentials of Free Radicals and Molecules. II. Theoretical Interpretation of δ_K Values for Alkyl Radicals and Amines^{1a}

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The constancy of δ_K values [which measure the change in ionization potential between a substituted molecule (or radical) and the parent compound] for alkyl radicals and amines is discussed in terms of the energies and possible wave functions for these species and their corresponding positive ions. For an alkyl radical it is possible to separate the σ - and π -electrons and, to a first approximation, deal with the wave function, Hamiltonian and orbital of only the π -electron. It is shown to be possible to describe the wave functions and Hamiltonians for the substituted and unsubstituted amines and their positive ions in a manner which emphasizes their close similarity to the alkyl radicals by making a formal separation into σ - and " π -like" electrons. The wave functions of the π - and " π -like" electrons are described and the effects of various perturbations on the Hamiltonians are shown. A comprehensive treatment of a pure inductive effect of a substituent group is given and the extension to substituent groups capable of mesomeric effects is indicated.

Introduction

In a recent article² the localized behavior of the free electron in saturated alkyl radicals was used to derive a simple method of calculating the ionization potentials of substituted radicals. Comparison of the ionization potentials of BY_2 ^{3a,b} radicals with those of the corresponding CY_3 radicals had shown a constant effect of substituent groups on ionization potentials of free radicals. From these data it was possible to formulate a semi-quantitative method for the estimation of ionization potentials of even fairly complex substituted free radicals by combining effects of substituent groups according to a non-linear relationship.

However, neither measurements of the ionization potentials of BY_2 radicals nor direct measurements of the ionization potentials of CY_3 radicals were readily available when the calculation described above^{3a,b} was performed. Therefore, to extend this line of reasoning into a quantitative method for the calculation of ionization potentials of substituted free radicals and certain substituted molecules, a new assumption was made that the ionization potentials of substituted amines would reflect almost the same behavior of change in ionization potential with substitution as did the CY_3 and BY_2 radicals (at least for $Y = H$ or alkyl substituents). Implicit in this discussion was the supposition that ionization of amines takes place by removal of a non-bonding electron of the nitrogen lone pair.⁴ Confirmation of this is the observation of strong excitation of the bending vibration in the NH_3^+ ion (as well as in the higher members of the Rydberg series) corresponding to the fact that NH_3^+ (like CH_3) is planar or nearly planar while NH_3 is not.⁵ The implication of the almost planar structure for NH_3^+ is that the one unpaired electron which remains after ionization of NH_3 is then in a π -type orbital just as the unpaired electron in the ground state of CH_3 is in the same kind of orbital.

The ionization potentials of a number of substituted amines had been measured by a photoionization technique⁶ and while photo measurements usually cor-

respond to Franck-Condon "vertical" processes, the extrapolated ionization potentials are very close to the adiabatic values. Using amines as the standard, δ_K values, a new set of constants which reflect the changes in ionization potential with changes in substituent groups, were calculated.²

δ_K Values.—To verify the assumption that the change in ionization potential on substitution would be the same for carbon radicals as for amines, δ_K values were also calculated from the measured direct ionization potentials of the alkyl free radicals, using the methyl radical as the standard.

The δ_K values calculated from the alkyl radicals were very close to those calculated from the amines. δ_K values calculated from amines combined with the ionization potential of the methyl radical were then used to calculate independently the ionization potentials of all the alkyl free radicals that had been measured directly⁷—as well as those of some which had not been measured at that time. The agreement between the calculated and measured values was excellent.²

It has already been pointed out that δ_K values are affected by a combination of inductive and resonance effects (where hyperconjugation is included in with the resonance effect).² One of the most intriguing questions which arises from a study of these δ_K values is why should there be such a close parallel in the effect of substitution on the ionization potentials of amines and alkyl radicals? Ordinarily one does not consider these two types of compounds as being closely related theoretically. A corollary to this question is the problem of how can one describe the valence structures of these two species and their corresponding ions in such a way as to emphasize this similarity in the effect of substitution on ionization potentials.

This article outlines a possible theoretical approach to this problem which has the virtue of preserving the constant character of the substituent groups regardless of the core on which they are placed.

Discussion of Wave Functions and Energies of Alkyl Radicals and Amines.—The ground state of alkyl radicals is agreed to be planar in most cases—the ethyl, isopropyl and *t*-butyl radicals have been considered as derived from a planar methyl radical.⁸ This means that the unpaired electron is a p - or π -type electron with the remaining electrons on the central carbon atom in sp^2 (or σ) hybridization.

A logical separation to make in order to simplify the problem is to assume that at least in the alkyl radicals one can separate the σ - and π -electrons and, to a first approximation, deal with the wave function and orbital of only the π -electron. This separation is

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(2) J. J. Kaufman and W. S. Koski, *J. Am. Chem. Soc.*, **82**, 3262 (1960).

(3) (a) W. S. Koski, J. J. Kaufman, C. F. Pachucki and F. J. Shipko, *ibid.*, **80**, 3202 (1958); (b) W. S. Koski, J. J. Kaufman and C. F. Pachucki, *ibid.*, **81**, 1326 (1959).

(4) R. S. Mulliken, *J. Chem. Phys.*, **3**, 584 (1935).

(5) G. Herzberg, "Molecular Electronic Spectra," *Ann. Rev. Phys. Chem.*, **9**, 330 (1958).

(6) (a) K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26**, 1773 (1957);

(b) K. Watanabe, T. Nakayama and J. Mottl, "Final Report on Ionization Potential of Molecules by a Photoionization Method," Dept. of the Army, Report No. 5B99-01-004, Dec., 1959.

(7) F. P. Lossing and J. B. deSousa, *J. Am. Chem. Soc.*, **81**, 281 (1959).

(8) N. Muller and R. S. Mulliken, *ibid.*, **80**, 3489 (1958).

the one commonly invoked in virtually all theoretical treatments of π -systems.

Alkyl Radicals.—The ground state of a radical having $2m - 1$ mobile electrons may be described by the function

$$\chi^0 = |\psi_1\bar{\psi}_1 \dots \psi_{m-1}\bar{\psi}_{m-1}\psi_m| \quad (1)$$

in which the space parts of ψ_1 and $\bar{\psi}_1$ are identical.⁹ This function is an eigenfunction of the Hamiltonian \mathcal{H} (assumed spin free), the spin component S_z and the total spin operator S^2 . Therefore, the wave function of the ground state of the π -electron of the methyl radical will be described by

$$\chi_{\pi}^0 = |\psi_1(1)\bar{\psi}_1(0)| \quad (2)$$

(CH₃)

where the $\psi_1(1)$ denotes the fact that the first orbital is occupied by one electron and $\bar{\psi}_1(0)$ denotes the fact that the other π -orbital with the identical spatial property and opposite spin property is unoccupied. This treatment implies also a proper antisymmetrization of the π -system. There are two ways in which a substituent group can influence π -orbitals and affect the behavior of the π -electrons: by an inductive effect or by a resonance (mesomeric) effect if the substituent group has π - or pseudo- π -electrons which can conjugate with the π -orbitals.

In the inductive effect the substituent group modifies the potential affecting the π -electrons. If a substituent existed which possessed only an inductive effect, it would be less difficult to treat theoretically, because a purely inductive substituent will not change the effective number of π -electrons. The wave function of the perturbed π -electron system may then be expanded in terms of those of the unperturbed system.¹⁰ It was emphasized that this procedure is only possible when the mesomeric effect is small, or can be taken into account. The substituent chosen in the original paper¹⁰ as most closely conforming to this requirement was fluorine because its valence electrons were considered to be very tightly bound. Therein lies one pitfall of all treatments of substituent groups. Fluorine, while it does have a very strong inductive electron-attracting effect, has since been shown to have almost as strong an opposite electron-donating effect when able to conjugate with a π -system. Several facts support this conclusion: (1) (a) The Hammett σ -value for a *m*-fluoro-substituent on benzoic acid is $+0.337$,¹¹ and for a *p*-fluoro-substituent is $+0.062$ where more positive values correspond to the greatest decrease in electron density. Since fluorine is known to be strongly electron-attracting inductively, it must be almost as strongly electron donating by a resonance effect to the *p*-position. (b) σ -Values can be separated into inductive and resonance parameters as shown by Taft,¹² where for F, $\sigma_I = +0.50$ and $\sigma_R = -0.44$. (2) The ionization potential of CF₃, 10.10 e.v., compared to that of CH₃, 9.95 e.v.,¹³ is surprisingly low. The inductive effect alone of fluorine in CF₃ on the radical and resulting positive ion would lead to a much higher ionization potential for CF₃ relative to the methyl radical. This indicates that both the inductive and resonance effects of a substituent group are of importance in determining ionization potentials.

Since it is hoped that it may still be possible to find substituent groups in which the mesomeric effect is small compared to the inductive effect, a treatment will be outlined in this article of the inductive effect

alone of substituent groups on the properties of the π -electron of the methyl radical. If an inductive perturbation is denoted by h' , the largest terms in the expression for the perturbed energy arise from terms of the type

$$\int \chi_r^0(1) h'(1) \chi_r^0(1) d\tau_1 \quad (3)$$

where χ_r^0 is the unperturbed 2p- π -orbital of the substituted carbon atom. In the discussion of substituted methyl radicals χ_{π}^0 denotes the unperturbed 2p- π -orbital of the methyl radical with the three hydrogen atoms already forming three σ -bonds to the carbon.

This will essentially take into account penetration integrals of the form (χ_{π}^0/U_H) where U_H is the potential due to a neutral hydrogen atom. The penetration integrals over both neutral hydrogen and neutral carbon atoms are usually assumed to be negligible; however, penetration effects are much more important than previously considered. It would seem that a substantial contribution to the lowering of the ionization potential from 11.16 e.v.,¹⁴ that of an sp² (tr tr' tr'' π)C atom, to 9.95 e.v., that of a planar methyl radical, must be due to a penetration effect of the hydrogen atoms. The form of the penetration integral makes it appear to correspond closely to the definition of an inductive effect—at least for a substituent group on a system which has π - or " π -like" electrons. The electronegativity (E.N.) of C, 2.5, and that of H, 2.05,¹⁵ would indicate that negative charge would tend to be transferred from H to C. In this connection it is of interest to note that for the BH₂ radical where B and H have very similar electronegativities (E.N._B = 2.0; E.N._H = 2.05), the effect of the two H atoms on the ionization potential of the unpaired π -electron of the B is almost negligible— $I(\text{BH}_2) = 8.12$ e.v.^{3a}

Valence state $I(\text{B})$ ¹⁶

$$\text{sp}\pi(\text{di di}'\pi) \quad (\pi) \quad 8.23 \text{ e.v.}$$

$$\text{sp}^2\pi(\text{tr tr}'\pi) \quad (\pi) \quad 8.33 \text{ e.v.}$$

For substituted alkyl radicals, substituents will then be treated as perturbations on the methyl radical.

Many methods for calculating ionization potentials assume that one can remove an electron from an occupied orbital in a molecule without affecting the potential due to the rest of the molecule.¹⁷ It has been

(14) I. J. Goldfarb and H. H. Jaffé, *ibid.*, **30**, 1622 (1959).

(15) L. Pauling, "The Nature of the Chemical Bond," 3rd Edition, Cornell University Press, Ithaca, N. Y., 1960, p. 93.

(16) H. H. Jaffé, private communication. The author is indebted to Professor Jaffé for calculating the valence state ionization potentials of boron.

(17) This assumption corresponds closely to the interpretation often made of Koopman's theorem, which theorem is presumed to imply that the ionization potential of an atom or molecule can be set equal to $-E$ of an electron in the highest occupied ground state Hartree-Fock orbital and that the resulting ion is insensitive to the presence or absence of this electron. It is usually implied that the theorem assumes that the orbitals of the ion are the same as those of the molecule. There may be a more subtle aspect of Koopman's theorem, however, based on the following point. It is tacitly assumed in the interpretation of Koopman's theorem that the phase space of a positive ion is completely contained in the phase space of the corresponding molecule. There is an almost unlimited number of different possible configurations available to the molecule whether it uses them or not—these may be defined as corresponding to the phase space of the molecule. The phase space of the corresponding positive ion may then be contained in this molecular phase space—the difference being in the coefficients of the various parts of the phase space used by the molecule or the ion. There can be elements utilized in the subspace of the ion which are not explicitly used in the larger subspace of the molecule; however, by making proper combinations of the elements of phase space available to the molecule, it may be possible to create a subspace which does span the whole phase space of the corresponding positive ion. The original derivation of Koopman's theorem [T. Koopmans, *Physica*, **1**, 104 (1934)] applies *only* to atoms; for the atomic case the phase space available to the atomic positive ion must necessarily be contained in the phase space of the atom itself. However, this is not so for molecules and their positive ions unless one makes an interpretation similar to the one above about the availability of a larger molecular phase space than might actually be considered as occupied by the molecule. This applies to "vertical" ionization potentials where "vertical" is the transition favored by the Franck-Condon principle.

(9) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc. (London)*, **66A**, 591 (1955).

(10) J. N. Murrell and H. C. Longuet-Higgins, *ibid.*, **68A**, 329 (1955).

(11) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(12) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

(13) J. B. Farmer, I. H. S. Henderson, F. P. Lossing and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

customary to suppose that the molecule and the ion have wave functions of the form

$$\Psi_M = |(\Sigma)(\Pi_M)| \text{ and } \Psi_{M^+} = |(\Sigma)(\Pi_{M^+})| \quad (4)$$

where (Σ) remains the same for both molecule and positive ion. Calculations for unsaturated systems using this assumption give values which are too high and it was suggested by Lykos and Parr¹⁸ that one should use a π -electron approximation with an adjustable core

$$\Psi_M = |(\Sigma_M)(\Pi_M)| \text{ and } \Psi_{M^+} = |(\Sigma_{M^+})(\Pi_{M^+})| \quad (5)$$

The Hamiltonians should also be different with an \mathcal{H}_M for the molecule and an \mathcal{H}_{M^+} for the ion.

Carbonium ions are believed to have greater stabilization due to charge redistribution and hyperconjugation than the parent radicals⁸ and, therefore, both the Σ - and Π -frameworks must be affected. For this reason an accurate method of treating even just the inductive effect of substituents on ionization potentials must treat the radical and ion as two separate entities—although hoping the differences might not be too great.

The ionization potential, I , of the radical, R , can be expressed as

$$I(R) = E(R) - E(R^+) \quad (6)$$

For the methyl radical as standard

$$I(\text{CH}_3) = E(\text{CH}_3) - E(\text{CH}_3^+) \quad (7)$$

In estimating just the inductive effect on the ionization potential of the π -electron, the equation to be used is

$$I(\text{CH}_3) = E_\sigma(\text{CH}_3) + E_\pi(\text{CH}_3) - E_\sigma(\text{CH}_3^+) \quad (8)$$

$I(\text{CH}_3)$ may be set equal approximately to $E_\pi(\text{CH}_3)$ only in the case where $E_\sigma(\text{CH}_3)$ is approximately equal to $E_\sigma(\text{CH}_3^+)$ which happens if and only if (iff) charge distribution is not too greatly different in the two species.

Similarly, for a substituted alkyl radical where Y has an inductive but no mesomeric effect and

$$E_\sigma(\text{YCH}_2) \sim E_\sigma(\text{YCH}_2^+) \quad (9)$$

then

$$I(\text{YCH}_2) = E_\pi(\text{YCH}_2) = \int \chi_\pi(1) \mathcal{H}_\pi(1) \chi_\pi(1) d\tau_1 \quad (10)$$

(YCH₂)(YCH₂)(YCH₂)

$$\mathcal{H}_\pi(\text{YCH}_2) = \mathcal{H}_\pi(\text{CH}_3) + \frac{h'}{(H \rightarrow Y)} \quad (11)$$

[($H \rightarrow Y$) denotes changing an H atom to a Y substituent] where $\chi_\pi(1) \sim \chi_\pi^0(1)$ in first-order perturbation theory

$$\frac{\chi_\pi(\text{YCH}_2)}{(\text{YCH}_2)} \sim \frac{\chi_\pi^0(\text{CH}_3)}{(\text{CH}_3)} \quad (12)$$

approximation.

$$\begin{aligned} \therefore \delta_K &= I(\text{YCH}_2) - I(\text{CH}_3) \quad (13) \\ &= \frac{\chi_\pi^0(1)}{(\text{CH}_3)} \frac{h'(1)}{(H \rightarrow Y)} \frac{\chi_\pi^0(1)}{(\text{CH}_3)} d\tau \end{aligned}$$

Amines.—Now, one should like to describe the wave functions and Hamiltonians for the substituted and unsubstituted amines and their positive ions in a manner which would emphasize their close similarity to the alkyl radicals. A possible method, which on first contemplation may seem a bit unusual but has been shown to have merit,¹⁹ is to consider the unshared pair of electrons on the nitrogen as being electrons in a π -type orbital. That this is not the true configuration may be seen from the bond angles in NH_3 ²⁰ which show approximately tetrahedral HNH bond angles corresponding closely to an almost sp^3 hybrid structure for the nitrogen. This formal separation into σ - and " π -like" electrons and orbitals, however, has proved to be

(18) P. G. Lykos and R. G. Parr, *J. Chem. Phys.*, **24**, 1166 (1956).

(19) J. J. Kaufman, *ibid.*, **37**, 759 (1962).

(20) I. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society (London) Special Publication No. 11 (1958), p. M45.

quite successful in discussing theoretical aspects of bonding in N-F compounds as they pertain to various properties of NF_3 and NH_3 such as their bond strengths, basicities and quadrupole coupling constants, as well as the differences in their ionization potentials.¹⁹ In this same article, a similar treatment was extended to an explanation of the properties of NH_2 and NF_2 .

The wave function of the ground state of the " π -like" electrons of the ammonia molecule will be described by

$$\chi_{\pi}^0(\text{NH}_3) = N |\psi_1(1)\bar{\psi}_1(1')| \quad (14)$$

where the two identical spatial orbitals are occupied by two electrons of opposite spin and the $||$ denote proper antisymmetrization.

This treatment of the lone pair electrons as " π -like" implies only the assumption that this " π -like" system is orthogonal to the other bonds in the molecule.²¹ This division depends on the proven fact that it is possible to write the wave function for the complete molecule as a product of wave functions which must be mutually orthogonal for the separate bonds or lone pairs so that certain orbitals may be associated with selected parts.²²

The treatment of the inductive effect of a substituent on a CY_3 outlined in the previous section is rigorous within the framework of the customary approximations used in π -electron theory where σ -electrons are considered part of a constant core. Using the separation of electrons in NY_3 molecules into " σ " and " π -like" and considering the " σ "-framework as part of the core, the expressions for the energy contributions caused by the identical inductive perturbation h' on the π - or " π -like" system of either a CY_3 radical or an NY_3 molecule turn out to be the same in first-order perturbation approximation

$$\int \chi_r^0(1) h'(1) \chi_r^0(1) d\tau$$

It will now be shown that this treatment leads to expressions of the same form of δ_K values of the identical substituent group on a CY_3 or an NY_3 core.

The ionization potential of ammonia can be expressed as

$$I(\text{NH}_3) = E(\text{NH}_3) - E(\text{NH}_3^+) \quad (15)$$

$$= E_\sigma(\text{NH}_3) + 2E_{\pi}(\text{NH}_3) - E_\sigma(\text{NH}_3^+) - E_{\pi}(\text{NH}_3^+)$$

If for the sake of simplicity $E_\sigma(\text{NH}_3)$ is set approximately equal to $E_\sigma(\text{NH}_3^+)$ and $E_{\pi}(\text{NH}_3)$ is equal to $E_{\pi}(\text{NH}_3^+)$ (which is the common assumption in LCAO-MO treatment of π -systems), then $I(\text{NH}_3)$ is approximately equal to $E_{\pi}(\text{NH}_3)$.

The analogy between species which are not isoelectronic but which still bear a formal similarity to one another is not without precedent. The higher electronic excitations of the free radical NH_2 have been reported to be almost identical with those of H_2O ,²³ except that one of the lone pair of electrons is missing in NH_2 .

(21) The original reason for the assumption of treating the lone pair electrons in NH_3 and NY_3 compounds as " π -like" was the experimentally observed constancy of substituent group effects on ionization potentials of CY_3 radicals and NY_3 molecules. The referee of this paper has made the following comment: "With regard to the interesting and at first sight rather mysterious equality of δ_K values for amines and alkyl radicals, possibly a simple explanation might be approached on the basis of the fact that for NH_3 only 0.25 e.v. is required to flatten out the pyramidal equilibrium structure to a planar (D_{3h}) structure. In a planar structure, the parallelism mentioned might be readily understandable in terms of inductive effect plus hyperconjugation, and plausibly this may remain essentially true for the actual non-planar structures. The fact that the equality of δ_K values for amines and hydrocarbon radicals does not extend to other molecular types [e.g., ethers, etc.; J. J. Kaufman, *J. Phys. Chem.*, **66**, 2269 (1962)] seems to be in harmony with the above proposal for the special case of the amines."

(22) C. A. Coulson and M. J. Stephen, *Trans. Faraday Soc.*, **53**, 272 (1957).

(23) G. W. Robinson, "Symposium on Light and Life," McElroy and Glass, Editors, Johns Hopkins University Press, Baltimore, Md., 1961, pp. 11-30.

This analogy could pertain equally well to the CH_3 radical and NH_3 .

For a substituted amine where Y has an inductive but no mesomeric effect and it is assumed that

$$I(\text{YNH}_2) \approx E_{\cdot\pi}(\text{YNH}_2) \quad (16)$$

$$\delta_K = I(\text{YNH}_2) - I(\text{NH}_3) \quad (17)$$

when the following relationships are used

$$\mathcal{I}C_{\cdot\pi} = \mathcal{I}C_{\cdot\pi} + \frac{h'}{(\text{H} \rightarrow \text{Y})} \quad (18)$$

and

$$\chi_{\cdot\pi} \approx \chi_{\cdot\pi}^0 \quad (19)$$

to first-order perturbation approximation

$$\delta_K \cong \int_{(\text{NH}_3)} \chi_{\cdot\pi}^0 \frac{h'}{(\text{H} \rightarrow \text{Y})} \chi_{\cdot\pi}^0 d\tau_{\cdot\pi} \quad (17a)$$

The form of the equation for the δ_K values of YCH_2 and YNH_2 turns out to be the same under the conditions invoked. It becomes apparent from the above treatment why the effect of substituent groups producing only inductive perturbations leads to exactly the same δ_K values for CY_3 and NY_3 .

Discussion

The ionization potentials of alkyl radicals and alkyl substituted amines are influenced by both the inductive and resonance effects.

$$\delta_K = a\sigma_I + b\sigma_R + c \quad (20)$$

Alkyl groups are known to have stronger inductive effects than resonance effects—even the resonance "hyperconjugation" of the methyl group is presumed to be weak compared to its inductive effect (for alkyl substituents both effects are in the same direction). To a first order the δ_K values for identical alkyl substituents on the methyl radical or ammonia are the same—the only slight discrepancies are noted in $\delta_K^{(2)}$ and $\delta_K^{(3)}$ (CH_3) (the effect of substituting two or three CH_3 groups for H atoms). δ_K values derived from the alkyl radicals are about 8% higher than those derived from the corresponding amines in these cases and this is no doubt due to the enhanced possibility for hyperconjugation in an alkylcarbonium ion compared to an alkylamine positive ion. Another type of δ_K value has also been defined: $\delta_{K-\text{Me}}$, which is the change in ionization potential caused by substituting a group for a methyl group. It has been shown that $\delta_{K-\text{Me}}$ values are integral multiples for any one substituent which would be the conclusion drawn from the result of the following equation where Y has only an inductive effect compared to X.

$$\delta_K = \int \chi_{\pi} \frac{h'}{(\text{X} \rightarrow \text{Y})} \chi_{\pi} d\tau_{\pi} \quad (21)$$

where $h' = \sum_i h_i'$.

Comparison of $\delta_{K-\text{Me}}$ values *vs.* Taft σ^* -values using $\text{CH}_3 = 0.00$ indicates a fairly linear relationship. This is not surprising since the methods both use the CH_3 group as the standard and presume to measure the inductive effect.

Use of δ_K Values in Finding Parameters for Incorporation into Quantum Chemical Calculations.—The difference between the ionization potential of a methyl radical and a substituted methyl radical has been proposed for quantum chemical calculations as an exact measure of the penetration integral of a substituent group²⁴ (a term which is usually neglected). The quantity $(\chi\chi/U_Y')$ may be used to evaluate the change in the valence state ionization potential of a carbon 2p- π -electron. In addition, there seems to be a

scarcity of theoretical calculations which incorporate the fact that there is a penetration effect due to the hydrogen atoms which affects the potential at the carbon 2p- π -electron and that it is this potential which is altered when a group is substituted for a hydrogen. The change in ionization potential as a function of substituent groups is almost constant for CY_3 and BY_2 free radicals since in each case the change is measured against H as a standard—which already takes into account any electronegativity differences between the central atom and the hydrogens.

There is yet another less direct, but very illuminating, way in which δ_K values and the concepts on which they are based may be of value in the field of quantum chemistry. A problem which has been pointed out recently by Hall²⁵ and by Boys²⁶ is the question of finding invariant parameters which can be used to give a quantum mechanical basis to empirical generalizations noted by chemists. Among the problems which this generalized application of quantum mechanics must solve, Hall²⁵ has considered the most important to be "to find suitable localized entities which can be used as invariant units to build up the properties of large complicated molecules from smaller simpler ones." If it could be shown that there are such entities, then their properties could be investigated by: (1) Reinterpreting existing properties in terms of these entities and finding their properties by calculation. (2) Treating integrals over these entities as parameters and finding their values by comparison with experiment.

δ_K values for specific substituents most assuredly refer to localized entities since the δ_K values can be carried over from one set of compounds to another different set of compounds. The integrals over the entities corresponding to δ_K values have been treated as parameters in the present article and their values found by comparison with experiment.

Boys²⁶ has discussed the possibility of constructing some molecular orbitals to be approximately invariant for changes from one molecule to another. These chemically invariant orbitals would have the smallest possible changes for variation in a distant change in the core. It was hoped that it might be possible to construct and tabulate chemically invariant orbitals for common radicals and then be able to write simple approximate wave functions for further molecules, without direct calculation, by taking appropriate orbitals from previous calculations. δ_K values serve as an indication of which groups display the property of chemical invariance from one molecule to another and thus would be suitable for description by chemically invariant orbitals.

δ_K values have been shown to be related to absolute Lewis acid and base strengths, chemical reactivities and σ -values, dipole moments and therefore nuclear quadrupole coupling constants, and absolute electronegativities of radicals.² Consequently, δ_K values have much wider possible applicability than just to the problem of predicting ionization potentials. By a higher order perturbation expansion than the simple first-order one used earlier in this article, it will be possible to see what changes in the wave function of a substituted molecule (or radical) relative to that of the parent remain consistent for the same substituent group on different parents. These consistent changes should then be of value in aiding one to determine the chemically invariant orbitals.

Acknowledgments.—The author wishes to thank Prof. R. Daudel for pointing out the use of δ_K values to evaluate penetration integrals and for several stimul-

(24) R. Daudel, Lecture delivered before the 3rd International Conference in Quantum Chemistry, Uppsala, Sweden, August, 1960.

(25) G. G. Hall, *Rept. Progr. Phys.*, **22**, 1 (1959).

(26) S. F. Boys, *Rev. Modern Phys.*, **32**, 296 (1960).

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[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., PLASTICS DIVISION, RESEARCH DEPARTMENT, SPRINGFIELD 2, MASS.]

The Free Radical, High Pressure Polymerization of Ethylene. II. The Evidence for Side Reactions from Polymer Structure and Number Average Molecular Weights

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Polyethylene polymerized isothermally in batch reactors at about 130 and 250° and at pressures of 800 to 3,000 atm. was characterized with respect to certain structural parameters and number average molecular weight. The methyl and vinylidene contents (per 1,000 CH₂) both decrease with pressure, and increase with temperature, but the vinylidene content is more strongly affected by these parameters than is the methyl content. Under most conditions the unsaturation occurs largely in the form of vinylidene groups, but the vinyl content becomes competitive at high temperatures and pressures. There is a close correspondence between vinylidene content and molecular weight. The data indicate, in fact, that under the conditions of this study the major molecular weight-controlling step is associated with the formation of vinylidene groups. The decomposition (β -elimination) of a tertiary radical could lead to this result and is a step which has already been suggested as participating in the thermal degradation of polyethylene at higher temperatures. This step, together with Roedel's "backbiting" mechanism, as subsequently modified, can account for most of the data on polymer structure and molecular weights reported in this study. Some difficulty is experienced, however, in accounting quantitatively for all experimental facts, and some doubt remains as to the adequacy of the steps which have been proposed.

Introduction

Several workers have attempted to gain information on the propagation and termination steps in the free radical polymerization of ethylene, yielding high molecular weight products, through kinetic studies carried out under isothermal conditions.¹⁻³ The existence in polyethylene, polymerized by free radical mechanisms, of branches and of unsaturation⁴ testifies to the importance of isomerization reactions and of radical decomposition reactions.⁵ In most cases the conclusions have been based on examination of commercial high pressure polyethylene, polymerized under conditions which are either unknown or not well defined, particularly with respect to temperature. The present study was undertaken to study branching, unsaturation and molecular weights of polyethylenes polymerized isothermally in batch reactors under known and well defined conditions, in an attempt to define more precisely some of the more important side reactions in the free radical high pressure polymerization of ethylene.

Polymerization rates are often strongly dependent on phase composition and their interpretation in heterogeneous systems is open to question.² Some doubt exists as to whether all samples for which data will be presented were polymerized under single-phase conditions. There was, however, no evidence that any heterogeneity which may have existed had any effect on the polymer properties measured.

Experimental

Sample Preparation.—The polymer samples used for the infrared measurements were prepared at two temperatures. The low temperature (130°) synthesis was represented by samples prepared in the presence of 15 to 30 mole % propane in an earlier kinetic study.² The (varying) amounts of propane had no measurable effect on the methyl and vinylidene contents. It may be concluded in view of this, and of unpublished data, that the values of methyl, vinyl and vinylidene concentrations

are, within experimental error, independent of the propane concentration, from undiluted monomer to the highest propane concentrations employed.

The high temperature samples (250°) were prepared in the absence of propane and without adding initiator to the ethylene. Under these conditions reproducible polymerization rates could not be obtained, especially at the higher pressures, and it must be concluded that most or all of the initiation was the result of interaction of the ethylene with the trace amounts of oxygen contained in it.⁶

The number average molecular weights were determined for several samples made in the high temperature (250°) synthesis just described. The samples made at 130° in the presence of propane were unsuitable for a molecular weight study, since the objective was to study molecular termination in the absence of added transfer agent. Several samples were, however, available which had been polymerized, using di-*t*-butyl peroxide at 140° in the absence of propane and at pressures of 1,600 to 1,800 atm., as well as a sample polymerized elsewhere under similar conditions and by a similar technique.⁷ In spite of the small difference in synthesis temperature, comparison of the molecular weights of these samples with the vinylidene contents of those polymerized at 130° in the presence of propane is relevant (see under Results). It will be for the 140° samples that the molecular weights, judged to be characteristic of the low temperature synthesis, in the absence of added transfer agent, will be reported. Reliable infrared determinations for the identical series could not be obtained because of difficulties in the sample preparation with this particular series, owing largely to the high molecular weights and limited amounts of polymer available.

The number average molecular weights were determined by osmotic pressure measurements.

Infrared Analyses.—Determinations of methyl, vinylidene, vinyl and *trans*-vinylene contents were made using a Beckman IR-7 spectrophotometer. Methyl content was determined from the 1378 cm.⁻¹ absorption, after compensating for methyl-ene absorptions at 1368 and 1352 cm.⁻¹, by means of a wedge of linear polyethylene containing less than 0.3 methyl/10³CH₂. Absorptions due to vinylidene, vinyl and *trans*-vinylene were measured at 888, 909 and 965 cm.⁻¹, respectively. In the case of the first two of these, corrections for the absorption by the RCH₂CH₂ group at 894 cm.⁻¹ had to be made, using the appropriate value of the methyl content measured at 1378 cm.⁻¹.

Although the absorptivity for the symmetrical C-H bending mode of methyl groups at 1378 cm.⁻¹ is known to decrease with increasing length of the pendant alkyl branch, this variation occurs only as the branch changes from methyl to butyl.⁸ Since the pendant branches are known to be primarily ethyl and butyl,^{9,10} the absorptivity of a hydrocarbon with a long alkyl chain was

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