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The Effect of Substitution on the Ionization Potentials of Free Radicals and Molecules. I. A New Set of Constants, the δ_K Values[1]

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RECEIVED OCTOBER 22, 1959

Several new applications of ionization potentials are presented. Ionization potentials of certain molecules are quantitative measures of the effect of substitution on ionization potentials in general. Ionization potentials of amines seem to be a measure of an "absolute" Lewis base strength uncomplicated by steric effects. Using substituted amines as a standard, a new set of constants, the δ_K values, has been calculated. δ_K values quantitatively reflect the change in ionization potential with substitution. Comparison of δ_K values for multiple substitutions definitely confirms the previously postulated "saturation" effects in the aliphatic series. Another series of constants, the $\delta_{K\text{-Me}}$ values which represent the change in ionization potential by substituting groups for methyl groups, was calculated and appears to be directly related to Taft σ^* values. The δ_K values when properly used are additive and as a check the ionization potentials of the alkyl radicals were calculated using the δ_K method; agreement with experiment was excellent.

The ionization potential of a molecule, radical or atom is defined as the energy required to remove an electron completely from one of the orbitals of the neutral particle in its ground state to form the corresponding ion also in its ground state. Ionization potentials are an important property of particles[2] and are of value in interpreting their electronic and molecular structure. Ionization potentials of molecules have been shown to be good criteria of bond energy,[3] indicative of electronegativity and bond order[4-6] and important in determining charge transfer spectra.[7-9] Ionization potentials of free radicals have been used to determine bond dissociation energies by the electron impact method.[10] The ionization potentials of free radicals have also been interpreted as a measure of reactivity in some theories of organic reactions[11] and the ionization potentials of radicals are related to the electronegativities (where electronegativity is defined as the power to attract electrons to itself) and to the electron affinities of the radicals.[12,13]

In addition to the uses mentioned above, the authors find several other very interesting applications of ionization potentials. The ionization potentials of certain molecules, for example those of some of the Group V compounds, are quantitative measures of the effect of substitution on ionization potentials in general. Also ionization potentials of Group V compounds such as amines seem to be a measure of what one may now call the "absolute" Lewis base strength—that is, the tendency of a molecule to donate electrons governed by the inductive and perhaps resonance effects but uncomplicated by steric effects. Knowledge of the ionization potentials of free radicals should make the mass spectrometric examination of free radical reactions much simpler than the present method of using the same high ionizing voltage that is used for the fragmentation of the parent compounds. By using an ionizing voltage only about 1 ev. higher than the ionization potential of the free radical in question (and this value is invariably lower than that of the parent molecule) only the free radicals present in the reaction should be ionized and measured by the mass spectrometer. The ionization potentials of BY_2 and CY_3 free radicals have confirmed the effect of substitution on ionization potentials. Ionization potentials of BY_2 radicals appear to be a very sensitive and delicate probe of the "absolute" Lewis acid strengths of corresponding BY_3 molecules.

And, most intriguing of all, there seems to be a relationship between ionization potentials, δ_K values (which are measures of the effect of substitution on ionization potentials) and various types of σ values.

Data

The true, or adiabatic, ionization potential of a molecule (or radical or atom) is by definition the energy difference between the ground vibrational level of the lowest electronic state of the molecule and the ground vibrational level of the lowest electronic state of the molecule-ion. The ionization potentials measured spectroscopically, usually by convergence of a Rydberg series, are the adiabatic ionization potentials. The ionization potentials measured by a photoionization technique[14] usually agree quite closely with the spectroscopic values and are also presumed to be adiabatic ionization potentials. On the other hand, ionization potentials measured by electron impact are the vertical ionization potentials (where "vertical" is taken to mean the transition favored by the Franck–Condon principle),[15] and these may exceed the adiabatic ionization potentials by the vibrational energy excited in the ion. The electron impact values are usually regarded as upper limits to the adiabatic values. However, comparison of a set of photoionization values and a set of electron impact values for ionization potentials of molecules show self-consistency within each set and the values usually agree to within 0.1–0.2 ev. (There are noticeable exceptions, namely, the ionization potentials of the amines by photoionization which agree with the spectroscopic values are several electron volts lower than those obtained by electron impact[16].)

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600)-1526. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] F. H. Field and J. L. Franklin, "Electronic Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

[3] R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

[4] A. D. Walsh, *Trans. Faraday Soc.*, **42**, 56. 779 (1946).

[5] A. D. Walsh, *Proc. Roy. Soc.* (*London*), **A207**, 13, 22 (1951).

[6] J. P. Teegan and A. D. Walsh, *J. Chem. Phys.*, **19**, 1070 (1951).

[7] R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950).

[8] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[9] S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, THIS JOURNAL, **75**, 2900 (1953).

[10] D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).

[11] E. Spinner, *J. Chem. Soc.*, 1590 (1956).

[12] R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).

[13] R. S. Mulliken, *ibid.*, **3**, 573 (1935).

[14] K. Watanabe, *ibid.*, **26**, 543 (1957).

[15] D. P. Stevenson and J. A. Hipple, Jr., THIS JOURNAL, **64**, 1588 (1942).

[16] K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26**, 1773 (1957).

For δ_K values calculated in this paper, ionization potentials of molecules obtained either spectroscopically or by a photoionization method were used whenever available. There is only one spectroscopic measurement of the ionization potential of a free radical, CH_3, and no photoionization measurements so a direct comparison of electron impact values with measurements made by other methods cannot be made.

The ionization potentials of radicals can be determined "directly" by generating the radical and measuring its ionization potential by electron impact or the ionization potentials can be calculated "indirectly" from appearance potentials by a dissociative electron impact method. If one represents the "indirect" electron impact process taking place as

$$R_1\text{–}R_2 + e^- \longrightarrow R_1^+ + R_2 + 2e^-$$

then by the equation

$$A(R_1^+) = D(R_1 - R_2) + I(R_1)$$

where $A(R_1^+)$ is the mass spectrometrically measured appearance potential of R_1^+, $D(R_1\text{–}R_2)$ is the bond dissociation energy of $R_1\text{–}R_2$ and $I(R_1)$ is the ionization potential of R_1, either the ionization potential of R_1 or the bond dissociation energy $R_1\text{–}R_2$ may be calculated directly from the measured $A(R_1^+)$ provided one knows the value of the other unknown in the equation. A necessary condition for the above equation to hold true is $I(R_1) < I(R_2)$.[10] If $I(R_1) > I(R_2)$ then $A(R_1^+) > D(R_1\text{–}R_2) + I(R_1)$. In order to correctly interpret the appearance potentials of fragment ions, it is necessary to know the structure of the ion, what other fragments are simultaneously formed, the states of electronic excitation of the fragments and the fragment ion and the excess kinetic or vibrational energy present.

Values for ionization potentials of some alkyl radicals had been derived indirectly by combining appearance potentials of the ions with thermochemical data.[2,10,17] Some uncertainties arise in the indirect method due to the difficulty of identifying the structure of the alkyl ions produced in the dissociative ionization process. The appearance potentials of these ions from normal paraffins were not found to be consistent with a primary structure for the ions. An isomerization which occurred prior to or during the dissociation of the parent ion has been postulated. However, the authors feel that an equally valid explanation for the structure of the alkyl ions formed by electron impact induced dissociation and ionization of normal paraffins is that a secondary hydrogen comes off in preference to a primary hydrogen in just the reverse order of the bond strengths then possibly followed by an isomerization (to a still different structure such as either a postulated cationated cyclopropane ring or a different cyclic structure in which one hydrogen is shared between the two end C atoms in the case of $C_3H_7^{+}$[18,19]). It should prove interesting to re-examine the data on appearance potentials of lower ions obtained by electron impact of hydrocarbons from the same point of view the authors used on the appearance potentials of lower ions from diborane, B_2H_6.[20] There are usually several possible energy values which can be calculated for ionization potentials of lower fragments formed by electron impact depending upon the choice of structure of the ion and what fragments are presumed to be formed in the dissociation. One must choose (sometimes on the basis of mere intuition) the most plausible process and the configuration of the resulting ion. Following this line of reasoning, one would really expect the ions formed from the normal hydrocarbons to have at least the secondary and not the primary structure. Recently the ionization potentials of propyl and butyl free radicals were measured directly on the free radicals generated by thermal decomposition of alkyl nitrites.[21] It was found that the ionization potentials of isopropyl[22] and *tert*-butyl[21] free radicals were about 0.5 ev. higher when measured directly than the values calculated by the indirect method. Due to the discrepancies between direct and indirect methods of measuring the ionization potentials of radicals, the authors have used only the direct ionization potentials of radicals in calculating or confirming δ_K values.

Calculations and Results

In an earlier paper on the mass spectroscopic appearance potentials of boron compounds,[23] the authors calculated the ionization potentials of a number of BY_2 radicals (where Y can be hydrogen, halogen or alkyl substituents) by the indirect method using appearance potentials and bond dissociation energies. There is less chance for rearrangement in boron radicals than in carbon radicals and it was felt that the ionization potentials of BY_2 radicals might indicate the effects of substituent groups on the ease with which the unpaired electron can be withdrawn assuming that the odd electron is the one involved in the ionization process. The ionization potentials calculated for the BY_2 radicals were compared with the then-available ionization potentials for corresponding CY_3 radicals (some of the CY_3 ionization potentials were direct and some were indirect). It was possible, even with the data then available, to formulate a semiquantitative method for the estimation of ionization potentials of even fairly complex substituted free radicals by combining the effects of substituent groups.

Now, as the result of a basic new assumption, the authors have been able to extend this line of reasoning into a quantitative method for the calculation of ionization potentials of substituted free radicals and substituted molecules. The new assumption made was that the ionization potentials of substituted amines would reflect the same behavior of change in ionization potential with substitution as did the CY_3 and BY_2 radicals.

Amine Series.—Fortunately, the ionization potentials of a number of substituted amines had been measured by a photoionization technique[16] and these values should be very close to the adiabatic values. Inspection of the ionization potentials of these amines showed a close parallel of the change in ionization potential with substitution to that noted in the CY_3 and BY_2 radicals. Using amines as the standard, a new set of constants, which the authors call the δ_K values, has been calculated.

δ_K values quantitatively reflect the change in ionization potential with substitution; in this paper δ_K values are given in ev. Although all the substituents reported in this paper lower the ionization potentials, there will be substituents which raise the ionization potentials and for this reason a sign convention must be established. The sign convention chosen is that all δ_K values which represent a lowering of ionization potential from that of the parent radical or molecule will be regarded as negative values and should be preceded by a minus sign. (Note that in this paper all δ_K values should be preceded by a minus sign since they all represent a lowering of ionization potential from that of the parent.)

In Table I are presented the δ_K values derived from the amine series. An explanation of the symbols used is given:

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[17] D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

[18] P. N. Rylander and S. Meyerson, THIS JOURNAL, **78**, 5799 (1954).

[19] M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, "Mass Spectra of Large Molecules. I. Saturated Hydrocarbons," Univ. Utah, 1951.

[20] W. S. Koski, Joyce J. Kaufman, C. F. Pachucki and F. J. Shipko, THIS JOURNAL, **80**, 3202 (1958).

[21] F. P. Lossing and J. B. de Sousa, *ibid.*, **81**, 281 (1959).

[22] J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

[23] W. S. Koski, Joyce J. Kaufman and C. F. Pachucki, THIS JOURNAL, **81**, 1326 (1959).

TABLE I

δ_K VALUES DERIVED FROM THE AMINE SERIES (IN EV.)

NH_3 PARENT COMPOUND

Substituent	$\delta_K^{(1)}$	$\delta_K^{(1-0)}$	$\delta_K^{(2)}$	$\delta_K^{(2-1)}$	$\delta_K^{(3)}$	$\delta_K^{(3-2)}$	$\delta_{K\text{-}Me}^{(1)}$	$\delta_{K\text{-}Me}^{(2)}$	$\delta_{K\text{-}Me}^{(3)}$
CH_3–	1.18		1.91		2.33		0	0	0
		1.18		0.73		0.42			
C_2H_5–	1.29		2.14		2.65		0.11	0.23	0.32
		1.29		0.85		0.51			
n-C_3H_7–	1.37		2.31		2.92		0.19	0.40	0.59
		1.37		0.94		0.61			
i-C_3H_7–	1.43		2.42				0.25	0.51	
		1.43		0.99					
n-C_4H_9–	1.44		2.46				0.26	0.55	
		1.44		1.02					

δ_K (or $\delta_K^{(1)}$), $\delta_K^{(2)}$, $\delta_K^{(3)}$ are the changes in ionization potential caused by substituting one, two or three identical groups respectively for H atoms (on the *same* central atom of the radical or molecule from which the electrons are being withdrawn in the ionization process). (Note that $\delta_K^{(2)}$ or $\delta_K^{(3)}$ are not simply twice or three times $\delta_K^{(1)}$.)

$\delta_{K\text{-}Me}^{(1)}$, $\delta_{K\text{-}Me}^{(2)}$, $\delta_{K\text{-}Me}^{(3)}$ are the changes in ionization potential caused by substituting one, two or three groups for methyl groups (under the same conditions as above).

An important type of δ_K value is the difference in ionization potential found by adding a second identical substituent group when a first substituent group is already present (or the difference in adding a third identical group when two groups are present). These differences are defined by:

$\delta_K^{(1-0)}$ (or δ_K or $\delta_K^{(1)}$), $\delta_K^{(2-1)}$, $\delta_K^{(3-2)}$ are the differences in ionization potential between the mono- and unsubstituted, the di- and monosubstituted and the tri- and disubstituted molecules or radicals (with identical substituent groups).

The above terminology is sufficient to describe δ_K values from the amine substitutions and from the alkyl radical substitutions discussed in this paper. However, a subsequent paper will present δ_K values and confirmation of δ_K values derived from the ionization potentials of alkenes. For these examples, in cases of ambiguity, further symbols must be used. The parent molecule of the alkenes is ethylene. In the case of just one substituent or if all the substituents are identical and are on one of the C atoms, the same symbols used for amines are applicable; but if the substituents are on different C atoms or are not identical then refinements must be made in the symbolism. This refined system is only used for molecules in which there is a chance of ambiguity. The simple nomenclature system described above is used wherever possible. The discussion of the complete symbolic system as applied to the ethylene and similar series will be deferred until the discussion of the ethylene series ionization potentials.

The δ_K values derived from amines are presented in Table I and these values will be used as standard values for many types of other compounds. A number of very interesting observations now become apparent from examination of these δ_K values.

First, the "saturation effect" in the aliphatic series, which had been mentioned[24,25] by some authors but the evidence called "not very convincing" by Taft,[26] seems to be definitely confirmed. The lowering of ionization potential by substitution of the first alkyl group for an H atom in the amines is larger than the change in ionization potential between substituting the first and the second groups, and the difference between substituting the first and the second groups is larger than that between substituting the second and the third groups.

$\delta_K^{(n)}$ values themselves, which represent the change in ionization potential found by substituting groups for H atoms, are governed by some combination of inductive and resonance effects (where any hyperconjugation effect[27] is included in with the inductive and resonance effects) but these $\delta_K^{(n)}$ values seem relatively uncomplicated by any steric effects. Numerous investigators have sought to establish a correlation between Lewis base strength (or Lewis acid strength) and substitution in a homologous series. A recent review paper[28] summarizes stability relationships among analogous molecular addition compounds of Group III elements. Sometimes the strength of the donor–acceptor bond is interpreted in terms of the magnitude of the equilibrium constant, *Kp*, for the reaction

$$D\cdot MX_3(g) \rightleftarrows D(g) + MX_3(g)$$

However, great care must be exercised in interpreting these results. Using the same MX_3 compound and a series of substituted amines, one would expect from purely electron donating effects that the *Kp* would decrease with increasing alkyl substitution or with increasing complexity of the alkyl substituents. *Kp* values decrease as one goes down the series $RNH_2\cdot MX_3$ where R is a normal alkyl radical, but *Kp* values increase as one goes down the series $RNH_2\cdot MX_3$, $R_2NH\cdot MX_3$, $R_3N\cdot MX_3$, or the series $RNH_2\cdot MX_3$ where the R's are alkyl radicals with branching on the α carbon atom. These results are explained easily if one looks back at the definition of *Kp*. The larger values of *Kp* simply represent the effect of steric hindrance in preventing the reverse reaction from taking place.

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(24) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice Hall, Inc., New York, N. Y., 1941.

(25) R. P. Smith and H. Eyring, THIS JOURNAL, **75**, 5183 (1953).

(26) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956.

(27) W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

(28) F. G. A. Stone, *ibid.*, **58**, 101 (1958).

The authors feel that the δ_K values derived from the amines may actually represent a measure of "absolute" Lewis base strength, the power to donate electrons governed by inductive and resonance effects but uncomplicated by the steric effects which plague the other measurements of Lewis base strengths. This should prove to be a useful method for the separation of steric effects from the other effects in determination of Lewis base strengths. A more thorough treatment of this phase of the use of δ_K values will be presented in a later paper.

While δ_K values are governed by inductive and resonance effects, $\delta_{K\text{-Me}}$ values should only be governed by inductive effects. The reasoning behind this assumption was that the resonance effects of a series of alkyl substituted compounds should be fairly constant from the methyl substituted compound up to the higher members. (Note that for alkyl substituents the σ_R value of CH_3 is -0.13 while the σ_R value of t-C_4H_9 is -0.12.) This assumption seems justified for if one looks at the $\delta_{K\text{-Me}}{}^{(n)}$ values, they seem to be integral multiples for any one substituent. Comparison of $\delta_{K\text{-Me}}$ values derived from the amine series *vs.* Taft σ^* values using CH_3 as 0.00[26] (these are also related to Taft σ_I values) indicates that there is fairly linear relationship between the two sets of values. (Please bear in mind that the $\delta_{K\text{-Me}}$ values are small differences between two fairly large numbers which both have large measuring errors. If the data were more accurate, presumably there would be even better correlation.) It seems quite probable that $\delta_{K\text{-Me}}$ values and σ^* values can be converted from one to another when enough data become available for comparison. This actually is not surprising since the methods both use the CH_3 group as the standard and presume to measure only the inductive effect.

There are several other quantitative relationships which are followed by these δ_K values for alkyl substituents:

$$\delta_K{}^{(1-0)} - 0.44 = \delta_K{}^{(2-1)} \text{ in ev.} \qquad (1)$$
$$\delta_K{}^{(2-1)} - 0.33 = \delta_K{}^{(3-2)} \text{ in ev.}$$

These equations are followed for the whole series of alkyl substituents studied by this method.

$$\delta_{K\text{-Me}}{}^{(2)} = 2\,\delta_{K\text{-Me}}{}^{(1)} \qquad (2)$$
$$\delta_{K\text{-Me}}{}^{(3)} = 3\,\delta_{K\text{-Me}}{}^{(1)}$$

Again, the relations are surprisingly accurate considering that these $\delta_{K\text{-Me}}$ values are a small difference between two large numbers with appreciable measuring errors.

Alkyl Radical Series.—The assumption that the δ_K values were actually a set of constants and could be carried over from one series of compounds to a *similar* series of compounds was confirmed by calculations of δ_K values derived from the alkyl radicals. Only "direct" values for ionization potentials of radicals were used because of the discrepancies of some of the "indirect" values noted earlier. In Table II are listed the δ_K values calculated from the alkyl radicals using CH_3 as the parent compound. The agreement between the δ_K values from amines and the δ_K values from alkyl radicals is excellent which might be expected since the two series are not too dissimilar. The only value for which there is even a slight discrepancy is that of the i-C_4H_9 radical which gives a δ_K for an i-C_3H_7- group and this value of $I(i\text{-}C_4H_9)$ was also questioned as being unexpectedly low by the investigators who performed the actual measurements of the ionization potentials of the radicals.[21]

TABLE II

δ_K VALUES DERIVED FROM THE ALKYL RADICAL SERIES $CH_3\cdot$ PARENT COMPOUND

Radical	Substituent	$\delta_K{}^{(1)}$	$\delta_K{}^{(2)}$	$\delta_K{}^{(3)}$
$CH_3\cdot$		0.00		
$C_2H_5\cdot$	CH_3–	1.18		
i-$C_3H_7\cdot$	$2CH_3$–		2.06	
t-$C_4H_9\cdot$	$3CH_3$–			2.54
n-$C_3H_7\cdot$	C_2H_5–	1.27		
n-$C_4H_9\cdot$	n-C_3H_7–	1.32		
i-$C_4H_9\cdot$	i-C_3H_7–	1.61		
sec-$C_4H_9\cdot$	CH_3– C_2H_5–		2.03	

A semi-empirical method of calculating ionization potentials in a homologous series has been developed,[29,30] and a "simplified" method in which group orbitals are employed[31] has been used to calculate ionization potentials for hydrocarbon derivatives, other types of compounds and alkyl-free radicals.[32-35] This "simplified" calculation as applied to the alkyl free radicals requires four parameters.

1. The potential parameter for a saturated alkane or alkyl CH_3 group, which is taken as the ionization potential of CH_4.
2. A saturate–saturate interaction, designated as b, which is taken as the difference $I(CH_4)$–$I(C_2H_6)$.
3. The parameter associated with a free CH_3 group, taken as $I(CH_3)$.
4. A saturate–unsaturate interaction, c, evaluated from the $I(C_2H_5)$ using the determinant.

$$\begin{vmatrix} e - E & c \\ c & -E \end{vmatrix} = 0$$
$$\text{where } e = I(CH_4) \qquad E = I(C_2H_5)$$

This "simplified" method, in addition to not being very simple, requires a knowledge of four parameters. These parameters while available for alkyl compounds are virtually unobtainable for many other types of compounds.

Since the δ_K values from the amines seem to carry over quantitatively into the alkyl radicals, the authors felt that calculation of the ionization potential of the *sec*-C_4H_9 radical by the δ_K method should indicate the versatility of this method since δ_K for the exact pair of substituents was not measured as such in the amine series. Considering the CH_3 radical as the parent compound, the substituents are a CH_3 group and a C_2H_5 group. Obviously the

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(29) G. G. Hall, *Proc. Royal Soc. (London)*, **A205**, 541 (1951).

(30) J. Lennard-Jones and G. G. Hall, *Discussions Faraday Soc.*, **10**, 18 (1951).

(31) J. Lennard-Jones and G. G. Hall, *Proc. Roy. Soc. (London)*, **A213**, 102 (1952).

(32) G. G. Hall, *Trans. Faraday Soc.*, **49**, 113 (1953).

(33) G. G. Hall, *ibid.*, **50**, 319 (1954).

(34) J. L. Franklin, *J. Chem. Phys.*, **22**, 1304 (1954).

(35) D. P. Stevenson, Preprint No. 29, Am. Chem. Soc. Meeting, March, 1954.

ionization potential had to obey the inequality

$$I(\mathrm{CH_3}) - |\delta_\mathrm{K}{}^{(1)}(\mathrm{CH_3})| - |\delta_\mathrm{K}{}^{(1)}(\mathrm{C_2H_5})| \neq I(sec\text{-}\mathrm{C_4H_9})$$

since the left-hand side of the equation would completely disregard the saturation effect of substituting a second group when a first group had already been substituted.

There are three possible approaches to calculating the ionization potential of the *sec*-C_4H_9 radical by use of the δ_K values. The first method is

$$I(\mathrm{CH_3}) - |\delta_\mathrm{K}{}^{(2)}(\mathrm{CH_3})| - |\delta_\mathrm{K\text{-}Me}{}^{(1)}(\mathrm{C_2H_5})| = I(sec\text{-}\mathrm{C_4H_9})$$
$$9.96 - 1.91 - 0.11 = 7.94 \text{ e.v.}$$

The second method is

$$I(\mathrm{CH_3}) - |\delta_\mathrm{K}{}^{(1)}(\mathrm{CH_3})| - |\delta_\mathrm{K}{}^{(2-1)}(\mathrm{C_2H_5})| = I(sec\text{-}\mathrm{C_4H_9})$$
$$9.96 - 1.18 - 0.85 = 7.93 \text{ e.v.}$$

The third method is

$$I(\mathrm{CH_3}) - |\delta_\mathrm{K}{}^{(1)}(\mathrm{C_2H_5})| - |\delta_\mathrm{K}{}^{(2-1)}(\mathrm{CH_3})| = I(sec\text{-}\mathrm{C_4H_9})$$
$$9.96 - 1.29 - 0.73 = 7.94 \text{ e.v.}$$

The experimentally measured value by direct electron impact of the *sec*-C_4H_9 radical is 7.93 ev. The three different methods of using the δ_K values to calculate ionization potentials seem to be all equally valid and to give excellent agreement with the experimentally measured value. The values calculated by other authors

$$I(sec\text{-}\mathrm{C_4H_9}) = 7.76^{35} \text{ or } 7.87^{21} \text{ e.v.}$$

using the SGO method ("simplified" group orbital method) while reasonably close to the experimental value are not in this case in as good agreement with the actual value as the $I(sec\text{-}C_4H_9)$ calculated by the δ_K method.

This particular approach to the additive use of δ_K values where ionization potential effects are governed by all the substituents interdependently should have a direct bearing on another most important field, reactivities as governed by σ^* or σ_I values. There does not seem to be much experimental work on σ^* or σ_I values for increasing substitution of the same group ($\sigma^{*(1)}$, $\sigma^{*(2)}$, $\sigma^{*(3)}$ or $\sigma_I{}^{(1)}$, $\sigma_I{}^{(2)}$, $\sigma_I{}^{(3)}$ would be the nomenclature) let alone work on σ^* or σ_I values for combinations of different groups. However, the same principles should govern the additivity of σ^* and σ_I values as governs the additivity of $\delta_{K\text{-}Me}$ and δ_K values and again the two sets of δ and σ values presumably can be interrelated when enough data become available for comparison.

This additive use of δ_K values certainly can be used in the amine series to calculate the ionization potentials of amines of the type $R_1R_2R_3N$ and consequently the "absolute" Lewis base strength of these amines.

In Table III is presented a comparison of the ionization potentials of the alkyl radicals calculated by the δ_K method, calculated by the "simplified" group orbital (SGO) method, observed by direct electron impact of radicals and observed by indirect electron impact of molecules. The ionization potentials calculated by the δ_K method are in excellent agreement with the experimentally measured direct values and most certainly would indicate a number of the indirect ionization potentials were in serious error.

TABLE III

IONIZATION POTENTIALS OF ALKYL RADICALS (IN EV.)

Radical	Substituent	I(radical) calcd. by δ_K method	I-calcd. by SGO method[21]	I-obsd. by direct e impact of radicals[21]	I-obsd. by direct e impact of molecules[21]
$CH_3\cdot$				9.96	
$C_2H_5\cdot$	CH_3-	8.78	8.78	8.78	
i-$C_3H_7\cdot$	$2CH_3-$	8.05	7.97	7.90	7.43
t-$C_4H_9\cdot$	$3CH_3-$	7.63	7.32	7.42	6.90
n-$C_3H_7\cdot$	C_2H_5-	8.67	8.68	8.69	7.94
n-$C_4H_9\cdot$	*n*-C_3H_7-	8.59	8.64	8.64	
i-$C_4H_9\cdot$	*i*-C_3H_7-	8.53	8.55	8.35	
sec-$C_4H_9\cdot$	CH_3-	7.94	7.87	7.93	8.0
	C_2H_5-	7.93			
		7.94			

Mulliken[12,13] defined an intrinsic electronegativity (the power of an atom or a radical in a molecule to attract electrons) as the average of the ionization potential and the electron affinity of the group. Taft[36] has stated the electron withdrawing power of a group is due to several factors and has concluded that polar substituent constants for groups, σ^*, strongly reflect the effect on reactivity of the intrinsic electronegativities of the atoms in the group as well as other constitutional factors.

The authors of the present paper wish to comment on an observation made during this study of δ_K values and ionization potentials of carbon radicals that there is a relation between electronegativity values[37] (as defined by

$$\mathrm{RHgR' + HCl \longrightarrow RH + R'HgCl}$$

or

$$\mathrm{R_2SnR_2' + 2HCl \longrightarrow 2RH + R_2'SnCl_2}$$

where the more electronegative radical turns up as RH) and ionization potentials and that there is another relation between ionization potentials and σ^* values (a slightly different relation apparently between σ^* values and electronegativities than the one proposed by Taft).

In Table IV are listed the ionization potentials, relative electronegativities,[37] σ^* values and relative σ^* values of some substituted methyl radicals. It can be seen that there seems to be a direct correlation between electronegativities of these radicals and their ionization potentials. This could not have been inferred directly from Mulliken's relationship since the electron affinities also play a role in that definition of electronegativity. While there is a correlation between ionization potentials and σ^* values for the alkyl radicals, this correlation completely breaks down in the case of the CCl_3 and $C_6H_5CH_2$ radicals. The CCl_3 radical gives $\delta_K{}^{(3)}(Cl) = 1.18$ and the lowering of the ionization potential can be explained on the basis of some interaction of the electrons in the $4p\pi$ non-bonding orbital of the Cl atoms and the $2p_z$ orbital of the central C atom and also partially to the greater stability of the CCl_3^+ ion over the CH_3^+ ion.[23] The δ_K for a C_6H_5 group (2.14 ev.) is in the correct direction as predicted by electronegativity of the benzyl group but completely in the wrong direction if predicted solely on the basis of σ^* values (or the related σ_I values).

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(36) R. W. Taft, Jr., *J. Chem. Phys.*, **26**, 93 (1957).

(37) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

The ionization potential of the benzyl radical was measured directly[38] and it is presumed that this measured ionization potential is that of the benzyl radical itself and not that of the isomeric tropylium ion which is formed in the mass spectrometric dissociations of all parent compounds such as toluene.[39–41] It seems apparent that δ_K values do not depend solely on inductive effects.

TABLE IV

Radical	I, ev.	Relative order electro-neg.	σ^*	Relative order σ^* values
CF_3	10.10	..	.....	1
CH_3	9.95	2	0	4
C_2H_5	8.78	3	−0.100	5
CCl_3	8.78	..	+2.65	2
n-C_3H_7	8.69	5	−0.115	6
n-C_4H_9	8.64	6	− .130	8
i-C_4H_9	8.35	..	− .125	7
sec-C_4H_9	7.93	8	− .210	10
sec-C_3H_7	7.90	9	− .190	9
$C_6H_5CH_2$	7.81	10	+ .215	3
t-C_4H_9	7.42	11	− .300	11

It has been shown that the values of σ_I and σ_R are quantitative and independent measures of electron withdrawing effects of substituents through inductive and resonance interactions, respectively.[42]

$$\sigma \equiv \sigma_I + \sigma_R$$

(σ values are the Hammett σ values derived from $\sigma = \log k/k_0$ for ionization of substituted benzoic acids).

By definition: σ_I is the inductive contribution of the substituent (relative to the H atom) resulting from its power to attract or repel electrons through space and the σ bonds of the benzene system; the resonance contribution, σ_R, may be regarded as resulting from the power of the substituent to attract or repel electrons through resonance interaction with the π orbitals of the benzene system.

A correlation of nuclear magnetic shielding effects in m- and p-substituted fluorobenzenes[42] follows the equation

$$\delta^F = \alpha\sigma_I + \beta\sigma_R$$

δ^F and σ values are related to σ_I and σ_R values by two different functions.

The authors wish to project these definitions a little farther and propose that δ_K values are related to inductive and resonance parameters by an equation of the type

$$\delta_K = \alpha\sigma_I + \beta\sigma_r + \gamma \text{ (a constant)} \qquad (3)$$

where σ_I is the previously defined inductive contribution of a substituent resulting from its power to attract or repel electrons through space and σ bonds, and σ_r is the resonance contribution of a substituent resulting from its power to attract or repel electrons through resonance interaction and participation in π bond or quasi-π bond formation (hyperconjugation effects would be included in the σ_r contribution).

The above proposal is based partly on observations in CY_3 radicals but even more conclusively on a recent calculation in BY_2 radicals. The appearance potentials of $B(OCH_3)_2^+$ from $B(OCH_3)_3$ and from $HB(OCH_3)_2$ had been measured previously.[43] The bond dissociation energy $D(B\text{–}OCH_3)$ was estimated from heat of formation data[44] combined with more recent data for heat of atomization of boron. The estimated value for $D(B\text{–}OCH_3)$ is 5.14 ev. This leads to a $I[B(OCH_3)_2] = 4.4_6$ ev. The B–H bond dissociation energy in $HB(OCH_3)_2$ has not been measured; however the limits for B–H bond dissociation energy should be somewhere between 4.04 and 4.66 ev. (terminal and bridge bond dissociation energies in boron hydrides). As a check, this would lead to an $I[B(OCH_3)_2]$ of 4.3_4 to 4.9_6 ev. which is in the same range as the 4.4_6 ev. calculated from dissociation of $B(OCH_3)_3$. The $I(BH_2)$ is 8.1_2 ev. which gives $\delta_K^{(2)}$ $(OCH_3) = 3.6_6$ ev. (actually a negative value since it represents a lowering of ionization potential from that of the parent radical).

All σ_I values which are negative increase electron density at a reactive center by donating electrons inductively. σ_R values which are negative increase electron density at a reactive center by donating electrons by resonance effects. Both σ_I and σ_R values for alkyl substituents are negative as are all of the δ_K values for alkyl substituents. However, the σ_I value for an (OCH_3) group is positive (+0.23) which means inductively the (OCH_3) group is electron attracting, while the σ_R value for an (OCH_3) group is negative (−0.50) which means that with respect to resonance effects the (OCH_3) group is electron donating.

Since the $\delta_K^{(2)}$ (OCH_3) is a negative value, this implies that a resonance effect is present in the effect of substitution on ionization potential as measured by δ_K values. σ_r and σ_R may not be the same value; however, it is felt that they will be in the same direction and perhaps fairly close to one another.

δ_K values derived from the amines carry over quantitatively to the alkyl radicals. δ_K values derived from the amines probably carry over to the BY_2 radicals almost quantitatively. This is difficult to state absolutely at this time because the value for $I(BH_2)$ was derived by the authors from $A(BH_2^+)$ from B_2H_6 and several assumptions regarding dissociation products and structure of fragments and ion had to be made.[20] A comparison of the ionization potentials[23] and corresponding δ_K values for CY_3 and BY_2 radicals shows that certainly at least semi-quantitatively δ_K values carry over into the BY_2 radicals.

The δ_K values for the BY_2 radicals have an intrinsic value beyond that of predicting their ionization potentials. These δ_K values seem to be a very sensitive and delicate probe of the "absolute" Lewis acid strengths of the corresponding BY_3 molecules, just as δ_K values for amines represent a measure of an "absolute" Lewis base strength.

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(42) R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957).

(43) R. W. Law and J. L. Margrave, *J. Chem. Phys.*, **25**, 1086 (1956).

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"Absolute" Lewis acid or base strength is defined as the power to donate or attract electrons governed by inductive and resonance effects but uncomplicated by the steric effects which plague the other measurements of Lewis acid and base strengths. Using δ_K values of amines or ethers and BY_3 molecules, one can predict on the basis of electron donating effects which pairs of molecules should be able to form donor-acceptor bonds and what the relative bond strengths should be. If a pair D–BY_3 should form a donor–acceptor bond on the δ_K basis, but does not or forms only a weak bond defined in terms of the equilibrium constant, K_P, for the reaction

$$D \cdot MX_3(g) \rightleftarrows D(g) + MX_3(g)$$

then one can also derive a measure of the steric effect.

In later papers the authors will discuss δ_K values in unsaturated compounds, substituted aliphatic compounds and aromatic compounds and the relation of δ_K values to the field of donor–acceptor bonding.

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Acceptor Infrared Band Intensities in Benzene–Halogen Charge-transfer Complexes[1]

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RECEIVED JULY 20, 1959

The previously developed "electron vibration" mechanism for the enhancement of intensity of molecular vibration bands in charge-transfer complexes is extended to a calculation of the halogen stretching mode intensities in the complexes of I_2, Br_2 and Cl_2 with benzene. The simultaneous enhancement by a "permanent dipole" mechanism also is treated.

Introduction

In a previous paper[2] it was proposed that the enhancement of the intensities of molecular vibration bands in charge-transfer complexes is due to a change in amount of charge transferred from donor to acceptor during molecular vibration. This change is a consequence of the change in vertical ionization potential (for donor bands) or vertical electron affinity (for acceptor bands) during the molecular vibrations. The mechanism might appropriately be called an "electron-vibration" spectrum, since infrared absorption is due to electron motion rather than to the motion of differently charged nuclei. With the electron-vibration model the direction of dipole moment change can be perpendicular to the directions of motion of nuclei involved in the vibration. In the previous paper,[2] a calculation of the intensity enhancement of the symmetric ring breathing vibrational mode of benzene complexed with iodine was shown to be in reasonable agreement with the observed value. In the present report is presented a similar calculation for the acceptor stretching mode intensity in the benzene complexes.

Theory

The Mulliken[3] charge-transfer theory assumes a wave function for the ground state of a weak complex

$$\Psi_c \sim \Psi_o + b\Psi_D \qquad (1)$$

where Ψ_o and Ψ_D are the wave functions for no-bond and dative states, respectively. Neglecting overlap, the dative coefficient is

$$b = \frac{H_{OD}}{W} \qquad (2)$$

where $H_{OD} = \int \Psi_o H \psi_D d\tau$, and $W = I - (A + C)$; I, A and C are the ionization potential of the donor, electron affinity of the acceptor and the coulomb and other energy terms, respectively. The dipole moment of the complex is

$$\mu_c = b^2 \mu_D \qquad (3)$$

where μ_D is the moment of the complex in the zero order dative state. The binding energy is (neglecting repulsive and dispersion forces which tend to cancel)

$$E_c \cong b^2 W \qquad (4)$$

The ultraviolet absorption frequency is

$$h\nu_{uv} = W(1 + 2b^2) \sim W \qquad (5)$$

The values of b conforming to (3), (4) and (5) are listed in Table I.

TABLE I

DATIVE COEFFICIENT, BENZENE–IODINE COMPLEX

$b = 0.17$	Dipole moment	$\mu_c = 0.72D$	ref. 3 (with $S = 0.1$)
.21	Dipole moment	$\mu_c = 0.72D$	with $S = 0$
.286	Dipole moment	$\mu_c = 1.80D$	G. Kortüm and H. Walz, *Z. Elektrochem.*, **57**, 73 (1953)
.13	Binding energy	$\Delta H = -0.057$	e.v., T. M. Cromwell and R. L. Scott, THIS JOURNAL, **72**, 3825 (1950)
.37	Ultraviolet spectra		S. H. Hasting, J. L. Franklin, J. Schiller and F. A. Matsen, THIS JOURNAL, **75**, 2900 (1953)

Calculation of B

The integrated intensity of an infrared absorption band is given by

$$B = \frac{N\pi}{3c^2}\left(\frac{\partial\mu}{\partial Q}\right)^2 \qquad (6)$$

Here N is the absorber concentration. From (3)

$$\frac{\partial\mu}{\partial Q} \cong \frac{\Delta\mu_c}{\Delta Q} = \mu_D 2b\frac{\Delta b}{\Delta Q} \qquad (7)$$

Using (2) and (3), assuming H_{OD} is approximately constant and setting $W \sim h\nu_{uv}$ (7) becomes

$$\frac{\Delta\mu_c}{\Delta Q} = \frac{2\mu_D b^2}{h\nu_{uv}L}\left(\frac{\Delta W}{\Delta r}\right) \qquad (8)$$

where L relates the normal coördinate to the symmetry coördinate. $L = \sqrt{\text{reduced mass}}$, for a diatomic molecule.

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[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] E. E. Ferguson and F. A. Matsen, *J. Chem. Phys.*, **29**, 105 (1958).

[3] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).