Spectroscopic Electronegativities of Alkyl Groups. A Method for Estimating Ionization Potentials of Di- and Triradicals

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A set of alkyl group parameters that are transferable and additive has been derived from the ionization potentials of the corresponding radicals. These parameters, which are related to spectroscopic electronegativities, have been correlated with ^{13}C NMR data of (a) alkyl halides, (b) aliphatic hydrocarbons, (c) aromatic hydrocarbons, (d) *p*-alkyl-substituted acetophenones, (e) olefinic compounds, (f) secondary alcohols, (g) aldehydes and ketones, and (h) 2,6-alkyl-substituted *p*-benzoquinones. Sequences of ^{13}C chemical shift data of monohalogen derivatives of acyclic, monocyclic, and bicyclic hydrocarbons are shown to be interrelated, a fact that permits the estimation of electronegativities of di- and trivalent alkyl substituents and ionization potentials of di- and triradicals. For example, the ionization potential of the triradical **11b** derived by "homolytically removing" the CX fragment from 1-haloadamantanes was estimated as 30.7 eV, from the fluoride, 29.3 eV, from the chloride, 29.2 eV, from the bromide, and 28.98 eV from the iodide, a range of 1.72 eV. In general, the estimated ionization potentials range between 0.23 and 1.72 eV for triradicals and 1.08 and 5.14 eV for diradicals. Correlations are also reported between sequences of ^{13}C chemical shift data and the corresponding thermochemical data, as a corollary of the correlations between spectroscopic electronegativities and ^{13}C chemical shift data.

Introduction

In organic chemistry, alkyl groups, like other functionalities such as atoms, may be introduced, transferred, rearranged, etc., and in all these transformations they retain their integrity. The question then arises as to whether there is a group parameter directly related to the energy of the group that retains its "integrity" as well. For atoms the spectroscopic electronegativity can be considered to be such a parameter.[1] Indeed, spectroscopic electronegativities, unlike other electronegativities, such as Pauling's[2] or Mulliken's,[3] do not[4] exhibit the property of equalization.[5] Thus, spectroscopic electronegativities have been shown to be transferable and additive parameters.[6] In other words, they can be used as additive substituent constants and, as such, can be correlated with physical and chemical data. For example, the ionization potentials of ferrocene and symmetrically substituted chloroferrocenes[7] correlate almost perfectly with the $\Sigma\chi_{spec}$(H,Cl), Figure 1 and regression eq 1.

$$\mathrm{IP}(\mathrm{Cp_2'Fe}) = 0.326_4\Sigma\chi_{spec}(\mathrm{H,Cl}) + 3.165_6 \quad (r = 0.996) \qquad (1)$$

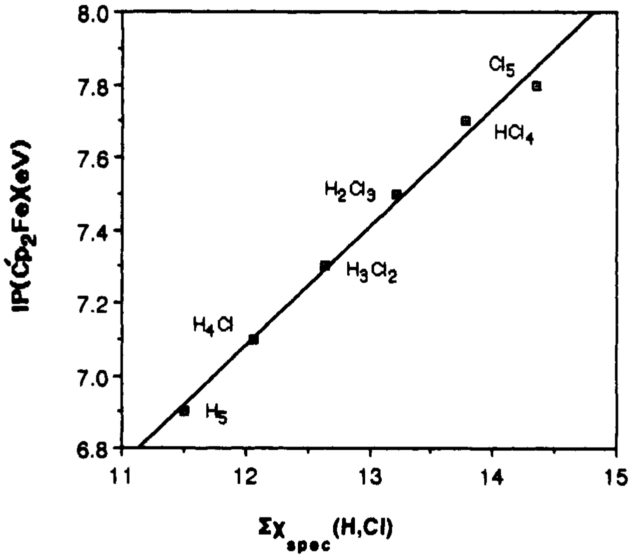

Figure 1. Ionization potentials of ferrocene and symmetrically substituted chloroferrocenes plotted against the respective sums of the spectroscopic electronegativities of hydrogen and chlorine atoms.

Spectroscopic electronegativities[1] are defined by eq 2, where *m* and *n* are the number of valence shell p and s electrons, respectively, and ϵ_p and ϵ_s are the multiplet-averaged ionization energies of a p or an s electron in a singly ionized atom. According to this definition, the s-block elements should have spectroscopic electronegativities that are directly proportional to the corresponding gas-phase ionization potentials, eq 3. It thus follows that

$$\chi_{spec} = \frac{m\epsilon_p + n\epsilon_s}{m + n} \qquad (2)$$

$$\chi_{spec} = 2.30016\mathrm{IP(E)}\ (\mathrm{IP\ in\ Ry}) \qquad (3)$$

a measure of the electronegativity of an s-block element, e.g., H, is the energy change of the gas-phase process (4).

$$\mathrm{H^\bullet \rightarrow H^+ + e^-} \qquad (4)$$

By analogy, we define the electronegativity of an alkyl group R as the energy change of the gas-phase process (5), i.e., the ionization potential of R•.

$$\mathrm{R^\bullet \rightarrow R^+ + e^-} \qquad (5)$$

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[1] Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.

[2] Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570.

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Table I

group R	IP(R$^\bullet$) (eV)	χ_{spec}(R)
H	13.598	2.300
CH_3	9.84	1.664
Et	8.39	1.419
n-Pr	8.09	1.368
n-Bu	8.02	1.357
i-Bu	7.93	1.341
n-C_5H_{11}	7.85	1.328
neo-C_5H_{11}	7.88	1.333
s-Pr	7.36	1.245
s-Bu	7.25	1.226
t-Bu	6.70	1.133
t-C_5H_{11}	6.60	1.116

In the past one of us has correlated IP(R$^\bullet$)'s with thermochemical and kinetic data.[8,9] In this work we report a set of χ_{spec}(R) parameters for various alkyls and show that these parameters are connected to atomic spectroscopic electronegativities via χ_{spec} for hydrogen. These new alkyl group electronegativity parameters, like their atomic counterparts, are transferable and additive, and their utility is demonstrated by a number of correlations between ^{13}C NMR data and χ_{spec}(R,H) or $\Sigma\chi_{spec}$(R,H). These correlations allow the estimation of spectroscopic electronegativities of di- and trivalent alkyls and the ionization potentials of di- and triradicals.

Spectroscopic Electronegativities of Alkyl Groups. Table I summarizes the presently accepted values for the ionization potentials[10] of various alkyl free radicals and the corresponding χ_{spec}(R) values derived from eq 3.

The χ_{spec}(R) were derived by multiplying the IP's in Ry by 2.300 16 so as to correspond directly to the χ_{spec}'s for atoms. It should be noted that ionization potentials, like other thermochemical parameters, are under continuous revision, and the same follows, therefore, for χ_{spec}(R). Specifically, for IP(Et) we favor the value 8.39 eV[10b] over the value 8.09 eV recommended by ref 10a. It is felt that the better agreement of the value 8.39 eV with the rest of the data in the correlations reported below could be indicative of its reliability.

We can demonstrate the utility of the above alkyl group electronegativities by correlating them with NMR spectroscopic data. The ^{13}C NMR shift of the α-carbon in $R^1R^2R^3CX$,[11] where R^i = an alkyl or hydrogen and X = halogen, exhibits a pronounced dependence upon the type of the substituent R^i. For example, in the series CH_3I, EtI, n-PrI, s-PrI, n-BuI, t-BuI, Et_2CHI, and Et_3CI, the range of the structural effect is 95.62 ppm! This, in turn, implies that the effect of an alkyl group on the shielding around C(α) of the alkyl halides is pronounced and very sensitive to structural changes on the alkyl group. It would be interesting, therefore, to find an alkyl parameter which is capable of expressing this phenomenon in a quantitative way. We now show that χ_{spec}(R) appears to be such a parameter. In Figure 2 the δ for C(α) is plotted versus the sum of $\chi_{spec}(R^i)$'s, i.e., *the sum of the spectroscopic electronegativities of the alkyl groups attached to C(α).* The linearity is very good indeed, and the important point is that the case for which $R^1 = R^2 = R^3 = H$ also fits the correlation. This implies that the reported χ_{spec}(R)'s are connected to the atomic χ_{spec} parameters.[1] Similar correlations hold for the sequences where X = F, Cl, and Br,[11] entries 1–4, Table II. Therefore, like the atomic χ_{spec} parameters, the χ_{spec}(R) parameters are also additive and transferable. Table II summarizes analogous correlations for aliphatic hydrocarbons, entry 5, aromatic hydrocarbons, entry 6, *p*-alkyl-substituted acetophenones, entry 7, olefinic compounds, entries 8, 9, secondary alcohols, entry 10, aldehydes and ketones, entry 11, and 2,6-alkyl-substituted *p*-benzoquinones,[12] entry 12.

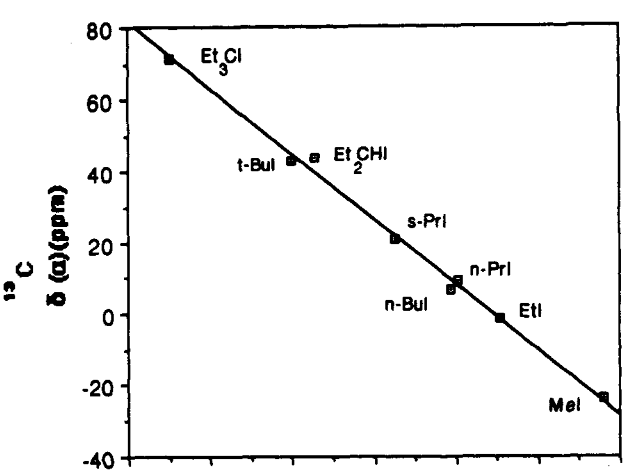

Figure 2. ^{13}C chemical shifts of C(α) in alkyl iodides plotted against the respective sums of the spectroscopic electronegativities of alkyls that are attached to C(α).

It is of interest to note that the magnitude of the slope of the regression equations reflects the range of the structural effect of the correlated data. Thus, in the series of alkyl halides, entries 1–4, Table II, we notice that the slope increases with decreasing electronegativity of the halogen. This may be understood on the basis of a competition between the alkyl groups and the halogen atom for shielding of the ^{13}C nucleus. This competition is more in favor of the alkyl groups in alkyl iodides than in alkyl fluorides, hence the large range of the structural effect in the sequence of alkyl iodides. These correlations have a number of important implications. If two sequences of data correlate with the same $\Sigma\chi_{spec}$(R)'s, then they should be linearly related to each other. This is indeed the case as shown, for example, in Figure 3, where the ^{13}C chemical shift of C(α) of alkyl chlorides is plotted against the corresponding chemical shift for alkyl fluorides, bromides and iodides. Interestingly enough, the correlations in Figure 3 appear to be of a broader scope than was expected, and besides simple alkyl halides, we may include monocyclic as well as bicyclic halides. Moreover, the same data cross-correlate. Namely, the sequence of ^{13}C chemical shifts for methyl halides, for example, plots linearly against the corresponding C(α) shifts for any RX, Figure 4, where for the sake of clarity the cases for which R = Et, cyclobutyl, and 1-bicyclo[2.2.2]octyl are included. The compliance, therefore, of mono- and bicyclic halides with the same correlations with the simple alkyl halides,

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[8] Screttas, C. G. *J. Org. Chem.* **1979**, *44*, 1471.

[9] Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1989**, *54*, 5132; *J. Org. Chem.* **1991**, *56*, 1615.

[10] IP's were taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. Levin, R. D.; Lias, S. G. Ionization Potential and Appearance Potential Measurements, 1971–1981; NSRDS-NBS 71.

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Table II. Regression Equations of $\delta^{13}C$ vs $\chi(R)$ or $\sum\chi(R)$ Correlations

entry no.[a]	sequence	regr eq	*r*	*n*
1	RF	$\delta(ppm) = 144.67 - 10.373\sum\chi(R)$	0.993	6
2	RCl	$\delta(ppm) = 171.31 - 20.995\sum\chi(R)$	0.994	9
3	RBr	$\delta(ppm) = 198.31 - 27.120\sum\chi(R)$	0.996	9
4	RI	$\delta(ppm) = 227.55 - 36.564\sum\chi(R)$	0.997	8
5	RH	$\delta(ppm) = 105.54 - 11.193\sum\chi(R)$	0.996	5
6	PhR	$\delta(ppm) = 170.61 - 18.790\chi(R)$	0.981	7
7	*p*-$RC_6H_4COCH_3$	$\delta(ppm) = 178.20 - 20.616\chi(R)$	0.995	5
8	$R^1R^2C^*{=}CH_2$	$\delta(ppm) = 76.96 + 9.832\sum\chi(R)$	0.960	10
9	$R^1R^2C^*{=}CHCOCH_3$	$\delta(ppm) = 194.29 - 12.798\sum\chi(R)$	0.986	5
10	R^1R^2CHOH	$\delta(ppm) = 129.95 - 19.879\sum\chi(R)$	0.999	9
11	$R^1R^2C{=}O$ (R=R,H)	$\delta(ppm) = 243.84 - 11.183\sum\chi(R)$	0.993	13
12	2,6-*p*-dialkylbenzoquinone	$\delta(ppm) = 177.96 - 9.212\sum\chi(R)$	0.995	5

[a] 1: MeF, EtF, n-BuF, s-PrF, t-BuF, Et_3CF. 2: MeCl, EtCl, n-C_5Cl, n-BuCl, n-PrCl, s-PrCl, t-BuCl, 3-pentyl Cl, Et_3CCl. 3: MeBr, EtBr, n-PrBr, i-BuBr, s-BuBr, Et_2CHBr, t-BuBr, Et_3CBr. 4: MeI, EtI, n-BuI, n-PrI, s-PrI, t-BuI, Et_2CHI, Et_3Cl. 5: n-PrC^*H_3, $Me_2C^*H_2$, Me_3C^*H, Me_4C^*, $Me_2(Et)_2C^*$. 6: PhH, C(1), $PhCH_3$, PhPr-n, PhEt, PhBu-s, PhPr-s, PhBu-t. 7: C(4), H, Me, Et, s-Pr, t-Bu. 8: H, H; H, Me; H, i-Bu; H, n-Pr; H, Et; H, s-Bu; Me, n-Pr; H, t-Bu; Me, Et; Et, Et. 9: H, H; H, Me; H, n-Pr; H, Et; Me, Me. 10: Me, Me; Et, Me; Me, s-Pr; Et, Et; Me, t-Bu; s-Pr, s-Pr; s-Pr, t-Bu; t-Bu, t-Bu. 11: H, Me; H, Et; H, n-Pr; H, n-Bu; H, s-Pr; H, s-Bu; Me, Me; Me, Et; Me, s-Pr; Et, Et; Et, s-Pr; s-Pr, s-Pr; s-Pr, t-Bu. 12: [C(2) + C(6)]/2; H, H; H, Me; Me, Me; s-Pr, s-Pr; t-Bu, t-Bu.

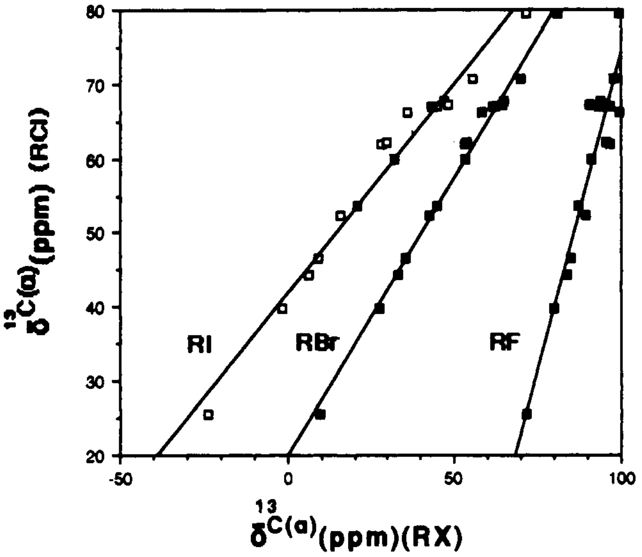

Figure 3. ^{13}C chemical shifts of C(α) in the chlorides of methyl, ethyl, n-propyl, *sec*-propyl, n-butyl, *tert*-butyl, 3-pentyl, 3-ethyl-3-pentyl, cyclobutyl, cyclopentyl, cyclohexyl, *exo*-2-norbornyl, 7-norbornyl, 1-bicyclo[2.2.2]octyl, 1-bicyclo[3.3.1]nonyl, 1-adamantyl, and 2-adamantyl plotted against the corresponding data of fluorides, bromides, and iodides.

implies, in turn, that the same data should correlate with $\chi_{spec}(R)$. Therefore, it appears to be legitimate to use certain correlations from Table II for obtaining estimates of $\chi_{spec}(R)$'s of "multivalent" substituents and ionization potentials of di- and triradicals. For example, from the sequence of the NMR data for cyclohexyl halides **3** and the correlations 1–4, Table II, we can estimate the $\chi_{spec}(R)$ of the "divalent" substituent **3a** and the IP of the corresponding diradical **3b** which results from "homolytically" removing the CHX fragment. Thus, the following estimates of the ionization potential of the latter diradical have been obtained: from the fluoride, by inserting $\delta[C(\alpha)]$ = 90.99 ppm into eq 1, Table II, we can obtain $\sum\chi_{spec}$ = 5.175, namely, the sum of the spectroscopic electronegativities of the "divalent" substituent **3a** and of the H atom. By subtracting 2.300, i.e., the spectroscopic electronegativity of hydrogen, we have an estimate of the spectroscopic electronegativity of **3a**, 2.875. From this value and eq 3 we obtain the estimate 1.25 Ry or 17.0 eV for the IP of **3b**. Similarly, from the corresponding NMR data of the cyclohexyl chloride, cyclohexyl bromide, and cyclohexyl iodide the following estimates for the IP of **3b** were obtained: 17.77, 18.07, and 17.99 eV, respectively. These estimates agree to within 1.08 eV or better and average to 17.71 eV. This value corresponds to an average value of $\chi_{spec}(R)$ = 2.996. It should be pointed out that the estimate of 17.71 eV corresponds to the enthalpy change for the *simultaneous* ejection of two electrons from the diradical **3b** and its transformation to the respective dication in the gas phase, at 298.15 K. An indication that the estimates of IP for **3b** are reasonable can be obtained from eq 10. By inserting the $\delta[C(\alpha)]$ of cyclohexanol (69.5 ppm) into eq 10, we extract the spectroscopic electronegativity parameter of **3a**, $\chi_{spec}(R)$ = 3.040. The latter gives an estimate for the IP of **3b** of 17.97 eV. Indeed, the latter number agrees to within 0.26 eV with the average value obtained from eqs 1–4, Table II, and the relevant NMR data of cyclohexyl halides. Further support for the method of estimating IPs of diradicals comes from the fair agreement between the average IP of **2b** obtained from eqs 1–4, Table II, and the value calculated from eq 10, Table II, and the $\delta[C(\alpha)]$ of cyclopentanol, 73.3 ppm, namely 16.94 versus 16.85 eV, respectively. Somewhat less satisfactory agreement between the above estimates and those obtained from eq 11, Table II, and the ^{13}C chemical shift of the carbonyl carbon in cyclohexanone and cyclopentanone, 18.68 and 19.0 eV, compared to 17.71

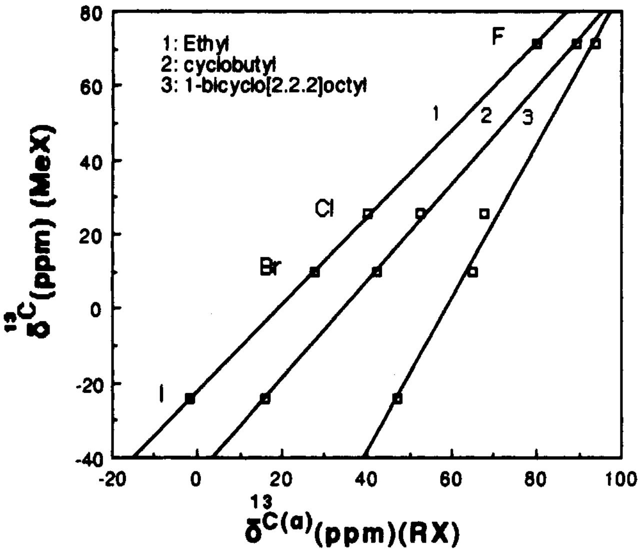

Figure 4. Sequence of ^{13}C chemical shifts of methyl halides plotted against the respective sequences of ethyl, cyclobutyl, and 1-bicyclo[2.2.2]octyl halides.

Chart I

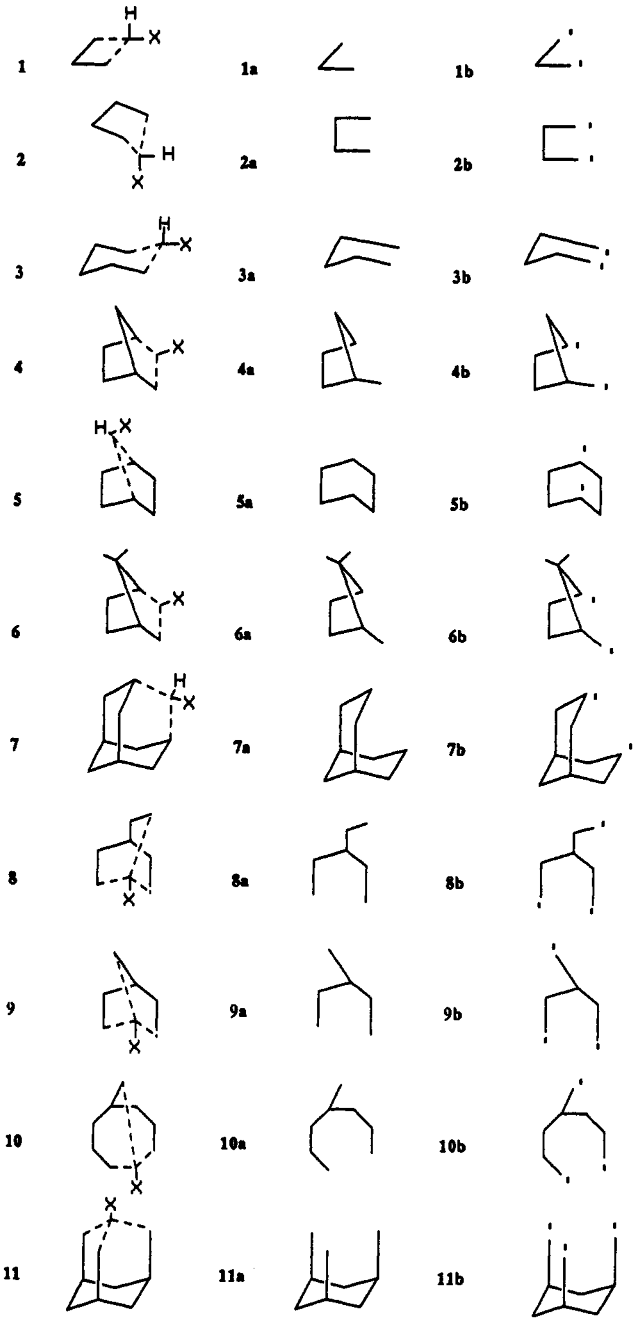

Table III. Spectroscopic Electronegativities of Di- and Trivalent Alkyl Substituents and Ionization Potentials of the Corresponding Di- and Triradicals

alkyl group	est. $\chi_{spec}(R)$[a]	radical	est. IP (eV)	range in est. IP's (eV)
1a	3.33 ± 0.24[b]	**1b**	17.85 (F)[c] 19.91 (Cl) 20.40 (Br) 20.64 (I) (ave, 19.70)	2.79
2a	2.87 ± 0.41	**2b**	13.83 (F) 17.23 (Cl) 18.06 (Br) 18.64 (I) (avg 16.94)	4.81
3a	2.996 ± 0.091	**3b**	16.99 (F) 17.77 (Cl) 18.07 (Br) 17.99 (I) (avg 17.71)	1.08
4a	2.86 ± 0.35	**4b**	14.26 (F) 17.10 (Cl) 17.93 (Br) 18.46 (I) (avg 16.91)	4.10
5a	2.66 ± 0.43	**5b**	12.29 (F) 15.97 (Cl) 16.92 (Br) 17.43 (I) (avg 15.73)	5.14
6a	3.07 ± 0.34[d]	**6b**	17.08 (Cl) 18.24 (Br) 19.08 (I) (avg 18.13)	(2.00)
7a	2.657 ± 0.097	**7b**	14.94 (F) 15.81 (Cl) 16.09 (Br) 15.98 (I) (avg 15.71)	1.15
8a	4.926 ± 0.019	**8b**	28.98 (F) 29.21 (Cl) 29.12 (Br) 29.15 (I) (avg 29.12)	0.23
9a	3.860 ± 0.017[d]	**9b**	22.87 (H) 22.77 (Me) (avg 22.82)	(0.10)
10a	4.69 ± 0.13	**10b**	26.76 (F) 28.34 (Cl) 28.05 (Br) 27.83 (I) (avg 27.75)	1.58
11a	4.997 ± 0.145	**11b**	30.70 (F) 29.30 (Cl) 29.19 (Br) 28.98 (I) (avg 29.54)	1.72

[a] The estimate was obtained from the average value of the estimated IP's using eq 3. [b] The indicated error was computed from 0.5 [range(in Ry) × 2.30016]. [c] In parentheses is shown the X in the parent compound, e.g., 1, from which the estimate was obtained. For example, from the $\delta[C(1)]$ of cyclobutyl fluoride, 89.49 ppm, and eq 1, Table II, we obtain an estimate for $\Sigma\chi_{spec}(R)$ of 5.320. From this is subtracted $\chi_{spec}(H) = 2.300$, which leaves $\chi_{spec}(R)$ for **1a**, i.e., 3.02. From this number and eq 3 we obtain an estimate for the IP of **1b** of 1.313 Ry or 17.85 eV. [d] The indicated error was calculated from [range (in Ry) × 2.30016].

and 16.94 eV, respectively. It appears reasonable to assume that the above estimates refer to the diradicals in the conformation that the corresponding fragments possess in the parent compounds, i.e., **2** and **3**. Conversely, the above results imply that the estimated $\chi_{spec}(R)$ for the divalent substituent **2a** and **3a** are fairly transferable. For example, by inserting the estimated electronegativity for **3a** from cyclohexyl halides, 2.996, into eq 10 we obtain the estimate $\delta[C(\alpha)] = 70.4$ ppm for cyclohexanol. The latter value agrees to within 0.9 ppm with the experimental value. However, the same parameter when used in conjunction with regression eq 5 to predict $\delta[C(1)]$, e.g., for 1,1-dimethylcyclohexane, gave a result that is in serious disagreement with the experimental value, i.e., 34.76 versus 30.05 ppm. It is felt that the lack of transferability of the $\chi_{spec}(R)$ of the divalent substituent **3b**, derived from the sequence of cyclohexyl halides, to 1,1-dimethylcyclohexane and the like is due to markedly different nonbonding interactions in the respective systems. Under the assumption that norbornane and 1-methylnorbornane **9** (X = H, Me) comply with the correlation for the aliphatic hydrocarbons, insertion of the appropriate $\delta(C(1))^{12}$ into regression equation 5, Table II, provides estimated $\chi_{spec}(R)$'s of 3.868 and 3.852, respectively, for the trivalent substituent **9a** corresponding to triradical **9b** which, in turn, gives us estimated IP's of 22.77 and 22.87 eV. Further results are summarized in Table III. An inspection of the data in Table III indicates that, in most cases, the estimated IP's of di- and triradicals vary in the same manner.

Namely, the estimate increases with decreasing electronegativity of the halogen. It can be noted also that the range of the estimates varies between 0.23 and 1.72 eV for triradicals and 1.08 and 5.14 eV for diradicals.

If we bear in mind that all the ^{13}C chemical shifts of monohalo derivatives of acyclic, monocyclic and bicyclic hydrocarbons are interrelated, Figures 3 and 4, it appears that the variation of the range of the estimated IP's from one sequence to another is not due to the degree of compliance of the sequences of data with the equations 1–4, Table II, but rather to factors such as strain energies, nonbonding interactions, and other factors which determine the thermochemical status of the system and that these factors depend considerably on the halogen in $R^1R^2R^3CX$. In any case, the range of the estimated values of ionization potentials from eqs 1–4, Table II, could be viewed as relatively small considering that di- and triradicals are rather high-energy species.

A comparison of the proposed set of group electronegativities with those in the literature[13] indicates that there are two important differences: (a) none of the literature sets of alkyl group electronegativities correlate with any of the data that have been correlated with χ_{spec}(R)'s, and (b) the χ_{spec}(R) parameter diminishes from primary to secondary to tertiary alkyl, whereas the opposite holds true for the respective literature parameters.[13] The lack of transferability of Mullay's values, for example,[13b] can be traced to the method of calculation, which assumes electronegativity equalization for the atoms constituting the alkyl group. The set of spectroscopic electronegativities of alkyl groups seem to correlate fairly well with the corresponding ϵ values derived over 30 years ago by Errede from bond dissociation energies.[14] In fact, the very near linearity between ϵ values and the corresponding χ_{spec}(R) is closely analogous to the correlation between ϵ values and the corresponding ionization potentials of free radicals which was reported by Neale.[15,16]

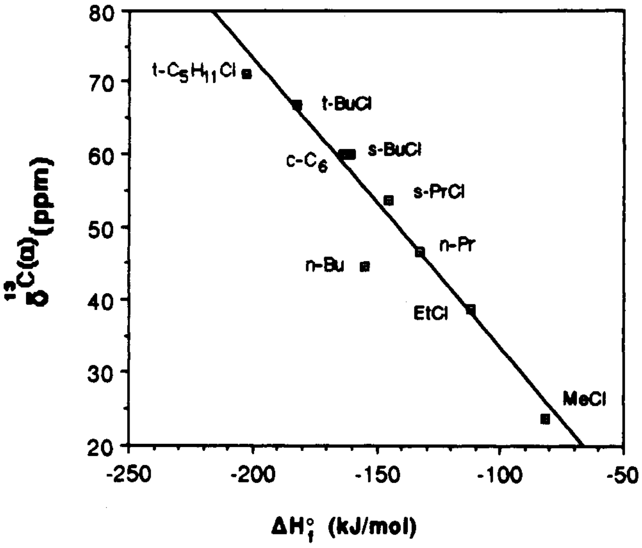

Figure 5. δC(a)'s of alkyl chlorides plotted against the corresponding enthalpies of formation (*g*, 298 K, kJ/mol).

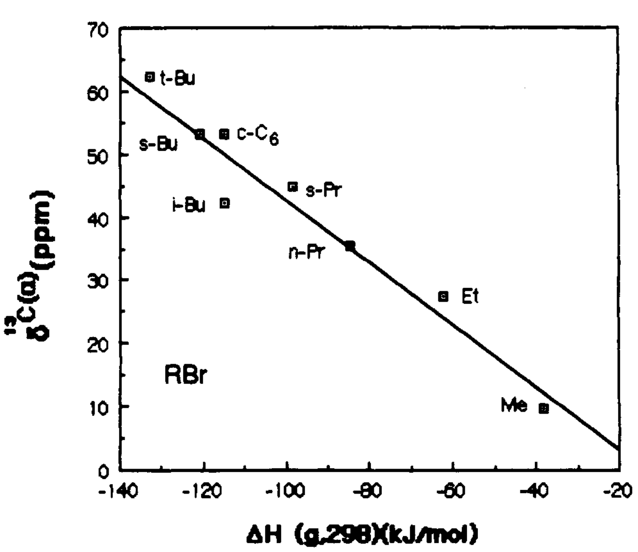

Figure 6. δC(α)'s of alkyl bromides plotted as in Figure 5.

The interrelation of sequences of ^{13}C chemical shift data recalls similar relationships involving thermochemical data,[9] and one is therefore tempted to try to combine the two sets of data. In Figures 5–7 it is shown that enthalpies of formation of alkyl chlorides, alkyl bromides, and aldehydes and ketones, respectively, plot linearly against the respective δ's for C(α). Another analogy between C-13 NMR data and thermochemical data is that ^{13}C chemical shifts of certain carbons appear to be transferable. For example, by writing an isodesmic[2,9,17] reaction such as eq 6, it can be shown that the sum of the δ's in the left-hand

$$2Et(Me)C^{*}HOH \rightarrow Et_2C^{*}HOH + Me_2C^{*}HOH \quad (6)$$

side of (6) is nearly equal to the sum of δ's in the right-hand side of the same equation, i.e., 137.4 versus 137.2 ppm. This property, which appears to be general for chemical shift of the secondary carbon of secondary alcohols and of secondary alkyl halides, can be used as an estimating scheme in relevant cases. Another way of demonstrating the transferability of the secondary carbon chemical shift in the series of secondary alcohols is the exchange reaction (7), in which an ethyl and a methyl

$$\begin{array}{llll} n\text{-}Bu(Et)C^{*}HOH + & Me_2C^{*}HOH & \rightarrow & \\ \quad 72.6 & \quad 63.4 & & \\ & \text{(sum 136.0 ppm)} & & \\ & n\text{-}Bu(Me)C^{*}HOH + & Me(Et)C^{*}HOH & (7) \\ & \quad 67.2 & \quad 68.7 & \\ & & \text{(sum 135.9 ppm)} & \end{array}$$

group exchange their positions in 3-heptanol and 2-propanol, respectively. Again, the sum of the chemical shifts on the left-hand side of (7) is very nearly equal to the sum of δ's on the right-hand side of the same equation. This property is analogous to thermoneutrality which holds, approximately, for certain isodesmic reactions.[2,9,16]

The correlation of ^{13}C NMR data with energy terms, such as χ_{spec}(R) and thermochemical data, can be understood by bearing in mind that σ_{param}, which is the dominant contribution to the shielding[17] of ^{13}C nuclei, is inversely proportional to the mean excitation energy.[18] We notice

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(13) (a) Allen, L. C.; Egolf, D. A.; Knight, E. T.; Liang, C. *J. Phys. Chem.* **1990**, *94*, 5602. (b) Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271. (c) Marriot, S.; Reynolds, W. F.; Taft, R. W.; Topsom, R. D. *J. Org. Chem.* **1984**, *49*, 959.

(14) Errede, L. A. *J. Phys. Chem.* **1960**, *64*, 1031; *Ibid.* **1961**, *65*, 2262; *J. Org. Chem.* **1962**, *27*, 3425.

(15) Neale, R. S. *J. Phys. Chem.* **1964**, *68*, 143.

(16) We are indebted to a reviewer for pointing this out.

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(18) Saika, A.; Slichter, C. P. *J. Chem. Phys.* **1954**, *22*, 26.

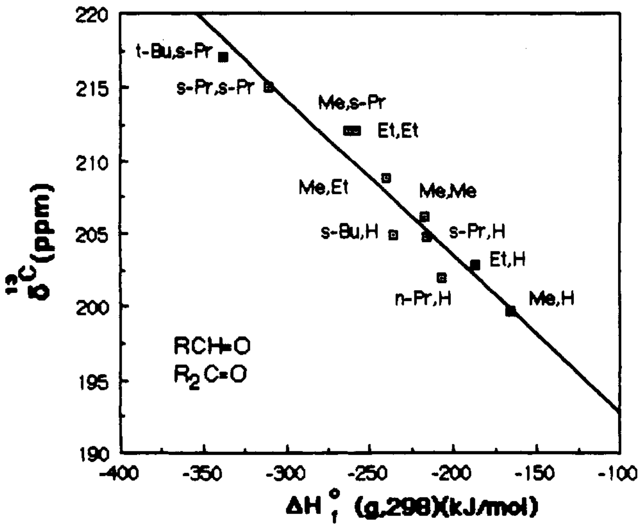

Figure 7. ^{13}C chemical shifts of the carbonyl carbon of aldehydes and ketones plotted against the respective enthalpies of formation (*g*, 298 K, kJ/mol).

that, with the exception of entry 8, Table II, the slopes of the regression equations are negative which, in turn, implies that there is an inverse relationship between δ's and $\Sigma\chi_{spec}(R)$'s. For example, for Me_2CH_2, $\Sigma\chi_{spec}(R) = 2\chi_{spec}(Me) + 2\chi_{spec}(H) = 7.928$, $\delta = 15.9$ ppm; for Me_4C, $\Sigma\chi_{spec}(R) = 4\chi_{spec}(Me) = 6.656$, $\delta = 31.4$ ppm. It appears, therefore, that there is a proportionality or linearity between $\Sigma\chi_{spec}(R)$ and mean excitation energy. This is true for all cases apart from entry 8, Table II.

Concluding Remarks

Ionization potentials of alkyl free radicals have been downscaled using eq 3 giving a set of alkyl substituent parameters which are connected to spectroscopic electronegativity parameters of atoms via hydrogen. The utility of these parameters is demonstrated by correlating them with ^{13}C chemical shifts of 12 different sequences of data. Thus, the proposed parameters, which are designated as $\chi_{spec}(R)$, appear to be transferable and additive. Corollaries of the reported correlations are the interrelation of sequences of ^{13}C chemical shift data and their connection to thermochemical data. Ionization potentials for diradicals derived from the homolytic detachment of a CHX fragment from a monocyclic halohydrocarbon and for triradicals derived from the homolytic detachment of a CX bridgehead fragment from a bicyclic halohydrocarbon may be estimated from the ^{13}C chemical shifts for the α-carbons.

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