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Could Ionization Potentials of Free Radicals Serve as Alkyl Inductive Substituent Constants?

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Four sets of heterolytic bond dissociation energies, eight sets of gas-phase ionization potentials of compounds having unshared electron pairs, five sets of activation energies of S_N2 reactions, one set of activation energies for alkaline hydrolysis of alkyl acetates, one set of activation energies for hydrogen abstraction by bromine atoms, and four sets of activation energies for gas phase unimolecular reactions, have been correlated with ionization potentials of alkyl free radicals, IP(R)'s. It has been shown that IP(R)'s can be treated as additive alkyl inductive substituent constants. For example, correlation $IP(R_1R_2C{=}O) = 0.148\Sigma IP(R_i) + 6.697$ ($r = 0.981$) covers (almost) all the available ionization data for a total of 19 aldehydes and ketones with eight different alkyl groups (plus hydrogen). Charton's steric constants υ_{OX} and $\upsilon_{NX_1X_2}$ are related to IP(R)'s as follows: $1/\upsilon_{OX} = 0.851IP(R) - 5.113$ ($r = 0.993$) and $\upsilon_{NX_1X_2} = -0.3455\Sigma IP(X_i) + 7.195$ (X = R, $r = 0.999$, eq 17). Equation 17 has been used to calculate 27 unavailable values of $\upsilon_{NX_1X_2}$. An attempt was made to rationalize most of the observed correlations.

Since the electron has been viewed as a "chemical entity",[1] it appears reasonable to wonder whether it could be considered as a substituent as well. Indeed, the presence of an odd electron in an organic chemical structure appears to impart to this structure properties, other than magnetic ones, that are markedly different from those of the parent molecule which has all its electrons paired. To limit this discussion to neutral radicals, the best, perhaps, known example that can be cited is the acidity of the radical $R_1R_2\dot{C}{-}OH$ and of the alcohol $R_1R_2CH{-}OH$ from which the radical derives. The pK_a values of these species can differ by 5–10 pK_a units, depending on the kind of R's. For example, although the alcohols ethyl, isopropyl, benzyl, and benzhydryl all have pK_a = 18,[2] the corresponding radicals, $CH_3\dot{C}HOH$, $(CH_3)_2\dot{C}OH$, $Ph\dot{C}HOH$, and $Ph_2\dot{C}OH$, differ significantly in their acidities,[3] i.e., 11.6, 12.2, 8.4, and 9.2, respectively. The structure-dependent pK_a values can be taken as the manifestation of the odd electron's ability to amplify the different contributions of R_1 and R_2 to the ionization of OH, in these radicals.

As a further example, one can compare bond dissociation energies, a molecular parameter widely used to rationalize reactivity,[4] with some other thermochemical data, such as gas phase ionization potentials. Namely, the bond dissociation energies for the series R–Br, *D*(R–Br), for R = CH_3, Et, *i*-Pr, and *t*-Bu, are respectively[5] 70, 68, 68, and 67 kcal/mol. The first gas phase ionization potentials[6] of the corresponding bromides, IP(R–Br), are respectively[7] 242.7, 236.0, 232.0, and 227.5 kcal/mol. We can see that the range of the structural effect, from CH_3Br to *t*-BuBr, in *D*(R–Br)'s is 3 kcal/mol only, as compared to 15.2 kcal/mol in IP(R–Br)'s. Again, it becomes apparent that in the case of the process where an odd electron species is involved, the effect of the alkyl substituent has been amplified to an extent which obviously depends on its structure. Even more pronounced is the difference between the range of the structural effects of *D*(R–Br)'s and of the ionization potentials of free radicals R·, IP(R)'s. Ionization potentials of free radicals are defined as the enthalpy change for reaction 1, and it is given by eq 2.

$$R\cdot \rightarrow R^+ + e^- \qquad (1)$$

$$IP(R) = \Delta H_f(R^+) - \Delta H_f(R\cdot) \qquad (2)$$

The IP(R)'s of CH_3, Et, *i*-Pr, and *t*-Bu are[7] 226.8, 193.2, 174.0, and 159.7 kcal/mol, respectively. In this case the range of the structural effect of 3 kcal/mol in *D*(R–Br)'s is compared to 67.1 kcal/mol in IP(R)'s. In the latter example the effect of the odd electron is dramatic.

The first gas phase ionization potential of a series R–X, where X is any group having unshared electron pairs or π electrons, and R = CH_3, Et, *n*-Pr, *n*-Bu, *i*-Bu, *i*-Pr, *s*-Bu, and *t*-Bu, shows a systematic decrease from R = CH_3 to R = *t*-Bu. In Table I is given the difference between the IP(CH_3-X) and IP(t-Bu-X) in kcal/mol and it is designated as range of the structural effect, RSE. It can be seen that RSE depends on X and it is maximal for X = odd electron.

Table I. Range of the Structural Effect in IP(R–X)[a]

series	RSE	series	RSE
$R–C_6H_5$	3.23	R–OH	19.82
$R–NH_2$	7.61	$R_2C{=}O$	22.36
$R–C(CH_3){=}O$	11.76	R–Cl	22.59
R–I	12.22	R_2O	23.05
R–SH	14.98	RCH=O	31.58
R–Br	15.21	R·	67.08
R_2S_2	18.44		

[a] Data taken from ref 7; RSE in kcal/mol.

Ionization potentials of free radicals derived from measurements in the dilute gas state are certainly free of complications due to solvation phenomena. It appears reasonable to believe that differences in IP(R)'s arise mainly from electronic factors and not at all from steric ones. The observed correlation between IP(R)'s and either $\sigma^*(R)$[8] or $\sigma_I(R)$ could be in support of this idea. Since IP(R)'s express the maximum possible RSE in the series of CH_3, Et, . . ., *t*-Bu radicals, then IP(R)'s could be taken as a measure of the alkyl inductive effect and be used as relevant substituent constant.

In fact, a number of linear free-energy relationships have been reported recently, relating kinetic and thermodynamic parameters for processes either in solution or in the gas phase and for polar or free-radical reactions.[9] More specifically, (a) activation energies of gas phase hydrogen abstraction from a series of hydrocarbons by a given radical were correlated with the ionization potentials of the conjugate radicals, (b) activation energies of gas phase hydrogen abstraction from a given substrate by a series of radicals were correlated with the ionization potentials of the radicals, (c) relative reactivities of organolithium compounds toward a given substrate were correlated with the ionization potentials of free radicals corresponding to the organolithium reagents, and (d) pK_a values of carbon acids were correlated with the ionization potentials of the derived radicals. Nugent and Kochi[10] have reported that log *k* for reaction 3 correlates with IP(R)'s.

$$R–Hg–R' + AcOH \rightarrow R'–HgOAc + R–H \qquad (3)$$

The purpose of this paper is to furnish further examples of correlations between IP(R)'s and various kinetic and thermodynamic parameters and to suggest the use of IP(R)'s as alkyl inductive or polar substituent constants.

Correlating IP(R)'s with Physical Parameters

A. Heterolytic Bond Dissociation Energies (HBD Energies). Beauchamp et al.[11] have defined gas-phase carbenium ion affinity for a given nucleophile as the enthalpy change in

$$R^+ + X^- \rightarrow R–X \qquad (4)$$

This parameter, which is called heterolytic bond dissociation energy, can be calculated from available thermochemical data from

$$D(R^+–X^-) = D(R–X) + IP(R) - EA(X) \qquad (5)$$

Although eq 5 does not warrant linearity between IP(R)'s and $D(R^+–X^-)$, they actually are linearly dependent on each other. For example, for the series R = CH_3, Et, *i*-Pr, and *t*-Bu and for X = Br, I, CH_3, and NH_2 the data correlated with r = 0.9996 or better. For $D(R^+–X^-)$ values and relevant data see the statement at the end of this paper. The observed linearity between $D(R^+–X^-)$ and IP(R)'s can be due to the nearly constant $D(R–X)$ in closely related series of R–X. In the case, for example, of alkyl chlorides $D(R–Cl)$ = 82 ± 2 kcal/mol. Due to the same reason, either the sum or the difference of $D(R^+–X^-)$ and $D(R–X)$ is linear to IP(R)'s. The linearity between HBD energies and IP(R)'s implies that ionization potentials of free radicals can adequately describe the relative carbenium ion stability order in the gas phase, with respect to *any* charged nucleophile.

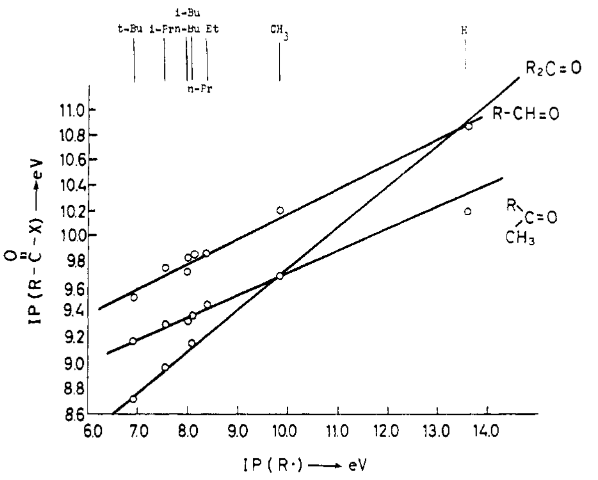

Figure 1. First gas phase ionization potentials of aldehydes, methyl ketones, and ketones plotted against the ionization potential of the relevant alkyl radical.

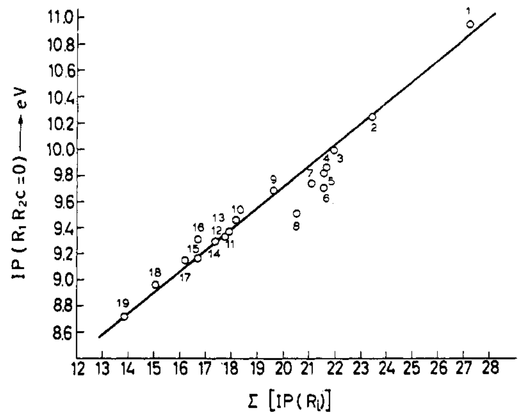

Figure 2. Plot of the first gas phase ionization potentials of the carbonyl compounds in Figure 1 against the sum of the ionization potentials of the free radicals that correspond to the two alkyl groups. The line was drawn through the points of formaldehyde, acetone, isopropyl methyl ketone, and di-*tert*-butyl ketone, with r = 0.9999: (1) H, H; (2) H, CH_3; (3) H, Et; (4) H, *n*-Pr; (5) H, *n*-Bu; (6) H, *i*-Bu; (7) H, *i*-Pr; (8) H, *t*-Bu; (9) CH_3, CH_3; (10) CH_3, Et; (11) CH_3, *n*-Pr; (12) CH_3, *n*-Bu; (13) CH_3, *i*-Bu; (14) CH_3, *i*-Pr; (15) CH_3, *t*-Bu; (16) Et, Et; (17) *n*-Pr, *n*-Pr; (18) *i*-Pr, *i*-Pr; (19) *t*-Bu, *t*-Bu.

B. Ionization Potentials. In this section are given examples of correlations between first gas phase ionization potentials of various compounds having unshared electron pairs and ionization potentials of alkyl-free radicals.[12] Considering the fact that the ionization data may originate from various laboratories and from different methods,[13] the observed correlation of the data is very good. Thus, the ionization potentials of alkyl halides, IP(R–X)'s, for X = Cl, Br, and I and R = CH_3, Et, *n*-Pr, *n*-Bu, *i*-Bu, *i*-Pr, *s*-Bu, and *t*-Bu, plot linearly with IP(R)'s with correlation coefficients r = 0.930, 0.989, and 0.983, respectively. For the ionization data used in the correlations and the regression equations see the statement at the end of this paper.

Similarly, ionization potentials of alcohols, ethers, and carbonyl compounds correlate with IP(R)'s. The ionization data for the carbonyl compounds fall on three lines, one for each subclass, i.e., for aldehydes, the ketones $R–C(CH_3){=}O$ and $R_2C{=}O$, including the cases for R = H, Figure 1. The regression lines are given by (IP's in eV)

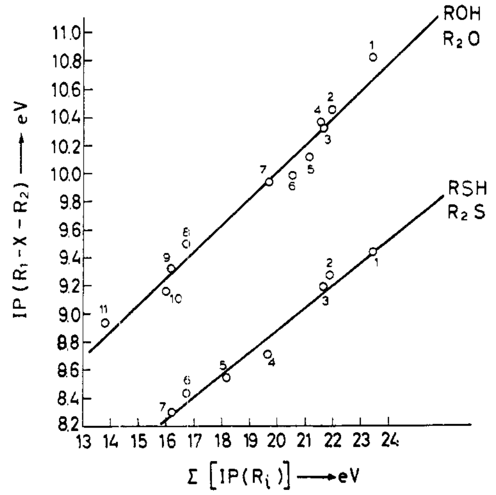

Figure 3. First gas phase ionization potentials of alcohols and ethers and thiols and thioethers plotted as in Figure 2. R_1R_2O: (1) H, CH_3; (2) H, Et; (3) H, *n*-Pr; (4) H, *n*-Bu; (5) H, *i*-Pr; (6) H, *t*-Bu; (7) CH_3, CH_3; (8) Et, Et; (9) *n*-Pr, *n*-Pr; (10) *n*-Bu, *n*-Bu; (11) *t*-Bu, *t*-Bu. R_1R_2S: (1) H, CH_3; (2) H, Et; (3) H, *n*-Pr; (4) CH_3, CH_3; (5) CH_3, Et; (6) Et, Et; (7) *n*-Pr, *n*-Pr.

$$\text{IP(RCH=O)} = 0.200\,\text{IP(R)} + 8.213 \quad (r = 0.986) \quad (6)$$

$$\text{IP(R}_2\text{C=O)} = 0.328\,\text{IP(R)} + 6.465 \quad (r = 0.998) \quad (7)$$

$$\text{IP(RC(CH}_3\text{)=O)} = 0.175\,\text{IP(R)} + 7.958 \quad (r = 0.994) \quad (8)$$

We notice that all data for the carbonyl compounds can be fitted to a single straight line, Figure 2, by treating the IP(R)'s as additive substituent constants, namely by plotting IP's for carbonyl compounds against the sum of $\text{IP(R}_1) + \text{IP(R}_2)$, where R_1, R_2 = alkyl or H. Similarly, alcohols and ethers and thiols and thioethers, respectively, fall on the same line, Figure 3. The lines in Figures 2 and 3 are expressed by (IP's in eV)

$$\text{IP(R}_1\text{R}_2\text{C=O)} = 0.148\textstyle\sum\text{IP(R)} + 6.697 \quad (r = 0.981) \quad (9)$$

$$\text{IP(R}_1\text{-O-R}_2) = 0.190\textstyle\sum\text{IP(R)} + 6.223 \quad (r = 0.987) \quad (10)$$

$$\text{IP(R}_1\text{-S-R}_2) = 0.162\textstyle\sum\text{IP(R)} + 5.644 \quad (r = 0.988) \quad (11)$$

This finding is particularly exciting because it indicates that ionization potentials of alkyl free radicals behave as alkyl inductive substituent constants.[14] The use of IP(R)'s as alkyl inductive substituent constants could be very desirable since such constants can be accessible by direct experimental methods, as contrasted to the ones which are derived from statistical analysis of kinetic data.

In fact, IP(R)'s by down scaling can be reduced to "substituent constants" designated as $\text{IP(R)}_{\text{reduced}}$, Table II, which are very close to those of Taft's new σ_I(R) values.[15] The down scaling was done by anchoring to $\text{IP(H)}_{\text{reduced}} = \sigma_I(\text{H}) = 0.000$ and $\text{IP}(s\text{-Bu})_{\text{reduced}} = \sigma_I(s\text{-Bu}) = 0.068$, according to eq 12 which reduces to eq 13.

$$-\text{IP(R)}_{\text{reduced}} = \frac{\text{IP(H)} - \text{IP(R)}}{\text{IP(H)} - \text{IP}(s\text{-Bu})}\,0.068 \quad (12)$$

$$-\text{IP(R)}_{\text{reduced}} = 0.1494 - 0.01098\,\text{IP(R)} \quad (13)$$

The most serious disagreement between $\text{IP(R)}_{\text{reduced}}$ and σ_I(R) is that for R = *i*-Bu, see Table II. The ionization potential consideration requires the *i*-Bu group to be the primary one, whereas in Taft's analysis it is viewed as a secondary one, $\sigma_I(i\text{-Bu}) \simeq \sigma_I(s\text{-Pr}) \simeq 0.065$. It should be noted that the derivation of the set of $\text{IP(R)}_{\text{reduced}}$'s is somewhat analogous to the method of Levitt and Widing[16] for deriving "sR" values. Their method is based on relating IP's of a series such as in Table I with IP(R–I)'s. Since there is a marked difference in RSE's between IP(R–I)'s and IP(R)'s, specifically 58.86 kcal/mol in favor of IP(R)'s, it is likely that the present method is more sensitive to structural effects and therefore affords a more consistent set of substituent constants. Perhaps the same could be said for the method which derives σ_I(R) values from proton affinities of primary amines.[15] Here the difference in RSE's between IP(R)'s and IP(R–NH_2)'s is 59.47 kcal/mol in favor of IP(R)'s.

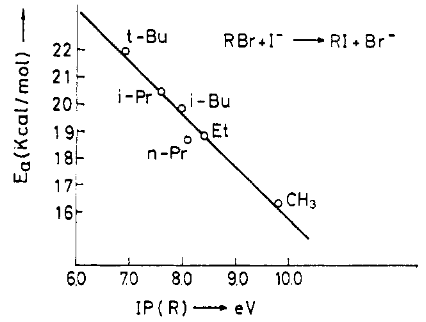

Figure 4. Activation energies of bromide displacement by iodide in acetone in a series of alkyl bromides plotted against the ionization potential of the relevant alkyl radical.

Table II

R	IP(R), eV[b]	$-\text{IP(R)}_{\text{reduced}}$	$-\sigma_I(\text{R})$[a]
H	13.60	0.000	0.000
CH_3	9.84	0.041	0.046
Et	8.38	0.057	0.056
n-Pr	8.10	0.060	0.061
n-Bu	8.01	0.061	0.063
i-Bu	8.01	0.061	0.065
i-Pr	7.55	0.067	0.066
s-Bu	7.41	0.068	0.070
t-Bu	6.93	0.073	0.074

[a] Taken from ref 15. [b] From ref 12.

Correlating IP(R)'s with Kinetic Parameters

A. Bimolecular Processes in Solution. Activation energies[17] of typical S_N2 reactions such as

$$\text{R-X} + \text{Y}^- \rightarrow \text{R-Y} + \text{X}^- \quad (14)$$

where X = halogen and Y = halogen or thiosulfate, vary linearly with IP(R)'s, with correlation coefficients ranging from *r* = 0.935 to 0.996, e.g., Figure 4. For data in the correlations and the regression equations see the statement concerning supplementary material.

Activation energies for alkaline hydrolysis of the ester series[18] such as CH_3CO_2R vs. IP(R)'s are linear with the exception of the point for R = CH_3, Figure 5. The regression line is given by

$$E_a = -2.227\,\text{IP(R)} + 29.006 \quad (r = 0.976) \quad (15)$$

E_a's in kcal/mol; IP(R)'s in eV

Charton's υ_{OX} steric constants,[19] derived from ester hydrolysis kinetic data, when plotted against IP(R)'s fall on a smooth curve, Figure 6. A plot, however, of $1/\upsilon_{\text{OX}}$ vs. IP(R) is a straight line, Figure 7, with the exception of X = CH_3. The regression equation is

$$1/\upsilon_{\text{OX}} = 0.851\,\text{IP(R)} - 5.113 \quad (r = 0.993) \quad (16)$$

X ≡ R; IP(R)'s in eV

A plot of the analogous steric constant[20] $\upsilon_{\text{NX}_1\text{X}_2}$ against IP(R)'s is linear, Figure 8. By treating IP(R)'s as additive substituent

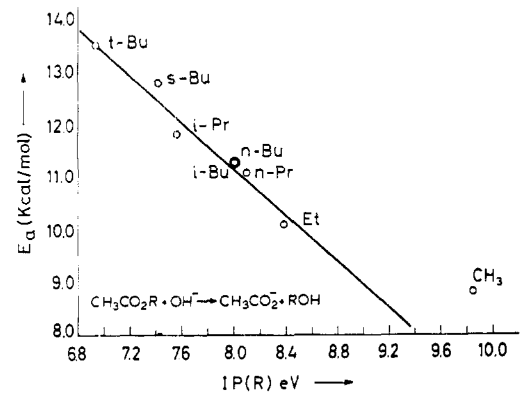

Figure 5. Activation energies for alkaline hydrolysis of a series of alkyl acetates plotted as in Figure 4.

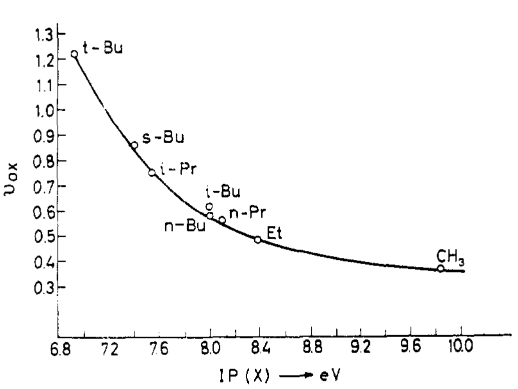

Figure 6. Charton's ν_{OX} constants plotted against the ionization potential of the radical corresponding to X.

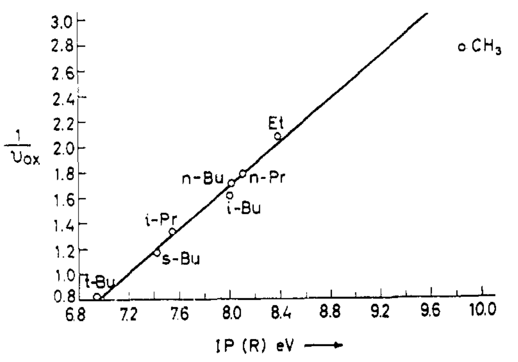

Figure 7. Plot of $1/\nu_{OX}$ against IR(R), X = R.

constants it became possible to include in the correlation the case for $X_1 = CH_3$, $X_2 = Et$. The relevant regression equation is

$$\nu_{NX_1X_2} = -0.3455(IP(X_1) + IP(X_2)) + 7.195 \quad (r = 0.999) \tag{17}$$

X_1, X_2 = alkyl; IP's in eV

The correlation covers a range of structural effects from CH_3 to *i*-Pr in IP(R)'s of 52.78 kcal/mol and therefore it does not seem too risky to use the regression equation to calculate the unavailable $\nu_{NX_1X_2}$ values. For a table with these values, a total of 27, see the statement at the end of this paper.

B. Bimolecular Processes in the Gas Phase. Hydrogen Abstraction. Activation energies[21] for hydrogen abstraction by bromine atoms from CH_3-H, Et-H, *i*-Pr-H, and *t*-Bu-H plot linear against IP(R)'s with correlation coefficient *r* = 0.999.

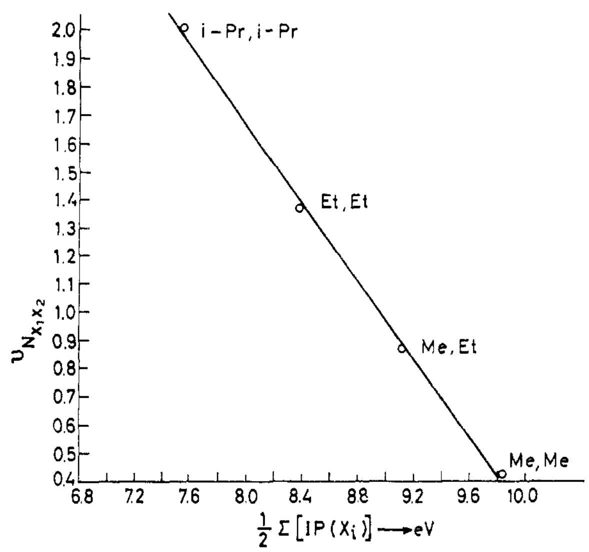

Figure 8. Plot of Charton's $\nu_{NX_1X_2}$ constant against the sum of the ionization potentials of the free radicals, corresponding to X_1, X_2.

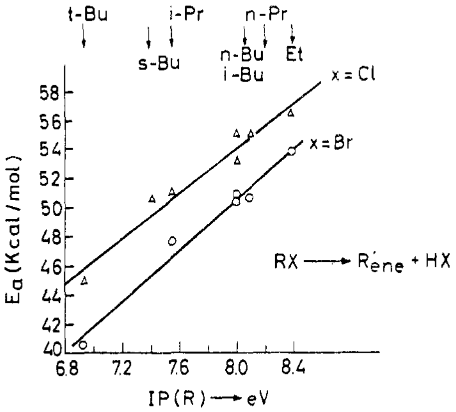

Figure 9. Activation energies of gas phase unimolecular decompositions plotted against IP(R)'s.

C. Unimolecular Processes in the Gas Phase. Activation energies[22] for reactions 18–21 are correlated with IP(R)'s, with *r* = 0.986, 0.988, 0.999, and 0.989, respectively, e.g., Figure 9. For data and regression equations see the statement at the end of the paper.

$$\text{R-Hg-R} \rightarrow \text{R}\cdot + \text{R-Hg}\cdot \tag{18}$$

$$\text{R-N=N-R} \rightarrow \text{R}\cdot + \text{R-N=N}\cdot \tag{19}$$

$$\text{R-Cl} \rightarrow \text{R'ene} + \text{HCl} \tag{20}$$

$$\text{R-Br} \rightarrow \text{R'ene} + \text{HBr} \tag{21}$$

Correlating Other Ionization Data with Kinetic Parameters

It has been observed that activation energies[21] for hydrogen abstraction by bromine atoms can be correlated with the first gas-phase ionization potential of the corresponding R-Br. Similarly, activation energies[23] for reaction 22 correlate with the ionization potentials of the corresponding alcohols, IP(R-OH)'s.

$$\text{R-H} + \text{CH}_3\text{O}\cdot \rightarrow \text{R}\cdot + \text{CH}_3\text{OH} \tag{22}$$

For data used in the correlations and regression equations see the statement at the end of this paper. It is very likely that E_a's of reactions such as (22) correlate with IP's of any series in Table I, due to the existing (possibly) linearity between the IP's of any two series in Table I. Therefore these types of correlations should be interpreted with great caution. For example, correlation between E_a's and IP(R–Br)'s by no means could be interpreted as meaning that in the transition state for hydrogen abstraction by bromine atoms there are contributions of the type $R–Br^{+\cdot} \ldots H^-$, just because E_a's correlate with IP(R–Br)'s, which, in turn, are related to the enthalpy of formation of $R–Br^{+\cdot}$ through

$$\mathrm{IP(R–Br)} = \Delta H_f(\mathrm{R–Br^{+}\cdot}) - \Delta H_f(\mathrm{R–Br}) \qquad (23)$$

General Discussion

In this section an attempt will be made to rationalize the observed correlations. The interpretation of the correlations between unshared electron pair ionization potentials and IP(R)'s appears to be rather straightforward: The observed decrease of IP's in all series of R–X, Table I, is from R = CH_3 to *t*-Bu. This decrease depends on X, as it can be seen by comparing the RSE values in Table I, and obviously parallels the ability of the R group to accommodate positive charge[24] in $R–X^{+\cdot}$. Since ionization potentials of free radicals are a direct measure of the ability of the group R to accommodate positive charge, then the observed linearity is hardly surprising.

The correlations between E_a's for both polar and free-radical reactions and IP(R)'s are certainly of the linear free energy relationship type. As such they should be expected to hold for reactions within series of structurally similar compounds in which entropy either remains constant or is linearly related to enthalpy.[9]

It is felt that these correlations could be rationalized on the basis of the relation of IP(R)'s to both homolytic and heterolytic bond dissociation energies, and through the latter to reaction enthalpies. Since it is unlikely that entropy change will vary significantly in a series of reactions involving similar reactants and products, and the transition states are presumably similar in the series, the rate constants will differ by virtue of the corresponding activation energies. If we make the reasonable assumption that reaction enthalpies are proportional to activation energies then the observed correlations can be understood. In fact, reaction enthalpies have been related to E_a's by Evans and Polanyi[25] for exoergic hydrogen abstraction reactions. Moreover, homolytic bond dissociation energies have been used to calculate E_a's either by empirical relations[26] or by semiempirical methods.[23] Very recently a relation of the Evans–Polanyi type has been reported[27] for gas phase ionic reactions. This could be a precedent for the application of the above considerations on interpreting the correlations between IP(R)'s and E_a's for ionic reactions in solution, making the additional hypothesis that contributions from solvation phenomena are nearly constant within the series of reactions where the correlations hold.

Concluding Remarks

A substantial amount of thermodynamic and kinetic data in this paper and in a previous one[9] has been correlated with ionization potentials of free alkyl radicals. These data were from processes either in the gas or the liquid phase and from polar, free radical, or unimolecular decomposition reactions. IP(R)'s can be used as additive alkyl inductive substituent constants and as such provide the first example of a set of substituent constants that can be obtained by *direct* experimental as well as theoretical[28] methods.

Supplementary Material: Table III, $\upsilon_{NX_1X_2}$ values from eq 17; Table IV, correlation of thermodynamic and kinetic parameters with ionization potentials of free radicals; Table V, IR and E_a data used in the correlations (6 pages). Ordering information is given on any current masthead page.

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