

Interpretation of Both Electron Pushing and Electron Withdrawing Inductive Effect of Alkyl Groups in Terms of Mulliken–Jaffe’s Charge Coefficient Parameters (*b*)*

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Alkyl groups can delocalize both the negative and positive charges through ion (charge)-induced dipole interaction with the polarizable alkyl groups. This charge induced polarization of the alkyl group to delocalize the charge is the origin of ‘inductive effect’ of the alkyl groups. The apparent less efficiency in negative charge delocalization compared to positive charge delocalization by a particular alkyl group is attributed to the less polarizing field strength of the anionic charge.

1. Introduction

The concept of inductive effect and its application are the important course components of organic chemistry taught at the high school and undergraduate level. Inductive effect actually delocalizes the charge [1, 2]. Depending on the properties of the atoms or groups, they can show electron withdrawing (i.e. $-I$ effect) or electron pushing (i.e. $+I$ effect) inductive effect [1, 2]. The $+I$ effect delocalizes the positive charge while the $-I$ effect delocalizes the negative charge. By considering the inductive effect of the groups or atoms, many important aspects of organic chemistry like the relative stabilities of carbocations and carbanions, acid-base strength, reaction mechanism, etc., are explained [1, 2] in the classrooms, and these are also discussed in all organic textbooks.

The inductive effect is generally explained in the conventional textbooks in terms of the simple electronegativities of the groups



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Keywords

Polarizability, inductive effect, charge capacity, charge delocalization, gas-phase acidity, solvation.

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or atoms concerned [1, 3]. The electronegativities of carbon and hydrogen are very much comparable ($\chi_C \approx 2.5$, $\chi_H \approx 2.2$ on Pauling scale) [4]. In the C–X bond, if X is less electronegative than carbon (i.e. $\chi_X < \chi_C$), then X is supposed to show the +I effect, and X is expected to show the –I effect if X is more electronegative than carbon (i.e. $\chi_X > \chi_C$). Thus the –I effect of the more electronegative substituents like halogens and the groups like OH, CN, NH₂, NO₂, CF₃, etc., is quite understandable [1]. When X is an alkyl group (R), the consideration of simple electronegativity cannot explain the nature of inductive effect of the alkyl group because the electronegativities of the alkyl groups, carbon and hydrogen are comparable (*cf.* electronegativity on Pauling scale: $\chi_C \approx 2.5$, $\chi_H \approx 2.2$, $\chi_R \approx 2.3$) [4]. In the C–R bond, the alkyl group (R) acts as an electron pushing group compared to hydrogen (H) in the C–H bond, though the alkyl group is slightly more electronegative than hydrogen. It is contradictory in terms of the simple electronegativity concept of inductive effect. But, in the common organic textbooks, the alkyl groups are described as the electron pushing groups (i.e. +I effect) to delocalize the positive charge through the inductive effect, and it explains a lot of experimental facts including the organic reaction mechanisms [1–3]. However, the origin of this +I effect of the alkyl groups is not very often explained there.

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In fact, phrases like ‘electron pushing inductive effect of the alkyl groups’, ‘positive charge delocalization by the alkyl groups’ [1–3], etc., are very often mentioned in the conventional organic textbooks, and this idea can actually explain a lot of experimental facts. But, the statement like ‘electron withdrawing inductive effect of alkyl groups to delocalize the anionic charge’ appears quite surprising to the students. In fact, the alkyl groups can delocalize both the negative and positive charges in the same way, and it has been established from the gas-phase studies [5–19] where there is no complication arising from the energetics of solvation and desolvation. Obviously, the +I and –I effect of the alkyl groups to delocalize the positive and negative charges respectively cannot be explained by considering the simple electronegativity effect. It

cannot also explain the order of inductive effect of the different alkyl groups and isomeric alkyl groups having the comparable group electronegativities on the Pauling scale ($\chi_P \approx 2.3$). Unfortunately, these aspects have been ignored for a long time in most of the organic textbooks. However, all these aspects can be nicely rationalized in terms of the inherent polarizability of the alkyl groups or any other substituents. The present article attempts to popularize this concept in terms of the Mulliken–Jaffe’s charge coefficient parameter (b) measuring the ease of polarizability [20–24].

2. Results of Gas-phase Studies

Before going into depth, let us cite the following, apparently striking observations [4–19] in gas-phase where complications from the energetics (both enthalpy and entropy factors) of solvation and desolvation do not arise.

- Stability order of the carbocationic and carbanionic centres [8–10]: $3^\circ > 2^\circ > 1^\circ$.
- Bronsted acidity order of the alcohols [11–13, 17, 25–27]: $R(3^\circ)\text{OH} > R(2^\circ)\text{OH} > R(1^\circ)\text{OH} > \text{H}_2\text{O}$; $\text{BrCH}_2\text{OH} > \text{FCH}_2\text{OH} > \text{CH}_3\text{OH}$.
- Bronsted acidity order of the carboxylic acids [5–7, 14–16, 19, 27, 28]: $\text{BuCO}_2\text{H} > \text{PrCO}_2\text{H} > \text{EtCO}_2\text{H} \approx \text{MeCO}_2\text{H}$; $\text{BrCH}_2\text{CO}_2\text{H} > \text{ClCH}_2\text{CO}_2\text{H} > \text{FCH}_2\text{CO}_2\text{H}$.

It may be noted that in aqueous phase, the above orders are reversed except in the case of carbocations. It may be noted that in solution phase, besides the inductive effect, the energetics (both enthalpy and entropy change) of solvation and desolvation contribute significantly to the overall observations.

3. Inductive Effect – Mulliken–Jaffe Electronegativity and Charge Coefficient Parameter

In terms of the group electronegativities, the electronegativity order (on Pauling scale, χ_P) is [4, 7, 20, 21]: $t\text{-Bu}$ (2.36) $>$ $i\text{-Pr}$



The alkyl groups are expected to show the more withdrawing inductive effect compared to hydrogen.

But this expectation contradicts our belief which we have learnt from the conventional organic text books.

(2.34) > Et (2.32) > Me (2.30) > H (2.25). It indicates that the alkyl groups are slightly more electronegative than hydrogen. More electronegative elements show more electron withdrawing inductive effect (*cf.* halogens vs. hydrogen). Consequently, the alkyl groups are expected to show more electron withdrawing inductive effect compared to hydrogen. But this expectation contradicts what we have learnt from the conventional organic text books. This apparent anomaly can be rationalized by considering the Mulliken–Jaffe electronegativity (χ_{MJ}) equation [20–24],

$$\chi_{MJ} = a + b\delta.$$

Here, δ denotes the partial charge (which may be cationic or anionic depending on the condition) on the group; ‘ a ’ and ‘ b ’ are the constants for a particular group or atom. The inherent or neutral atom electronegativity is measured by ‘ a ’ (in eV) which is actually Mulliken electronegativity (χ_M) given by the average value of ionization energy and electron affinity expressed in electron volt per atom or group. χ_P (electronegativity on Pauling scale) is related to the a -parameter of Mulliken–Jaffe electronegativity as follows [4, 7, 20],

$$\chi_P = 1.35 \sqrt{\chi_{MJ}} - 1.37 = 1.35 \sqrt{a} - 1.37, \text{ (for } \delta = 0\text{)}.$$

The constant ‘ b ’ actually represents the charge coefficient measuring the rate of change of electronegativity with the charge (δ), i.e. $b = d(\chi_{MJ})/d\delta$ which is the first derivative of electronegativity (χ_{MJ}) with respect to charge. Thus electronegativity is highly sensitive to δ when ‘ b ’ is large. Obviously, for the positive value of δ , the electronegativity increases linearly with the increase of the value of δ , while it decreases linearly for the negative value of δ . The effect of partial charge on electronegativity is illustrated by an example: χ_{MJ} of iodine with a partial charge of about +0.4 is almost the same as that of neutral fluorine [4].

The Mulliken–Jaffe’s charge coefficient parameter (b) is related to the charge capacity or polarizability (κ) of the group as follows

[29, 30]:

$$b = 1/\kappa.$$

Smaller value of b indicates higher value of charge accommodating capacity of the group, and in such cases, the electronegativity does not change remarkably with the accumulation of charge (δ).

For the alkyl groups, the Mulliken–Jaffe group electronegativity (χ_{MJ}) equation may be written as follows [4, 7, 31]:

$$\begin{aligned}\chi_{MJ} &= a_{\text{alkyl}} + b_{\text{alkyl}}\delta; \\ a_{\text{alkyl}} &= \frac{1}{n} \sum_{i=1}^n a_i = a_{\text{av}}; \\ b_{\text{alkyl}} &= \frac{1}{n} \times \frac{1}{n} \sum_{i=1}^n b_i = b_{\text{av}}/n,\end{aligned}$$

where a_i and b_i denote the parameters of the constituent atoms. Thus, a_{alkyl} is simply the average value of the inherent atomic electronegativities (a_i) while b_{alkyl} is the average of the charge coefficient parameters (b_i) of the constituent atoms but at the same time, inversely proportional to the number of constituent atoms. This is why, the a_{alkyl} value (measuring the inherent electronegativity) remains almost the same for different alkyl groups, but the b_{alkyl} value decreases with the increase in number of the constituent atoms, i.e. b_{alkyl} is smaller for larger groups. It is illustrated in *Table 1*.

It indicates that the inherent electronegativities (measured by the a -value) of the alkyl groups and hydrogen are more or less the same ($a \approx 7.2$ eV), but the alkyl groups being more polarizable (i.e. smaller b value), show the better charge accommodating capacity, and the larger alkyl groups with smaller values of b (*Table 1*) can accommodate the charge better. Compared to the hydrogen atom (assuming $b = 1$), the relative charge accommodating or delocalizing capacities of the alkyl groups are: H = 1, Me = 3.96, Et = 6.94, Pr = 9.88 and Bu = 12.85. The alkyl groups with smaller b -values (*Table 1*) are the better electron donors (when attached to more electronegative centres with higher a -values) and

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Table 1. Comparison of the a and b values of Mulliken–Jaffe group electronegativities (χ_{MJ}) of hydrogen, halogens (for the p -orbitals) and some representative alkyl groups [4, 7, 20, 21, 31].

Group/Atom	a (ev)	b (ev)
H	7.18	12.85
CH ₃	7.37	3.24
CH ₃ CH ₂	7.40	1.85
n -C ₃ H ₇	7.41	1.30
i -C ₄ H ₉	7.42	1.00
t -C ₄ H ₉	7.42	1.00
F	12.2	17.57
Cl	10.95	11.40
Br	8.63	10.22
CF ₃	12.85	3.90
CCl ₃	10.24	2.88

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are better electron acceptors (when attached to less electronegative centres with smaller a -values). The more or less same a -value (measuring the inherent electronegativity) of the alkyl groups and hydrogen suggests that with respect to hydrogen, the alkyl groups have no strong tendency to accommodate a particular type of charge. In fact, they can almost equally accommodate both types of charge depending on the conditions.

For the halogens, the inherent electronegativity order is: F > Cl > Br (χ -value on Pauling scale, $\chi_P = 4.0, 3.2$ and 3.0 for F, Cl and Br respectively; $a = 12.20, 10.95$ and 8.63 for F, Cl and Br respectively; [4, 7, 20]). But their charge accommodating capacity order measured by the b -value (= 17.57, 11.4 and 10.22 for F, Cl and Br respectively; Table 1) dating is in the reverse order, i.e. Br > Cl > F. Similarly, the CF₃ group ($\chi_P = 3.35$) is more electronegative than the CCl₃ group ($\chi_P = 3.03$) but their charge accommodating capacity order is reverse as the b -value of the CCl₃ group is smaller (Table 1).



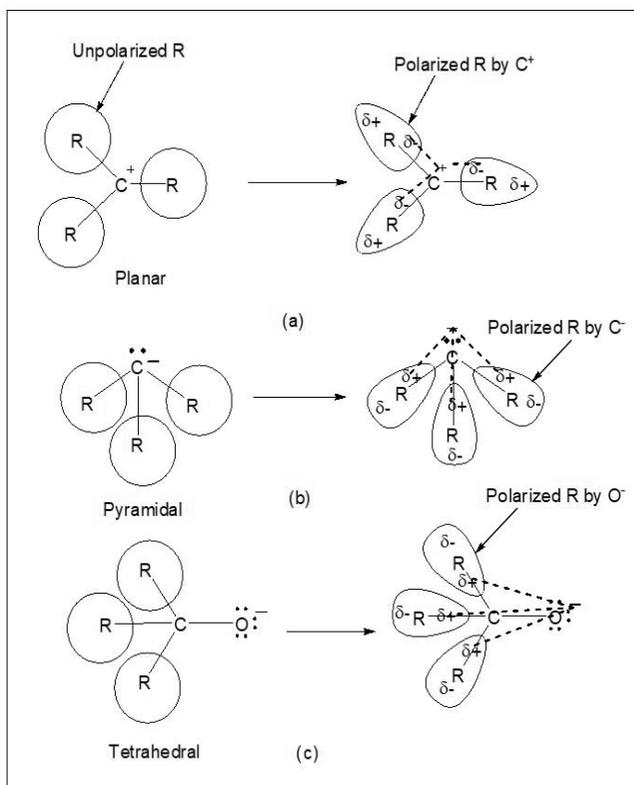


Figure 1. Illustration of charge (ion) induced dipole interaction to delocalize the charge by alkyl groups. **(a)** Delocalization of the positive charge of carbocation. **(b)** Delocalization of the negative charge of carbanion. **(c)** Delocalization of the negative charge of alkoxide

4. Charge Delocalizing Capacity and Polarizability

The charge (both positive and negative) delocalizing power of the alkyl groups can be rationalized by considering their polarizability ($\kappa = 1/b$) (*cf.* larger alkyl groups are more polarizable because of their smaller b -values). In fact, the charge delocalization occurs due to the ion or charge-induced dipole interaction [7]. This is illustrated in *Figure 1*.

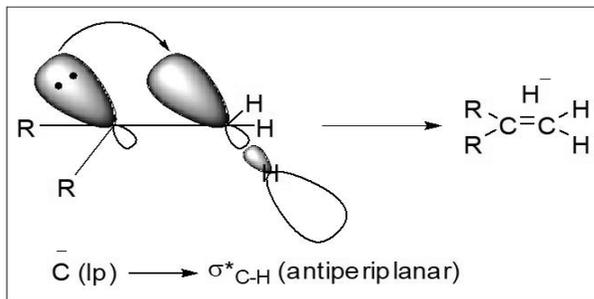
5. Charge Delocalization – Stability of Carbocations, Carbanions, Carboxylate and Alkoxide Ions

(A) Stability Order in Gas-phase

Through the polarization of the alkyl groups, they can delocalize the positive charge of the carbocations and negative charge of



Figure 2. Orbital picture of negative hyperconjugation to stabilize carbanion.



the carbanions and it can explain their stability order ($3^\circ > 2^\circ > 1^\circ$) [8–10] in gas phase where there is no complication from the energetics of solvation and desolvation. Positive hyperconjugation (i.e. heterolytic cleavage of the C–H bond to generate H^+ ion) can also delocalize the positive charge of carbocation, and negative hyperconjugation (i.e. heterolytic cleavage of the C–H bond to generate H^- ion) can also delocalize the negative charge of the carbanion. For this negative hyperconjugation [7, 27], the lone pair (housed in an sp^3 hybrid orbital) is donated to the vacant antiperiplanar σ^* -MO of the C–H bond at the alpha position to release hydride (*Figure 2*).

Here it is worth mentioning that both the negative and positive hyperconjugation share equal probabilities of delocalizing the charge in gas-phase. Due to the comparable inherent electronegativities [4, 7] (measured by the a -values; *cf.* a -value on the Pauling's scale = 2.25 and 2.50 for hydrogen and carbon respectively) of carbon and hydrogen, there is no strong permanent polarization in any direction in the C–H bond.

Delocalization of the negative charge of the alkoxides (i.e. conjugate bases of the alcohols) through the polarization of the alky groups (*Figure 1*) can explain the stability order (in gas phase): $\text{R}(3^\circ)\text{O}^- > \text{R}(2^\circ)\text{O}^- > \text{R}(1^\circ)\text{O}^- > \text{HO}^-$ which is the stability order of the conjugate bases of the alcohols. It justifies the acidity order of the alcohols in gas-phase: $\text{R}(3^\circ)\text{OH} > \text{R}(2^\circ)\text{OH} > \text{R}(1^\circ)\text{OH} > \text{H}_2\text{O}$. That the polarizability factor is the most important factor to determine the gas-phase acidity order has been supported by both qualitative [18, 26–28, 32–36] and quantitative

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[17, 25, 26, 28, 33–36] treatments. It may be noted that Pearson's HSAB (hard and soft acids and bases) principle [37–39] – “hard acids prefer to bind the hard bases while the soft acids prefer to bind the soft bases” – can also explain the experimental findings in gas-phase. The more substituted alkoxides, being softer, are more reluctant to bind the hard proton, and it reduces their basicity. On the other hand, the primary alkoxide being relatively harder prefers to bind the hard proton to show higher basicity. It makes the basicity order in gas-phase: $R(3^\circ)O^- < R(2^\circ)O^- < R(1^\circ)O^- < HO^-$. The absolute hardness ($\eta = 0.5b$) or softness ($\sigma = 1/\eta$) actually gives the measure of polarizability ($\kappa = 1/b = 0.5/\eta = 0.5\sigma$) [4, 7]. The absolute hardness (η) is defined in terms of the energies of the FMOs (frontier molecular orbitals), i.e. HOMO (highest occupied molecular orbital) and LUMO (lowest molecular orbital), as follows [40].

$$\eta = \frac{1}{2}(E_{\text{LUMO}} - E_{\text{HOMO}}) = \frac{b}{2}.$$

Obviously, higher energy difference between the HOMO and LUMO makes the species harder and less polarizable (i.e. higher b value, *cf.* polarizability, $\kappa = 1/b$) while smaller energy difference makes the species softer and more polarizable (i.e. smaller b value). When the HOMO-LUMO energy gap is smaller, a small perturbation can excite the electron from the HOMO to the LUMO, and thus the species become more polarizable. Thus the polarizability factor measured by absolute hardness (η) can explain the Bronsted acid strength order of the alcohols in gas phase [12, 13, 17, 18, 25–27, 32, 35, 36]. In the same way, by considering the delocalization of the negative charge of the carboxylates (i.e. conjugate bases of the carboxylic acids), we can explain the acid strength order in gas-phase [5–7, 14–16, 19, 27, 28]: $BuCO_2H > PrCO_2H > EtCO_2H \approx MeCO_2H$; $BrCH_2CO_2H > ClCH_2CO_2H > FCH_2CO_2H$. It may be noted that the polarizability (determined by the size and the b -values; b -value = 17.57, 11.4 and 10.22 for F, Cl and Br respectively; [4, 7, 20]) order of the halogens is: $Br > Cl > F$. In the same way, the Bronsted acidity

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order of the halogen substituted alcohols in gas-phase ($\text{BrCH}_2\text{OH} > \text{FCH}_2\text{OH} > \text{HCH}_2\text{OH}$) can be explained [26].

(B) *Stability Order in Solution Phase*

It may be noted that in the solution phase, a reverse order is noted very often as in the following cases [1–7, 16]:

1. Carbanion stability order: $3^\circ < 2^\circ < 1^\circ$.
2. Bronsted acidity order of the alcohols: $\text{R}(3^\circ)\text{OH} < \text{R}(2^\circ)\text{OH} < \text{R}(1^\circ)\text{OH} < \text{H}_2\text{O}$; $\text{CH}_3\text{OH} < \text{BrCH}_2\text{OH} < \text{FCH}_2\text{OH}$.
3. Bronsted acidity order of the carboxylic acids: $\text{BuCO}_2\text{H} < \text{PrCO}_2\text{H} < \text{EtCO}_2\text{H} < \text{MeCO}_2\text{H} < \text{HCO}_2\text{H}$; $\text{CH}_3\text{CO}_2\text{H} < \text{BrCH}_2\text{CO}_2\text{H} < \text{ClCH}_2\text{CO}_2\text{H} < \text{FCH}_2\text{CO}_2\text{H}$; $\text{CH}_3\text{CO}_2\text{H} < \text{ClCH}_2\text{CO}_2\text{H} < \text{Cl}_2\text{CHCO}_2\text{H} < \text{Cl}_3\text{CCO}_2\text{H}$.

Findings (i.e. the reverse orders) in the solution phase does not mean that in aqueous phase, the alkyl groups fail to delocalize the negative charge of carbanion, alkoxide or carboxylate anion through the polarization of alkyl groups. But the energetics of solvation and desolvation factor including the entropy factor can override the effect of charge delocalization [1, 3, 7, 11–13, 16, 32, 35, 36]. This is why, in solution phase, the observed orders are different compared to those found in the gas-phase. In fact, with the increase of the non-polar hydrophobic organic portion, the anions like tertiary carbanion (pyramidal structure), and tertiary butoxide (tetrahedral structure) become like wax-balls which are less hydrated (i.e. enthalpic disfavor) than their neutral unionized molecules, and consequently, the anions (i.e. conjugate bases) more readily undergo protonation in solution phase to produce the neutral species. In fact, water molecules cannot approach the oxygen site of the bulky wax-ball like anions (e.g. Me_3C^- , Me_3C^-). Thus $\text{R}_3\text{C-H}$ and $\text{R}_3\text{C-OH}$ are stabilized better through solvation than their corresponding conjugate bases (i.e. R_3C^- and $\text{R}_3\text{C-O}^-$). The enhanced basicity of tertiary carbanion or tertiary butoxide ion is not due to the enhanced negative charge density but because of their poorer solvation compared to that of their corresponding conjugate acids. In fact, in such cases, the negative

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charge is also delocalized to stabilize the anions (i.e. conjugate bases) but the anions are not stabilized sufficiently through solvation [11–13, 16, 27, 32, 35, 36]. Consequently, the enthalpic disfavor due to the solvation effect (i.e. poorer hydration of the wax-ball like conjugate base anions) in the deprotonation process predominates over the enthalpic favor due to the electronic effect (i.e. stabilization of the conjugate base anion through charge delocalization or dispersal). This overall enthalpic disfavor (i.e. total ΔH becomes more positive) thermodynamically controls the process, i.e. the said deprotonation process is enthalpically driven as discussed below.

Here, it may be pointed out that better charge delocalization by the larger number of alkyl groups as in tertiary carbanion, tertiary butoxide, etc., reduces the charge density of the anions and consequently, it disfavors the solvation of anions (i.e. conjugate bases) through ion-dipole interaction and H-bonding interaction. Thus, better charge delocalization by the alkyl groups lead to more enthalpic disfavor in the solvation of conjugate base in the said deprotonation process. It is obvious that the said deprotonation processes experience an entropic benefit due to the inefficient solvation of the anion or conjugate base (i.e. inefficient ordering of solvent molecules around the anion through the ion-dipole interaction). However, the enthalpic disfavor (ΔH) overrides the entropic favor ($T\Delta S$) in the present cases at ordinary temperature. Thus the said deprotonation processes of the alcohols and alkanes are mainly driven by the enthalpy factor. In other words, Gibbs free energy change ($\Delta G = \Delta H - T\Delta S$) of the process is mainly controlled by the enthalpy factor. This is why, the wax-ball like anions (tertiary carbanion, tertiary butoxide, etc.) undergo protonation more readily in solution phase to produce the neutral species which is solvated better to enjoy the enthalpic benefit in the protonation process. Consequently, such anions show the enhanced Bronsted basicity. Here, it is worth mentioning that for the basicity order of amines (i.e. primary, secondary and tertiary) in aqueous phase, solvation of the protonated species (i.e. conjugate acids) through H-bonding also plays a crucial role [4, 7], and

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their basicity order is enthalpy-driven.

It has been noted that for the simple aliphatic and halogenated aliphatic acids in aqueous media, at ordinary temperature, the entropy factor ($T\Delta S$) contributes much more than the enthalpy factor (ΔH) (*Table 2*) to the Gibbs free energy change ($\Delta G = \Delta H - T\Delta S$) [1, 3, 7, 16]. In fact, ΔG actually determines the position of the equilibrium. The halogen substituted alkyl groups show the electron withdrawing inductive effect when they are connected to the less electronegative sp^2 -C of the carboxylic acid group, but the unsubstituted alkyl group shows electron pushing inductive effect towards the carboxylic acid group. It is quite reasonable in terms of inherent electronegativity (*cf.* $\chi_P = 3.03$ for CCl_3 , 2.3 for unsubstituted R, 2.7 for sp^2 -C; [4]).

Poorer solvation of the conjugate base causes more enthalpic disfavor, but at the same time, more entropic favor which is the most predominant thermodynamic factor in the acid dissociation process of aliphatic carboxylic acids.

The halocarboxylate ion delocalizes the negative charge towards more electronegative halogens and it reduces charge density on the carboxylate group. Consequently, the conjugate base (i.e. halocarboxylate anion) becomes less efficient to undergo solvation (compared to unsubstituted alkyl carboxylates) because of the reduced charge density [7], and it brings about an entropic favor along with an enthalpic disfavor in the acid dissociation process. In fact, better solvation of the conjugate base (i.e. carboxylate anion) puts a higher electrorestriction over the solvent molecules (i.e. more ordering of the solvent molecules around the conjugate base anion through ion-dipole electrostatic interaction including the H-bonding interaction), and it introduces more entropic disfavor. In other words, poorer solvation of the conjugate base (e.g. halocarboxylate anion) causes more enthalpic disfavor, but at the same time, more entropic favor which is the most predominant thermodynamic factor (*Table 2*) in the acid dissociation process of aliphatic carboxylic acids [1,7,16]. The importance of entropy factor over the enthalpy factor in determining the relative acid strengths of aliphatic acids in aqueous phase can be understood from the following discussion.

The effect of charge delocalization or charge dispersal in the conjugate base (i.e. carboxylate anion) by the electron withdrawing group produces two opposing contributions to the total enthalpy

Acid	ΔH° (kJ mol ⁻¹)	$T\Delta S$ (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	pK _a
HCO ₂ H	-0.084	-22.0	+21.9	3.85
CH ₃ CO ₂ H	-0.37	-27.6	+27.2	4.78
ClCH ₂ CO ₂ H	-4.5	-21.0	+16.5	2.90
Cl ₃ CCO ₂ H	+ 6.3	+ 2.5	+3.8	0.65
C ₂ H ₅ CO ₂ H	-0.67	-28.4	+27.7	4.87

change (ΔH). That means stabilization of the conjugate base by charge dispersal (an electronic effect) generates an enthalpic favor but the poorer solvation of the conjugate base due to reduced charge density (a consequence of charge delocalization) generates an enthalpic disfavor. Consequently, because of these two opposing contributions, in general, in the said acid dissociation process, the overall enthalpy factor (ΔH) becomes less important compared to the entropy factor ($T\Delta S$) to the Gibbs free energy change (ΔG). Thus the acid dissociation process of carboxylic acids becomes entropically driven (Table 2). Effect of the electron withdrawing group on the thermodynamic parameters of acid dissociation process is illustrated for CH₃CO₂H vs. CCl₃CO₂H. Compared to CH₃CO₂H, for CCl₃CO₂H, the ΔH factor is disfavored by about 6.7 kJ mol⁻¹ while the $T\Delta S$ factor is favored by about 30 kJ mol⁻¹ (Table 2). It makes the halocarboxylic acids stronger. Thus it is quite interesting to note that in aqueous phase, for aliphatic carboxylic acids, the order of acid dissociation constant is entropically driven while for aliphatic alcohols, it is enthalpically driven.

Several theoretical and experimental investigations have been carried out [14, 15, 19, 28, 34] to explore the major contributing factors to determine the acid strength order of substituted aliphatic carboxylic acids. Proft *et al.* [34] have carried out a quantum mechanical study using the density functional theory (DFT) based descriptors to interpret the relative acid strengths of substituted acetic acids (CH₂XCO₂H) in both gas and aqueous phases. The results have been rationalized using the Pearson's HSAB princi-

Table 2. Thermodynamic data for the acid dissociation constants of some representative carboxylic acids (25°C) ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0 - RT \ln K_a = RT \times 2.3 \text{ pK}_a$) [1, 7, 16].

Several theoretical and experimental investigations have been carried out to explore the major contributing factors to determine the acid strength order of substituted aliphatic carboxylic acids.



In aqueous phase, the inherent electronegativity (measured by the a -value of χ_{MJ}) of X plays an important role while in gas phase, the b -value of χ_{MJ} plays the more important role in determining the relative acid strengths.

ple [37–39]. The acidities in aqueous phase have been found to be almost independent of the softness or polarizability (measured by the b -value of χ_{MJ}) of group X while the polarizability of group X has been found to play an important role in determining the gas-phase acidity. Thus in aqueous phase, the inherent electronegativity (measured by the a -value of χ_{MJ}) of X plays an important role while in gas phase, the b -value of χ_{MJ} plays the more important role in determining the relative acid strengths. Perez *et al.* [33] have also analyzed the relative gas-phase acidity of different halosubstituted acetic acids like $\text{CH}_2\text{XCO}_2\text{H}$, $\text{CHX}_2\text{CO}_2\text{H}$ and $\text{CX}_3\text{CO}_2\text{H}$ (X = F, Cl and Br) in terms of global and local descriptors of reactivity. The relative acidity strength of the said haloacetic acids has also been rationalized in the same way. All these strongly support the view that polarizability causes charge delocalization.

In fact, in gas phase, though the stability order is the same for both the carbocations and carbanions, the stability differs by only about 42 kJ/mole between the primary and tertiary carbanions while this difference is about 315 kJ/mole in the case of carbocations.

Here it is worth noting that for the carbocations, the stability order (pri < sec < tert) is the same in both the gas and solution phase. Probably, solvation of the planar carbocation enriched with the nonpolar alkyl groups (as in the tertiary carbocation) is not so disfavoured compared to the case of pyramidal carbanions which appear wax-ball shaped for the tertiary carbanion. Some workers have also argued that the charge delocalizing effect is more important for the carbocations than for the carbanions [8–10]. In fact, in gas phase, though the stability order is the same for both the carbocations and carbanions, the stability differs by only about 42 kJ/mole between the primary and tertiary carbanions while this difference is about 315 kJ/mole in the case of carbocations [8–10]. But, it does not really reflect that the alkyl groups are relatively less efficient in delocalizing the negative charge of carbanions (through polarization) compared to delocalizing the positive charge of carbocations. The degree of polarization of alkyl groups in delocalizing the charge (+ve or -ve) depends on two factors [4, 7]: the polarizability (determined by b -value) and the square of the strength of the polarizing field (i.e. field intensity determined by charge to radius ratio). Thus, the extent of polarization of a particular alkyl group depends on the square of the strength of the

polarizing field and not on the sign of charge of the polarizing field [7]. In fact, a carbanion being larger in size possesses less polarizing power (i.e. lesser value of charge to radius ratio) compared to the relatively smaller corresponding carbocation having the stronger polarizing power due to the higher charge to radius ratio.

Thus it is reasonable to expect that for the carbocations, the charge delocalizing factor (an electronic factor) being predominant because of the higher polarizing field strength probably controls the stability order in both gas and solution phases. On the other hand, for carbanions, the charge delocalization factor being relatively less important because of the relatively smaller polarizing field strength cannot override the solvation effect in the aqueous phase, though it controls the stability order in the gas phase where there is no question of solvation.

It is reasonable to expect that for the carbocations, the charge delocalizing factor being predominant because of the higher polarizing field strength probably controls the stability order in both gas and solution phases.

6. Conclusion

The present article attempts to popularize the concept among the students and instructors that the alkyl groups can delocalize both the positive and negative charges depending on the condition through the charge induced polarization of the alkyl groups. Thus the origin of both electron withdrawing and electron pushing inductive effect (i.e. charge delocalizing effect) shown by the alkyl groups can be rationalized in terms of the polarizability of the alkyl groups. Polarizability is determined by the Mulliken–Jaffe charge coefficient b -parameter. Higher polarizability is indicated by lower b -value. Without this concept, we cannot understand clearly the organic chemistry phenomena, specially, occurring in gas phase and aprotic nonpolar solvents where the solvation effect is absent.

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