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Gas-phase acidity of *para*-substituted benzoic acids—a triadic analysis of substituent effects[†]

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ABSTRACT: Deprotonation energies *in vacuo* of a large number of *para*-substituted benzoic acids encompassing a wide variety of substituents [F, Cl, Br, CH_3, $C(CH_3)_3$, $CH{=}CH_2$, $C{\equiv}CH$, CHO, COOH, CF_3, BH_2, $B(CH_3)_2$, NH_2, $N(CH_3)_2$, OH, OCH_3, SH, CN and NO_2] were studied by a reliable *ab initio* method. It is shown by using a triadic formula analysis that the enhanced acidity of these compounds is a consequence of the final state as a rule, i.e. it is a result of the greater stability of the conjugate bases. There are just a few exceptions to this rule, involving $C(CH_3)_3$, OCH_3, OH and SH substituent groups. In the last two cases molecules deprotonate at the O and S substituent atoms, respectively. The ring-substituted pentacyano derivative of benzoic acid was also examined. It is shown that it exhibits highly pronounced acidity owing to a strong anionic resonance effect in the resulting final state anion. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: acidity; benzoic acid; deprotonation; substituent effects; triadic formula analysis

INTRODUCTION

The origin of the stronger acidity of carboxylic acids relative to the corresponding alcohols has been a much debated theme with a controversial outcome. A large body of the work was focused on the simplest representatives of these two families of compounds: formic acid and methanol. In his classic book, Wheland[1] pointed out that the difference in acidity might be due to the (anionic) resonance stabilization and the electrostatic stabilization of the negative charge by the positively charged carbon atom in the formate anion. Wheland concluded that 'We cannot be sure how much of the observed effect must be attributed to each cause'. It seems that this statement holds even nowadays. Despite Wheland's caution on a possible dichotomy, the prevailing interpretation has attributed the higher acidity of carboxylic acids to the resonance effect in the resulting anions, as can be found in many contemporary textbooks.[2–5] This conventional view was challenged by Siggel, Thomas and Streitwieser,[6–10] who claimed that the greater acidity of carboxylic acids compared with alcohols is a consequence of the properties of the initial neutral molecules. More specifically, the higher polarized carbonyl of the carboxylic acid repels the hydroxyl proton in the neutral acid and stabilizes the negative charge in the conjugate base due to a highly pronounced positive charge of its carbon atom. Unfortunately, most of the analyses were based on Bader's electron populations and net atomic charges,[11] which are highly unrealistic. Maslen and Spackman found that Bader's AIM scheme yields appreciable charge transfer even within promolecules, where the interatomic interactions are set equal to zero by definition.[12,13] In other words, Bader's charges do not exhibit a proper asymptotic behavior. It is not surprising, therefore, that the gross atomic populations of oxygen are between 9 and 9.5 electrons, suggesting a charge drift of 1.0–1.5 electrons to the O atom even in small molecules such as CO, H_2CO and CH_3OH. Clearly, interpretations employing topological atom charges are not viable. Since the definition of the atomic charge in a molecular environment is not unique, it should be used with extreme care.[14] A recent analysis by Baerends, Bickelhaupt and co-workers[15] showed that the atomic charges calculated using Hirshfeld's 'stockholder' recipe[16] and the Voronoi deformation density method[17,18] (a) were similar and (b) provided physically and chemically meaningful values. It would therefore be interesting to re-examine earlier results, which have claimed a decisive importance of the initial state by using more realistic atomic charges of Hirshfeld[16] and Voronoi.[17,18] However, there is also another kind of critique put forward by Exner,[19] who employed isodesmic reactions to show that the origin of enhanced acidity of formic acid is the low energy of the CH_3COO^- anion and not the high energy of the initial

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CH_3COOH acid. To put it another way, it is a consequence of the final state rather than the effect of the initial state as advocated by Thomas and co-workers[6–10] Dewar and Krull addressed the same problem in a typically ingenious way by designing a set of vinylogs of formic acid, COH—(CH=CH)$_n$—OH, with varying number n of vinyl fragments.[20] The electrostatic interaction of the C=O group at one end of the molecules and the OH group on the other is negligible for large n and yet the acidity increases with the size of the acid molecule. It is obvious that the anionic resonance becomes progressively more important with increasing n, which is in harmony with the standard interpretation. Subsequently, it gradually turned out that both the electrostatic (inductive) and resonance effects are of importance in determining the amplified acidity of carboxylic acids. For example, the valence bond SCF method was employed by Hiberty and Byrman[21] to show that the inductive effect and π-electron delocalization contribute equally to the acidity of the carboxylic acid. Rablen,[22] on the other hand, used MO theory and a series of isodesmic reactions in studying the acidity of acetic acid and concluded that 75% of its amplified acidity comes from electrostatic stabilization, whereas 25% arises from π resonance. Qualitatively similar, but quantitatively different, results were obtained by Taft *et al.*[23] by multilinear analysis, which showed that 36% of the acidity of formic acid could be ascribed to the resonance effect of the general O-acids. To epitomize the mainstream discussion, one could say together with Exner and Čarsky[24] that the acidity of carboxylic acids originates in the low energy of their anions. It is more difficult to estimate the relative contributions of the anionic resonance and the electrostatic effects, since it cannot be done in an unequivocal manner. Obviously, it would be useful to approach the problem from another angle.

Our approach in rationalizing the proton affinities of bases and deprotonation energies of acids is somewhat different, offering a new point of view. It is embodied in the triadic formula based on dissection of the (de)protonation process into three stages corresponding to the initial, intermediate and final state events.[25,26] Let us consider the acidic dissociation of the proton as a reverse reaction: protonation of the anionic conjugate base. One should keep in mind that in this case the final state in deprotonation becomes the initial state in the protonation of the anions. If the genuine properties of the latter are desired, then Koopmans' ionization energy of the anions $(IE)_n^{\mathrm{Koop}}$ should be calculated in the fixed nuclei and frozen electron density approximation. Consistent application of this model has conclusively shown that carboxylic acids X—COOH are more acidic than alcohols X—OH (X = H, CH_3, F, CF_3), because of considerably larger Koopmans' ionization energies.[26] To put it succinctly, the enhanced acidity of carboxylic acids X—COOH (X = H, CH_3, F, CF_3) is a consequence of the final state (anionic) features.

In view of the great interest in this topic, we felt it worthwhile to extend the triadic analysis to *para*-substituted benzoic acids X—COOH, where X = Ph(p-Y) with Y encompassing a large number of widely different atoms or atomic groups [Y = F, Cl, Br, CH_3, $C(CH_3)_3$, $CH{=}CH_2$, C≡CH, CHO, COOH, CF_3, BH_2, $B(CH_3)_2$, NH_2, $N(CH_3)_2$, OH, OCH_3, SH, CN and NO_2]. In addition, the ring-substituted pentacyano derivative of benzoic acid is examined, since it represents a good candidate for a very strong neutral organic acid.

THEORETICAL FRAMEWORK

Acidity is defined as the change in enthalpy ΔH_{acid} for the reaction

$$\mathrm{AH(g)} \longrightarrow \mathrm{A^-(g)} + \mathrm{H^+(g)} \tag{1}$$

which is given by

$$\Delta H_{\mathrm{acid}} = \Delta E_{\mathrm{acid}} + \Delta(pV) \tag{2}$$

where ΔE_{acid} is the change in the total molecular energy of the species participating in reaction (1). It includes the zero-point vibrational energy (ZPVE) and the finite temperature thermal correction (from 0 to 298.15 K), whereas $\Delta(pV)$ denotes the pressure–volume work term. It is worth noting that stronger acids have smaller numerical values of ΔH_{acid}, thus implying easier release of the proton. A theoretical model offering a very good compromise between accuracy and feasibility combined with practicality is given by the MP2(fc)/6–311+G(d,p)//B3LYP/6–31G(d) approach, hereafter denoted MP2. This computational procedure yields acidities which compare reasonably well with experiment and much more demanding G2 method.[27–31]

We have shown that a very useful tool for interpretation of acidities is provided by the triadic formula:[26,32,33]

$$\begin{aligned} PA(\mathrm{A^-})_\alpha = {} & -IE(\mathrm{A^-})_n^{\mathrm{Koop}} + E(ei)_{\mathrm{rex}}^{(n)} \\ & + (BDE)^{\cdot}_\alpha + 313.6\,\mathrm{kcal\,mol^{-1}} \end{aligned} \tag{3}$$

(1 kcal = 4.184 kJ), which describes protonation of the conjugate base (anion A$^-$). In other words, it is conceptually convenient to consider a reversed process instead of deprotonation. Here, the electron affinity of the proton is 313.6 kcal mol^{-1}, the site of protonation is denoted α and $IE(\mathrm{A^-})_n^{\mathrm{Koop}}$ is the nth Koopmans' ionization energy of the anion A$^-$ calculated in the clamped nuclei and frozen electron density approximation (that is to say, a sudden ionization from the nth occupied molecular orbital is considered counting HOMO as the first). The reorganization of both the nuclei and electron density, due to the fact that ionization is not a sudden event in reality, is denoted $E(ei)_{\mathrm{rex}}^{(n)}$. Actually, the picture

underlying the triadic description of the $A^- + H^+$ protonation event implies a completion of the relaxation before the $H^{\cdot}$ atom and $A^{\cdot}$ radical start to interact yielding ultimately an A—H bond. Hence the relaxation energy $E(ei)^{(n)}_{\mathrm{rex}}$ is defined by the equation

$$E(ei)^{(n)}_{\mathrm{rex}} = IE(A^-)^{\mathrm{Koop}}_{n} - IE(A^-)^{\mathrm{ad}}_{1} \qquad (4)$$

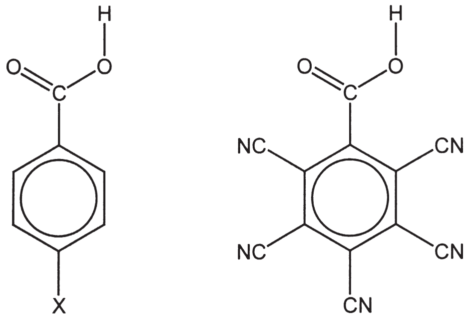
where $IE(A^-)^{\mathrm{ad}}_{1}$ is the first adiabatic ionization energy. One should keep in mind that Koopmans' ionization energy is calculated by the HF wavefunction, implying that the relaxation energy $E(ei)^{(n)}_{\mathrm{rex}}$ includes the correlation energy contribution inherent only in the first adiabatic ionization energy $IE(A^-)^{\mathrm{ad}}_{1}$ term. In other words, it is not a 'clean' relaxation effect. One could, of course, single out and separate the correpation energy contribution to the $-IE(A^-)^{\mathrm{ad}}_{1}$ adiabatic ionization energy as an idenpendent term. However, we would prefer to keep the picture and formulae as simple as possible. This standpoint is supported by the fact that $-IE(A^-)^{\mathrm{Koop}}_{n}$ does reflect the energy price to be paid in the ionization process, because the relaxation and correlation effects tend substantially to cancel out. Finally, the bond dissociation energy in deprotonation (or association energy in a reverse protonation) process describing homolytic X_α—H scission at the X_α atom is denoted $(BDE)^{\cdot}_{\alpha}$.

It should be mentioned that the three-step process, introduced for interpretation purposes and embodied in the trichotomy formula (3), is a simple extension of the usual thermochemical cycle, where a single $IE(A^-)^{\mathrm{ad}}_{1}$ term is replacing a sum of $IE(A^-)^{\mathrm{Koop}}_{n} - E(ei)^{(n)}_{\mathrm{rex}}$. This is conceptually very important, since Koopmans' ionization energy mirrors the influence of the final state, i.e. it reflects intrinsic features of the conjugate base produced as a result of deprotonation in its ground state. Moreover, in contrast to the first adiabatic ionization energy $IE(A^-)^{\mathrm{ad}}_{1}$, Koopmans' $IE(A^-)^{\mathrm{Koop}}_{n}$ term corresponds to the *n*th ionization energy, which is related to a specific MO that participates in the protonation process in the most direct way. The latter MO is closely associated with the site X_α in anion A^- that is protonated. For example, in the case of a lone pair localized on the atom under proton attack, it is the very molecular orbital describing this lone pair. Identification of such MOs is usually unambiguous and poses no problem. It should be strongly pointed that triadic formula (3) is exact and that errors arise solely from the approximate theoretical methods employed in calculating the $PA(A^-)_\alpha$ values. However, one should keep in mind that partitioning of the total $PA(A^-)_\alpha$ into three terms is not unique, because the calculation of the ionization energy $IE(A^-)^{\mathrm{Koop}}_{n}$ in the sudden Koopmans' approximation is not rigorous. The inherent error, given by a deviation from the exact cancelation of the electron correlation and relaxation contributions calculated in the sudden picture, is remedied by its absorption in the relaxation $E(ei)^{(n)}_{\mathrm{rex}}$ energy term. Hence, the latter should be also taken treated with a due caution (see above). This is the price one has to pay for conceptual gain obtained by considering the frozen distributions of the nuclei and electrons in the anion A^-, in order to extract the genuine features of the final state in an approximate, but satisfactory, way.

The triadic analysis applied here is executed at the ROMP2(fc)/6–311+G(d,p)//B3LYP/6–31G(d) level of theory. Koopmans' ionization energies are calculated by the restricted HF/6–311+G(d,p)//B3LYP/6–31G(d) model, which represents a simplified form of the procedure proposed earlier.[26] Bond dissociation energies are obtained by use of the restricted open-shell MP2 approach. All calculations were carried out by employing the Gaussian 98 suite of programs.[34]

RESULTS AND DISCUSSION

The systems examined here are schematically depicted in Fig. 1. In addition to a series of *para*-substituted benzoic acids with substituents X = F, Cl, Br, CH_3, $C(CH_3)_3$, $CH_2{=}CH_2$, C≡CH, BH_2, $B(CH_3)_2$, CHO, COOH, CF_3, NH_2, $N(CH_3)_2$, OH, OCH_3, SH, NO_2 and CN, we considered the pentasubstituted cyano derivative **2**, which should exhibit a very strong acidity. The calculated proton acidities (*PA*) of their conjugate bases are given in Table 1 together with results of the triadic analysis. We note that the theoretical proton affinities (i.e. acidities) are in excellent agreement with available experimental data taken from Ref. 35, being in all cases within the error bars. An interesting finding is that deprotonation takes place at oxygen and sulfur atoms for the *para* substituents X = OH and SH. If compound **2** is excluded, then the range of *PA* values is fairly narrow, extending from 328.9 (X = NO_2) to 342.3 kcal mol^{-1} (X = NH_2 or $N(CH_3)_2$). In other words, the variation in *PA* caused by a large variety of widely different *para* substituents spans a range of only 12 kcal mol^{-1}. A strong decrease in *PA* and a concomitant increase in acidity is found in **2**, as expected in view of a very strong anionic resonance in A^- anions possessing a large number of CN groups, which seems to be a general feature.[32,36–39]



1 **2**

Figure 1. Schematic representation of the studied substituted benzoic acids

Table 1. Triadic analysis of proton affinities (*PA*) of conjugate bases of *para*-substituted benzoic acids obtained by applying the ROMP2(fc)/6–311+G(d,p)//B3LYP/6–31G(d) method and triadic formula (3) (all data in kcal mol^{-1})[a,b]

Substituent	$(IE)_n^{Koop}$	$(IE)_1^{ad}$	$E(ei)^{(n)}_{rex}$	$(BAE)^{\cdot}$	PA(thr)	PA(exp)[c]
H	$(139.4)_4$	74.1	65.3	100.0	339.5	340.2 ± 2.2
F	$(143.6)_4$	77.5	66.1	100.4	336.5	337.0 ± 2.1
Cl	$(146.0)_4$	78.4	67.6	100.3	335.5	335.5 ± 2.1
Br	$(146.8)_4$	79.0	67.8	100.4	335.0	
CH_3	$(138.3)_4$	73.0	65.3	99.9	340.5	340.7 ± 2.1
$C(CH_3)_3$	$(139.2)_4$	73.8	65.4	100.0	339.8	340.0 ± 2.2
$CH{=}CH_2$	$(142.6)_4$	75.7	66.9	100.2	338.1	
$C{\equiv}CH$	$(145.7)_4$	78.0	67.7	100.3	335.9	
CHO	$(150.4)_4$	81.6	68.8	100.4	332.4	332.8 ± 2.1
COOH	$(149.4)_4$	79.9	69.5	100.3	334.0	
CF_3	$(150.1)_4$	82.5	67.6	100.6	331.7	332.3 ± 2.1
BH_2	$(146.8)_4$	79.6	67.2	100.2	334.2	
$B(CH_3)_2$	$(144.5)_4$	76.8	67.7	100.0	336.8	
NH_2	$(137.0)_4$	71.2	65.8	99.9	342.3	343.4 ± 2.1
$N(CH_3)_2$	$(136.6)_4$	70.9	65.7	99.6	342.3	
OH	$(146.3)_3$	61.2	85.1	82.7	335.1	335.9 ± 2.1
OCH_3	$(138.8)_4$	72.6	66.2	99.9	340.9	340.8 ± 2.1
SH	$(93.9)_2$	58.7	35.2	75.8	330.7	
CN	$(153.5)_4$	84.9	68.6	100.9	329.6	327.8 ± 2.1
NO_2	$(156.7)_4$	85.4	71.3	100.7	328.9	328.1 ± 2.2
$(CN)_5$	$(189.1)_2$	112.8	76.3	102.9	303.7	

[a] Koopmans' ionization energies $(IE)_n^{Koop}$ correspond to HF/6–311+G(d,p)//B3LYP/6–31G(d) calculations.

[b] $(IE)_n^{Koop}$ and $(IE)_1^{ad}$ are Koopmans' *n*th and the first adiabatic ionization energies, respectively.

[c] Experimental data are taken from Ref. 35.

Analysis of various contributions to the deprotonation energies reveals some interesting features. In the first place, the homolytic bond dissociation energy $(BDE)^{\cdot}_{OH}$ of the OH bonds belonging to the carboxylic fragment is fairly constant, being around 100 kcal mol^{-1}. The $(BDE)^{\cdot}_{OH}$ and $(BDE)^{\cdot}_{SH}$ values of the *para*-hydroxy and *para*-sulfoxy derivatives, respectively, are notable exceptions being smaller assuming 82.7 and 75.8 kcal mol^{-1}, respectively. Second, the molecular orbitals undergoing the largest change in deprotonation of the acids or, alternatively, playing a pivotal role in protonation of the corresponding anions of conjugate bases, are HOMO-3 as a rule as exemplified by the parent benzoic acid (Fig. 2). The latter describes the σ-electron distribution of the lone pairs in the carboxylic acid. There are only three exceptions, which are given by *para*-substituted OH and SH derivatives and pentacyano derivative of benzoic acid **2**. In the first case (OH substituent), the MO participating directly in de/protonation is the HOMO-2 antibonding orbital describing the in-plane interaction between the lone pair of the oxygen atom belonging to the OH group and the two vicinal CC bonds within the benzene ring. In the last two molecules the crucial MOs are HOMOs-1 of the S^- and COO^- groups in **2** as depicted in Fig. 2. The orbital energies in question, taken with the opposite sign, represent the energetic cost to be paid in the protonation process of anions. It is related to ionization of the conjugate bases estimated within Koopmans' approximation. The largest ionization energies $(IE)_n^{Koop}$ in monosubstituted benzoic acids are found for NO_2 (156.7), CN (153.5), CHO (150.4), CF_3 (150.1) and COOH (149.4 kcal mol^{-1}) substituents. The absolute maximum is identified in the pentacyano derivative **2**, being 189.1 kcal mol^{-1}. In contrast, the lowest $(IE)_n^{Koop}$ value is found in the monosubstituted system involving the SH group (93.9 kcal mol^{-1}). Interestingly, this compound possesses the lowest relaxation energy (32.5 kcal mol^{-1}) too, which is in harmony with a strong localization of the S^- lone pair (Fig. 2). Hence the loss of an electron does not appreciably affect the molecular and electronic rearrangement. On the other hand, the $E(ei)^{(n)}_{rex}$ term achieves a maximum value of 85.1 kcal mol^{-1} for the OH substituent and a sizeable 76.3 kcal mol^{-1} in the ring-pentacyano derivative **2**.

Relative contributions of all three terms appearing in the triadic formula (3) for acidity of derivatives of benzoic acid, gauged by the parent compound benzoic acid, are given in Table 2. Let us focus on halides first. It is obvious that acidity increases along the series F, Cl and Br owing to the greater stabilization of HOMO-3 orbitals. Whether this is a consequence of the greater polarizability of Cl and Br atoms, as usually stated in numerous textbooks, is an open question. Mulliken[40] and Löwdin[41] (in parentheses) charges for F, Cl and Br atoms in anions are −0.43 (−0.24), −0.09 (−0.07) and −0.16 (−0.09). Caution has to be exercised, however, in view of the fact that both Mulliken[14] and Löwdin (based on orthogonalized AOs) charges exhibit considerable imperfections.[42] They definitely do not reflect a greater ease of larger halogen atoms accommodating the negative charge.

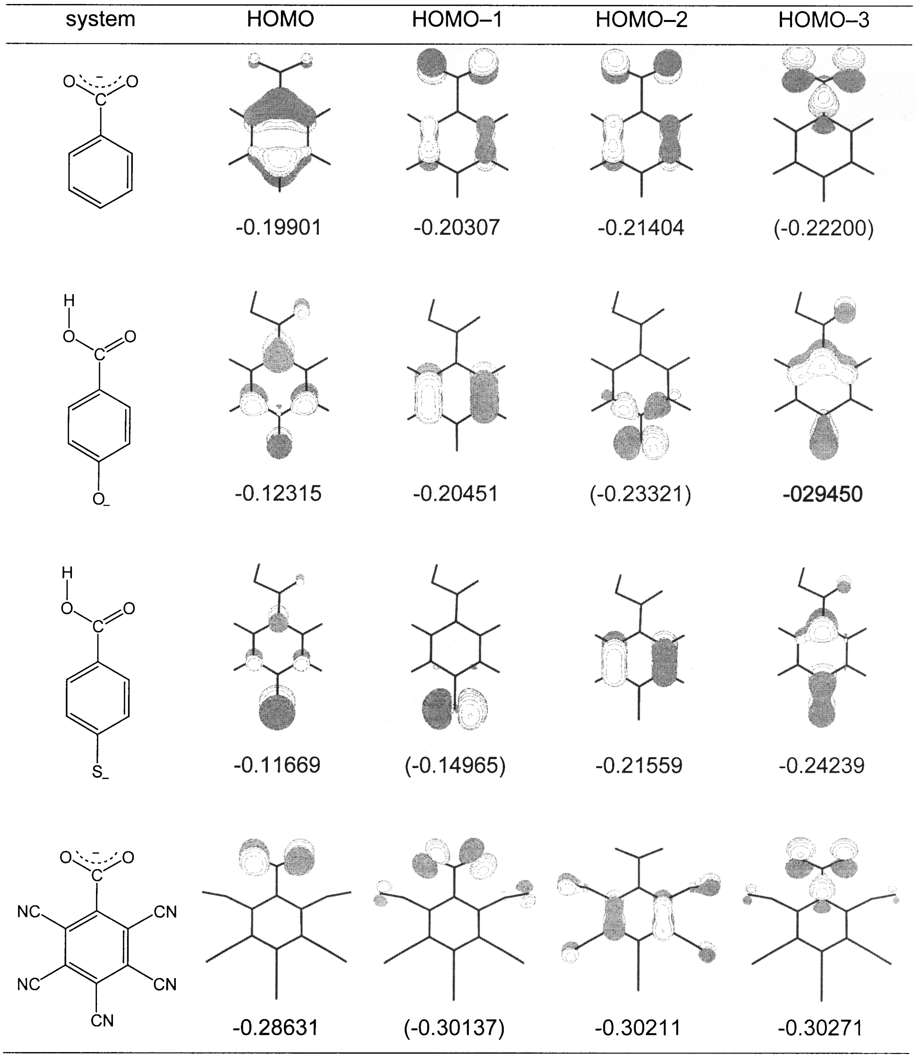


Figure 2. Schematic representation of the first four occupied molecular orbitals for some characteristic conjugated bases under consideration together with their orbital energies (in a.u.) obtained at the HF/6–311+G(d,p)//B3LYP/6–31G(d) level of theory in Koopmans' approximation. The orbital energies of MOs participating in protonation of anions the most are given in parentheses

It is convenient to analyze variation in acidity by a triad of numbers, $\Delta PA = [\Delta(-IE_n^{\text{Koop}}), \Delta E(ei)_{\text{rex}}^{(n)}, \Delta(BDE)^{\cdot}_{\alpha}]$, where $\Delta PA = PA(\text{X—C}_6\text{H}_4\text{—COO}^-) - PA\ (\text{C}_6\text{H}_5\text{—COO}^-)$, $\Delta(-IE_n^{\text{Koop}}) = -IE(\text{X—C}_6\text{H}_4\text{—COO}^-)_n^{\text{Koop}} + IE(\text{C}_6\text{H}_5\text{—COO}^-)_n^{\text{Koop}}$, $\Delta E(ei)_{\text{rex}}^{(\text{n})} = E(ei)_{\text{rex}}^{(\text{n})}(\text{X—C}_6\text{H}_4\text{—COO}^-) — E(ei)_{\text{rex}}^{(\text{n})}(\text{C}_6\text{H}_5\text{—COO}^-)$ and $\Delta\ (BDE)^{\cdot}_{\alpha} = (BDE)^{\cdot}_{\alpha}(\text{X—C}_6\text{H}_4\text{—COO}^-) - (BDE)^{\cdot}_{\alpha}(\text{C}_6\text{H}_5\text{—COO}^-)$, where the squared brackets imply summation of the three terms. The increased acidity of COOH, CHO and CF_3 derivatives by 5.5–7.8 kcal mol^{-1} is a consequence of the increased Koopmans' ionization energies, which are spaced in a close interval between 10 and 11 kcal mol^{-1}, as easily deduced from the data given in Table 2 by using triads sketched above. In other words, it is the effect of the final state. The same holds for derivatives involving BH_2 and $B(CH_3)_2$ substituents. On the other hand, NH_2, $N(CH_3)_2$ and OCH_3 substituents decrease the acidity of the *para*-substituted benzoic acid, which in the first two cases is predominantly due to decreased $IE(\text{A}^-)_4^{\text{Koop}}$ values. This is illustrated by triads $[2.4, 0.5, -0.1] = 2.8$ and $[2.8, 0.4, -0.4] = 2.8$ for NH_2 and $N(CH_3)_2$ substituents, respectively. Interestingly, the OH and SH are very special cases, for two reasons: first because they deprotonate at the substituent O and S positions (see above) and second because the final state is not the primary cause of the increased acidity. The former substituent enhances acidity by a synactive combination of the increased Koopmans' ionization (-6.9 kcal mol^{-1}) and, more importantly, by a considerably lower bond dissociation energy $(BAE)^{\cdot}$ by ~17 kcal mol^{-1}. In contrast, the amplified acidity by the *para*-substituted SH group is a result of a substantial decrease in the relaxation and bond dissociation energies $E(ei)_{\text{rex}}^{(2)}$ and $(BAE)^{\cdot}_{\text{SH}}$, respectively, which overcome a dramatic destabilization of the HOMO-1 orbital (45.5 kcal mol^{-1}) measured within Koopmans' approximation by its orbital energy. Finally, a strong acidifying effect of both CN and NO_2 substituents

Table 2. Relative contributions to proton affinities (*PA*) of the investigated molecules obtained by triadic formula (3) taking benzoic acid as a gauge molecule (all data in kcal mol^{-1})

Substituent	$\Delta(IE)_n^{\mathrm{Koop}}$	$\Delta E(ei)^{(n)}_{\mathrm{rex}}$	$\Delta(BAE)^{\cdot}$	ΔPA(thr)
H				
F	−4.2	0.8	0.4	−3.0
Cl	−6.6	2.3	0.3	−4.0
Br	−7.4	2.5	0.4	−4.5
CH_3	1.1	0.0	−0.1	1.0
$C(CH_3)_3$	0.2	0.1	0.0	0.3
$CH{=}CH_2$	−3.2	1.6	0.2	−1.4
$C{\equiv}CH$	−6.3	2.4	0.3	−3.6
CHO	−11.0	3.5	0.4	−7.1
COOH	−10.0	4.2	0.3	−5.5
CF_3	−10.7	2.3	0.6	−7.8
BH_2	−7.4	1.9	0.2	−5.3
$B(CH_3)_2$	−5.1	2.4	0.0	−2.7
NH_2	2.4	0.5	−0.1	2.8
$N(CH_3)_2$	2.8	0.4	−0.4	2.8
OH	−6.9	19.8	−17.3	−4.4
OCH_3	0.6	0.9	−0.1	1.4
SH	45.5	−30.1	−24.2	−8.8
CN	−14.1	3.3	0.9	−9.9
NO_2	−17.3	6.0	0.7	−10.6
$(CN)_5$	−49.7	11.0	2.9	−35.8

and a dramatic amplification of acidity by pentacyano substitution in **2** originate from a very large stabilization of HOMO-3 orbitals in the resulting anions, the latter assuming a value as high as 49.7 kcal mol^{-1}. Consequently, it is a result of the final state effect.

It follows as a corollary that the stabilization of the anionic conjugate bases is a prime cause of the enhanced acidity of *para*-substituted benzoic acids, in agreement with results obtained by Exner[19] and by us.[25,26] There are very few exceptions to this rule encompassing $C(CH_3)_3$, OCH_3, OH and SH groups. The first two substituents exert a minor effect on the acidity of benzoic acid.

CONCLUSIONS

To put the present results into a proper perspective, it is worth pointing out that Hammett chose the ionization of benzoic acids (in water) to design his famous equations, which established relationship between the rate (or equilibrium) constants and the substituent constants σ.[43] Multiple regression analysis performed by Ehrenson has split the σ constants into the 'dual substituent parameter' contribution involving inductive σ_I and resonance σ_R components.[44] Slightly different procedures were put forward by Exner[45] and Charton.[46] All these results are based on experimental measurements in solvents. In our view, the system of σ constants should be developed *in vacuo* in a consistent way by using high-level *ab initio* computational methods. We shall defer this discussion to later papers. The most important outcome of the present discussion is that the origin of increased acidity in substituted benzoic acids is the higher stability of the corresponding conjugate bases in most cases with only a few exceptions involving $C(CH_3)_3$, OCH_3, OH and SH substituent groups. The last two compounds deprotonate at OH and SH positions placed on the benzene ring *para* to the carboxylic fragment. Consequently, their different behavior is not surprising. Another interesting finding is very high acidity of the ring-substituted pentacyanobenzoic acid, which is a consequence of a strong anionic resonance effect in its conjugate base. This is in accordance with the spectacular acidifying effect of other polycyano substituents in planar hydrocarbons, as was conclusively shown recently.[36–39]

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