Interpretation of Brønsted Acidity by Triadic Paradigm: A G3 Study of Mineral Acids

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Deprotonation enthalpies and the gas-phase acidities of 24 inorganic acids are calculated by using composite G3 and G2 methodologies. The computed values are in very good accordance with available measured data. It is found that the experimental ΔH_{acid} values of the FSO_3H and CF_3SO_3H are too high by some 6 and 7 kcal mol^{-1}, respectively. Furthermore, a new ΔH_{acid} value for $HClO_4$ of 300 kcal mol^{-1} is recommended and suggested as a threshold of superacidicity in the gas phase. The calculated deprotonation enthalpies are interpreted by employing the trichotomy paradigm. Taking into account that the deprotonation enthalpy is a measure of acidity, it can be safely stated that the pronounced acidities of mineral acids are to a very large extent determined by Koopmans' term with very few exceptions, one of them being H_2S. To put it in another way, acidities are predominantly a consequence of the ability of the conjugate bases to accommodate the excess electron charge, since Koopmans' term in trichotomy analysis is related to conjugate base anion. The final state is decisive in particular for superacids like $ClSO_3H$, CF_3SO_3H, $HClO_4$, HBF_4, HPF_6, $HAlCl_4$, and $HAlBr_4$. However, in the latter two molecules the bond dissociation energy of the halogen−H bond substantially contributes to their high acidity too. Therefore, acidity of these two most powerful superacids studied here is determined by cooperative influence of both initial and final state effects. It should be emphasized that acidity of hydrogen halides HCl and HBr is a result of concerted action of all three terms included in triadic analysis. A byproduct of the triadic analysis are the first adiabatic ionization energies of the anionic conjugate bases. They are in fair to good agreement with the experimental data, which are unfortunately sparse. A fairly good qualitative correlation is found between the gas-phase deprotonation enthalpies of six mineral O−H acids and available Hammett−Taft σ_p^- constants of the corresponding substituent groups.

Introduction

Acidity is one of the pillars of chemistry and biochemistry. Brønsted acidity is a measure of the propensity of a molecule to donate a proton and ability to accommodate the negative charge in the resulting conjugate Brønsted base. This qualitative description of acidity is intuitively appealing being in accordance with common sense. However, intuitive notions developed by experimental work should be put on more rigorous basis and interpreted by sound physical models. In order to achieve that, we need in the first place theoretical tools capable of quantitative description of the molecular structure and energetics. Computational chemistry has developed such methods in the last two decades, which offer results comparable in accuracy to those obtained by various experimental techniques. This development is a consequence of the pioneering work of Pulay,[1] which enabled ab initio calculations of stationary points on the potential energy surfaces (PES) in an analytic way. Moreover, the gradients made possible calculations of many properties defined by the higher order derivatives of the total molecular energy.[2] Provided reasonably accurate molecular wavefunctions and energies are available, one can address the next fundamental question related to interpretation and rationalization of the measured and/or computed molecular features.[3] It is exactly this link which makes possible understanding of natural phenomena on the molecular scale.

The early efforts of rationalization of the acidity of hydrocarbons were based on the simple hybridization model. Cram found that acidity of the C−H acids increased linearly with the s-character of the hybrid orbital describing the localized C−H bond.[4] The argument was that the lone pair of electrons formed upon deprotonation were more stable, if placed in the hybrid orbitals possessing higher s-content. Cram's qualitative conjecture based on canonical sp^3, sp^2, and sp^1 hybridizations were confirmed later by the variable hybridization model obtained by the maximum overlap[5] and NBO calculations.[6]

Hammett[7] examined deprotonation of para-substituted benzoic acids in water and established the famous equation based on the empirical substituent σ-constants, which are proportional to the $\log(k_S/k_0)$. Here k_S denotes either a rate or equilibrium constant of a substituted reactant, whereas k_0 stands for the corresponding value of the unsubstituted parent compound. This work triggered a cascade of papers, which laid down the basis of physical organic chemistry. At the beginning Hammett−Taft σ-constants were empirical in nature,[8] but availability of computer codes for the gradient ab initio methods enabled their theoretical estimates.[9−12] A lot of insight into acidity of organic acids has been gained by controversial discussion over the origin of the higher acidity of carboxylic acids relative to the corresponding alcohols.[13−24] The heart of the problem was the question whether the higher acidity of the formic acid over the methanol was a consequence of the increased stability of the anions (conjugate base HCOO$^-$) or the decreased stability of the initial HCOOH molecule due to unfavorable electrostatic interactions. The mainstream discussion was summarized by Exner and Čarsky[25] by stating that the acidity of carboxylic acids

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TABLE 1: G3 Deprotonation Enthalpies, Their Resolution into Triadic Components, and the Gas-Phase Acidities of Selected Mineral Acids (in kcal mol^{-1})

molecule	$(IE)_n^{Koop}$	$(IE)_1^{ad}$	$(IE)_1^{ad}exp^a$	$E(ei)^{(n)}_{rex}$	$(BAE)^\bullet$	ΔH_{acid}	$\Delta H_{acid,exp}{}^a$	ΔG_{acid}	$\Delta G_{acid,exp}{}^a$
H_2O	$(66.5)_1$	41.0	42.1	25.5	118.6	391.2	390.3	384.7	383.7 ± 0.3
HF	$(111.3)_1$	78.4	78.4	32.9	137.0	372.2	371.3	366.6	365.5 ± 0.2
HClO	$(89.6)_1$	53.4	52.5 ± 0.03	36.2	96.0	356.2	355.6 ± 1.1	349.7	349.2 ± 1.2
H_2S	$(59.3)_1$	53.5	53.4 ± 0.05	5.8	90.9	351.0	351.3 ± 0.1	344.8	344.4 ± 3.0
HNO_2	$(105.0)_1$	52.6		52.4	78.2	339.2	340.2 ± 0.2	332.3	333.7 ± 0.3
H_2CO_3	$(138.6)_2$	89.1		49.5	114.1	338.6		331.2	
$HClO_2$	$(87.1)_1$	51.8	49.6 ± 0.7	35.3	73.2	335.0		328.3	
HCl	$(94.1)_1$	83.2	83.3	10.9	103.6	334.2	333.4	328.7	328.1 ± 0.1
H_3PO_3	$(152.4)_2$	104.5		47.9	119.7	328.8		323.7	
H_3PO_4	$(154.5)_1$	104.1		50.4	118.7	328.2	330.5 ± 5.0	321.6	323.5 ± 5.0
H_2SO_3	$(114.9)_1$	77.1		37.8	87.8	324.3		316.8	
HNO_3	$(146.5)_1$	95.4		51.1	105.8	324.0	324.5 ± 0.2	317.8	317.8 ± 0.2
HBr^b	$(87.5)_1$	80.2	77.6	7.3	90.4	323.8	323.5 ± 0.1	318.7	318.3 ± 0.2
$HClO_3$	$(133.2)_1$	97.2	98.0 ± 2.3	36.0	99.0	315.4		309.0	
H_2SO_4	$(159.9)_1$	116.1	109.5 ± 2.3	43.8	113.9	311.4	309.6 ± 2.6	303.8	302.3 ± 2.5
HPO_3	$(156.7)_1$	118.7	114.1 ± 1.4	38.0	115.8	310.7	310.8 ± 2.6	303.5	303.5 ± 2.5
FSO_3H	$(169.0)_1$	127.4		41.6	114.8	301.0	307.1 ± 2.6	293.9	303.9 ± 0.3
$HClO_4$	$(176.5)_1$	127.0	121.1 ± 2.3	49.5	112.6	299.2	288.0 ± 14	292.5	281.0 ± 14.0
CF_3SO_3H	$(172.4)_1$	143.9		28.5	128.7	298.4	305.4 ± 2.2	291.5	299.5 ± 2.0
$ClSO_3H$	$(173.0)_1$	136.7		36.3	120.9	297.8		290.5	
HBF_4	$(240.3)_1$	159.0		81.3	137.2	291.8		287.6	
HPF_6	$(262.1)_1$	170.2		91.9	136.5	279.9		276.8	
$HAlCl_4$	$(178.1)_1$	142.6		35.5	94.0	265.0		258.9	
$HAlBr_4{}^b$	$(159.8)_1$	130.9		28.9	79.7	262.4		256.7	

[a] Experimental data for adiabatic ionization energies and acidities are taken from the NIST database (ref 54). [b] Results for HBr and $HAlBr_4$ are obtained with G2 methodology.

originates in the low energy of their anions. This conclusion was corroborated by triadic analysis of the acidity of carboxylic acids X−COOH and alcohols $X-CH_2OH$ (X = H, CH_3, F, CF_3). It was unequivocally demonstrated that the increased acidity of carboxylic acids relative to alcohols can be traced down to considerably larger Koopmans' ionization energies of carboxyl anions $X-COO^-$.[26] In other words, the excess electron is stabilized in the conjugate base and the amplified acidity is a result of the predominant influence of the final state effect. It should be mentioned that triadic analysis proved useful in discussing gas-phase acidity of para-substituted benzoic acids,[27] phenols,[28] substituted cyclopentadienes,[29] azoles,[30] some substituted benzenes,[31] and cyclopropa-fused quinones.[32] The comparative merits of different modes of interpretation of the acidity were assessed and discussed in extenso by Deakyne.[33]

Unlike numerous studies of the acidity of organic neutral acids, in particular with the C−H bond as a proton donor,[34−45] systematic analyses of their inorganic counterparts are scarce.[46−50] In order to fill the gap we report here on the attempt to interpret acidity of the most common inorganic acids and superacids by using triadic paradigm.[26]

Computation Method

Protonation of a neutral and anionic base is given by eq 1:

$$B^{n-1}(g) + H^+(g) \rightarrow BH^n(g) \qquad (1)$$

where *n* assumes values 1 or 0 and (g) stands for the gas phase. If protonation of the negatively charged conjugate base is considered, then $n = 0$. The negative of the standard free energy change in reaction 1 yields the gas-phase basicity of the conjugate base $B^-(g)$, whereas the negative of the standard enthalpy change for the same reaction gives the proton affinity of $B^-(g)$. The latter is calculated at room temperature (298 K) via eqs 2 and 3:

$$\mathrm{APA} = \Delta E_{el} + \Delta(\mathrm{ZPVE}) + \Delta E_t + \Delta E_r + \Delta E_v + \Delta(pV) \qquad (2)$$

where APA denotes the absolute proton affinity and ΔE_{el} is given by

$$\Delta E_{el} = [E_{tot}(B^-) + E_{tot}(H^+) - E_{tot}(BH)] \qquad (3)$$

Here $E_{tot}(B^-)$ and $E_{tot}(BH)$ stand for the total energies of the conjugate base in question and its protonated form BH, respectively. Δ(ZPVE) is the difference in the zero-point vibrational energy of the reactants and products. The term absolute proton affinity refers to the fact that it is calculated from the first principles without reference to a standard gauge acid/base as is usual in the experimental work. Further, $\Delta E_v + \Delta E_t + \Delta E_r$ are the changes in the vibrational, translational, and rotational energy differences of the reactants and products, respectively, at 298 K. The $\Delta(pV)$ term is the change in the pressure−volume work contribution. Finally, $\Delta(pV) = RT$, $\Delta E_t = -(3/2)RT$, and $\Delta E_r = (\Delta N)(1/2)RT$, where ΔN is a gain in the number of rotational degrees of freedom upon protonation. A brief comment on the terminology is in place here. Brønsted acidity is by definition given by the negative Gibbs free energy change ΔG_{acid} in eq 1 as already pointed out earlier. However, the standard enthalpy change $\Delta H_{acid}(BH) = \mathrm{APA}(B^-)$ defined via eq 4 (vide infra) is a very good measure of acidity. We shall, therefore, use $\mathrm{APA}(B^-)$ in the forthcoming discussion as an equivalent of acidity, unless it is explicitly stated that ΔG_{acid} values are considered. In an attempt to work out a general procedure for prediction of accurate molecular energies, which can reproduce known experimental data with accuracy higher than ±2 kcal mol^{-1}, including acidity, Pople and co-workers developed G2[51] and G3[52] composite methods. They were used in the present work as implemented in GAUSSIAN 03 suite of computer codes.[53]

Results and Discussion

The calculated gas-phase absolute proton affinities ΔH_{acid} and the corresponding gas-phase acidities ΔG_{acid} of OH^- and 23 other conjugate bases of inorganic acids are given in Table 1.

The G3 composite scheme is employed in all molecules but in HBr and $HAlBr_4$, since the Br atom is not parametrized in that particular method. The G2 approach is, therefore, used instead. Computed values are in very good agreement with NIST experimental data as a rule.[54] In fact, theoretical estimates are within the measured error margin in most cases, but there are exceptions. Rare cases are given by CF_3SO_3H and FSO_3H, where the calculated value seems to be too low by 7 and 6 kcal mol^{-1}, respectively. We believe that the theoretical results are closer to the true proton affinity. In this connection it should be mentioned that our result for FSO_3H (301.0 kcal mol^{-1}) is in very good accordance with G2 calculation of Koppel et al.[46] ($\Delta H_{\mathrm{acid}} = 301.3$ and $\Delta G_{\mathrm{acid}} = 294.7$ in kcal mol^{-1}) and CBS-Q calculations of Steudel and Otto[55] ($\Delta H_{\mathrm{acid}} = 300.2$ and $\Delta G_{\mathrm{acid}} = 292.3$ in kcal mol^{-1}). Thus, it is likely that the experimental value for $\Delta H_{\mathrm{acid}} = 307.1 \pm 2.6$ kcal mol^{-1} is too high by at least 3−4 kcal mol^{-1}. The earlier experimental ΔH_{acid} value[54] of 311.0 kcal mol^{-1} is definitively wrong. Further, the error bars for the experimental acidity of $HClO_4$ are extremely high being ±14 kcal mol^{-1}. Hence, a theoretical value for its acidity of 300 kcal mol^{-1} is recommended by the present calculations. We note in passing that this value can be conveniently used as a threshold of superacidity in the gas phase. Finally, it should be mentioned that CBS-Q results for H_2SO_3 ($\Delta H_{\mathrm{acid}} = 325.3$ and $\Delta G_{\mathrm{acid}} = 316.9$ in kcal mol^{-1})[56] are in good accordance with our computations (Table 1). The same holds for $\Delta H_{\mathrm{acid}}(H_2CO_3) = 337.8$ kcal mol^{-1} obtained by Remko[57] using the CBS-Q method. Thus, acidities of other mineral acids computed here and not submitted to measurements as yet, can be used as fairly reliable data instead of the experimental values. New experimental measurements of the acidity of $HClO_4$, CF_3SO_3H, and FSO_3H are strongly recommended.

As to the agreement of the calculated first adiabatic ionization energies with the experimental IE_1^{ad} values, it is good for H_2O, H_2S, HF, HCl, HBr, HClO, $HClO_2$, and $HClO_3$ but the computed first adiabatic ionization energies are by far too large for H_2SO_4, HPO_3, and $HClO_4$. The reasons for these discrepancies are not known. However, since the theoretical values for HClO, $HClO_2$, and $HClO_3$ are in good agreement with experiment, it is likely that the measured value for $HClO_4$ is too low. It would be very useful to have more experimental data for this important molecular property, since available values are sparse. The G3 (G2 in the case of Br atom(s)-containing molecules) estimated first adiabatic ionization energies can be used in the meantime, if a due care is exercised.

Before the computed APA values are interpreted, some preliminaries are necessary. Adopting the trichotomy paradigm[26] one obtains

$$\Delta H_{\mathrm{acid}}(\mathrm{BH}) = \mathrm{APA}(\mathrm{B}_\alpha^-) = -\mathrm{IE}(\mathrm{B}^-)_{n,\alpha}^{\mathrm{Koop}} + E(\mathrm{ei})^{(n)}_{\mathrm{rex}} + (\mathrm{BAE})_\alpha^{\bullet} + 313.6\ \mathrm{kcal\ mol^{-1}} \quad (4)$$

where α denotes the site of protonation, while 313.6 kcal mol^{-1} is the electron affinity of proton (1 kcal mol^{-1} = 4.184 kJ mol^{-1}). Here the first term represents Koopmans' ionization energy of the conjugate base B^- calculated from the *n*th molecular orbital in the clamped nuclei and frozen electron density approximation. It is obtained by the Hartree−Fock model [HF/GTLarge//MP2(full)/6-31G(d)]. The accuracy and limitations of Koopmans' approximation were discussed by us[58] and by Pradie and Linnert.[59] It should be pointed out that ionization of the B^- conjugate base is considered to be a sudden event at the Koopmans level. However, it actually occurs in a real time. This is taken into account by the second term in eq 4, which describes relaxation of the nuclei and electrons during the ionization process. It is given by

$$E(\mathrm{ei})^{(n)}_{\mathrm{rex}} = \mathrm{IE}(\mathrm{B}^-)_n^{\mathrm{Koop}} - \mathrm{IE}(\mathrm{B}^-)_1^{\mathrm{ad}} \quad (5)$$

where $\mathrm{IE}(\mathrm{B}^-)_1^{\mathrm{ad}}$ is the first adiabatic ionization energy. Finally, the bond association energy $(\mathrm{BAE})_\alpha^{\bullet}$ gives the amount of stabilization released by the formation of a new X_α−H bond by attachment of the hydrogen atom to the X_α atom. It absorbs the Δ(ZPVE) and the small $\Delta E_t + \Delta E_r + \Delta E_v + \Delta(pV)$ terms given in eq 2. Finally, it should be mentioned that protonation of the conjugate base B_α^- can be visualized by the three-step process: (1) instantaneous pruning of an electron from the conjugate base (anion), (2) reorganization of the electron density and relaxation of the nuclei during ionization in the real time, and (3) homolytic creation of a new X_α−H bond between neutral radical $B^{\bullet}$ and hydrogen atom $H^{\bullet}$. It represents a slight generalization of the customary thermodynamic cycle, where a single $\mathrm{IE}(\mathrm{B}^-)_1^{\mathrm{ad}}$ term, yielding the first adiabatic ionization energy, is replaced by a sum of $\mathrm{IE}(\mathrm{B}^-)_n^{\mathrm{Koop}}$ and $E(\mathrm{ei})^{(n)}_{\mathrm{rex}}$. This elementary operation is, however, conceptually extremely important. Since deprotonation is considered here as reversed protonation, Koopmans' term mirrors properties of the final state of the acid, which donates the proton. It corresponds to an instantaneous snapshot picture of the electron distribution in the anion. On the other hand, the bond association energy $(\mathrm{BAE})_\alpha^{\bullet}$ describes the first step in the deprotonation process, thus reflecting properties of the initial state. The relaxation term provides description of the intermediate stage.

The *n*th MO energy occurring in Koopmans' term deserves a few words of a comment. It corresponds to the molecular orbital that is most closely related to the X_α atom in anion B^- to be protonated. For example, in the case of a lone pair localized on the atom X_α, it is the very MO accommodating this lone pair. Identification of such MOs, termed principal molecular orbitals (PRIMOs),[60] is usually unambiguous and poses no problem. It should be noticed that the PRIMO is not necessarily HOMO but could be placed lower on the orbital energy scale.

Finally, it should be stressed that formula 4 is exact in its complete form and the errors occurring in the results arise due to the approximate nature of the theoretical and computational methods applied. Dissection of the total APA into three contributions is not exact, but only rough instead. For instance, the one-particle picture underlying Koopmans' term is more realistic for higher occupied principal MOs than for the lower ones. In this context, it is interesting to point out that the HOMO orbitals can be even visualized by modern experimental techniques.[61−64] In conclusion, it is noteworthy that triadic analysis proved useful in interpreting absolute proton affinities of neutral organic bases and superbases as well as *mutatis mutandis* hydride affinities as reviewed recently.[65]

In order to interpret the trend of changes along a family of acids, it is convenient to select a standard molecule serving as a reference. Then the variations in APAs, denoted by $\Delta[\mathrm{APA}(\mathrm{B}_\alpha^-)]$ are measured relative to APA(st), where "st" stands for the gauge compound. In our case the latter will be the water molecule, or to put it more precisely, its deprotonated form hydroxyl anion OH^-. The difference $\Delta[\mathrm{APA}(\mathrm{B}_\alpha^-)]$ can be resolved into three contributions according to the trichotomy formula:

$$\Delta[\mathrm{APA}(\mathrm{B}_\alpha^{\,-})] = \mathrm{APA}(\mathrm{B}_\alpha^{\,-}) - \mathrm{APA}(\mathrm{OH}^-) = [-\Delta(\mathrm{IE})_{\alpha,n}^{\ \mathrm{Koop}};\quad \Delta E(\mathrm{ei})^{(n)}_{\ \alpha,\mathrm{rex}};\quad \Delta(\mathrm{BAE})_\alpha^{\ \bullet}] \tag{6}$$

where the square parentheses imply summation of the three bordered terms, which in turn explicitly read:

$$\Delta(\mathrm{IE})_{\alpha,n}^{\ \mathrm{Koop}} = \mathrm{IE}(\mathrm{B}^-)_{\alpha,n}^{\ \mathrm{Koop}} - \mathrm{IE}(\mathrm{OH}^-)_m^{\ \mathrm{Koop}} \tag{7a}$$

$$\Delta E(\mathrm{ei})^{(n)}_{\ \alpha,\mathrm{rex}} = E(\mathrm{ei})(\mathrm{B}^-)^{(n)}_{\ \alpha,\mathrm{rex}} - E(\mathrm{ei})(\mathrm{OH}^-)^{(m)}_{\ \mathrm{rex}} \tag{7b}$$

$$\Delta(\mathrm{BAE})_\alpha^{\ \bullet} = \mathrm{BAE}(\mathrm{B}^\bullet)_\alpha - \mathrm{BAE}(\mathrm{OH}^\bullet) \tag{7c}$$

It should be noted that indices n and m are different in general. The changes in triadic components relative to H_2O molecule are summarized in Table 2. Water is considered in the liquid state to be neither acidic nor basic within the Brønsted definition, although it can act as a proton donor (Brønsted acid) or a proton acceptor (Brønsted base). It is, therefore, convenient to use it as a standard in the gas state as well, particularly since it is an inorganic compound. Theoretical APA of the OH^- anion is very high being 391.2 kcal mol^{-1}, which is in very good accordance with the experimental value of 390.3 kcal mol^{-1}. It comes, therefore, as no surprise that APAs of all other conjugate bases of mineral acids lie below this gauge value. It is important to notice that very significant contribution to the increased acidity of all mineral acids is provided by the stabilization of the principal MOs, which offer residence to the excess electron, H_2S being a notable exception. Let us consider first superacids $ClSO_3H$, CF_3SO_3H, $HClO_4$, HBF_4, HPF_6, $HAlCl_4$, and $HAlBr_4$. The corresponding $\Delta(\mathrm{IE})_n^{\mathrm{Koop}}$ contributions are −106.5, −105.9, −110.0, −173.8, −195.6, −111.6, and −93.3 kcal mol^{-1}, respectively. It follows that Koopmans' term decreases APAs of the conjugate bases (i.e., increases acidity) by more than 100 kcal mol^{-1}, except in the case of $HAlBr_4$, where this decrease is "only" 93.3 kcal mol^{-1}. The latter is peculiar, because $HAlBr_4$ is the strongest acid considered here (see later). The highest enhancements of acidity by the Koopmans' term are found in HBF_4 and HPF_6 being 173.8 and 195.6 kcal mol^{-1}, respectively, which is remarkable indeed. Perusal of other data presented in the first column of Table 2 provides conclusive evidence that Koopmans' term exerts a decisive influence on the acidity of mineral acids in general with very few exceptions. It is, therefore, safe to conclude that acidity of mineral acids is predominantly determined by the properties of the final state, or in other words by the ability to distribute the excess electron density in deprotonated forms in an advantageous way. A few words on PRIMOs are in place here. They are the highest occupied molecular orbitals (HOMOs) in all but two cases (H_2CO_3 and H_3PO_3). The HOMO of OH^- is one of two degenerate MOs describing lone pair electrons (Figure 1). In HCO_3^- the PRIMO orbital is HOMO−1 in-plane combination of two local atomic AOs belonging to planar lone pairs. Since the proton attacks one of two oxygen atoms in the $HOCOO^-$ conjugate base in the molecular plane, HOMO−1 is the principal molecular orbital instead of HOMO. Analogously, in $H_2PO_3^-$ anion the HOMO−1 orbital has the lone pair MOs on oxygen atoms in the direction of the proton attack. Hence, it represents the PRIMO orbital for this anion (Figure 1). It is interesting to observe that it has a significant fraction of the hydrogen AO, which is directly bonded to phosphorus atom.

TABLE 2: Relative Contributions to Deprotonation Enthalpies of Selected Mineral Acids via Triadic Formulas 7a−7c in kcal mol^{-1} [a]

molecule	$\Delta[(\mathrm{IE})_n^{\mathrm{Koop}}]$	$\Delta[E(\mathrm{ei})^{(n)}_{\mathrm{rex}}]$	$\Delta(\mathrm{BAE})^\bullet$	$\Delta(\Delta H_{\mathrm{acid}})$
H_2O	0.0	0.0	0.0	0.0
HF	−44.8	7.4	18.4	−19.0
HClO	−23.1	10.7	−22.6	−35.0
H_2S	7.2	−19.7	−27.7	−40.2
HNO_2	−38.5	26.9	−40.4	−52.0
H_2CO_3	−72.1	24.0	−4.5	−52.6
$HClO_2$	−20.6	9.8	−45.4	−56.2
HCl	−27.6	−14.6	−15.0	−57.0
H_3PO_3	−85.9	22.4	1.1	−62.4
H_3PO_4	−88.0	24.9	0.1	−63.0
H_2SO_3	−48.4	12.3	−30.8	−66.9
HNO_3	−80.0	25.6	−12.8	−67.2
HBr	−21.0	−18.2	−28.2	−67.4
$HClO_3$	−66.7	10.5	−19.6	−75.8
H_2SO_4	−93.4	18.3	−4.7	−79.8
HPO_3	−90.2	12.5	−2.8	−80.5
FSO_3H	−102.5	16.1	−3.8	−90.2
$HClO_4$	−110.0	24.0	−6.0	−92.0
CF_3SO_3H	−105.9	3.0	10.1	−92.8
$ClSO_3H$	−106.5	10.8	2.3	−93.4
HBF_4	−173.8	55.8	18.6	−99.4
HPF_6	−195.6	66.4	17.9	−111.3
$HAlCl_4$	−111.6	10.0	−24.6	−126.2
$HAlBr_4$	−93.3	3.4	−38.9	−128.8

[a] Water molecule is taken as a reference.

TABLE 3: Acidities of Selected Mineral Acids (in kcal mol^{-1}) and Their Relation to Hammett−Taft σ_p and σ_p^- Parameters

substituent (X−OH)	acid	ΔH_{acid} (X−OH)	σ_p(X)	σ_p^-(X)
H	H_2O	391.2	0.00	0.00
Cl	HClO	356.2	0.23	0.19
NO	HNO_2	339.2	0.91	
CO_2H	H_2CO_3	338.6	0.45	0.77
ClO	$HClO_2$	335.0		
H_2PO_2	H_3PO_3	328.8		
H_2PO_3	H_3PO_4	328.2		
SO_2H	H_2SO_3	324.3	−0.07	
NO_2	HNO_3	324.0	0.78	1.27
ClO_2	$HClO_3$	315.4		
SO_3H	H_2SO_4	311.4		
PO_2	HPO_3	310.7		
SO_2F	FSO_3H	301.0	0.91	1.54
ClO_3	$HClO_4$	299.2		
SO_2CF_3	CF_3SO_3H	298.4	0.96	1.63
SO_2Cl	$ClSO_3H$	297.8	1.11	

In a couple of molecules the bond association energy plays a more important role than Koopmans' term, such as in HNO_2, $HClO_2$, H_2S, and HBr, implying that in the latter two S−H and Br−H bond scission energies are much lower than the O−H bond energy in H_2O. In these four molecules the initial state is the crucial factor, but it should be noted that in HNO_2 its contribution is equivalent to the Koopmans' term. In this connection it is fitting to say that superacidity of $HAlCl_4$ and $HAlBr_4$ is a result of a combined effect of the final and initial state effects, which both act in harmony. A decrease in their Cl−H and Br−H bond energies relative to those of the water molecule is −24.6 and −38.9 kcal mol^{-1}, respectively. This explains the fact that $HAlCl_4$ and $HAlBr_4$ are more potent superacids than HBF_4 and HPF_6 in spite of a lesser contribution of Koopmans' term, together with less favorable contribution of the relaxation energy in the latter two molecules (Table 2). Substantial influence of the $(\mathrm{BAE})^\bullet$ term is also found in H_2SO_3 and HClO. Finally, it should be emphasized that concerted influence of all three triadic terms, leading to enhanced acidity, is found only in halides HCl and HBr. Acidity of HF is, on the other hand, exclusively determined by Koopmans' term. The

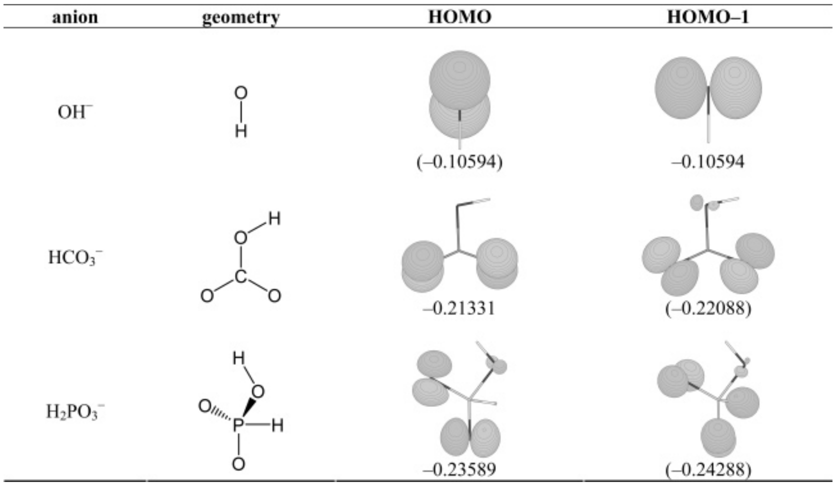

Figure 1. Schematic representation of highest two occupied molecular orbitals for some characteristic conjugated bases, together with their orbital energies (in au) obtained by HF/GTLarge//MP2(full)/6-31G(d) level of theory. The orbital energies of the principal MOs participating in protonation of anions the most are given within parentheses.

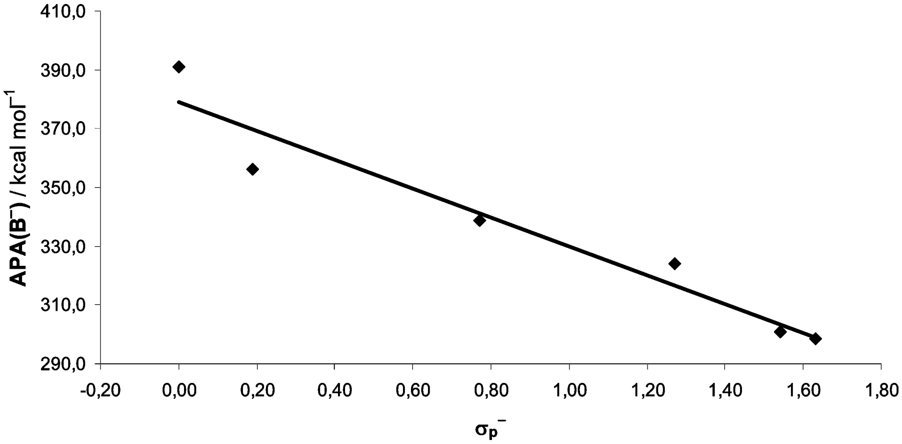

Figure 2. Approximate linear relationship between APA(B^-) and Hammett−Taft σ_p^- constants [APA(B^-) = $-49.22\sigma_p^- + 379.2$ kcal mol^{-1}).

relaxation energy contributes toward increase in acidity of H_2S relative to H_2O by 19.7 kcal mol^{-1} (Table 2). In all other molecules the intermediate relaxation step diminishes acidity.

It is interesting to examine a homologous series of compounds HClO, $HClO_2$, $HClO_3$, and $HClO_4$. Their acidity increases (absolute proton affinity of conjugate bases decreases) along the series, implying that it is enhanced by each oxygen atom added to the central chlorine atom. Taking the least acidic molecule HClO as a new reference system for this set of acids, this increase in acidity is regular and practically additive being −21.2, −40.8, and −57.0 kcal mol^{-1}. In other words, each oxygen atom amplifies the acidity by roughly 20 kcal mol^{-1}. The reasons behind this are intriguing. Applying triadic formula 6 one obtains the following: APA($HClO_2$) − APA(HClO) = −21.2 = [2.5; −0.9; −22.8], APA($HClO_3$) − APA(HClO) = −40.8 = [−43.6; −0.2; 3.0], and APA($HClO_4$) − APA(HClO) = −57.0 = [−86.9; 13.3; 16.6]. In all four systems the PRIMO orbital corresponds to the HOMO orbital, since these orbitals have electron densities at oxygen atoms in the plane of protonation. However, in hypochlorous and chlorous acids the energies of PRIMO orbitals are practically the same. In the other two molecules Koopmans' ionization energy term substantially contributes toward enhancement of acidity, meaning that the final state effect is overwhelming. It appears that upon sequential attachment of the oxygen atoms to HClO, the principal molecular orbital of the anion (describing the lone pair to be protonated) becomes gradually more and more stabilized, which leads to higher acidities. It should be noticed that individual terms in triadic analysis are not additive, but their sum, i.e., their interplay, leads to a constant increment in acidity. The relaxation energy contribution is very small for $HClO_2$ molecule and, being of the opposite sign, practically cancels out Koopmans' term. It turns out that the bond association energy term (−22.8 kcal mol^{-1}) exerts the final and decisive effect in this molecule making it more acidic than HClO by almost the same amount (−21.1 kcal mol^{-1}). The situation in the other two molecules is, however, quite different. In $HClO_3$ and $HClO_4$ the relaxation energy decreases, whereas the Δ(BAE) term becomes higher acting against the decrease in the APA values. It can be concluded that consecutive additions of an oxygen atom to the HClO molecule leading to $HClO_n$ (n = 2, 3, 4) series result in a linear increase of acidity, which in the case of $HClO_2$ is clearly a consequence of the initial state effect, whereas in the case of $HClO_3$ and $HClO_4$ acids it is a pure final state effect. There is a distinct difference, however, since in $HClO_3$ the influence of the relaxation and bond association terms is almost negligible. On the contrary, in $HClO_4$ these two terms jointly act to diminish acidity by 30 kcal mol^{-1}, which is overcome by the overwhelming Koopmans' effect (−86.9 kcal mol^{-1}), yielding a net increase in acidity by 57 kcal mol^{-1}. Interestingly, attachment of the oxygen atom to the central atom in HNO_2 and H_2SO_3 leads to increase in acidity too, but for different reasons. Specifically, APA(HNO_3) − APA(HNO_2) = −15.2 = [−41.5; −1.3; 27.6] and APA(H_2SO_4) − APA(H_2SO_3) = −12.9 = [−45.0; 6.0; 26.1], in kcal mol^{-1}. In HNO_3 and HNO_2 the relaxation energies are practically identical, whereas in H_2SO_4 it is higher than in H_2SO_3 by 6 kcal mol^{-1}. In both cases the BAE term diminishes acidity by roughly 27 kcal mol^{-1}. However, a predominant effect is exerted by Koopmans' term leading to amplified acidity of HNO_3 and H_2SO_4 relative to their HNO_2 and H_2SO_3 counterparts by −15.2 and −12.9 kcal mol^{-1}, respectively, which is consequently the final state effect.

It is of some importance to relate the APA values to Hammett−Taft σ_p and σ_p^- constants.[9] Unfortunately, they are sparse for constituents of mineral acids. Considering only compounds deprotonated at hydroxyl group O−H, we present the data for substituents X−OH in Table 3. The σ_p constants show very poor correlativity with the APA values as evidenced by regression coefficient $R^2 = 0.62$ and exhibit the absolute average deviation of 13.8 kcal mol^{-1} (not shown here). However, a fair correlation is found between the σ_p^- constants and absolute proton affinities (Figure 2), as could be expected. It reads:

$$\mathrm{APA(B^-)} = -49.22\sigma_p^- + 379.2\ \mathrm{kcal\ mol^{-1}} \qquad (8)$$

The number of points in Figure 2 is small, and the quality of correlation is fairly low as reflected by $R^2 = 0.936$ and the absolute average error of $\Delta_{abs}[\mathrm{APA(B^-)}] = 6.4$ kcal mol^{-1}. Nevertheless, this is the best correlation at present. The qualitative trend of changes is easily discernible though. Unfortunately, the inverse relationship would be too inaccurate to be used for estimates of the σ_p^- constants of other substituents.

Conclusions

It is shown that the G3 and G2 computational scheme yield acidities of inorganic acids in very good agreement with available measured data. Discrepancies found for CF_3SO_3H, $HClO_4$, and FSO_3H indicate that new measurements are desirable. The calculated deprotonation energy of $HClO_4$ of 300 kcal mol^{-1} is recommended as a threshold of superacidity in the gas phase. The first adiabatic ionization energies of their conjugate base anions are in fair to good accordance with the experimental values, which are unfortunately scarce. Some more computational and experimental work is needed here. The origin of acidity of inorganic acids is explored by using triadic formula. It is conclusively shown that it arises predominantly due to the final state effect. In other words, they are properties of deprotonated forms mirrored by Koopmans' theorem and the corresponding HOMO and HOMO−1 orbitals (PRIMOs), which offer themselves as the best molecular orbitals to accommodate the excess electron density. The principal molecular orbitals HOMO−1 enter the game in only two cases: H_2CO_3 and H_3PO_3 (Figure 1). Taking water molecule as a gauge system, it is shown that only H_2S is more acidic as a consequence of the combined action of the relaxation and bond dissociation terms. Koopmans' term acts in opposite direction since HOMO is destabilized in SH^- relative to the corresponding highest occupied molecular orbital in OH^-. The underlying effects leading to acidity below the borderline of 300 kcal mol^{-1} for $HClO_4$, as found in $ClSO_3H$, CF_3SO_3H, HBF_4, HPF_6, $HAlCl_4$, and $HAlBr_4$ molecules, are of particular importance. In all cases the Koopmans' term is decisive. However, in the last two compounds the bond dissociation energy makes substantial contribution to the acidity too, which makes them the most powerful superacids studied here. It turns out that their acidity, measured by the APA values of 265.0 and 262.4 kcal mol^{-1}, respectively, is a result of cooperative action of the final and initial state effects. A concerted interplay of all three triadic terms leads to enhanced acidity of HCl and HBr, which in turn are quite acidic, but they are not superacidic species.

Finally, a linear, albeit very approximate relation is found between absolute proton affinities of deprotonated conjugate bases (APAs) and Hammett−Taft σ_p^- constants, where the latter are available.

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