Using Hydrocarbon Acidities To Demonstrate Principles of Organic Structure and Bonding

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A recent article in this *Journal (1)* discusses the properties of acidic substances not containing a formal carboxylic acid functionality. The authors elaborate on a number of carbon-based acids, such as Meldrum's acid and dimedone. Other compounds that could be considered in this context are hydrocarbons (substances containing only hydrogen and carbon). Conant and Wheland undertook the first "study of extremely weak acids" in 1932 and by colorimetric methods were able to arrange 10 hydrocarbons in a scale of increasing acid strength *(2)*. McEwen *(3)* extended this work by quantifying the acidity of these compounds (and many others) with respect to the acid dissociation constant of methanol. The most acidic hydrocarbon noted by these researchers was 9-phenylfluorene[1] (Figure 1) with a $pK_a = 21$ *(3)*.

The pK_a values[2] of many structurally diverse hydrocarbons have been measured during the last 70 years. A striking feature of the collected data is the enormous acidity range covered. Hydrocarbon acidities encompass an astonishing 50 orders of magnitude (minimum) and thus span the majority of known acid behavior. Examination of such wide-ranging acidities facilitates a classroom discussion concerning fundamental principles of organic structure and bonding. This review article highlights the acidity of different types of hydrocarbons and rationalizes observed trends. Emphasis is placed upon undergraduate concepts of hybridization, resonance, induction, and aromaticity.
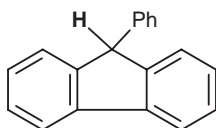

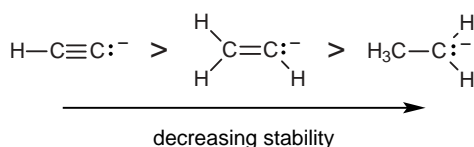Figure 1. 9-Phenylfluorene. The most acidic proton is highlighted by a bold **H**.

decreasing stability

Figure 2. Relative order of conjugate base stability of two-carbon hydrocarbons.

Table 1. pK_a and Hybridization of Two-Carbon Hydrocarbons

Molecule	Carbon Hybridization	pK_a
Ethane	sp^3	49–62
Ethene	sp^2	42–45
Ethyne	sp	25.5

Hybridization Effects

Acidities of alkanes, alkenes, and alkynes are discussed in most introductory organic chemistry textbooks *(4)*. The pK_a of ethyne (acetylene) is well established (25.5 in DMSO[3]; ref *5*). Acidities of ethane ($pK_a = 49$–62; ref *6*) and ethene (ethylene, $pK_a = 42$–45; ref *7*) are less well known owing to experimental difficulty in accurately measuring pK_a values of such weakly acidic compounds.[4]

Hydrocarbon acidity increases as the percentage s character in hybrid orbitals of carbon increases; that is, a correlation exists between hybridization and acidity as shown in Table 1. Walsh *(8)* has suggested that carbon electronegativity towards hydrogen is greatest for an acetylenic carbon atom. A C–H bond in ethyne therefore has a comparatively high bond dipole of sign $C^{\delta-}$–$H^{\delta+}$. The ability of an sp hybridized carbon to attract electrons is related to conjugate base stabilization. The relative base stability order formed by proton loss from each hydrocarbon is shown in Figure 2.
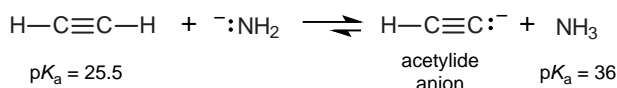
The acetylide anion formed by deprotonation of ethyne is more stable than corresponding anions derived from ethene and ethane. An sp hybrid orbital (present in the acetylide anion) possesses 50% s character and 50% p character. As an s orbital is lower in energy and closer to the carbon nucleus than a p orbital, the negative charge developed on hydrocarbon deprotonation is stabilized most for the acetylide anion. This effect leads to increased dissociation of ethyne compared to ethene and ethane and thus increased acidity. A sufficiently strong base such as an amide ion can deprotonate ethyne (Scheme I).

The equilibrium constant for this equilibrium is 3.16×10^{10} meaning that ethyne is essentially completely deprotonated (> 99.9%) under these conditions. This behavior is extended to any terminal alkyne (one possessing an acetylenic hydrogen, R–C≡C–**H**). Anions derived from terminal alkynes are useful in constructing carbon chains, as they act as excellent nucleophiles in S_N2 reactions *(9)* (Scheme II). An sp^3 hybrid orbital (25% s character) cannot stabilize a negative charge developed in the resulting anion as effectively and alkanes are observed to be much less acidic than alkynes.
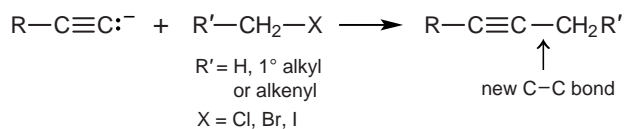
A linear relationship between acidities of 10 nonconjugated hydrocarbons and hybrid orbital composition has been reported *(10)*. In this study hybridization parameters were calculated by the scaled maximum overlap (SMO) method.[5] This approach defines hybrid orbitals in the form sp^n, where n often represents a noninteger hybridization index exponent (second-order hybridization). A general wave function for an sp^n hybrid (n being an integer or not) is given by the expression
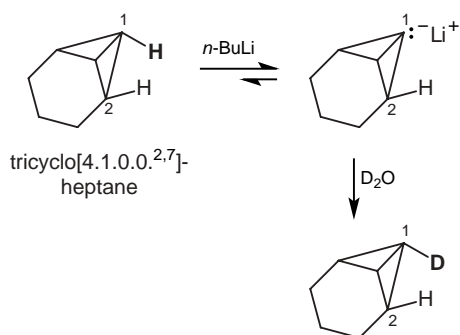
$$\psi = \left(2s + n^{1/2}2p\right)(n+1)^{-1/2}$$

Even for a simple molecule such as ethyne the use of integer

$$H-C{\equiv}C-H \quad + \quad ^{-}{:}NH_2 \quad \longrightarrow \quad H-C{\equiv}C{:}^{-} \quad + \quad NH_3$$

pK_a = 25.5 ... acetylide anion ... pK_a = 36

Scheme I. Formation of an acetylide anion.

$$R-C{\equiv}C{:}^{-} \quad + \quad R'-CH_2-X \quad \longrightarrow \quad R-C{\equiv}C-CH_2R'$$

R' = H, 1° alkyl
or alkenyl

X = Cl, Br, I

new C–C bond

Scheme II. Carbon–carbon bond formation.

tricyclo[4.1.0.0.^{2,7}]-
heptane

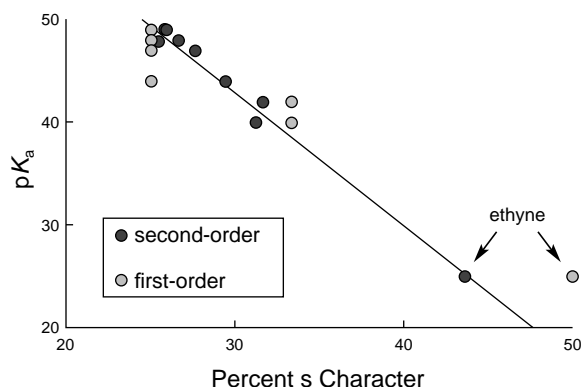Scheme III. Acidity of tricyclo[4.1.0.0.^{2,7}]heptane

Figure 3. Plot of hybrid orbital % s character versus measured acidity for first-order hybridization and second-order hybridization (10a).

Table 2. Relationship between the Rates of H–T Isotopic Exchange and ^{13}C–H Coupling Constants[a]

Hydrocarbon	Exchange Rate[b]	$J_{13C\text{-}H}$ /Hz
Cyclopropane	7.0×10^4	161
Cyclobutane	28	134
Cyclopentane	5.7	128
Cyclohexane	1	123, 124
Cycloheptane	0.76	123
Cyclooctane	0.64	122

[a]Data from ref 14. [b]The exchange rate is relative to cyclohexane.

hybrids to describe covalent bonds has no quantitative basis. There is no reason to suppose the "best" hybrid orbital to form a C–H bond in ethyne has an identical s:p ratio as present in the triple bond. According to the SMO method an acetylenic carbon forms a C–H bond with a hybrid orbital described as sp$^{1.29}$, corresponding to 43.6% s character. When hybrid orbitals are idealized (sp, sp^2, or sp^3; first-order hybridization) the correlation with hydrocarbon acidity is much poorer (Figure 3).

Highly strained cycloalkanes possess C–H bonds containing an unusually high degree of s character. Carbon orbital hybridization used for C–H bonding in cyclopropane is calculated as sp$^{2.36}$ rather than sp^3 (11). The hybridization index for an sp^n hybrid orbital is related to the NMR ^{13}C–H coupling constant ($J_{13C\text{-}H}$) by (12):

$$J_{13_{C\text{-}H}}\,(\text{Hz}) \;=\; \frac{500}{n+1}$$

Cycloalkanes forming C–H bonds with hybrid orbitals of greater than 25% s character ($J_{13C\text{-}H} > 125$ Hz) exhibit enhanced acidity. The strained tricyclic hydrocarbon tricyclo[4.1.0.0.^{2,7}]heptane (Scheme III) should theoretically be more acidic than a saturated alkane such as n-heptane. $J_{13C\text{-}H}$ for the C1–H bond has been measured as 200 Hz, while $J_{13C\text{-}H}$ for the C2–H bond is 146 Hz (13). This corresponds to a hybrid orbital of composition sp$^{1.50}$ involved in the C1–H bond (40% s character) and a hybrid orbital of composition sp$^{2.42}$ involved in the C2–H bond (29% s character). Increased acidity of tricyclo[4.1.0.0.^{2,7}]heptane is verified by salt formation on treatment with n-butyllithium, followed by deuteration on addition of D$_2$O (Scheme III).

Streitwieser has noted a correlation between $J_{13C\text{-}H}$ and kinetic acidities of cycloalkanes (14). Rates of hydrogen–tritium (T) isotopic exchange were measured in N-tritiated cyclohexylamine catalyzed by cesium cyclohexylamide (Table 2). The dominant factor determining cycloalkane acidity is the quantity of s character in the C–H bond hybrid orbital. Cycloheptane and cyclooctane are slightly less acidic than cyclohexane (smaller s character). More highly strained rings appear more acidic than cyclohexane (larger $J_{13C\text{-}H}$, greater s character).

Resonance and Inductive Effects

The preceding section highlights factors increasing anionic stabilization that promote increased hydrocarbon acidity. Another stabilizing effect is resonance delocalization of charge. This effect is illustrated by comparing the acidities of cyclohexane (pK_a = 52; ref 15) and cyclohexene (pK_a = 46; ref 16). Deprotonation at an allylic position in cyclohexene forms a resonance stabilized anion (Figure 4). Formation of this conjugate base is energetically more favorable than generation of the corresponding anion from cyclohexane, hence cyclohexene exhibits greater acidity.

Similarly, formation of the resonance stabilized benzyl anion rationalizes the greater acidity of toluene (pK_a = 42; ref 17) compared to methane (pK_a ≈ 55; ref 18). Toluene is at least 13 orders of magnitude more acidic than methane. Four canonical forms can be drawn for the benzyl anion (Figure 5), where the negative charge is delocalized to ortho and

para ring positions. A greater degree of charge dispersion in this anion than the cyclohexenyl anion leads to toluene appearing more acidic than cyclohexene by a factor of 10^4.

Implicit in construction of such canonical forms is coplanarity of the ring with an sp^2 hybridized carbon, as maximal p orbital overlap will ensue. Charge delocalization lowers the energy of the benzyl anion. A proton is more readily lost from toluene than from methane since no resonance stabilization of the methyl anion is feasible. This concept is extended to diphenylmethane, Ph_2CH_2, $pK_a = 32$ *(19),* and triphenylmethane, Ph_3CH, $pK_a = 30$ *(19b, 20).*

One can construct 7 and 10 canonical forms for the anions derived from diphenylmethane and triphenylmethane, respectively. The acidities of these compounds are a function of contributing steric and inductive effects *(21, 22),* illustrating caution should be exercised in making simple correlations between canonical structures and delocalization energy. It has been concluded that "more than half of the enhanced acidity of triphenylmethane over saturated hydrocarbons is due to the inductive effect of three benzene rings and that less than half can be attributed to resonance stabilization of the carbanion" *(22).*

The example of triptycene (Figure 6A) demonstrates that inductive effects can play a role in determining hydrocarbon acidity. The pK_a of triptycene (44; ref *23)* is comparable to that of toluene and much greater than that of a saturated hydrocarbon. Despite the presence of three aromatic rings resonance delocalization of the triptycyl anion cannot occur (Figure 6B). Proton abstraction from a bridgehead carbon atom generates the conjugate base that is forced to adopt a pyramidal conformation. An absence of necessary coplanarity precludes successful p orbital overlap. Stabilization of the triptycyl anion occurs by an inductive electron withdrawal mechanism through σ bonds involving the benzene rings. This effect is apparent for other benzylic anions, including the benzyl anion itself. Greater s character in the bridgehead C−H bond makes an additional acidifying contribution *(23).*

Aromaticity Effects

Cyclopentadiene (Figure 7) is a remarkably acidic hydrocarbon having an experimentally measured pK_a of 18 *(24).* Deprotonation results in delocalization of the cyclopentadienyl anionic charge over all five carbon atoms (Figure 8). Resonance delocalization of charge and inductive electron withdrawal are clearly small contributory acidifying factors. The cyclopentadienyl anion obeys Hückel's rule—it is planar, has a total of six π electrons and a p orbital associated with each carbon. An aromatic species is generated from a nonaromatic hydrocarbon (cyclopentadiene) that has an sp^3 hybridized carbon atom present. The driving force of aromaticity leads to the parent hydrocarbon having an acidity comparable to some aliphatic alcohols. The enormous size of this "aromatic effect" is evident on examining pK_a values of other cycloalkenes (Scheme IV). Seven canonical forms can be drawn for the tropylium anion. Addition of π electrons in this species shows there are eight ($4n$, an anti-aromatic number, where $n = 2$). The extremely weak acidity of cycloheptatriene is attributable to great instability of its conjugate base. Neither the parent hydrocarbon nor the conjugate base adopts a planar conformation with the latter anion
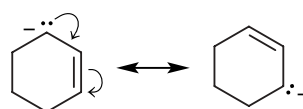

Figure 4. Resonance delocalization of charge in the cyclohexenyl allylic anion.
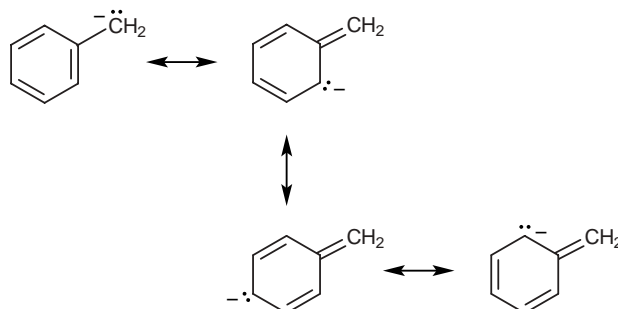

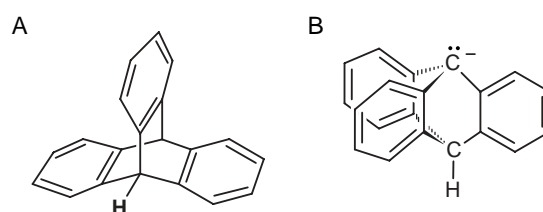Figure 5. Resonance delocalization of charge in the benzyl anion.
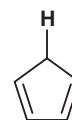

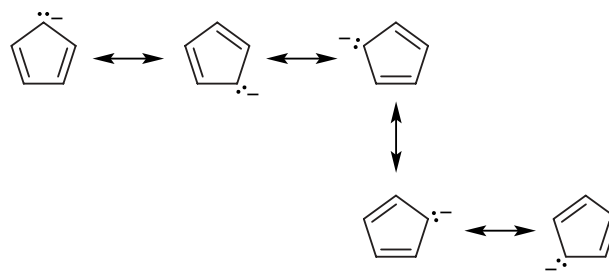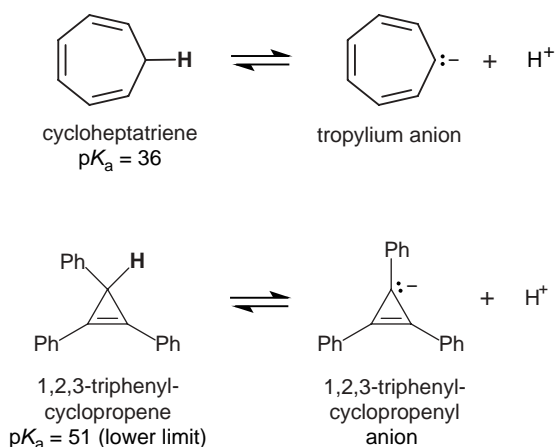Figure 6. (A) Triptycene and (B) triptycyl anion.

Figure 7. Cyclopentadiene.

Figure 8. Five canonical forms of the cyclopentadienyl anion.

cycloheptatriene
$pK_a = 36$

tropylium anion

Scheme V. Generation of the aromatic fluorenyl anion from fluorene.

1,2,3-triphenyl-
cyclopropene
$pK_a = 51$ (lower limit)

1,2,3-triphenyl-
cyclopropenyl
anion

Scheme IV. Generation of anti-aromatic anions from cycloheptatriene and 1,2,3-triphenylcyclopropene. The pK_a values are from ref *25*.
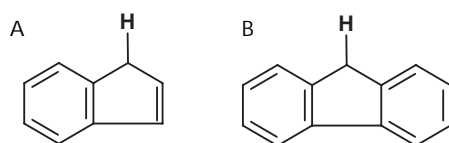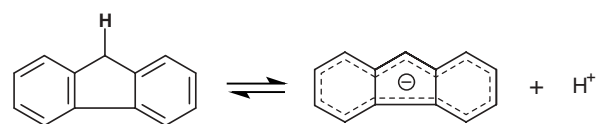

Scheme VI. Generation of the fluoradenyl anion from fluoradene.

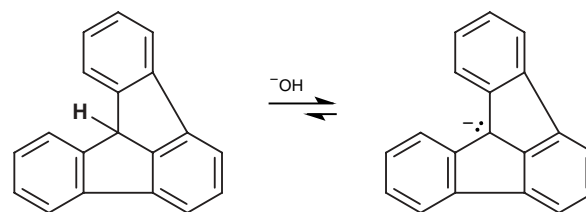Figure 9. (A) Indene and (B) fluorene.

Figure 10. Fluoradenyl anion.

additionally representing an anti-aromatic species. The 1,2,3-triphenylcyclopropenyl anion has four π electrons ($n = 1$, analogous to cyclobutadiene). Enormous angle strain exists leading to an acidity similar to an unsubstituted alkane such as ethane.

Indene ($pK_a = 20.1$; ref *26*) and fluorene ($pK_a = 22.6$; ref *19b*) are viewed as structural derivatives of cyclopentadiene (Figure 9). The successive decrease in acidity of cyclopentadiene, indene, and fluorene is linked to a progressive decrease in aromatic character of the conjugate bases. This overshadows the acidifying effects of the benzene ring(s). The fluorenyl anion has a total of 14 delocalized π electrons with each of its 13 carbon atoms bearing a 0.077 negative charge (Scheme V).

Fluoradene ($pK_a = 13.8$; ref *27*) has two fluorene rings fused together resulting in enhanced acidity compared to cyclopentadiene. There exists the possibility of forming a planar anion on deprotonation and extensive charge delocalization taking place. The highlighted proton is removed by treatment with aqueous NaOH (Scheme VI). A sharp-eyed student will notice that the fluoradenyl anion in Scheme VI has 20 π electrons associated with it (a $4n$, or anti-aromatic, number). One might predict the formation of this anion to be energetically disfavored, and fluoradene to be correspondingly *weakly* acidic. It is however possible to draw canonical structures containing only 18 electrons spread over 18 car-
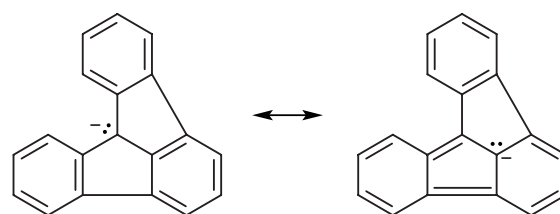
bon atoms that represent an aromatic species. The negative charge is localized and each of the 18 carbons bears a negative charge of 0.00 (Figure 10).

A plot of experimental pK_a values against aromatic stabilization energies (delocalization energies, ΔE_π) calculated by Hückel molecular orbital (HMO) theory yields a linear correlation (Figure 11; ref *28*). The HMO approach assumes acidity is solely proportional to changes in π-bond energy resulting from conjugation differences between a hydrocarbon and its corresponding anion. This implies that σ-bond energy changes are constant and that any strain energies in the hydrocarbon are the same as those in the anion. Any solvation or hyperconjugation effects are also neglected. The ΔE_π of the cyclopentadienyl anion is calculated by the Hückel method to be 2.000β *(29)*. The empirical aromatic stabilization energy (derived from the heat of hydrogenation of benzene relative to cyclohexene) equals 36 kcal mol^{-1} *(30)* and also corresponds to 2β. Conversion of cyclopentadiene to its anion results in a large increase in delocalization energy (36 kcal mol^{-1}). Significantly the correlation only holds for anions predicted to be coplanar. Triphenylmethane (whose anion is subject to steric effects and deviates from coplanarity) is considerably less acidic than predicted by HMO theory.

Increasing electronic delocalization while maintaining aromatic character on deprotonation further increases hydrocarbon acidity (Table 3). Three of the four compounds in
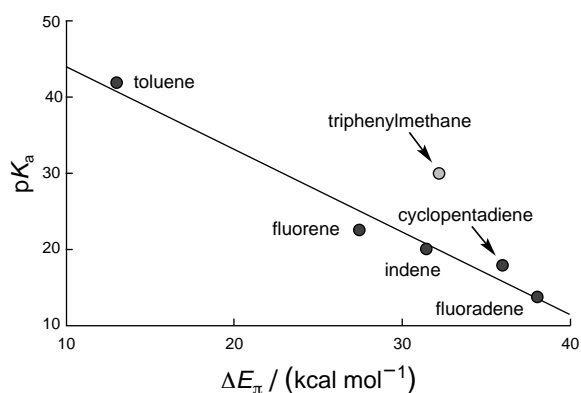
Figure 11. Plot of hydrocarbon aromatic stabilization energy (ΔE_π) versus measured acidity (28).
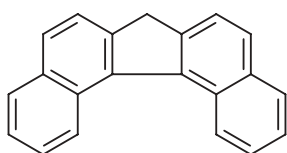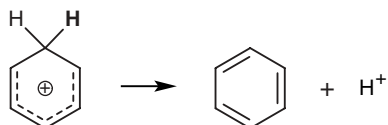

Figure 12. 7*H*-Dibenzo[*c,g*]fluorene.

Scheme VII. Deprotonation of the benzenium ion.

Table 3 are based on the structure of 7*H*-dibenzo[*c,g*]fluorene (Figure 12). An undergraduate exercise is to construct all canonical forms of the anions derived from these molecules in an attempt to link anionic stability with electronic delocalization. This reinforces concepts of resonance stabilization and "curly-arrow" notation.

Conclusions

This article illustrates the remarkable range of experimentally measured hydrocarbon acidities. Discussion is limited to neutral compounds containing solely the elements hydrogen and carbon. An even more acidic "hydrocarbon" is the benzenium ion (Scheme VII), which forms benzene on deprotonation. This species is only stable in superacid media and has an estimated pK_a of < −10 (32).

Acidity differences are reasoned by applying fundamental principles encountered by the students enrolled in an introductory organic chemistry course. The data provide an ideal springboard to discuss concepts of hybridization, resonance, induction, and aromaticity. Opportunities exist to outline limitations of these concepts when considered in isolation from one another. Although hydrocarbons are generally considered nonacidic, this is clearly not necessarily the case. Compound 3.4, Table 3, has a pK_a of 5.9, meaning it is at least four orders of magnitude more acidic than phenol

Table 3. pK_a of Some Polycyclic Aromatic Hydrocarbons

Compound	Structure	pK_a
3.1		10.4
3.2		9.1
3.3		8.2
3.4		5.9

NOTE: Solvent is a mixture of DMSO/HOAc/NaOAc. Data from ref 31.

(aqueous pK_a of 9.89; ref *1*), although the latter pK_a is substantially lowered in the presence of DMSO ($pK_a = 12.4$ in 70% DMSO; ref *33*). As an extension students can be challenged to "design their own hydrocarbon" that may prove to be even more acidic than the ones discussed herein. Several software programs exist that allow prediction of pK_a values, often to an accuracy of ±0.5 pK_a units *(34)*.
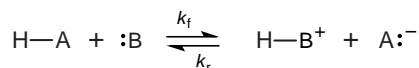
Acknowledgment

WSupplemental Material

A table containing the pK_a values for all hydrocarbons mentioned in this article is available in this issue of *JCE Online*.

Notes

1. The most acidic proton in each structure is highlighted by a bold **H**.

2. pK_a represents $-\log_{10} K_a$, where $K_a = k_f / k_r$ for the equilibrium:

$$H{-}A \; + \; :B \; \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \; H{-}B^+ \; + \; A{:}^-$$

K_a is related to the rate constant for protonation of B (k_f) and deprotonation of BH$^+$ (k_r). Since pK_a values are recorded in solution, anionic solvation makes k_r the more significant rate constant. k_f and k_r are measures of kinetic rather than thermodynamic acidity.

3. For comparison purposes, all quoted pK_a values < 32 are in dimethylsulfoxide (DMSO) unless otherwise stated.

4. Generally pK_a determinations up to 33 are obtained by equilibrium methods involving colorimetry or spectroscopy. pK_a evaluation of less acidic hydrocarbons is achieved by electrochemical or isotopic exchange (H–D or H–T) techniques.

5. The SMO method involves optimizing parameters for all hybrid orbitals of all atoms in a molecule that maximizes the sum over all bonds of suitably scaled bond overlaps (*10b*).

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