PROTIC ACIDITY OF SOME ALIPHATIC AND ALICYCLIC HYDROCARBONS IN THE GAS PHASE AND IN SOLUTION. AN EMPIRICAL AND COMPUTATIONAL LINK

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This work is dedicated to Professor Otto Exner on the occasion of his 80th birthday in recognition of his outstanding contributions to physical organic chemistry.

Here we report the results of the study of a set of thirteen hydrocarbons R–H not leading to extensively charge-delocalized anions R^- upon ionization, R–H → $R^- + H^+$. It essentially involves the following: (i) The computation at the G2 level of the changes in thermodynamic state functions for this process in the gas phase. The reliability of the computational method was further assessed by comparison with CCSD(T)/Aug-cc-pVTZ results. (ii) A direct comparison of the experimentally available thermodynamic (gas phase) and kinetic (solution) data pertaining to this reaction. (iii) A careful re-examination of the experimental data sets and the Brønsted-type relationships derived therefrom by using the computed thermodynamic data. This treatment suggests the existence of mechanistic features affecting the experimental data and indicates the need for further experimental and computational work.

Keywords: Carbanions; Thermodynamics; Gas-phase reactivity; Charge-delocalized anions; Alicyclic hydrocarbons; Protic acidity; Ab initio calculations; CCSD(T).

Carbanions are important species in organic chemistry and the investigation of structural effects on their thermodynamic stability in solution and in the gas phase is a topic of conceptual relevance[1] and, as we discuss below, an experimental challenge in a number of cases. State-of-the-art computational techniques allow rather accurate (generally within 1–2 kcal mol^{-1}) estimates of the acidities of the corresponding hydrocarbons in the gas phase[2].

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In this work we have examined the ionization of a group of hydrocarbons, for which solution data are available. This data set was compared to with their experimental acidities in the gas phase. Furthermore, a computational study at the G2 level[3] was conducted for the same systems with the goal of having a reliable benchmark for examination of some energetic and structural factors pertaining to the ionization of these compounds. Because of our interest in cubane, cyclobutane and some of their derivatives[4], attention was particularly focused on cyclic compounds.

COMPUTATIONAL DETAILS

In all cases, the initial structures were fully optimized at the HF/6-31G(d) level and the harmonic vibrational frequencies were also computed at this level. The structures thus optimized were used as input for the calculations at higher levels. In all cases use was made of the Gaussian 98 package[5]. Detailed computational information (including coordinates) are available on request from the authors.

RESULTS AND DISCUSSION

Experimental Gas-Phase Data and Computational Results

Consider a hydrocarbon, R–H. Its acidity in the gas phase and in solution can be measured by the standard enthalpy or Gibbs energy changes for the ionization processes (*1*) and (*2*):

$$\text{R–H(g)} \rightarrow \text{R}^-\text{(g)} + \text{H}^+\text{(g)} \quad \longrightarrow \quad \Delta_r H^o_m\,(1),\ \Delta_r G^o_m\,(1) \tag{1}$$

$$\text{R–H(sln)} \rightarrow \text{R}^-\text{(sln)} + \text{H}^+\text{(sln)} \quad \longrightarrow \quad \Delta_r H^o_m\,(2),\ \Delta_r G^o_m\,(2) \tag{2}$$

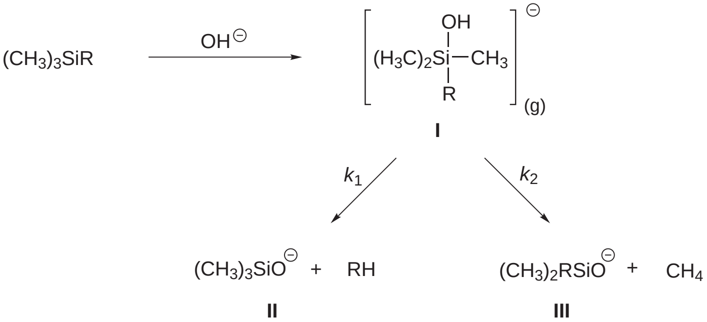
$\Delta_r H^o_m$ (*1*) is the proton affinity of R^-(g), PA(R^-); $\Delta_r G^o_m$ (*1*) is the corresponding gas-phase acidity of RH(g), ΔG^o_{acid}(RH) or, alternatively, the gas-phase basicity of R^-, GB(R^-)[6].

The difficulties inherent to the experimental study of the acidity of aliphatic and alicyclic hydrocarbons are consequences of the two facts: (i) Their extremely weak acidity and, (ii) a number of their corresponding carbanions are unstable with respect to the electron loss (Eq. (*3*))[7]. This implies that the electron affinities (EA) of the corresponding radicals, EA($R^\bullet$), defined as EA($R^\bullet$) = $\Delta_r H^o_m$ (*3*), are negative.

$$R^-(g) \rightarrow R^\bullet + e^- \qquad (3)$$

This is the case of a variety of aliphatic and alicyclic carbanions. Methyl and phenyl anions are two useful exceptions. Schleyer[8] and coworkers indicated some years ago that negative EA values are associated with short lifetimes of the isolated species in the gas phase. As discussed below, there are experimental (albeit indirect) means to estimate the thermodynamic stability of many of them. Thus, it is important to ascertain whether or not the results of these studies have a true physical meaning. Computational studies at various levels (ranging from HF/6-31+G(d)[9a] to B3LYP/6-311++G(2d,p)[9b]) show that the Hessians for the structures of a number of anions (including all those reported in Table I), as optimized at the same levels, indicate that they are true minima on the corresponding potential energy surfaces (PES), irrespective of the sign of the electron affinity.

There are several methods for the experimental study of properties of carbanions in the gas phase, including the determination of their PA values. In Table I, a number of experimental PA and/or GB values are collected for the ions examined in this work and originating in different laboratories. It is obvious that in many cases, both precision and accuracy are quite limited. For our present purposes,results obtained using DePuy's reaction[10] (Eq. (*4*)) are particularly useful. It involves the attack by hydroxide anion on relevant alkyltrimethylsilane, $(CH_3)_3Si–R$.



(*4*)

The mechanism currently accepted for this reaction involves the formation of the pentacoordinate siliconate ion **I**, followed by its decomposition to yield the ion–dipole complexes **II** and **III** involving alkyl (R^-) or methyl (CH_3^-) anions, respectively. These complexes should readily decompose

TABLE I
Thermodynamic stabilities of selected carbanions in the gas phase[a]

Hydrocarbon	Anion	PA(G2)[b,c]	$\Delta_r G°_{acid}$(G2)[b,c]	PA(exp)[b,c]	$\Delta_r G°_{acid}$(exp)
Methane (**1**)	CH_3^-	418.4	410.1	416.7 ± 0.7[d] 418.0 ± 3.5[e]	408.60 ± 0.08[a] 409.9 ± 3.6[e]
Ethane (**2**)	$C_2H_5^-$	420.6 419.6[t]	411.9 410.9[t]	420.1 ± 2.0[f] 421.0 ± 2.0[g] (420.6 ± 2.8)[h]	411.7 ± 2.1[f]
Propane (**3**)	n-$C_3H_7^-$	416.5	408.5	415.6 ± 2.0[f] (415.6 ± 2.0)[h]	407.2 ± 2.1[f]
Isobutane (**4**)	*t*-$C_4H_9^-$	412.2	404.7	412.9 ± 2.0[g] 414.7 ± 2.4[i] (413.8 ± 3.1)[h]	404.3 ± 2.1[f]
Neopentane (**5**)	neo-$C_5H_{11}^-$	412.7	403.6	408.9 ± 2.0[f] 411 ± 10[e]	400.1 ± 2.0[f]
Cyclopropane (**6**)	c-$C_3H_5^-$	413.4	404.6	411 ± 7[j] 410.7 ± 1.6[k] 411.5 ± 2.0[f] 412.0 ± 2.0[g] 416.9 ± 4.9[e] (412.8 ± 2.8)[h]	401 ± 10[j]
Cyclobutane (**7**)	c-$C_4H_7^-$	414.7 (eq-H) 416.9 (ax-H)	406.4 (eq-H) 408.3 (ax-H)	417.4 ± 2.0[f] 419.9 ± 2.4[i] (418.7 ± 3.1)[h]	408.4 ± 2.1[f]
Cyclopentane (**8**)	c-$C_5H_9^-$	411.8 (eq-H) 413.4 (ax-H)	406.1 (eq-H) 406.2 (ax-H)	416.1 ± 2.0[f] 418.3 ± 2.4[i] (417.2 ± 3.1)[h]	407.4 ± 2.1[f]
Cyclohexane (**9**)	c-$C_6H_{11}^-$	413.6 (eq-H) 415.9 (ax-H)	403.7 (eq-H) 405.8 (ax-H)	418.3 ± 2.4[i] 404.0 ± 0.9[l]	>398[l]
Cycloheptane (**10**)	c-$C_7H_{13}^-$	409.3 (eq-H) 413.3 (ax-H)	401.4 (eq-H) 405.1 (ax-H)	415.6[i]	
Cubane (**11**)	$C_8H_7^-$	407.1	398.1	404.3 ± 3.1[m]	396.5 ± 3.0[m]
Ethene (**12**)	$C_2H_3^-$	408.5		409.40 ± 0.60[n] 407.5 ± 2.0[f] 407.0 ± 3.0[e] (408.0 ± 2.6)[h]	400.10 ± 0.50[n]
Acetylene (**13**)	C_2H^-	377.5	369.5	377.9 ± 0.70[n] 378.0 ± 0.70[o] 378.0 ± 0.50[p] 379.8 ± 0.50[q] (378.4 ± 0.7)[h] 379 ± 5[j]	369.70 ± 0.80[n] 369.80 ± 0.60[o] 369.80 ± 0.60[p] 370 ± 6[j]
Benzene (**14**)	$C_6H_5^-$	400.1	391.2	401.70 ± 0.50[r] 401.80 ± 0.50[s] 400.7 ± 2.5[q] (401.4 ± 1.8)[h]	392.90 ± 0.40[r] 390.9 ± 2.0[q]

[a] All values in kcal mol^{-1}. [b] Defined in the text. [c] This work. [d] From lit.[11]. [e] From lit.[18]. [f] From lit.[10b]. [g] From lit.[10a]. [h] Average of experimental values taken from lit.[16]. [i] From lit.[13]. [j] From lit.[16]. [k] From lit.[19]. [l] From lit.[20]. [m] From lit.[14]. [n] From lit.[21]. [o] From lit.[22]. [p] From lit.[23]. [q] From lit.[24]. [r] From lit.[12a]. [s] From lit.[12b]. [t] Calculated at the CCSD(T)/Aug-cc-pVTZ//MP2/Aug-cc-pVTZ level.

through internal proton transfer to yield either hydrocarbon R–H or methane. According to experimental evidence, the statistically corrected relative rates of formation of ions $(CH_3)_3SiO^-$ and $(CH_3)_2RSiO^-$ and the gas-phase acidities of RH and CH_4 are related through Eq. (*5*).

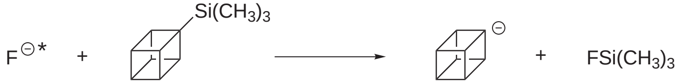
$$\ln (k_1/k_2) = -\beta[\mathrm{PA}(R^-) - \mathrm{PA}(CH_3^-)] \qquad (5)$$

The scaling factor β is determined by using as anchoring values, the PAs for methyl[11] and phenyl[12] anions for which independent, accurate PA values are available.

There are two important experimental data sets of gas-phase acidities for the hydrocarbons examined in this work. While based on an experimental study of reaction (*4*), they differ in the experimental techniques used and, hence, in the experimental conditions. They were respectively obtained by means of flowing afterglow-selected ion flow tube, a "high-pressure"[10,12] technique and by Fourier transform ion cyclotron resonance spectroscopy (FT ICR)[13]. The results are presented in Table I.

In the case of cubane, reaction (*1*) proceeds too slowly, possibly because rehybridization accompanying the formation of cubanyl anion significantly reduces its rate of formation, and this prevents the use of Eq. (*3*). This difficulty was overcome in an elegant FT ICR study[14] in which fluoride anion was kinetically (translationally) excited by SORI[15] (sustained off-resonance irradiation) pulses and allowed to react with (trimethylsilyl)-cubane to yield cubanyl anion (Eqs (*6*) and (*7*)). Its PA value (reported in Table I) was estimated by applying the bracketing technique to the proton (or deuteron) exchanges with a variety of proton donors and ND_3.

$$\mathrm{F}^{\ominus} \xrightarrow{\text{SORI}} \mathrm{F}^{\ominus *} \qquad (6)$$



(*7*)

We have used the G2 computational method to determine the reliability of the experimental data in the case of negative EA values. This is important because, to our knowledge, cycloalkyl carbanions (with the exception of cyclopropyl anion) belong to this subset. To this end, we have determined $\Delta_r H^{\circ}_{\mathrm{m}}$ (*1*) and $\Delta_r G^{\circ}_{\mathrm{m}}$ (*1*) for a small group of ions having both positive and negative EAs. We present in Fig. 1 a comparison of experimental and computed PA values for selected alkyl carbanions and other anions derived from stronger hydrocarbon acids (chloride, fluoride and hydroxide anion were also included in order to widen the range of acidities as well as to refer to some totally independent benchmark values). For the sake of consistency, the experimental values used are those recommended in the latest NIST compilation[16]. The agreement between computed and experimental data is remarkably good. A similar excellent agreement has been reported for a variety of acidic compounds studied at the B3LYP/6-311+G(d,p) level[17]. These results lend confidence to the extension of the method to cycloalkyl carbanions. For the latter, we have used, as much as possible, experimental data originating in the same laboratory, with the hope of minimizing systematic errors. (The raw computational results are presented in Table II.)

Inspection of the data presented in Table I shows the following:

1. Using the computed $\Delta_r G^{\mathrm{o}}_{\mathrm{m}}$ (*1*) values as a quantitative criterion, the stability of cyclic carbanions is larger for the isomers in which the electronic "lone pair" is in an axial position. However, the difference in stabilities is relatively small, and so a mixture of both isomers should be expected under equilibrium conditions. In the case of cyclobutyl anion the energetic barrier for the equatorial–axial interconversion amounts to 4.71 kcal mol^{-1} (at the B3LYP/6-311++G(d,p) level)[4a].

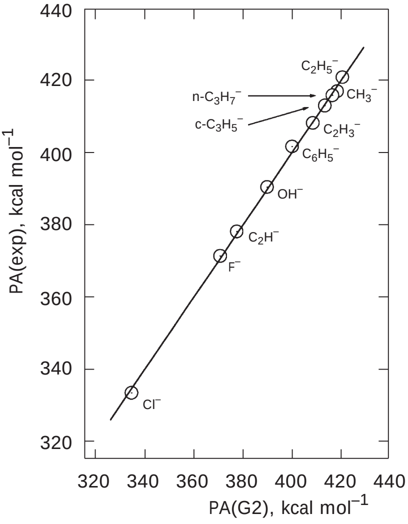


FIG. 1
Experimental vs G2-computed gas-phase PA of selected anions. Slope = 0.997 (0.013), intercept = 0.9 (4.8), s.d. = 0.99, R^2 = 0.999

2. Structure effects on both experimental and calculated $\Delta_r G^{\text{o}}_{\text{m}}$ (*1*) and $\Delta_r H^{\text{o}}_{\text{m}}$ (*1*) values clearly show that a significant increase in the s character of the acidic carbon brings about an enhancement of the acidity. This trend was first reported as a good linear relationship holding in the case of a limited set of hydrocarbons[17]. The correlation is less clear when examining a large group of compounds of closely related structures[9b]. This finding is not too surprising because of the complexity of the situation. For instance, (i) long-range effects are likely to be important[9b] and, (ii) the hybridization of the acidic carbon in the neutral molecule and in the anion are different[25]. It is of interest that in the case of cubane the s character is large and further increases on going from the neutral molecule to the anion. On the other hand, in the case of cyclobutane, the s character in the neutral mole-

TABLE II
Computed[a] thermodynamic state functions for relevant acidic species A–H and their corresponding anions[b] A^-

Anion	H_{298}	G_{298}	Acid	H_{298}	G_{298}
Cl^-	–459.80664	–459.82402	HCl	–460.32832	–460.34948
F^-	–99.75824	–99.77476	HF	–100.34670	–100.36639
OH^-	–75.70947	–75.72903	H_2O	–76.32827	–76.34965
CH_3^-	–39.74268	–39.76461	CH_4	–40.40708	–40.42819
$C_2H_5^-$	–78.95850 –78.93890[c]	–78.98584 –78.96624[c]	C_2H_6	–79.62631 –79.60513[c]	–79.65233 –79.63106[c]
n-$C_3H_7^-$	–118.18891	–118.21989	C_3H_8	–118.85023	–118.88088
t-Butyl	–157.42299	–157.45606	Isobutane	–158.07751	–158.11102
Neopentyl	–196.65134	–196.68848	Neopentane	–197.30672	–197.34169
Cyclopropyl	–116.97043	–116.99899	Cyclopropane	–117.62678	–117.65374
Cyclobutyl	–156.19488 (eq-H) –156.19142 (ax-H)	–156.22589 (eq-H) –156.22285 (ax-H)	Cyclobutane	–156.85341	–156.88349
Cyclopentyl	–195.45198 (eq-H) –195.45153 (ax-H)	–195.48592 (eq-H) –195.48605 (ax-H)	Cyclopentane	–196.10793	–196.14327
Cyclohexyl	–234.68755 (eq-H) –234.68395 (ax-H)	–234.72312 (eq-H) –234.71972 (ax-H)	Cyclohexane	–235.34231	–235.37644
Cycloheptyl	–273.90657 (eq-H) –273.90010 (ax-H)	–273.93926 (eq-H) –273.94527 (ax-H)	Cycloheptane	–274.55642	–274.59491
Cyclooctyl	–308.20122	–308.23409	Cyclooctane	–308.84766	–308.87847
Ethenyl	–77.71775	–77.74277	Ethene	–78.41193	–78.43678
Ethynyl	–79.58283	–76.60581	Ethyne	–77.18204	–77.20464
Phenyl	–231.13993	–231.17221	Benzene	–231.77509	–231.80568

[a] At the G2 level. [b] All values in hartrees. [c] Calculated at the CCSD(T)/Aug-cc-pVTZ//MP2/Aug-cc-pVTZ level.

cule is small and even more so in the case of the anion[4a,9b]. Last, anionic hyperconjugation has been suggested to be a stabilizing factor in the case of carbanions. This effect (confirmed by NBO analyses) involves the interaction between the "lone pair" and antibonding C–H and C–C σ^* orbitals β to the anionic center and leads to a lengthening of the corresponding bonds[4a,9,17]. The subject seems to deserve further study, perhaps using the methods of correlation analysis.

3. Irrespective of the sign of their EAs, the apparent experimental PA values for bulky aliphatic or alicyclic carbanions are significantly different from the computed values and this difference seems to increase with the bulkiness of the anion. This is best seen by consideration of Fig. 2, a plot of all the computed values of $\Delta_r H^{\mathrm{o}}_{\mathrm{m}}$ (*1*) against the corresponding experimental data (all values taken from Table I). It is clear that, with the exception of the anions of some cycloalkanes, the agreement between experimental and computed values is again quite satisfactory. Cyclopropyl anion also behaves well, but cyclobutyl, cyclopentyl, cyclohexyl and cycloheptyl anions seem "too weak" by some 4 to 5 kcal mol^{-1}. This feature supports the concept that the carbanions within complexes **II** and **III** (reaction (*4*)) are "solvated" by the trialkylsilanol molecules[10b]. Because of the strong electrostatic interaction, the carbanion could thus avoid decomposition through electron loss. For Eq. (*5*) to hold, the "solvation" of the carbanions within the complexes should be of the same strength. This is likely to be the case for species of small steric requirements; a possibility exists that this stabilizing effect de-

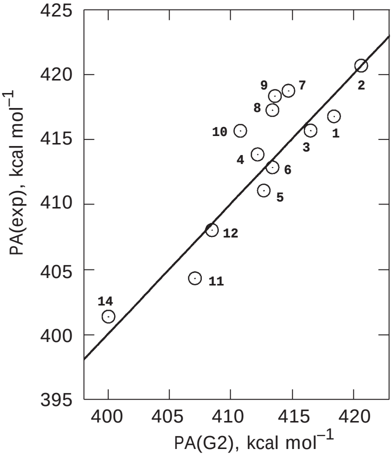


FIG. 2
Overview of experimental vs G2-computed gas-phase PA of aliphatic and alicyclic carbanions. Species are numbered as in Table I

creases as the bulk of the carbanionic moiety increases. In the absence of further information, this provides a seemingly satisfactory rationale for these facts. Note, however, that our computational results show an intriguing point, namely that the departures from the good correlation portrayed in Fig. 2 are of the same size as the equatorial–axial interconversion barrier mentioned above. One can then envisage the possibility of the effect originating in the energetic barrier associated to a phenomenon closely related to this inversion and taking place in the reaction **I** → **II**. Here we mention that we have recently undertaken a computational study of the mechanism of reaction (*4*) and that it proceeds slowly because of the considerable size of the species involved.

Solution Acidity

Acidities (as measured by $\Delta_r G^{\circ}_{\mathrm{m}}$ (*2*)) for a number of hydrocarbons leading to charge-delocalized carbanions have been determined in DMSO[1] solution. Unfortunately, aliphatic and alicyclic hydrocarbons are too weak acids for this method to be applicable. An alternative approach of great importance is the Streitwieser kinetic technique. It is based on the study of the kinetics of the cyclohexylamide-catalyzed (cesium cyclohexylamide) deuterium or tritium exchanges between the relevant carbanions and cyclohexylamine, reaction (*8*)[26]

$$\mathrm{RH}_{n-1}\mathrm{L(sln)} + \mathrm{R'NH_2(sln)} \rightarrow \mathrm{RH}_n\mathrm{(sln)} + \mathrm{R'NHL(sln)}\ , \qquad (8)$$

where L = D, T; R, R′ = cyclohexyl

TABLE III
Kinetic acidities in solution for selected hydrocarbons relative to cyclohexane

Hydrocarbon	k/k_0	$(k/k_0)_{323.15\ \mathrm{K}}$
Cyclopropane[a,b]	$(7.0 \pm 0.9) \times 10^4$	$(7.0 \pm 0.9) \times 10^4$
Cyclobutane[a,b]	28 ± 10	28 ± 10
Cyclopentane[a,b]	5.72 ± 0.27	5.72 ± 0.27
Cyclohexane[a,b]	(1.00)	(1.00)
Cycloheptane[a,b]	0.76 ± 0.09	0.76 ± 0.09
Cubane[c,d]	6.3×10^4	6.6×10^4 [e]
Benzene[c,d]	$(9.1 \pm 0.7) \times 10^7$	$(3.8 \pm 0.3) \times 10^8$ [e]

[a] At 50 °C. [b] From lit.[26a]. [c] At 25 °C. [d] From lit.[26c]. [e] Corrected as indicated in the text.

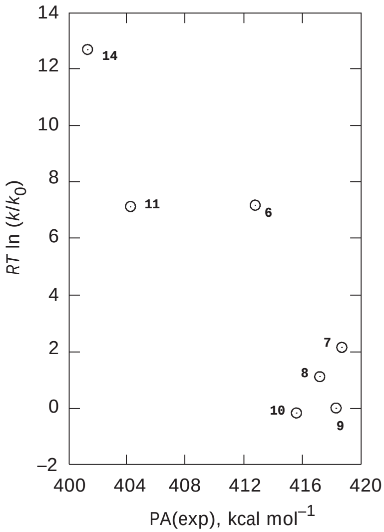


FIG. 3

Experimental Gibbs energies of activation for deuterium exchange of several hydrocarbons, relative to cyclohexane vs the experimental PA values of the corresponding anions. Species are numbered as in Table I

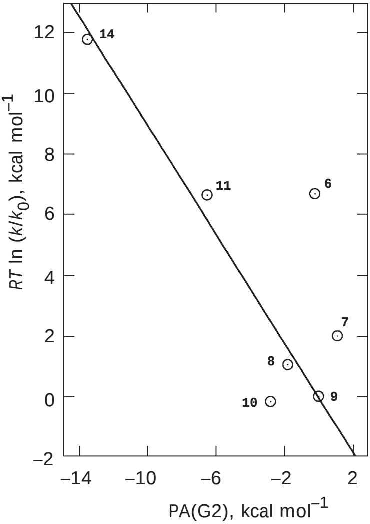


FIG. 4

Experimental Gibbs energies of activation for deuterium exchange of several hydrocarbons, relative to cyclohexane vs the computed PA values of the corresponding anions. Species are numbered as in Table I

Representative experimental results, in terms of relative rates referred to the ionization of cyclohexane, are summarized in Table III. Note that the experimental reaction rates were obtained at different temperatures. However, the datum for cyclohexane was also determined at these temperatures and this allowed to unify the results at 50 °C (most values were obtained at this temperature) by assuming that $\Delta\Delta G^{o\neq} \approx \Delta\Delta H^{o\neq}$.

Figures 3 and 4 are plots of the relative activation energies, $RT \ln (k/k_0)$ (k_0 stands for the reaction rate of cyclohexane) vs the intrinsic (thermodynamic) acidities in the gas phase. In Fig. 3 we have used the experimental PA values while those in Fig. 4 are the computed (G2) values.

Inspection of Fig. 3 indicates similar trends of structure effects on acidity in the gas phase and in solution. It is clear, however, that the solution kinetic acidities of cyclopropane and (to a lesser extent) cyclobutane seem to be affected by some different factors. In particular, the seemingly higher solution acidity of cyclopropane relative to cubane does not reflect the ranking of intrinsic acidities of these compounds.

Figure 4 shows a somewhat clearer pattern. Thus, benzene, cubane, cyclopentane and cyclohexane define an excellent linear relationship with a range of some 14 kcal mol^{-1} and a slope close to 0.90. It is obvious that the number of data points is small and that this "local order" might well be fortuitous. However, it is tempting to consider that it reflects a real fact and to explore the reasons for the departures from linearity. The simplest hypothesis is to admit that the line is the locus of species involving comparable solvation effects. Then, the positions of cyclopropane (**6**), cyclobutane (**7**) and cycloheptane (**10**) with respect to this line are exactly those one would expect on the basis of increasing steric hindrance to solvation.

It is clear that the fundamental condition for the discussion given above being meaningful is for the computational method to be reliable. A referee has expressed doubts about the ability of the G2 method to properly account for the properties of species such as ethide anion, known to be unstable. In view of this, we have computed the PA of this ion at the CCSD(T)/Aug-cc-pVTZ//MP2/Aug-cc-pVTZ level[27,28]. The results are presented in Table I and the raw data in Table II. As it can be seen, the value obtained by this method nicely agrees within 1 kcal mol^{-1} with both the G2 value and the experimental (indirect) datum.

CONCLUSIONS

Our study, however, severely limited by the moderate size of the experimental database and the difficulties inherent to the high-level calculations on large, flexible species, leads to the following preliminary conclusions:

1. The experimental thermodynamic (gas phase) and kinetic (solution) acidities of hydrocarbons not leading to extensively charge-delocalized anions examined herein do seem to be physically meaningful.

2. Brønsted-type correlations are somewhat blurred by the relatively large experimental uncertainties and, particularly by "solvation" effects in solution and/or mechanistic side-effects in the gas phase. This notwithstanding, these correlations seem to appear under conditions of nearly constant solvation.

3. The above results suggest that more computational and possibly experimental studies are needed and that the field is not yet closed.

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