Thermodynamic Acidity of $(CF_3)_3CH$ and 1H-Undecafluorobicyclo[2.2.1]heptane: The Concept of Anionic (Fluorine) Hyperconjugation

Ilmar A. Koppel,[*,†] Viljar Pihl,[†] Juta Koppel,[†] Frederick Anvia,[‡] and Robert W. Taft[*,‡]

Contribution from the Institute of Chemical Physics, Tartu University, EE2400 Tartu, Estonia, and Department of Chemistry, University of California at Irvine, Irvine, California 92717

Received September 13, 1994. Revised Manuscript Received June 6, 1994[⊗]

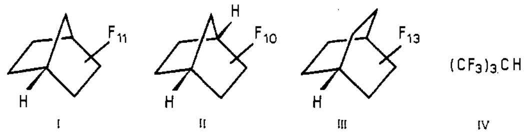
Abstract: The gas-phase equilibrium acidity of 1H-undecafluorobicyclo[2.2.1]heptane (I), 1H,4H-decafluorobicyclo-[2.2.1]heptane (II), and tris(trifluoromethyl)methane (IV) has been determined by pulsed FT-ICR technique. Also, a comparison study of the thermodynamic acidities of I and IV in DMSO solution has been made. These experiments have long been considered crucial for the evaluation of the role of the anionic (fluorine) hyperconjugation on the stability of aliphatic fluorosubstituted carbanions. Substituent field/inductive, polarizability, and steric effects for I, II, and IV can be assumed to be similar. The significantly greater observed acidity of the open-chain IV, compared to its bridgehead counterparts I and II, can be reasoned to be the inability of the latter acids to form planar anionic structures (Bredt's rule) that is a requirement for maximum hyperconjugation. Both the new gas-phase and the DMSO measurements show that IV is by many powers of 10 more acidic than I and II. Together with the existing experimental and the theoretical work, important evidence is provided that qualitatively favors the concept of anionic hyperconjugation.

In 1950 J. D. Roberts used the concept of anionic hyperconjugation to explain *m*- and *p*-trifluoromethyl substituent effects.[1] The valence bond picture suggested by Roberts involves a no-bond resonance structure (e.g., $CF_3CH_2^- \leftrightarrow F^- F_2C{=}CH_2$). In terms of MO theory[2] the effect is based on the interaction of the lone pair (n or p) electrons on the anionic or the neutral reaction center with the antibonding (vacant, σ^*_{CF} or π^*_{CX}) and bonding (filled, σ_{CF} or π_{CX}) orbitals of the β-CF bonds. The overall effect of these interactions will be determined by the relative contribution of the stabilizing (n-σ^*_{CX} or p-π^*_{CX}) or destabilizing (n-σ_{CX} or p-π_{CX}) interactions which are accompanied by the steric repulsion between fluorine atoms.

Alternative interpretations of the β-fluorine stabilization effect, mostly due to A. Streitwieser and D. Holtz et al.,[3–5] are based primarily on the inductive and field effects. Both concepts usually assume that the effects of β- and, even more so, of α-fluorine atoms are accompanied by the destabilizing steric lone pair repulsion between fluorine atoms and by stabilizing polarizability effects.

During the last 40 years a great number of experimental and theoretical studies of the aforementioned effect on chemical, electrical, and spectroscopic properties of the neutral molecules, reactive intermediates, ionic species, and free radicals have been undertaken. Numerous experimental and theoretical arguments for and against two major hypotheses regarding the interpretation of the effect of β- and α-fluorine-substituted alkyl groups have been published.[2–13]

Chart 1



One of the most powerful tests for the evaluation of the importance of the contributions of hyperconjugation, field/inductive, and steric repulsion effects on the reactivity of fluorine-substituted compounds was suggested by S. Andreades[14] who called for a comparison of kinetic (isotope exchange) or thermodynamic acidities of the hydrogen in the bridgehead positions of fluorinated bicyclic systems: I, II, and their open-chain analog IV (Chart 1).

It is assumed that bridgehead hydrogen acidities in I–III cannot be influenced by the fluorine (anionic) hyperconjugation (the interaction of the filled anion lone pair orbital with the CX bonding or antibonding orbitals) on the basis of the Bredt's rule due to inability of those bicyclic systems to assume the planar structure in the anionic form. Evidently, no such restrictions are present in the anion of IV which is believed to be planar (C_{3v} symmetry)[10,15] and stabilized by nine resonance structures of the type:

$$(CF_3)_3C^- \leftrightarrow F^- F_2C{=}C(CF_3)_2$$

The stabilization of anions of I, III, and IV by the field/inductive effect and the polarizability of the substituents, on one hand, and destabilization by the repulsive interactions between the anionic center and fluorine atoms, on the other hand, could be considered to be rather similar because the former two acids have six β- and five γ- or six β- and seven γ-fluorines, respectively, whose electron-withdrawing ability could be estimated to be approximately the same as that of nine β-fluorines in $(CF_3)_3C^-$. Hence, it could be expected that if fluorine (anionic) hyperconjugation is an

---

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

[1] Roberts, J. D.; Webb, R. L.; McElhill, E. A. *J. Am. Chem. Soc.* **1950**, *72*, 408 and references therein.

[2] (a) Schleyer, P. v. R.; Kos, A. *Tetrahedron* **1983**, 1141 and references therein. (b) Salzner, U.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1992**, *190*, 401.

[3] Holtz, D. *Prog. Phys. Org. Chem.* **1971**, *8*, 1.

[4] Holtz, D. *Chem. Rev.* **1971**, *71*, 1.

[5] Streitwieser, A., Jr.; Holtz, D.; Ziegler, G. R.; Stroffer, J. O.; Brokaw, M. L.; Guibe, F. *J. Am. Chem. Soc.* **1976**, *98*, 5229.

[6] Stock, L. M.; Wasilewski, M. R. *Prog. Phys. Org. Chem.* **1981**, *13*, 253.

[7] Streitwieser, A., Jr.; Holtz, D. *J. Am. Chem. Soc.* **1967**, *89*, 692.

[8] Sleigh, J. H.; Stephens, R.; Tatlow, J. C. *J. Fluorine Chem.* **1980**, *15*, 411.

[9] Friedman, D. S.; Francl, M. M.; Allen, L. C. *Tetrahedron* **1985**, *41*, 499.

[10] Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 4027. (b) Farnhan, W. B., Smart, B. E.; Middleton, W. J.; Calabrese, J. C.; Dixon, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 4565.

[11] Klabunde, K. J.; Burton, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 820, 5985.

[12] Wiberg, K.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 614.

[13] DeFrees, D. J.; Bartmess, J. E.; Kim, J. K.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *99*, 6451.

[14] Andreades, S. *J. Am. Chem. Soc.* **1964**, *86*, 2006.

[15] Koppel, I. A.; Burk, P.; Trummal, A.; Rummel, A.; Anvia, F.; Taft, R. W. Unpublished Gaussian 88/90 and MOPAC (PM3, AM1) calculations.

0002-7863/94/1516-8654$04.50/0

important stabilizing factor, $(CF_3)_3CH$ would have thermodynamic and kinetic acidities that exceed by several orders of magnitude those of the bicyclic acids **I**, **II**, or **III**. (The latter has six β- and four γ-fluorines and one hydrogen atom on each of the two bridgehead positions.)

Unfortunately, the measurement of the kinetic acidity of **I**–**III** and **IV** has led to the controversial results. Streitwieser, Holtz, et al. have made indirect comparison of the second-order rate constants for the sodium methoxide catalyzed deuterium incorporation into **IV** in deuteriomethanol solution[14] with the corresponding measurements for the sodium methoxide catalyzed tritium incorporation into **I**–**III** in methanol-*t* solvent[3–5,7] but, unfortunately, not in the same reaction conditions. The following kinetic acidity order was deduced from this comparison: **III** > **I** > **IV** ≫ **II** (**III** was 200 times more reactive than **IV**, whereas **I** was about twice more acidic than **IV**). This was used as a basis for ruling out the hypothesis regarding fluorine hyperconjugation.[3–5] This interpretation of the results is, however, complicated because Andreades work[14] was performed under conditions where very high (up to 17–52 wt %) substrate concentrations were used. Thus, an unaccountable solvent effects might have been introduced. Also, the approximate rate constant listed for **IV** by Andreades was measured only at a single temperature (–29 °C) and assumed Arrhenius parameters were used to extrapolate to 0 °C, i.e. to the same temperature used by Holtz and Streitwieser. Finally, Andreades noted that an extensive side reaction (E2 elimination of HF by sodium methoxide from **IV** in methanol at –29 °C) accompanied the deuterium exchange even in relatively dilute solutions.

An extremely fast isotope exchange rate for **IV** was noticed by Klabunde and Burton[11] in 50:50 mol % mixture of DMSO with methanol in presence of triethylamine as a catalyst. However, no comparisons were made with **I**–**III**. These circumstances led Tatlow et al.[8] to perform direct competitive experiments of deuterium incorporation into **I**, **III**, and **IV** under neutral conditions (without the presence of CH_3O^-) in the mixture (9:1) of acetone-d_6 and D_2O at 50 °C. The comparison of these results with those of Holtz and Streitwieser led to a drastically inverted reactivity order. These new results show that **IV** had at least 2 powers of 10 higher rate of deuterium incorporation than **I** and about 10 times more than that for **III**. On the basis of these results the authors concluded, contrary to Holtz and Streitwieser that fluorine hyperconjugation should be considered as a reasonable mechanism for the interpretation of their data.

In addition to the deuterium incorporation rates, the equilibrium cesium ion pair acidities of six substituted analogues of **I**, as well as of **III** and 1H-perfluorobicyclo[2.2.1]hept-2-ene in cyclohexylamine were measured.[5] However, no experimental results under the same conditions were reported for **IV**. It is worthwhile to mention that the estimated pK_a values (7, 11, and 20.3)[5,14,16] for the latter compound are themselves in very significant disagreement with each other.

In short, no direct comparative measurements of the thermodynamic equilibrium acidities of compounds **I**–**IV**, in solution or gas phase, have been made.

The goal of the present work was to make direct experimental determination of the thermodynamic acidity of **I**, **II**, and **IV** in the gas phase and to clarify the above-mentioned controversy regarding the pK_a values of **IV**. More definitive evidence on the nature of the influence of fluoroalkyl substituents and the role of anionic hyperconjugation on the chemical reactivity could be expected to result. For comparison purposes, the gas-phase acidities of $(CF_3)_2CH_2$, $(CF_3)_3CNH_2$, and CF_3SH were also measured. An unsuccessful attempt to determine the intrinsic acidity of $(CF_3)_3CCH_3$ was made (See Experimental Section). Therefore, the theoretical calculations of that quantity for the latter compound were undertaken.

Experimental Section

The *gas-phase* acidity measurements reported in this paper are performed with a FT-ICR mass spectrometer (IonSpec Corporation). The details of the experimental techniques used for the measurements of the equilibrium constants (*K*) for the following reversible proton transfer reactions are described elsewhere:[17,18]

$$A_iH + A_o^- \overset{K}{\rightleftharpoons} A_oH + A_i^-$$

$$\delta\Delta G_{acid} = -RT \ln K$$

where A_iH refers to a given acid and A_oH is a reference acid. All measurements were performed at 100 °C at 1 T magnetic field. The partial pressures of the components were in the 10^{-8} to 10^{-7} Torr range. Usually, isoamyl nitrite (10^{-7} Torr) was used for the initiation of the proton-transfer reaction. However, the ionization of **IV** and $(CF_3)_3COH$ occurred to the same extent with or without the presence of the isoamyl nitrite. Each experiment was performed at several ratios of partial pressures and at different overall pressures of the reagents. Arithmetic mean values of *K* were used for the calculation of $\delta\Delta G°$ at 373 K, the average uncertainty is ±0.1 kcal/mol. The multiple overlaps were performed to insure the internal consistency of the data. Positive and negative ion mass scans were performed to check the purity of compounds. The relative acidities $\delta\Delta G°$ are given in the Table 1. The $\Delta G°_{acid}$ values for the reference compounds were taken from the literature.[18,19] Not shown in the Table 1 are following results obtained for $(CF_3)_2CH_2$: weaker than fluorene ($\Delta G°_{acid}$ = 344.0 kcal/mol) by 0.2 kcal/mol, weaker than p-$CH_3C_6H_4OH$ (343.4 kcal/mol) by 0.3 kcal/mol, weaker than 9-methoxyfluorene (343.3 kcal/mol) by 0.5 kcal/mol. These results give an average $\Delta G°_{acid}$ of 343.9 ± 0.1 kcal/mol for $(CF_3)_2CH_2$. The following results were also obtained for $(CF_3)_3CNH_2$: stronger than m-$ClC_6H_4NH_2$ (351.6 kcal/mol) by 1.5 kcal/mol, weaker than m-$CF_3C_6H_4NH_2$ (349.6 kcal/mol) by 0.6 kcal/mol, weaker than CH_3NO_2 (349.7 kcal/mol) by 0.1 kcal/mol. These results give an average $\Delta G°_{acid}$ of 350.1 ± 0.1 kcal/mol for $(CF_3)_3CNH_2$. (See also ref 18.)

In DMSO the pK_a of **IV** is measured at 293 K using potentiometric titration of the acid with standard ca. 0.01 molar solution of Bu_4NOH in the mixture (1:4, v/v) of *i*-PrOH and benzene. The detailed description of the technique is given in refs 20–22. $C_6H_5CO_2H$ was used as a reference compound (pK_a = 11.0).[23] The concentration of **IV** in DMSO solution was about millimoles/liter. The pK_a values calculated for the different ionization ratio [AH/A⁻] remained constant within 0.02–0.04 pK_a unit. The average value of pK_a was calculated to be 12.6 ± 0.2. A single measurement was also performed in order to obtain an estimate of the pK_a of **I** in DMSO. This result gives pK_a ca. 20 showing that the bicyclic compound is a weaker acid by approximately two units than phenol (pK_a = 18.0).[23] It is suggested that the modified transmetalation technique[23] would give a more exact pK_a value for **I**.

Chemicals. The compound **IV** (bp 11.0 °C) was synthesized as described in ref 18. The sample of $(CF_3)_3CCH_3$ (mp 20.0 °C) was kindly provided by Dr. N. I. Delyagina, Institute of Organoelement Compounds, Moscow. The negative ion FT-ICR spectrum of **IV** shows an excellent very intense signal for the anion of **IV** (m/e = 219), indicating no impurities. The potentiometric titration of this acid shows at least 99.8% purity of the sample. $(CF_3)_3CCH_3$ fragments very extensively under ICR conditions giving in the negative ion mass spectrum predominantly M – 19 ions. This result is characteristic of poor M – 1 stability.

---

(16) (a) Butin, K. P. Beletskaya, I. P.; Reutov, O. A. *Elektrokhimistry* **1966**, *2*, 635. (b) Reutov, O. A.; Butin, K. D.; Beletskaya, I. P. *Usp. Khim.* **1974**, *43*, 35.

(17) Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017.

(18) Koppel, I. A.; Taft, R. W.; Anvia, F.; Zhu, S.-Z.; Hu, L.-Q.; Sung, K.-S.; DesMarteau, D. D.; Yagupolskii, L. V.; Yagupolskii, A. Yu.; Ignatev, N. V.; Kondratenko, N. V.; Volkonskii, A. Yu.; Vlasov, M. V.; Notario, R.; Maria, P.-C. *J. Am. Chem. Soc.* **1994**, *116*, 3047.

(19) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, G. W. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

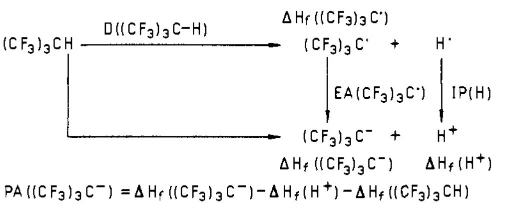
(20) Koppel, I. A.; Koppel, J. B.; Degerbeck, F.; Grehn, L.; Ragnarsson, U. *J. Org. Chem.* **1991**, *56*, 7172.

(21) Koppel, I. A.; Koppel, J. B.; Pihl, V. O. *Org. React.* (*Tartu*) **1988**, *25*, 77.

(22) Gyenes, I. *Titration in Non-aqueous Media*; Van Nostrand: Princeton, NJ, 1967.

(23) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

Scheme 1



Highly fluorinated bicyclic acids I and II were obtained from Prof. A. Streitwieser, Jr., UC Berkeley, and were originally synthesized by Prof. J. C. Tatlow and his co-workers,[8] at the University of Birmingham; $(CF_3)_2CH_2$, from Prof. D. D. DesMarteau, University of Clemson; $(CF_3)_3CNH_2$, from Prof. D. Aue, UC Santa Barbara. CF_3SH was prepared according to the literature.[24] $(CF_3)_3COH$, $CH_2(CN)_2$, $C_6H_5COCH_2CN$, p-$CF_3C_6H_4OH$, $(CH_3CO)_2CH_2$, and m-$CF_3C_6H_4CH_2CN$ were commercial products. $C_6F_5CH_2CN$ was from ref 18, and CF_3CH_2COOH, from ref 25.

DMSO was purified as described earlier.[20,21]

Results and Discussion

Gas Phase. Table 1 shows that **IV** in the gas phase is a stronger acid (ΔG°_{acid} = 326.6 kcal/mol) than most of the CH acids.[18,19] It is a much stronger acid than methane (by 81.9 kcal/mol) or fluoroform (by 42 kcal/mol), still 2.1 kcal/mol stronger than malononitrile, only slightly weaker than fluoradene (by 1.4 kcal/mol), and much weaker than CH superacids such as $(CF_3SO_2)_2CH_2$ (by 25.1 kcal/mol)[18] and $(CF_3SO_2)_3CH$ (by 37.6 kcal/mol).[18]

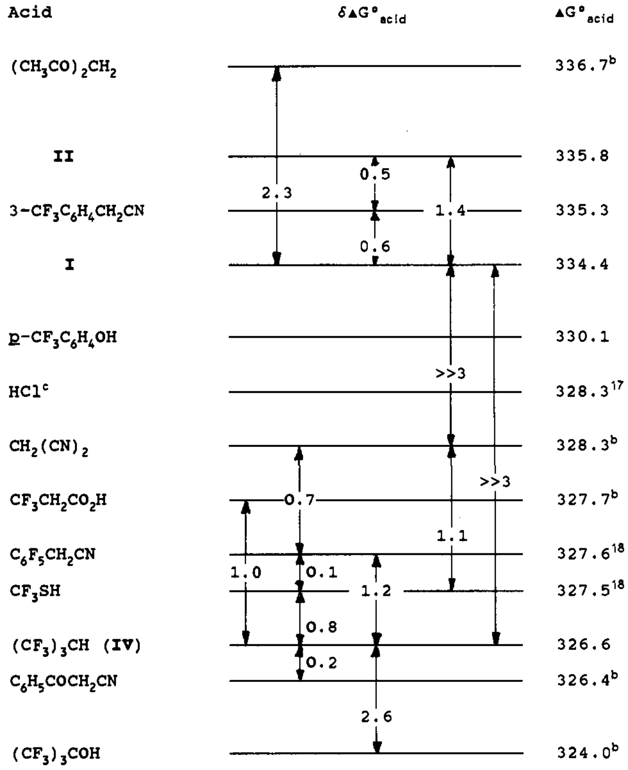
It is interesting to note that intrinsic gas-phase acidity of **IV** exceeds even the acidity of such a traditionally strong acid as hydrochloric acid by 1.7 kcal/mol.[17]

The analysis of the effect of the consecutive introduction of CF_3 group into methane shows a definite nonadditivity: the first CF_3 group increases the acidity of methane by ca. 38 kcal/mol,[18] the addition of the second CF_3 group increases the acidity of CF_3CH_3 further by 27 kcal/mol (the ratio is 1.70 or 15% short from additivity), and the third addition of CF_3 group increases the acidity yet further by 17.1 kcal/mol which falls even shorter from the additivity.[18]

Comparing with the other neutral aliphatic acids containing the $(CF_3)_3C$ group, **IV** is much stronger than $(CF_3)_3CNH_2$ (by 23.6 kcal/mol) and only slightly weaker than $(CF_3)_3COH$ (by 2.6 kcal/mol). It may be estimated that **IV** will be found to be much weaker than $(CF_3)_3CSH$ ($\Delta G^\circ_{acid} \leq 300$ kcal/mol). The ab initio estimate of ΔG°_{acid} for $(CF_3)_3CCH_3$ (using a HF/3-21G//3-21G level of calculations) is 364.0, which is ca. 6 kcal/mol stronger acidity than for CF_3CH_3 (ΔG°_{acid} is ca. 370 kcal/mol).[18,26] This difference somewhat resembles the difference in acidities of CF_3OH (ΔG°_{acid} = 341 kcal/mol)[27] and $(CF_3)_3COH$ (ΔG°_{acid} = 324.0 kcal/mol)[18,19] and originates from similar structural effects.

In addition to present experimental measurements and theoretical calculations,[15] the acidity of **IV** could be estimated by the thermodynamical calculations using the cycle shown in Scheme 1 and the available literature data. So, the use for compound **IV** of the reported[28,29] lower limit for $EA[(CF_3)_3C^\bullet] \geq 3.4$ eV and $D[(CF_3)_3CH]$ value (109 ± 5 kcal/mol) suggested by Lias et al.[19] [$IP(H^\bullet)$ = 312.6 kcal/mol][19] gives for $(CF_3)_3C^-$ the PA = $-EA[(CF_3)_3C^\bullet] + IP(H^\bullet) + D[(CF_3)_3CH] \leq 344$ kcal/mol.

Chart 2. Multiple Overlap Sequences Used To Obtain Gas-Phase Acidities ΔG°_{acid} of **I**, **II**, and **IV** at 373 K[a]



[a] The values are in kcal/mol. The error for $\delta\Delta G$ is ±0.1 kcal/mol unless otherwise stated.[b] See refs 18 and 19.[c] The acidity of HCl is indicated for comparison.

On the other hand, $PA[(CF_3)_3C^-]$ could be calculated from $\Delta H_f[(CF_3)_3C^\bullet] = -433.3$ kcal/mol,[30] $EA[(CF_3)_3C^\bullet] \geq 3.4$ eV (vide supra), and $\Delta H_f[(CF_3)_3CH)] = -473$ kcal/mol[31] as ≤330 kcal/mol. The use of the above-used $\Delta H_f[(CF_3)_3CH)] = -473$ kcal/mol,[31] together with $\Delta H_f[(CF_3)_3C^-] = -513.9$ reported by Christophorou,[28,29] gives a third estimate (324 kcal/mol) of $PA[(CF_3)_3C^-]$, whereas the use of the alternative formation enthalpy value for $\Delta H_f[(CF_3)_3C^-]$ (−504.3 kcal/mol) suggested by Dixon et al.[10] leads to additional estimate (334 kcal/mol) of the proton affinity of $(CF_3)_3C^-$ carbanion. An average value 333.0 ± 4 kcal/mol, from these four independent estimates gives a ΔG°_{acid} value of ca. 326 kcal/mol ($\Delta H - T\delta S$ = 333−7)[19] and this is practically identical with the experimental value measured in this work.

The comparison of the intrinsic acidities of **IV** and the highly fluorinated bridgehead bicyclic acid **I** shows that **IV** is a much stronger acid (by 7.6 kcal/mol, or 5.6 pK_a units). The substitution of the bridgehead hydrogen in **II** by a fluorine atom to give **I** results in a modest increase in the intrinsic acidity by 1.4 kcal/mol. This difference is roughly of the same order as predicted by Holtz[3] on the basis of the electrostatic model for this pair of acids. However, it may be noted that this is significantly smaller than a similar bridgehead substitution of a fluorine atom for hydrogen in 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids[32,33] where, the effect on gas-phase acidity is 5.6 kcal/mol.

Qualitatively, the acidity order **IV** > $(CF_3)_3CH_3$ > **I** > **II** is also predicted from MOPAC PM3 calculations[15] which show that **IV** is by 17 kcal/mol more acidic than **I**, by 23 kcal/mol

---

(24) Tatlow, J. C. *J. Chem. Soc.* **1953**, 3219.

(25) Jinfeng, C.; Topsom, R. D.; Headley, A. D.; Koppel, I. A.; Mishima, M.; Ueji, S.; Taft, R. W. *J. Mol. Struc. (THEOCHEM)* **1988**, *168*, 141.

(26) Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1160.

(27) Taft, R. W.; Koppel, I. A.; Topsom, R. D.; Anvia, F. *J. Am. Chem. Soc.* **1990**, *112*, 2047.

(28) Spyrou, S. M.; Sauers, I.; Christophorou, L. G. *J. Chem. Phys.* **1983**, *18*, 7200.

(29) Spyrou, S. M.; Hunter, S. R.; Christophorou, L. G. *J. Chem. Phys.* **1985**, *83*, 641.

(30) Takhistov, V. V. D.Sc. Thesis, Leningrad, 1989 (in Russian).

(31) Calculated on the basis of the group additivity scheme suggested by: Palm, V. A.; Hiob, R. J. *Org. React. (Tartu)* **1983**, *20*, 147.

(32) Koppel, I. A.; Korgesaar, A. O.; Koppel, J. B.; Pihl, V. O. *Org. React. (Tartu)* **1988**, *25*, 272.

(33) Koppel, I. A.; Mishima, M.; Stock, L. M.; Taft, R. W.; Topsom, R. D. *J. Phys. Org. Chem.* **1993**, *6*, 685.

more acidic than II, and by 42 kcal/mol stronger acid than $(CF_3)_3CH_3$.

Acidity of IV in DMSO. The pK_a value 12.6 (this work) for IV in DMSO is rather close to the value estimated by Andreades on the basis of his deuterium incorporation data.[14] However, the present pK_a value disagrees significantly with the two other estimates suggested by Butin et al.[16] and Streitwieser, Holtz, et al.[3–5,7] Like in the gas phase, IV displays its rather pronounced acidic properties also in DMSO solution. Its DMSO pK_a acidity is slightly weaker than that of malononitrile (11.0), fluoradene (10.5), $(CF_3)_3COH$ (10.7), and benzoic acid (11.0). It is essentially of equal acidity to that of acetic acid (12.3).[21,23] It exceeds the acidity of fluorene (22.6), Ph_3CH (30.6), fluoroform (estimated pK_a 26, 31, and 30.5)[5,14,16] and has much lower acidity than several stronger gas-phase CH superacids [e.g., $PhCH(CN)_2$ (pK_a = 4.2) and $(CF_3SO_2)_3CH$, $(CF_3SO_2)_2NH$, $(CF_3CO)_2CH_2$, $(CF_3CO)_3CH$ which are at the limit of the DMSO scale (pK_a = 2.00 ± 0.3)].[34]

Rather crude estimation of the effect of consecutive substitution of the hydrogen atoms in methane (an estimated pK_a is ca. 56)[23] for CF_3 groups is possible. On the grounds of closeness of σ_F and σ_R substituent constants for CF_3 (0.44 and 0.07) and CH_3SO (0.40 and 0.08)[35] and somewhat higher polarizability of the latter group, the pK_a's for CF_3CH_3 and DMSO (in its own medium) could be considered very roughly equal, i.e. 35.[23] Literature estimate on the grounds of the polarographic scale of Butin et al.[16] for the pK_a of $(CF_3)_2CH_2$ is 22. These estimates give for the effect of introduction of the first CF_3 ca. 21 pK_a units, for the transfer from CF_3CH_3 to $(CF_3)_2CH_2$ 13 pK_a units, and for a third step from $(CF_3)_2CH_2$ to $(CF_3)_3CH$, 9.4 pK_a units less than follows from additivity principle. Keeping in mind the very approximate nature of the estimated pK_a values for methane, CF_3CH_3 and $(CF_3)_2CH_2$, this picture practically repeats the situation in the gas phase.[18]

Only a very approximate comparison of the thermodynamic acidities of I and IV in DMSO solution is possible. As in the gas phase, the acidity of IV exceeds I by several powers of 10. The same conclusion, which qualitatively confirms the acidity order found by Tatlow,[8] could be reached assuming the rough equality of the numerical values of pK_a on the ionic acidity scale in DMSO[23] and those on the ion-pair acidity scale in cyclohexylamine (CHA)[36] and keeping in mind the pK_a value (20.5) determined for (I) in CHA.[5]

Conclusions

The present findings, besides several other experimental arguments[6,8,11,14] and theoretical calculations[2,9,10,15,37] of electronic structure, charge distribution, and geometry of fluorinated molecules, ions, and free radicals definitely provide additional experimental basis for the study of the role of anionic negative hyperconjugation in stabilizing appropriate aliphatic fluorosubstituted carbanions.

The present experimental evidence is qualitatively at variance with the concept which assumes that the stabilization of alkyl anions by F atoms is due entirely to a dipolar effect.

At the present time there is no strictly unambiguous way to differentiate quantitatively between the contributions of different structural effects (anionic hyperconjugation, field/inductive effect, polarizability, steric repulsion) for the gross effect of β- and α-fluorination.

---

(34) Koppel, I. A.; Yagupolskii, L. M.; Taft, R. W., and associates. Unpublished data.

(35) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(36) Streitwieser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1980; p 382.

(37) (a) Koppel, I. A.; Molder, U. H. *Org. React.* (*Tartu*) **1983**, *20*, 3. (b) Koppel, I. A. *Org. React.* (*Tartu*) **1987**, *24*, 263.