Tetrahedron Letters,Vol.27,No.37,pp 4411-4414,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

THE ETHYL, 1- AND 2-PROPYL, AND OTHER SIMPLE ALKYL "CARBANIONS" DO NOT EXIST[1]

Paul von Ragué Schleyer* and Günther W. Spitznagel
Institut für Organische Chemie der Friedrich-Alexander-Universität
Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany

Jayaraman Chandrasekhar
Department of Organic Chemistry, Indian Institute of Science
Bangalore, 560 012, India.

Summary. A combination of experimental data and theoretical calculations has been used to estimate the electron affinities of simple primary, secondary, and tertiary alkyl radicals and the proton affinities of the corresponding anions. With the exception of cyclopropyl, such "carbanions" are indicated to be unstable towards loss of an electron and are not expected to exist as long-lived species in the gas phase.

Although "carbanions" are the most widely used reactive intermediates in organic synthesis, they are the least well understood. Simple primary, secondary, and tertiary alkyl anions are as yet unknown as free entities. Their pK values in solution are only roughly estimated.[2] Most of the species designated in oversimplified terms as "carbanions" are, in reality, polar organometallic derivatives (e.g., organolithium or Grignard reagents) which react as monomeric or aggregatated entities, rather than as free anions.[3]

CH_3^- is the only simple alkyl anion which has been observed in the gas phase. The very small electron affinity, 1.8±0.7 kcal/mol,[4] indicates that the extra electron is weakly bound. The lone pair extends far from the carbon nucleus and has little effect on the geometry. Indeed, the most sophisticated recent calculation even indicates CH_3^- may be planar rather than pyramidal.[5] Adequate mathematical representations of carbanions require the inclusion of diffuse s and p orbitals in the ab initio basis sets.[6,7] Our earlier calculations at such levels have shown that carbanions are destabilized by alkyl substituents.[6,8] Since the methyl anion is barely bound, this implies that the ethyl, isopropyl, etc. carbanions should be unstable as isolated entities towards loss of an electron.[6-8] This rather startling conclusion has also been reached recently by DePuy, et al.[9a] and by Brauman, et al.,[9b] who both used indirect methods to deduce the relative acidities of hydrocarbons in the gas phase.[10] We now provide quantitative estimates of electron affinities of alkyl radicals and proton affinities of the corresponding carbanions.

By combining the experimental PA (CH_3^-)=416.6 kcal/mol with our calculated (4-31+G basis set) stabilization energies relative to CH_3^- (eq 1), the proton affinities of various carbanions can be evaluated easily with an accuracy of a few kcal/mol. The cyclopropyl anion is an exception, as basis sets augmented with d-type polarization functions are needed to describe three membered carbon rings.[11] Hence, 6-31+G*-optimized data was used in this case.[12] The data in Table I show that the higher alkyl carbanions are destabilized relative to CH_3^-. That this result is not an artifact of using finite basis sets for potentially unbound species is confirmed by the data on the corresponding metallated derivatives which are quite stable towards loss of an electron. Thus the calculated methyl stabilization energies of the alkyl lithium compounds (eq 2, M=Li) correlate with a slope of about 0.7 with the methyl stabilization energies of the carbanions (eq 1).[8a,b] A similar correlation has been found for the corresponding sodium (eq 2, M=Na) compounds; the more covalent magnesium derivatives (eq 2, M=MgH) give a lower slope.[8c] We are thus confident in asserting that such simple primary, secondary, and tertiary free carbanions (as well as their polar organometallic counterparts) are destabilized relative to the methyl anion. This conclusion is supported experimentally by the recent results of DePuy, Brauman, and their associates[9] in the gas phase, and has long been deduced from data in solution,[2a] e.g. via "kinetic acidity"[2b] and other measurements.

$$CH_3^- + RH \rightarrow CH_4 + R^- \qquad (1)$$

$$CH_3M + RH \rightarrow CH_4 + RM \qquad (2)$$

In contrast, alkyl substituents are well known experimentally to stabilize alkyl free radicals relative to methyl (eq. 3, Table I).[13] The opposite methyl substituent effects on $R^\cdot$ and on R^- enhance the tendency of R^- to lose an electron. This conclusion can be quantified by evaluating the electron affinities of $R^\cdot$ by means of eq. 4. This combines eq. 1 and eq. 3, and assumes the experimental $EA(CH_3\cdot)=1.8$ kcal/mol.[4]

$$CH_3\cdot + RH \rightarrow CH_4 + R^\cdot \qquad (3)$$

$$R^\cdot + CH_3^- \rightarrow R^- + CH_3^\cdot \qquad (4)$$

The EA's of alkyl radicals estimated in this manner are given in Table I. Comparison with the experimental EA of the more stable allyl species, as well as with DePuy's estimates,[9a] shows satisfactory agreement generally well within 2 kcal/mol. The largest discrepancy (2.6 kcal/mol) found with DePuy's results is probably due to the overestimation of the stability of the t-butyl anion experimentally, due to relief of strain in the cleavage reaction.[9a] Brauman's inference that t-Bu-H is more acidic than Me-H is suspect.[9b]

Even granting errors of ±4 kcal/mol, our predictions are quite conclusive: the ethyl, 1- and 2-propyl, and the isomeric C_4H_9 radicals should have negative (unfavorable) electron affinities. This means that the corresponding anions should not be observable as long-lived species in the gas phase. The same can be expected of similar saturated alkyl and cycloalkyl anions.

The cyclopropyl carbanion is an exception. The apparent earlier disagreement with experimental conclusions,[2,3] that the cyclopropyl carbanion and its organometallic derivatives have unfavorable methyl stabilization energies,[6,8,12,15] is resolved at higher levels of theory.[11] $c\text{-}C_3H_5^-$ is 2.1 (4.0) kcal/mol more stable than CH_3^- at 6-31+G*//6-31+G* (MP2/6-31+G*//6-31+G*). The stability of the cyclopropyl anion is even larger when compared with other secondary carbanions, such as 2-propyl or cyclobutyl.[12] Significantly, the cyclopropyl radical is destabilized relative to methyl and the other alkyl or cycloalkyl radicals in Table I;[13] hence, the EA is positive (favorable) and we predict that the cyclopropyl carbanion should be observable in the gas phase. After this conclusion was reached,[1] the experimental detection of $c\text{-}C_3H_7^-$ in the gas phase was achieved.[15]

The effect of methyl substituents on anions depends on the electronegativity of the atom to which the CH_3 group is attached. This determines whether the four electron negative hyperconjugative interaction[16] involving the anion lone pair and the methyl π_{CH_3} and $\pi^*_{CH_3}$ orbitals is stabilizing or destabilizing. Thus, while CH_3O^- is more stable than OH^- (the proton affinities (PA's) are 379.2 and 390.8 kcal/mol, respectively), the stabilities of NH_2^- and of CH_3NH^- are comparable (PA's 403.6 and 403.2 kcal/mol) and SH^- is more stable than CH_3S^- (PA's 353.4 and 359.0 kcal/mol).[17] The calculated variation of PA's in $CH_3CH_2^-$ and CH_3^- (Table I) fits in very well with this trend, as the electronegatives of carbon and sulfur are nearly the same.

Conclusions: Many simple "carbanions" are viable species only as components of ion pairs, R^-M^+, or higher aggregates $(R^-M^+)_n$, even though the relative energies of such species may be parallel.[8] Polar organometallic representations, which emphasize the nature of the reacting species in solution, are much to be preferred over oversimplified and misleading "R^-" designations. The metal cations are of critical importance mechanistically.[18]

Acknowledgments. We thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for support of this work. C.H. DePuy and R.R. Squires kindly provided information prior to publication.

Table I. Stabilization Energies (vs Methyl) of Anions and Radicals. Proton Affinities of Anions and Estimated Electron Affinities of Radicals (kcal/mol)

R	Energy of Reaction 1[a]	Energy of Reaction 3[b]	Electron Affinity		Proton Affinity	
			Predicted[c]	Exp.	Calc.[d]	Exp.[f]
Ethyl	5.6[e]	-4.6	-8.4[e]	-9[f]	422.2	421
Cyclopropyl	-2.1(-4.0)	1.2	5.1(7.0)	8[f]	414.5(412.6)	412
1-Propyl	2.7	-4.0	-4.9	-	419.3	-
2-Propyl	5.9	-5.8	-9.9	-11[f]	422.5	419
2-Butyl	5.3	-6.1	-9.6	-	421.9	-
tert-Butyl	3.0	-8.4	-9.6	(-7)[f,g]	419.6	(414)[g]
Cyclobutyl	4.6	-8.6	-11.4	-	421.2	-
Cyclopropylmethyl	-2.7	-7.7	-3.2	-	413.9	-
Vinyl	-9.7	4.9	16.4	17[f]	406.9	408±3,406
Ethynyl	-47.9	26.9±5[h]	76.6±5[h]	67.8±2[j]	368.7	375.4[i]
Allyl	-28.0[k]	-18.8	11.0	8.3[k],12.7[i]	388.6	391±1[k]

[a] For C_1-C_3 systems, calculated at 4-31+G//4-31+G;[8] for C_4 systems at 4-31+G//3-21G;[8] cyclopropyl at 6-31+G*//6-31+G*(MP2/6-31+G*//6-31+G*). For other calcs, see refs 5-7,10,12, 15,16,19. [b] From experimental BDE data from ref. 13b for acyclic alkyl systems; data from ref. 13a for the rest. [c] Obtained as $1.8-\Delta E_1+\Delta E_3$; EA of CH_3, ref. 4. [d] Obtained as PA CH_3^- (416.6, ref. 17) $+\Delta E$ (eq 1). [e] At the highest theoretical level we have employed (MP2/6-31+G*//6-31+G*), ΔE (eq 1) = 3.2 kcal/mol and the predicted EA of C_2H_5=-6.0 kcal/mol. [f] From ref. 9a. [g] This value is doubtful, see text. [h] Experimental error bars are significantly less in all other cases. [i] Ref. 17. [j] Ref. 14. [k] See ref. 19 for discussion of available data.

References and Notes

(1) Presented, in part, at the Royal Society of Chemistry, Perkin Division, International Symposium, "Chemistry of Carbanions", Durham, England, July 1984.

(2) (a) Review: A Streitwieser, Jr., E. Juaristi, and L.L. Nebenzahl, in E. Buncel and T. Durst, Eds., "Comprehensive Carbanion Chemistry", Part A, Elsevier, Amsterdam 1980, Chapt. 7. (b) A. Streitwieser, Jr., private communication.

(3) See P.v.R. Schleyer, Pure Appl. Chem. **55**, 355 (1983); **56**, 151 (1984); W.N. Setzer and P.v.R. Schleyer, Adv. Organomet. Chem. **24**, 353 (1985); C. Schade and P.v.R. Schleyer, ibid., in press, and lit. cited.

(4) G.B. Ellison, P.C. Engelking, P.C. Lineberger, J. Am. Chem. Soc. **100**, 2556 (1978).

(5) J. Kalcher and R. Janoschek, Chem. Phys. **104**, 251 (1986).

(6) (a) J. Chandrasekhar, J.G. Andrade, P.v.R. Schleyer, J. Am. Chem. Soc. **103**, 5609 (1981). (b) G.W. Spitznagel, T. Clark, J. Chandrasekhar, P.v.R. Schleyer, J. Comput. Chem. **3**, 363 (1982). (c) T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P.v.R. Schleyer, ibid **4**, 294 (1983).

(7) H. Kollmar, J. Am. Chem. Soc. **100**, 2660 (1978).

(8) (a) P.v.R. Schleyer, J. Chandrasekhar, A.J. Kos, T. Clark, G.W. Spitznagel, J. Chem. Soc., Chem. Commun. 882 (1981). (b) P.v.R. Schleyer, E. Kaufmann, G.W. Spitznagel, R. Janoschek, G. Winkelhofer, Organometallics **5**, 79 (1986). (c) C. Rohde, Diplomarbeit (Masters Thesis), Erlangen, 1980.

(9) (a) C.H. DePuy, V.M. Bierbaum, R. Damrauer, J. Am. Chem. Soc. **106**, 4051 (1984). (b) W. Tumas, R.F. Forster, J.I. Brauman, Ibid. **106**, 4053 (1984). Also see: G. Klass, V.C. Trennery, J.C. Sheldon, J.H. Bowie, Aust. J. Chem. **34**, 519 (1981).

(10) This conclusion is also implied (but not explicitly stated) in the analysis of anion stabilization energies by G. Leroy, C. Wilante, D. Peeters, M.M. Uyewa, J. Mol. Struct. (Theochem.) **124**, 107 (1985).

(11) W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, "Ab Initio Molecular Orbital Theory", Wiley, New York, 1986, p. 293f.

(12) For a recent theoretical evaluation of the relative stabilities of the cyclopropyl and isopropyl anions see: A.C. Hopkinson, M.A. McKinney, M.H. Lien, J. Comput. Chem. **4**, 513 (1983).

(13) (a) D.F. McMillen, D.M. Golden, Ann. Rev. Phys. Chem. **33**, 493 (1982). (b) W. Tsang, J. Am. Chem. Soc. **107**, 2872 (1985).

(14) P.S. Drzaic, J. Marks, and J.I. Braumann, in "Gas Phase Ion Chemistry"; M.T. Bowers, Ed.; Wiley, New York, 1984, Vol. 3, Chapter 21.

(15) S.W. Froelicher, B.S. Reiser, R.R. Squires, J. Am. Chem. Soc., **108**, 2853 (1986).

(16) A.J. Kos and P.v.R. Schleyer, Tetrahedron **39**, 1141 (1983). Also see D.A. Forsyth and J.-R. Yong, J. Am. Chem. Soc. **108**, 2157 (1986) and refs. cited.

(17) J.E. Bartmess and R.T. McIver, Jr., in ref. 14, Vol. 2, (1979), Chapter 11.

(18) K.N. Houk, N.G. Rondan, P.v.R. Schleyer, E. Kaufmann, and T. Clark, J. Am. Chem. Soc. **107**, 284 (1985); E. Kaufmann, P.v.R. Schleyer, K.N. Houk, and Y.-D. Wu, ibid. **107**, 6393 (1985).

(19) P.v.R. Schleyer, J. Am. Chem. Soc. **107**, 4793 (1985).

(Received in Germany 26 June 1986)