Tetrahedron Vol. 33, pp 775 to 778 Pergamon Press 1977 Printed in Great Britain

MOLECULAR ORBITAL STUDIES OF THE ACIDITY OF SUBSTITUTED METHANES

HERMANN M. NIEMEYER
Institute of Organic Chemistry, University of Lausanne, Rue de la Barre 2, 1005-Lausanne, Switzerland

(*Received in the UK* 21 *October* 1976; *Accepted for publication* 16 *November* 1976)

Abstract—CNDO/2 MO studies have been carried out on CH_4, C_2H_6, $CHCl_3$, CH_3CN, CH_3NO_2, CH_3CHO, CH_3COCH_3, and their corresponding anions, both in the gas phase and in "aqueous solution". The results closely parallel related experimental studies.

The development and increasing use of methods for determining gas phase acidities have produced in recent years several reports comparing gas phase acidities with the more traditional solution values.[1-8] A molecular orbital study of the acidity of some simple hydrocarbons both in the gas phase and in solution has been undertaken.

Methods

We have chosen to study simple substituted methanes as model systems. Presumably these systems will show the basic patterns of behaviour found experimentally in analogous but more complex systems, with the advantage that they will not be overshadowed by superficial effects and that the computation time is reduced to a minimum.

Supermolecules composed of the hydrocarbon or its anion and a varying number of H_2O molecules have been considered in the solvation studies. Although most of the anions studied will not survive in aqueous solution, the choice of H_2O as a solvating agent is justified since in these MO calculations H_2O is a relatively simple molecule to treat and also one which should represent the limiting case of solvation owing to its small size and high polarity and dielectric constant.

Since the size of our systems precludes the use of *ab initio* MO methods, the CNDO/2 semiempirical method was employed.[9] It has been shown that this method yields better results when experimental or standard[10] geometries are used[11] but the lack of knowledge of the geometries of most of the structures studied renders this approach impossible. Instead, the energies of the species studied were minimized through successive optimization of each of the geometrical parameters involved.

Numerous CNDO/2 MO calculations have been reported which included one or more of the molecules now studied. Nevertheless, the emphasis has been on other properties of the system.

RESULTS

Table 1 summarizes values of parameters for which a direct comparison can be established with experimental values or with results from *ab initio* calculations when experimental values are not available.

The bond lengths and angles calculated in this work generally agree to within 4% with the values determined experimentally. The geometries calculated for pyramidal and planar Me and Et anions compare reasonably well with *ab initio* results employing large basis sets.[13,14] The preferred geometries of Me, Et and trichloromethyl anions in the gas phase are pyramidal, as expected from the tendency of a negative charge to reside in an orbital with the largest s-character, in the absence of conjugative effects. Experimental data on hydrogen ion transfer from chloroform to hydroxide ion in H_2O/DMSO solution has been interpreted by invoking a pyramidal trichloromethyl anion with a highly localized negative charge.[15]

The effects of solvation of the carbanionic center on the stability of anions has been studied in greater detail in the case of Me anions. Equations (1) and (2) refer to the models **1** and **2** (Fig. 1) studied for the first solvation shell of pyramidal Me anions, where $(H_2O)_{solv}$ represents a solvated H_2O molecule.

$$CH_3^-(\text{pyramidal}) + (H_2O)_{solv} \rightarrow CH_3^-(\text{pyramidal})\cdot H_2O\ (\mathbf{1}) \quad (1)$$

$$CH_3^-(\text{pyramidal}) + 2(H_2O)_{solv} \rightarrow CH_3\ (\text{pyramidal})\cdot 2H_2O\ (\mathbf{2}) \quad (2)$$

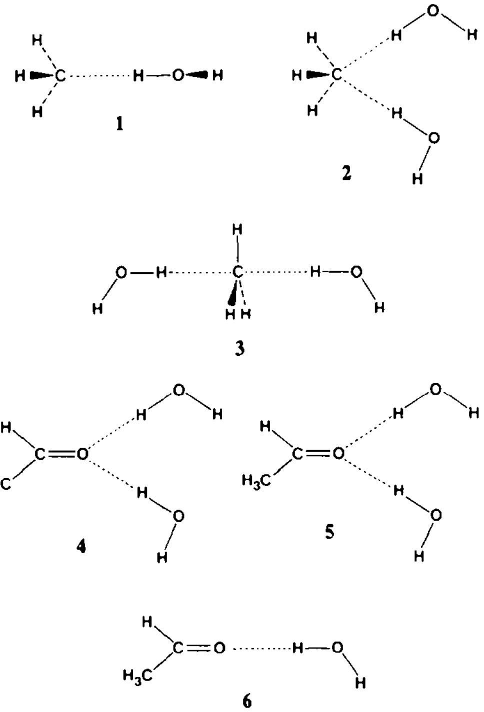

Fig. 1. Models for solvation.

Table 1. Geometrical parameters[a]

CH_4	CH = 1.114, 1.093(E)
CH_3 planar	CH = 1.115, 1.130(4G), 1.082(ss), 1.079(ss + d), 1.080(ss + d, p)
CH_3^- pyramidal	CH = 1.134, 1.189(4G), 1.105(ss), 1.101(ss + d), 1.102(ss + d, p); HCH = 105.4, 97.5(4G), 107.3(ss), 104.4(ss + d), 104.2(ss + d, p)
CH_3CH_3	CH = 1.120, 1.093(E); CC = 1.458, 1.534(E); CCH = 112.1, 109.8(E)
CH_3CH_2 [b]	C(1)H = 1.129, 1.179(4G); C(2)H = 1.137, 1.126–1.128 (4G)[c]; HC(1)H = 106.4, 99.6(4G); C(2)C(1)H = 111.0, 107.0(4G); C(1)C(2)H = 115.7, 116.0(4G); CC = 1.433, 1.551(4G)
$CHCl_3$	CH = 1.120, 1.073(E); CCl = 1.739, 1.762(E); ClCCl = 110.1, 110.9(E)
CH_3CN	CH = 1.119, 1.103(E); CC = 1.422, 1.458(E); CN = 1.190, 1.157(E); CCH = 110.3, 109.5(E)
CH_3CHO[b]	C(1)H = 1.119, 1.114(E); C(2)H = 1.123, 1.086(E); CC = 1.443, 1.501(E); C(2)O = 1.261, 1.216(E); CCO = 126.2, 123.9(E); C(2)C(1)H = 111.2; C(1)C(2)H = 117.4, 117.5(E)
CH_3NO_2	CH = 1.117, 1.09(E); CN = 1.417, 1.49(E); NO = 1.224, 1.22(E); NCH = 110.1, 109.5(E); ONO = 121.9, 127(E)
CH_3COCH_3	CH = 1.119, 1.086(E); CC = 1.455, 1.515(E); CO = 1.275, 1.215(E); CCO = 120.3, 121.9(E); CCH = 111.7, 110.3(E)

[a] The value resulting from this work is followed by the experimental value (E)[12] or by results from *ab initio* calculations with the following basis sets: 4G = STO − 4G; ss = (8s, 4p) for C and (4s) for H contracted into (4, 2, 1, 1; 3, 1) and (3, 1) respectively; ss + d = ss augmented with d orbitals on C; ss + d, p = ss + d augmented with p orbitals on H. For details see Ref. 13. Bond lengths are given in Å and angles in degrees.

[b] C(1) refers to the acidic carbon.

[c] While our calculations impose C_{3v} symmetry to the methyl groups, the *ab initio* studies allow it to relax to its optimal geometry.

For eqn (1), the solvation energy calculated is 64.3 kcal/mol,† while for eqn (2), it increases to 70.3 kcal/mol.‡ Thus, of the two models studied, **2** is energetically favoured§ and hence it is used as a general model for studying the solvation of substituted pyramidal anions.¶ For simplicity secondary solvation has been left out of the calculations.

In the case of planar Me anion, **3** was the only model considered for the first solvation shell and it has adopted for the study of the substituted planar anions. Other arrangements of lower symmetry are expected to be of higher energy.‖ The energy (81.0 kcal/mol) for the solvation of **3** (eqn 3) is greater than that for the pyramidal anion,

$$CH_3^-(\text{planar}) + 2(H_2O)_{\text{solv}} \rightarrow CH_3^-(\text{planar})\cdot 2H_2O(\mathbf{3}) \qquad (3)$$

reflecting the difference is charge present on the C atom (−0.608 in the planar anion and only −0.500 in the pyramidal one).

The heteroatoms in the substituents in β-position with respect to the acidic carbon show a substantial concentration of negative charge. Their solvation was studied in greater detail in the case of acetaldehyde where comparable data from *ab initio* calculations is available.[20] Structures **4**, **5** and **6** were examined. In **4**, the optimal COH angle calculated is 116.4° and the H-bond represents a stabilization energy of 9.7 kcal/mol. In **5**, the second H-bond represents only 91% of the first one. These results are in good agreement with similar *ab initio* calculations on formaldehyde[20] where the COH angle in the structure analogous of **4** was calculated to be 116.1° and the stabilization energy of the second H-bond in model **5**, 73% of the first one in model **4**. Although the calculations on structure **6** show a stabilization energy of only 8.8 kcal/mol, **6** can serve as a model for further calculations owing to its structural simplicity. Furthermore, **6** gives results directly comparable with the solvation of the CN group where only one H_2O molecule is expected to solvate the N atom with a CNH angle of 180°, and with the substituted anions, where the directional preference of the highly electronegative O and N atoms is not likely to be as clear-cut as in the neutral species. Detailed studies on H-bonded systems have led to the conclusion that directionality of the H-bond is not important.[21]

Solvation of the H atoms through direct interaction with the solvent was not considered, since they support little charge and thus their solvation is not energetically important. Other CNDO/2 studies support this choice.[22]

DISCUSSION

CNDO/2 calculations have been carried out on substituted phenyl anions and also on anions of highly unsaturated hydrocarbons.[23] The results were considered reliable in the latter species but the treatment of

---

†We have used the experimental value for the heat of evaporation of H_2O (10.5 kcal/mol[16]) as the energy required to desolvate one mole of H_2O. A CNDO/2 study of several H_2O aggregates[17] gives a value of 10–12 kcal/mol for this energy.

‡Experimental solvation energies for inorganic anions lie in the range 60–120 kcal/mol.[18]

§The entropy change for pulling out of solution the additional H_2O molecule in eqn (2) works in the direction opposite to the enthalpy changes. Nevertheless, its magnitude is small (the entropy of evaporation of H_2O is 26 e. u.) and does not change our conclusion.

¶Earlier studies[17] have shown that the heats of hydration of anions calculated by the CNDO/2 method are in reasonable agreement with experimental data.

‖MO studies both at the *ab initio* and semiempirical levels have shown for example, that the minimum energy for the CH_3^- anion corresponds to a species with D_{3h} symmetry, both in the gas phase and in solution.[19]

substituent effects, in particular the effects of electron-donating groups, was generally less satisfactory. In addition, it has been pointed out that the electron correlation problem implicit in the CNDO/2 approximation, which is more important in studies involving species differing in charge, especially negatively charged species, represents a limitation of the method.[23,24] Nevertheless, CNDO/2 calculations on alcohol-alkoxide as well as amine-ammonium equilibria[25–28] have proved to be in good agreement with gas phase equilibrium measurements. It would seem that when treating a series of related compounds and making the comparison with experimental quantities determined in the gas phase, the approximations of the method cancel out to give reasonable over-all results. We have tested the applicability of the CNDO/2 method to the particular case at hand by comparing the differences in energy between anion and hydrocarbon with the experimental pK values. Ideally one should compare the acidities calculated (which correspond to gas phase values) with the results of measurements in the gas phase. Unfortunately in the present case the literature shows few and sometimes even contradictory values for acidities in the gas phase. Thus the acidity of acetonitrile has been reported as larger[8] as well as smaller[1] than that of acetone. We have thus chosen to compare our results with the pK values measured in DMSO solution.[29] It has been shown that these results refer to ionized carbanions[30] and furthermore, in some instances they parallel gas phase measurements within families of related compounds.[31] The fair correlation obtained (correlation coefficient = 0.96) can be interpreted as a success of the CNDO/2 method in dealing with acidities of substituted methanes (Table 2 and Fig. 2). The pK of malononitrile is known in DMSO[32] but has been excluded from the correlation since it is well known that CNDO/2 gives unreliable values for the energies of compounds containing conjugated triple bonds, a fact that remains true even in the most recent version of the MINDO sequence.[33]

The comparison of methane and ethane equilibria and of acetaldehyde and acetone equilibria (Table 2) shows that relative to hydrogen the Me group acts as an electron-attracting group towards a cabanionic center, in agreement with more elaborate *ab initio* calculations using basis sets of various degrees of complexity,[14,34] as well as with gas phase measurements of comparable equilibria.[1,28,35]

Table 2. Energy differences and experimental acidities[a]

Compound	$(\Delta E)^{b}_{\text{gas phase}}$	$(\Delta E)^{c}_{\text{solv}}$	pK[d]
CH_4	1.0347	0.8892	50
CH_3CH_3	0.9912		
CH_3CN	0.9403	0.8154	31.2
CH_3COCH_3	0.8928		26.7
CH_3CHO	0.8870	0.7765	
CH_3NO_2	0.8719	0.7620	17.2
$(CH_3CO)_2CH_2$	0.8750		13.4
$CHCl_3$	0.9241		24[e]

[a] Energies in atomic units. The pK values have not been statistically corrected.

[b] $E(R^-) - E(RH)$.

[c] $E(R\ \cdot nH_2O) - E(RH\cdot[n-2]H_2O) - 2E(H_2O)$.

[d] In DMSO (Refs. 29 and 32).

[e] In H_2O/DMSO (Ref. 1).

Hydrocarbons giving rise to localized carbanions have been shown to exhibit similar pK values in DMSO and in H_2O.[32] The pK of chloroform, which is believed to give rise to a localized anion,[15] has been determined in H_2O/DMSO solution[15] and indeed this pK value puts chloroform on the line of correlation.

A comparison of the calculated acidities in the gas phase with those calculated in solution (Table 2 and Fig. 3) shows that a linear relationship exists between them (correlation coefficient = 0.999) as has been found experimentally for other hydrocarbons when acidities in the gas phase and in DMSO were compared.[31]

The finding of Bronsted coefficients outside the normal range of 0–1,[36] has been described for aliphatic nitro compounds.[37] Several explanations are available for this observation.[37–41] Recently Bordwell has presented further evidence for a mechanism of deprotonation where a H-bonded complex is transformed in the rate-determining step to an "essentially" pyramidal nitro carbanion which then rehybridizes and resolvates to form a nitronate anion.[41] The CNDO/2 energy surface for the isolated anion was throughly searched and no minimum was found corresponding to a pyramidal structure. Nevertheless a minimum indeed appears when solvation by H_2O molecules through H-bonding to the lone pair on the C atom is included in the calculation and it corresponds to model 2 with a Me hydrogen replaced by a nitro group. This solvated pyramidal species is higher in energy than the corresponding solvated planar carbanion, thus providing further support for the mechanism proposed by Bordwell.

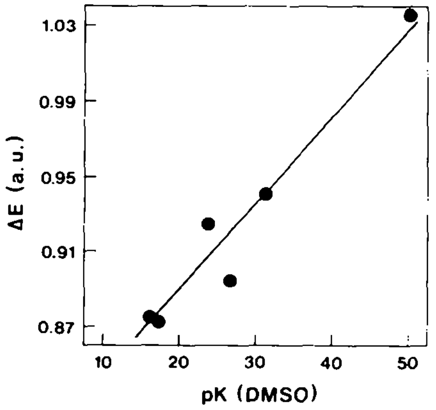

Fig. 2. Correlation of calculated (see Table 2) and experimental acidities.

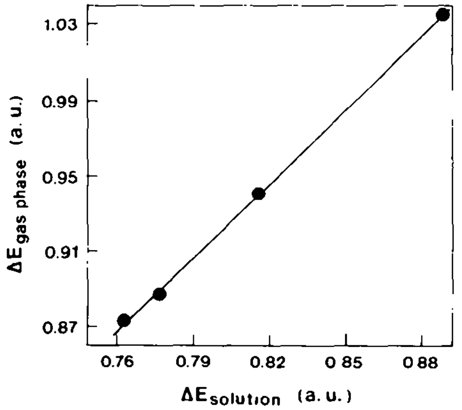

Fig. 3. Correlation of acidities calculated in the gas phase and in solution (see Table 2).

Acknowledgements—The author wishes to express his gratitude to Prof. H. Dahn for his encouragement and advice. The financial support given to Prof. Dahn by the Fonds National Suisse pour la Recherche Scientifique (Project No. 2.772.72) is gratefully acknowledged.

REFERENCES

[1] D. K. Bohme, E. Lee Ruff and L. B. Young, *J. Am. Chem. Soc.* **94**, 5153 (1972).

[2] R. T. McIver, Jr., J. A. Scott and J. M. Riveros, *Ibid.* **95**, 2706 (1973).

[3] R. T. McIver, Jr. and J. H. Silvers, *Ibid.* **95**, 8462 (1973).

[4] I. Dzidic, D. I. Carroll, R. N. Stilwell and E. C. Horning, *Ibid.* **96**, 5258 (1974).

[5] R. Yamdagni and P. Kebarle, *Ibid.* **95**, 4050 (1973).

[6] K. Hiraoka, R. Yamdagni and P. Kebarle, *Ibid.* **95**, 6833 (1973).

[7] R. Yamdagni, T. B. McMahon and P. Kebarle, *Ibid.* **96**, 4035 (1974).

[8] T. B. McMahon and P. Kebarle, *Ibid.* **96**, 5940 (1974).

[9] J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys* **54**, 508 (1971); J. A. Pople and G. A. Segal, *Ibid.* **44**, 3289 (1966); P. A. Dobosh, CNINDO, QCPE program No. 141.

[10] J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory.* McGraw-Hill, New York (1970).

[11] L. B. Kier, *Molecular Orbital Studies in Chemical Pharmacology*, Symposium held at Battelle Seattle Research Center, 20–22 Oct. 1969. Springer-Verlag, Berlin (1970).

[12] L. E. Sutton, *Tables of Interactomic Distances*, The Chemical Society, London (1958) and Supplement 1965.

[13] J. E. Williams, Jr. and A. Streitwieser, Jr., *J. Am. Chem. Soc.* **97**, 2634 (1975).

[14] A. Streitwieser, Jr., P. H. Owens, R. A. Wolff and J. E. Williams, Jr., *Ibid.* **96**, 5448 (1974).

[15] Z. Margolin and F. A. Long, *Ibid.* **95**, 2757 (1973).

[16] O. A. Hougen, K. M. Watson and R. A. Ragatz, *Chemical Process Principles*, Part I, p. 279. Wiley, New York (1954).

[17] P. Cremaschi, A. Gamba and M. Simonetta, *Theoret. Chim. Acta* **25**, 237 (1972).

[18] D. F. C. Morris, *Structure and Bonding* (Edited by C. K. Jorgensen, J. B. Neilands, R. S. Nyholm, D. Reinen and R. P. J. Williams) Vol. 4, p. 163 (1968).

[19] P. Cremaschi and M. Simonetta, *Theoret. Chim. Acta* **37**, 341 (1975); and refs therein.

[20] K. Morokuma, *J. Chem. Phys.* **55**, 1236 (1971).

[21] P. A. Kollman and L. C. Allen, *Chem. Revs.* **72**, 283 (1972).

[22] P. Cremaschi, A. Gamba and M. Simonetta, *Theoret. Chim. Acta* **31**, 155 (1973).

[23] A. Streitwieser, Jr., P. C. Mowery, R. G. Jesaitis, J. R. Wright, P. H. Owens and D. M. E. Reuben, *Quantum Aspects of Heterocyclic Compounds in Chemistry and Biochemistry.* The Jerusalem Symposia on Quantum Chemistry and Biochemistry. II, Jerusalem (1970).

[24] J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.* **93**, 4315 (1971).

[25] T. P. Lewis, *Tetrahedron* **25**, 4117 (1969).

[26] D. H. Aue, H. M. Webb and M. T. Bowers, *J. Am. Chem. Soc.* **94**, 4726 (1972).

[27] M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz and R. W. Taft, *Ibid.* **94**, 1369 (1972).

[28] See however P. H. Owens, R. A. Wolf and A. Streitwieser, Jr., *Tetrahedron Letters* 3385 (1970).

[29] F. G. Bordwell and W. S. Matthews, *J. Am. Chem. Soc.* **96**, 1216 (1974).

[30] T. E. Hogen-Esch and J. Smid, *Ibid.* **88**, 307 (1966); J. I. Brauman, J. A. Bryson, D. C. Kahl and N. J. Nelson, *Ibid.* **92**, 6678 (1970); A. Streitwieser, Jr., C. J. Chang and D. M. E. Reuben, *Ibid.* **94**, 5730 (1972); E. M. Arnett, T. C. Moriarity, L. E. Small, J. P. Rudolph and R. P. Quirk, *Ibid.* **95**, 1492 (1973); F. G. Bordwell and W. S. Matthews, *Ibid.* **96**, 1214 (1974).

[31] F. G. Bordwell, J. E. Bartness, G. E. Drucker, Z. Margolin and W. S. Matthews, *Ibid.* **95**, 3226 (1975).

[32] F. G. Bordwell, paper presented at the 10th Faraday Symposium, held at Stirling, Scotland, September (1975).

[33] R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.* **97**, 1285, 1294, 1302 (1975).

[34] W. J. Hehre and J. A. Pople, *Tetrahedron Letters* 2959 (1970); L. Radom, *Chem. Commun.* 403 (1974).

[35] J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.* **90**, 6562 (1968).

[36] R. P. Bell, *The Proton in Chemistry* (2nd Edition). Chapman & Hall, London (1973).

[37] F. G. Bordwell, W. J. Boyle and J. A. Hautala, *J. Am. Chem. Soc.* **91**, 4002 (1969).

[38] R. A. Marcus, *Ibid.* **91**, 7224 (1969).

[39] A. J. Kresge, *Ibid.* **92**, 3210 (1970); A. J. Kresge, *Chem. Soc. Quart. Revs.* **2**, 475 (1973).

[40] B. G. Cox and A. Gibson, *Chem. Commun.* 683 (1974).

[41] F. G. Bordwell and W. J. Boyle, Jr., *J. Am. Chem. Soc.* **97**, 3447 (1975).