

MNDO STUDY OF THE PROTON AFFINITY OF FLUORINATED FORMALDEHYDES AND ACETONES

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ABSTRACT

The MNDO molecular orbital method is employed to calculate the proton affinities of fluorinated formaldehydes and acetones. Agreement with experimentally reported proton affinities is good. In the acetone series a decrease in proton affinity is calculated for each successive fluorine substituent. The calculated strength of the intramolecular hydrogen bond in the protonated fluoro-formaldehydes and acetones is 0.6–2.7 kcal mol⁻¹, in good agreement with the experimental value of 2–3 kcal mol⁻¹ in the protonated fluoroacetones. Examination of the calculated charge distribution shows that the trends in proton affinity can be understood qualitatively both in terms of initial-state and final-state effects caused by the fluorine substituents. Protonation at the fluorine atom is less stable by about 25 kcal mol⁻¹ than protonation at the oxygen atom for mono-fluoroacetone.

INTRODUCTION

Drummond and McMahon [1] have recently reported the gas phase proton affinities (PA's) of acetone and six fluorinated acetones from ion-cyclotron resonance spectroscopy experiments. The principle results of their work were; (a) that there is a regular decrease in PA of 6.1 ± 0.4 kcal mol⁻¹ for each successive fluorine substituent; (b) that this result can be interpreted in terms of an inductive effect of the fluorine atoms, and (c) that an intramolecular hydrogen bond with a strength of 2–3 kcal mol⁻¹ is present in each of the protonated fluoroacetones.

The present study was undertaken as part of a larger PA study being conducted using semiempirical molecular orbital methods and was intended to assess the validity of the MNDO approach for such studies. Besides the energetics of the protonation (for which experimental data are available), it was intended to analyze the results in terms of charge redistributions, relative energetics of different protonation sites, and structural changes that result from protonation.

PA's were also calculated for the fluoroformaldehydes in order to test the sensitivity of PA to the proximity of the fluorine substituent, and to compare our results with the 4–31G ab initio results of Del Bene [2].

A few reports utilizing the MNDO method for PA studies have been

published [3] and the results generally have been in good agreement with experiment. A systematic study of the strengths and weaknesses of the MNDO method with respect to PA studies has already been conducted [4].

METHOD OF CALCULATION

We have employed the usual MNDO computer program available from the Quantum Chemistry Program Exchange [5]; its development has been described by Dewar and Thiel [6]. All bond angles and bond lengths were optimized for both the neutral substrates and the protonated species. Of course, such an optimization always runs the risk of finding a local energy minimum rather than the (quasi) global value which one hopes to find in a particular region of the hypersurface [7]. In this particular study, if the protonated molecule had two geometrical isomers (*syn* and *anti* substituents to the proton) a geometry search was carried out for each structure in order to determine their relative stabilities. In the case of more subtle geometrical differences such as rotation about a C—C bond, the optimization was started from several different geometries to ensure that the optimum final geometry was reached. The experimental heat of formation of H⁺ was used in calculating the PA's: $\Delta H_f(\text{H})^+ = 365.7 \text{ kcal mol}^{-1}$ [8].

RESULTS AND DISCUSSION

Pertinent results from the MNDO calculations are presented in Table 1 for the formaldehyde and acetone series of molecules. The ionization energies are Koopmans' theorem values. A comparison of experimental and calculated PA values is presented in Table 2. Except for the one exploratory calculation with fluorine protonation, all results refer to proton attack at the carbonyl oxygen atom.

In the following discussion we consider first the fluoroacetone molecules. Plots of PA versus number of fluorine substituents, versus calculated ionization energy, versus charge on the oxygen atom of the neutral molecule, and versus charge on the added proton of the protonated molecules, are presented in Figs. 1, 2, 3 and 4, respectively. Figures 1 and 2 bear a striking resemblance to the corresponding plots presented by Drummond and McMahon [1]. That is, increasing fluorine substitution results in a decreasing PA and an increasing ionization energy. Figures 3 and 4 illustrate that within the calculational framework it is not possible to ascribe the trends in PA solely to either initial-state or final-state effects caused by the fluorine substituents. If only initial-state effects were important there should be a linear correlation with charge on the oxygen atom of the neutral molecule. On the other hand, final-state effects should be manifest as a linear correlation with charge on the carbonyl proton of the protonated molecule.

Figures 1 and 2 deviate in some particulars from the experimental

TABLE 1

MNDO results on the fluorinated acetones and formaldehydes

Molecule	ΔH_f (kcal mol ⁻¹)	Ionization energy (eV)	q_H	q_O	q_C	q_{syn}^a	q_{anti}^b
H ₂ CO	-33.0	11.0	-	-0.29	0.29	0.00	0.00
H ₂ COH ⁺	155.5	-	0.31	-0.08	0.47	0.13	0.17
FHCO	-88.9	12.4	-	-0.30	0.41	-0.21 _s	0.10
FHCOH ⁺	106.3	-	0.33	-0.14	0.63	-0.08	0.25
F ₂ CO	-138.8	13.6	-	-0.27 _s	0.60 _s	-0.16 _s	-0.16 _s
F ₂ COH ⁺	73.2	-	0.34 _s	-0.12	0.81	-0.04	0.00
(CH ₃) ₂ CO	-49.5	10.8	-	-0.28	0.19	0.04 _s	0.04 _s
(CH ₃) ₂ COH ⁺	127.2	-	0.29	-0.10	0.37	0.20	0.24
(CH ₂ F)(CH ₃)CO	-93.3	11.0	-	-0.25	0.17	0.02	0.06
(CH ₂ F)(CH ₃)COH ⁺	90.2	-	0.31	-0.08	0.32	0.20	0.25
(CH ₂ FH)(CH ₃)CO ⁺	114.1	-	0.48	0.00 ^c	0.20	-	-
(CH ₂ F) ₂ CO	-136.4	11.3	-	-0.25	0.15	0.05	0.05
(CH ₂ F) ₂ COH ⁺	54.5	-	0.31	-0.05 _s	0.26 _s	0.22	0.26
(CH ₃)(CF ₃)CO	-189.9	12.0	-	-0.20 _s	0.20	0.12	-0.12
(CH ₃)(CF ₃)COH ⁺	14.5	-	0.32	-0.06	0.32	0.26	0.16
(CHF ₂) ₂ CO	-228.2	11.9	-	-0.16	0.12	0.02	0.02
(CHF ₂) ₂ COH ⁺	-19.0	-	0.33	-0.02	0.21	0.22	0.27
(CHF ₂)(CF ₃)CO	-276.1	12.4	-	-0.15	0.14	0.06 _s	-0.06
(CHF ₂)(CF ₃)COH ⁺	-57.3	-	0.34	-0.02	0.23	0.26	0.20
(CF ₃) ₂ CO	-322.7	13.0	-	-0.12	0.16	-0.02	-0.02
(CF ₃) ₂ COH ⁺	-93.5	-	0.34 _s	-0.01	0.24	0.18 _s	0.24

^aThe charge on the group *syn* to the proton. In the case of different groups, the *syn* group is listed on the left of the chemical formula in the first column. ^bThe charge on the group *anti* to the proton. ^cCharge on the protonated fluorine atom.

results. First, the calculations do not show as regular a decrease as is exhibited experimentally [1]. Second, acetone itself fell beneath the graphical lines by about 2 kcal mol⁻¹ in the experimental presentations. This phenomenon was attributed to the formation of an intramolecular hydrogen bond (F···H—O) for each of the fluorinated acetones. No such observation is evident from our results in Figs. 1 and 2. Nevertheless, we do believe that that interpretation of Drummond and McMahon [1] is correct. Calculations on monofluoroacetone in which the formation of an intramolecular hydrogen bond was allowed, exhibited an extra stability of about 0.65 kcal mol⁻¹ compared to molecular configurations in which such bonding was not allowed. Corresponding calculations on protonated 1,3-difluoroacetone resulted in an intramolecular hydrogen bond strength of 2.7 kcal mol⁻¹. Typically the F···H distance is optimized to be about 2.5 Å, which is probably overestimated by several tenths of an angstrom in the MNDO method. Surprisingly, we find that for protonated 1,1,1-trifluoroacetone conformation 1 is more stable than 2 by 1 kcal mol⁻¹. Since the major purpose of this work was to examine trends in the PA values, we did not

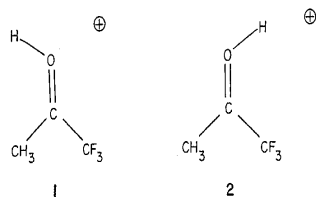


TABLE 2

Comparison of MNDO calculated and experimental proton affinities (kcal mol⁻¹)

Molecule	Calculated proton affinity	Experimental proton affinity
H ₂ CO	177.2	174.6 ^a
HFCO	170.5	—
F ₂ CO	153.7	—
(CH ₃) ₂ CO	189.0	193.9 ^b
(CH ₂ F)(CH ₃)CO	182.2	190.0
(CH ₂ F) ₂ CO	174.8	183.5
(CF ₃)(CH ₃)CO	161.3	177.1
(CHF ₂) ₂ CO	156.5	171.1
(CF ₃)(CHF ₂)CO	146.9	165
(CF ₃) ₂ CO	136.5	159.3

^aJ. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp and R. W. Taft, *J. Am. Chem. Soc.*, 99 (1977) 5417. ^bRef. 1.

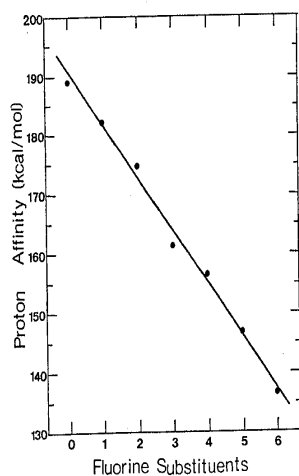


Fig. 1. Plot of calculated proton affinity versus number of fluorine substituents.

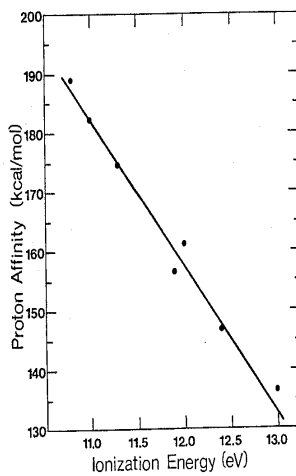


Fig. 2. Plot of calculated proton affinity versus calculated ionization energies.

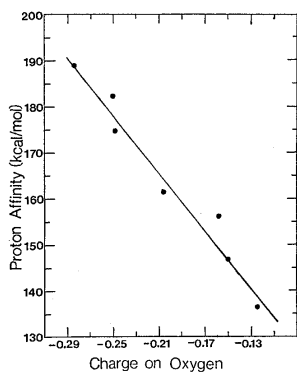


Fig. 3. Plot of calculated proton affinity versus calculated charge on the oxygen atom in the neutral acetone.

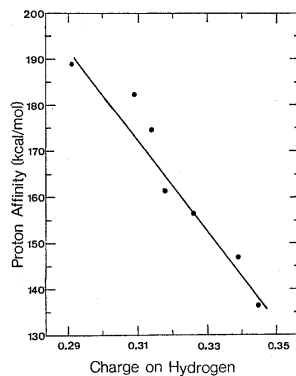


Fig. 4. Plot of calculated proton affinity versus calculated charge on the added hydrogen in the protonated molecule.

pursue this study of the intramolecular hydrogen bond. It is sufficient to note that the MNDO method was not parameterized to reproduce hydrogen bond strengths [9].

The slope of Fig. 1 is $-8.75 \text{ kcal mol}^{-1}$ per fluorine substituent compared to the experimental slope of $-6.1 \text{ kcal mol}^{-1}$. This difference is exemplified well by the PA results presented in Table 2, which shows that there is good agreement between the calculated and observed PA of acetone but for hexafluoroacetone the difference is more than 20 kcal mol^{-1} , i.e., the MNDO method overestimates the effect of the fluorine substituents. Dewar and Rzepa report calculated MNDO PA values for the fluorinated ethylenes [10] and their results also show that the fluorine substituent effect on PA is overestimated. However, in comparing the PA of acetone and formaldehyde we see that MNDO underestimates the alkyl substituent effect. These two conclusions are further substantiated by earlier studies [4].

Turning next to the fluoroformaldehydes, Table 2 shows that the fluorine substituent effect is predicted to be larger than for the fluoroacetones. The atomic charge results presented in Table 1 for the fluoroformaldehydes would indicate that the trend can be understood better on the basis of final-state than initial-state effects. An intramolecular hydrogen bond of 2 kcal mol^{-1} has been calculated for monofluoroformaldehyde, perhaps in acci-

dental agreement with the ab initio 4-31G result of 2.5 kcal mol⁻¹ [2]*. In both the MNDO and ab initio studies the fluorine effect is not additive in the series H₂CO, F₂CO, and F₂CO.

Geometrical parameters

Table 3 presents pertinent geometrical parameters. Notice that the calculated COH angle in the protonated species is 120–125°. The OH bond length tends to increase slightly with the number of fluorine substituents. The CO

TABLE 3

Geometrical parameters calculated by the MNDO method

Molecule	R _{OH} (Å)	R _{CO} (Å)	θ (COH) (degrees)
H ₂ CO	—	1.22	—
H ₂ COH ⁺	0.96	1.27	121
HF ₂ CO	—	1.22	—
HF ₂ COH ⁺	0.96	1.29	124
F ₂ CO	—	1.22	—
F ₂ COH ⁺	0.97	1.29	121
(CH ₃) ₂ CO	—	1.23	—
(CH ₃) ₂ COH ⁺	0.96	1.29	120
(CH ₃ F)(CH ₃)CO	—	1.22	—
(CH ₃ F)(CH ₃)COH ⁺	0.96	1.29	122
(CH ₃ F) ₂ CO	—	1.22	—
(CH ₃ F) ₂ COH ⁺	0.96	1.28	122
(CF ₃)(CH ₃)CO	—	1.22	—
(CF ₃)(CH ₃)COH ⁺	0.96	1.28	122
(CHF ₂) ₂ CO	—	1.21	—
(CHF ₂) ₂ COH ⁺	0.97	1.27	124
(CF ₃)(CHF ₂)CO	—	1.21	—
(CF ₃)(CHF ₂)COH ⁺	0.97	1.27	124
(CF ₃) ₂ CO	—	1.21	—
(CF ₃) ₂ COH ⁺	0.97	1.26	125

*In ref. 2b Del Bene and Radovick indicate in a footnote that their ab initio calculations do not indicate an intramolecular hydrogen bond as the reason for the stability of *syn* HF₂COH⁺ over the *anti* isomer. They base this statement on the small but negative F...H Mulliken overlap population and on the lack of geometrical changes to indicate the formation of such a hydrogen bond. In fact, charge density difference maps more accurately portray bond formation than do Mulliken population analyses (see ref. 11). However, in the case of these proton affinity studies such charge density difference maps could not be readily interpreted to indicate whether or not an intramolecular hydrogen bond has formed. Whether or not the extra stability of the *syn* isomer is strictly due to an intramolecular hydrogen bond, we use that term to describe it here for convenience.

bond distance is increased by about 0.05 Å as a result of protonation. The geometries mimic the ab initio 4-31G results very well, agreeing to within 5° in angles and 0.03 Å in lengths. Geometrical changes as a result of protonation agree even better, to within 1° and 0.01 Å.

Charge redistribution

The charges presented in Table 1 show that protonation results in a charge redistribution throughout the entire molecule. Invariably we find that for equivalent methyl or substituted methyl groups, the group *anti* to the carbonyl proton is more electron-releasing than the group that is *syn*. In spite of the protonation, the oxygen atom remains negatively charged which is in agreement with the 4-31G ab initio calculations [2].

Detailed analysis of the charge redistribution for monofluoroacetone and its protonated counterpart shows that the proton removes 0.50 electrons from the oxygen atom σ orbitals. This charge loss is partially offset by an increase of 0.33 electrons in the oxygen atom π orbital. Almost all of this was taken from the carbonyl carbon atom π orbital. The carbonyl carbon atom suffered a loss of only 0.1 electron in the σ framework. Similar conclusions regarding the redistribution of σ and π electrons result from an analysis of the Wiberg bond indices [12]. That is, protonation results in a decrease of 0.12 in the CO σ bond index and of 0.30 in the CO π bond index. Such a charge redistribution also has been reported in the MNDO study of protonation in methylsydnone [3c].

CONCLUSIONS

The present calculations show that the experimental trends in PA of the fluoroacetones can be reproduced reasonably well. These trends can be understood in terms of both initial-state and final-state effects and there is evidence for the formation of an intramolecular hydrogen bond in both the protonated fluoroacetones and fluoroformaldehydes. Analysis of the charge redistribution caused by protonation shows that the proton attacks an oxygen lone pair which results in a weakening of the CO π bond and the CO bond is lengthened by about 0.05 Å.

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REFERENCES

- 1 D. F. Drummond and T. B. McMahon, *J. Phys. Chem.*, **85** (1981) 3746.
- 2 (a) J. E. Del Bene, *J. Am. Chem. Soc.*, **100** (1978) 1673; (b) J. E. Del Bene and S. Radovick, *J. Am. Chem. Soc.*, **100** (1978) 6936.
- 3 (a) M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc.*, **99** (1977) 5231; (b) P. Brint, E. F. Healy, T. R. Spalding and T. Whelan, *J. Chem. Soc., Dalton Trans.*, (1981) 2515; (c) M. Eckert-Maksić and Z. B. Maksić, *J. Chem. Soc., Perkin Trans. 2*, (1981) 1462; (d) S. Olivella and J. Vilarrasa, *J. Heterocycl. Chem.*, **18** (1981) 1189; (e) R. Chadha and N. K. Ray, *Theor. Chim. Acta*, **60** (1982) 579.
- 4 R. L. DeKock and C. P. Jasperse, *Inorg. Chem.*, accepted for publication.
- 5 W. Thiel, Quantum Chemistry Program Exchange (QCPE), Bloomington, Indiana, U.S.A., Program No. 353.
- 6 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99** (1977) 4899, 4907.
- 7 M. J. S. Dewar and M. L. McKee, *Inorg. Chem.*, **17** (1978) 1569.
- 8 S. Lias, in P. Ausloos (Ed.), *Kinetics of Ion-Molecule Reactions*, Plenum, New York, 1978, p. 233.
- 9 T. J. Zielinski, D. L. Breen and R. Rein, *J. Am. Chem. Soc.*, **100** (1978) 6266; G. Klopman, P. Andreozzi, A. J. Hopfinger, O. Likucki and M. J. S. Dewar, *J. Am. Chem. Soc.*, **100** (1978) 6267.
- 10 M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **100** (1978) 58.
- 11 P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51** (1969) 3286; P. J. Desmeules and L. C. Allen, *J. Chem. Phys.*, **72** (1980) 4731.
- 12 K. B. Wiberg, *Tetrahedron*, **24** (1968) 1083.