

GAS PHASE PROTON AFFINITIES OF OXIRANE AND THIIIRANE MOLECULES: AN AB INITIO STUDY

Luiz Carlos Gomide Freitas

Departamento de Física
Universidade Federal de Pernambuco
50.739 - Recife - PE
Brasil

Received July 14, 1987

ABSTRACT

This paper reports ab initio results for the electronic structure and gas phase proton affinities (PA) of Oxirane (C₂H₄O) and Thiirane (C₂H₄S) molecules.

The SCF calculations are performed using 4-31G basis set and correlations effects are included by Many-Body Perturbation Theory (MBPT) up to fourth-order within the Möller-Plesset formalism.

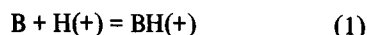
For both molecules the results obtained for the PA compare well with experimental values available in the literature.

1. INTRODUCTION

The interaction of protons with atoms and molecules in the gas phase and solution plays a very important role in many processes of chemical interest. In the last decades, the growing interest in the experimental aspects of gas phase acid-base chemistry and recent advances in instrumentation and experimental methods have produced a wealthy number of proton affinity measurements and therefore making possible a comparative study of gas phase protonation processes in the absence of perturbative effects due to solvent interaction¹. An interesting question raised by such studies was the discovery that for some class of molecules the acid-base properties in gas phase are radically different from their solution behaviour². These observations have also stimulated many theoretical studies toward an understanding of the electronic aspects of the acid-base reactions^{3,4}. The aim of the present paper is the theoretical investigation of the gas phase proton interaction with Oxirane and Thiirane molecules by using basis sets of a moderately small size and an attempt is made to access the need of including electron correlation effects to reproduce the energetics of the proton binding process.

Oxirane and Thiirane are examples of three-membered heterocycles with strongly strained rings and this particular aspect of the ring structure creates favourable conditions for the interaction with electrophilic reagents⁵. These molecules are isovalent and belong to the same point group symmetry (C_{2v}). From a preliminary electron distribution analysis it is expected a favourable contribution of lone pair type molecular orbital to the proton binding process. As the Sulphur atom is less electronegative than Oxygen it is also expected that the proton binding to the Thiirane molecule should be energetically more favourable if compared to Oxirane.

For a protonation process described by equation 1.



the proton affinity PA of the base B is defined as the reaction enthalpy ΔH and can be calculated from the expression⁶:

$$PA(B) = -\Delta E_{el} - \Delta ZPE + 5/2RT \quad (2)$$

where the ΔE_{el} includes all electronic effects, the term ΔZPE is the zero point energy difference between B and BH(+) and the last term is required to convert from ΔE to ΔH .

In the next section (2) we will describe the methodology used in the present calculation and in section (3) results and conclusions will be presented.

2. METHODOLOGY

In the present study ab initio SCF molecular orbital calculation were performed with the Gaussian 82 program⁷. The geometries of both molecules and of each correspondent protonated ion were optimized at the HF-SCF level with 4-31G basis set⁸⁻⁹ by using gradient algorithms incorporated into the Gaussian program.

Vibrational frequencies were then calculated at the HF/SCF level with this same basis set in order to get the zero point energy (ZPE) for each molecule and ion which are being studied in the present work.

Correlation energy contributions were calculated by Many-Body / Möller-Plesset Perturbation Theory¹⁰ (MP) from second (MP2) to fourth-order (MP4) within the frozen core approximation. At the MP4 level single, double and quadruple excitations from the SCF reference state were allowed to take part in the correlation energy calculation. The MP calculations were performed at the HF/4-31G optimized geometry with the 4-31G basis set (Oxirane and Thiirane) and 4-31G* (Thiirane). The 4-31G* basis set includes d-type Gaussian functions on the heavy atom. No attempt was made to reoptimize the geometries at the MP level in the grounds that such a process would be very time consuming. However, it is well accepted¹² that the effects originated by extending the basis set size and including MP correlation energy corrections to the optimization process nearly cancel each other and therefore the HF/4-31G optimized geometry is a good approximation to a MP/4-31G* level calculation.

3. RESULTS

In figure 1 the structural shape of the molecules and ions studied in the present paper is displayed and in Table I all the optimized geometry parameters are presented. Both protonated molecules belong to the C_s point

group symmetry. By comparing the geometry parameters for the neutral and corresponding protonated molecule one can see that protonation strongly affects the ring structure.

In Table II the calculated SCF and MP total energies obtained with 4-31G and 4-31G* basis set are presented. The values of ΔE_c , that is, the correlation energy correction introduced by different levels of perturbation theory are also shown in Table II. As expected, the MP corrections shift down the total energy values and the amount of correlation energy introduced increases from second (MP2) to fourth-order (MP4). At the fourth-order MP4 level the correlation energy correction calculated with single, double and quadruple excitations gives the best value for the total energy. Its noteworthy however the fact that, compared to the fourth-order MP4SDQ, the total energy values on Table II calculated at the second-order MP2 level includes more than 85 percent of the correlation energy and the computer time expended by a MP2 calculation is considerably lower than the one needed by higher orders of perturbation theory.

The values of the zero point energies (ZPE) calculated at the HF/4-31G level are also presented in Table II.

In Table III the calculated proton affinities for Oxirane and Thiirane molecules are presented and compared against the experimental data available in the literature¹²⁻¹³.

For both molecules the HF/4-31G* values for the PA is in excellent agreement with the experimental data. Such good performance of the HF theory to predict proton affinities has also been observed by other author¹⁴ and could be originated by the systematic error cancellations since correlation energy is not included.

In the set of results calculated with MP corrections to the correlation energy contribution from the valence electrons the experimental data is better at higher orders of perturbation theory.

For the Thiirane molecule the inclusion of d-type Gaussian functions on the heavy atoms was necessary to improve the agreement with the experimental data.

Other point to be discussed concerns the ZPE calculation: as a general trend the HF vibrational frequencies are larger than the experimental ones and therefore our calculated ZPE should be scaled by a factor of 0.9 which is the scaling value generally accepted for the HF/4-31G basis set results¹⁵. This scaling correction decreases the values of the zero point energy differences and therefore the proton affinities calculated by using Equation 2 will increase.

As our calculated PA values are almost systematically lower than the experimental results the use of scaled ZPE values brings on a slight improvement on the present theoretical data. The magnitude of this improvement can be verified by comparing the MP4SDQ(s) with the experimental data, as shown on Table III.

In Table IV we present the calculated HF/4-31G total atomic charges for each atomic center present on the neutral and protonated molecules. The values of Δq indicates the magnitude of charge density modifications on the neighbourhood of each atom. In an "atom in molecule" terminology one should say that in the protonation process of the Oxirane molecule charge is transferred from the carbons and hydrogens atoms to the incoming proton and in the Thiirane molecule proton binding process the contribution from the Sulphur atom is the dominant one. Therefore, as far as the arguments generated by this localized charge analysis are valid in a molecular orbital context, it is possible to perceive differences in the proton binding process by these two molecules, that is, an overall ring dominant contribution in the Oxirane molecule case and for the Thiirane molecule a more localized contribution from an atomic center.

The results of the present paper shows that a calculation using moderately small basis set that is, the 4-31G and 4-31G* including correlation energy corrections by MBPT/Möller-Plesset is able to predict the gas phase proton affinities of small heterocycle rings. The average error of 1.5kcal/mol found in the PA calculations is sufficiently small to encourage further Quantum Chemistry studies of the energetics of gas phase proton binding processes. Even the inclusion of a small number of hydrations molecules to probe solvent effects seems to be computationally feasible, at least at the less time consuming MP2 level of theory. In this case, the inclusion of solvent molecule could be done by using the supermolecule approach.

Some of these studies are in progress and will be reported soon.

ACKNOWLEDGEMENTS

This paper is dedicated to Prof. Ricardo Ferreira on the occasion of his 60th birthday.

The author wishes to thank Dr. Y. Takarata and Dr. Alfredo N. Simas for facilities.

This work was partially supported by CNPq and FINEP.

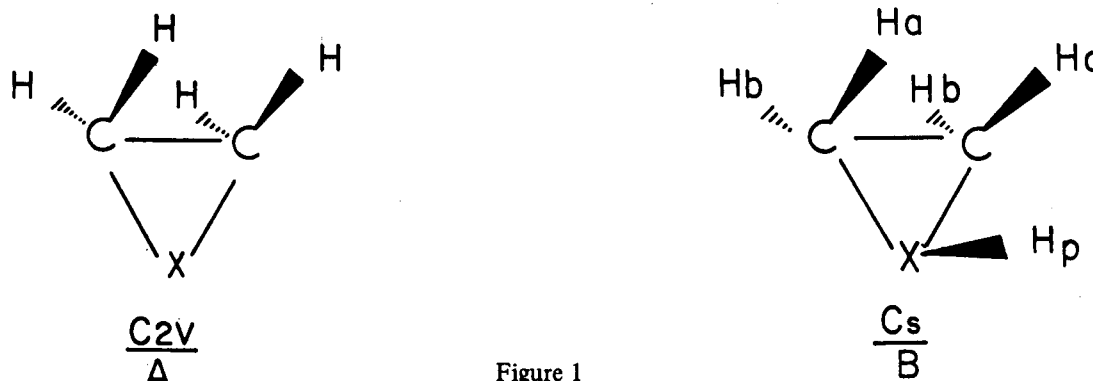


Figure 1

TABLE I

HF/4-31G Geometry parameters.

	Oxirane	Thiirane	Protonated Oxirane	Protonated Thiirane
RCC	1.4604	1.4594	1.4586	1.4356
RCX	1.459	1.9204	1.542	2.026
RCH	1.069	1.069	1.069	1.071
∠CXC	60.06	44.7	56.44	41.49
∠HCC	119.78	118.97	120.16	120.24
∠HCCX	102.74	105.03	98.67	100.17
RXP	—	—	0.962	1.356
∠PXD	—	—	129.35	98.1

Rab = bond length (angstroms)

∠abc = bond angles (degrees)

∠abcd = dihedral angles (degrees)

TABLE II

Total Energies (au) and ZPE (Kcal/mol)

Method	Oxirane				Protonated Oxirane			
	4-31-G	ΔE_c^a	4-31G*	ΔE_c	4-31G	ΔE_c^a	4-31G*	ΔE_c
HF	-152.626759	—	-152.715504	—	-152.945731	—	-153.025358	—
MP2	-152.934446	.3077		.4398	-153.242530	.2968		.4268
MP3	-152.945212	.3185		.4551	-153.255664	.3099		.4462
MP4DQ	-152.952359	.3256		.4585	-153.263349	.3176		.4503
MP4SDQ	-152.955675	.3289		.4633	-153.267326	.3216		.4553
ZPE	38.7565				46.7137			

	Thiirane				Protonated Thiirane			
	4-31G	ΔE_c	4-31G*	ΔE_c	4-31G	ΔE	4-31G*	ΔE_c
HF	-474.971358		-475.054248		-475.2752		-475.373196	
MP2	-475.210265	.2389	-475.437898	.3836	-475.512810	.2376	-475.747627	.3744
MP3	-475.230142	.2588	-475.464944	.4107	-475.536123	.2609	-475.779493	.4063
MP4DQ	-475.235333	.2640	-475.467174	.4129	-475.541750	.2666	-475.782054	.4088
MP4SDQ	-475.237769	.2664	-475.471337	.4171	-475.552826	.2776	-475.786884	.4137
ZPE	36.9700				42.833			

^a $\Delta E_c = E(\text{MPi}) - E(\text{HF})$

TABLE III

Proton Affinities in Kcal/mol at T = 300K

Method	OXIRANE		THIIRANE	
	4-31G	4-31G*	4-31G	4-31G*
HF	193.671	187.969	186.291	195.770
MP2	186.857		185.477	189.985
MP3	188.344		187.633	193.01
MP4DQ	188.681		187.907	193.217
MP4SDQ	189.096		193.328	193.636
MP4SDQ(S)	189.892		193.914	194.222
Exp.	189.6 ^a		195.8 ^a	(S) Scaled ZPE
	187.9 ^b			a ref. 12
				b ref. 13

TABLE IV

Total Atomic charges and Dipole Moment^a

	OXIRANE			THIIRANE		
	Neutral	Protonated	Δq	Neutral	Protonated	Δq
C	6.0805	6.0436	-36.9	6.4495	6.3759	-73.6
X	8.6081	8.6961	88.0	16.001	15.7614	-239.6
Ha	0.8077	0.6975	-110.2	0.7750	0.6821	-92.9
Hb	0.8077	0.6758	-131.9	0.7750	0.6692	-105.8
Hp	-	0.4699	-	-	0.7841	-
D ^b	3.0135			2.6142		-

a HF/4-31G

b Dipole Moment (Debye)

 $\Delta q = [\text{Charge (Protonated)} - \text{charge (Neutral)}] \times 1000$

Hydrogens Ha, Hb, Hp are defined in the structure B of figure 1.

REFERENCES

- C.R. Moylan and J.I. Brauman, *Ann. Rev. Phys. Chem.* **34**, 187 (1983).
- P. Kebarle, *Ann. Rev. Phys. Chem.* **28**, 445 (1977).
- P.G. Jasien and W.J. Stevens, *J. Chem. Phys.* **83**(6) 2984 (1985).
- H. Fujimoto, T. Yamasaki, I. Hatane and N. Koga, *J. Phys. Chem.* **89**, 779 (1985).
- R. Bonaccorsi, E. Scrocco and J. Tomasi, *J. Chem. Phys.* **52**, 5270 (1970).
- R.A. Eades, K. Scalon, M.R. Ellenberger, D.A. Dixon and D.S. Marynick, *J. Phys. Chem.* **84**, 2840 (1980).
- J.S. Binkley, M. Frish, K. Raghavachari, D. DeFrees, H.B. Schlegel, R. Whiteside, E. Fluder, R. Seeger and J.A. Pople, "Gaussian-82 Program, Release A", Carnegie-Mellon University, 1982.
- R. Ditchfield, W.J. Hehre and J.A. Pople, *J. Chem. Phys.* **54**, 724 (1971).
- S. Huzinaga, *Comp. Phys. Reports* **2**, 280 (1985).
- R.J. Bartlett, *Ann. Rev. Phys. Chem.* **32**, 359 (1981); C. Möller and M.S. Plesset, *Phys. Rev.* **46**, 618 (1934).
- W.J. Hehre and J.A. Pople, *J. Chem. Phys.* **56**, 4233 (1972).
- D.H. Ane, H.M. Webb, W.R. Davidson, M. Vidal and M.T. Bowers, *J. Am. Chem. Soc.* **102**, 5151 (1980).
- S.G. Lias, J.F. Liebman and R.D. Levin, *J. Phys. Chem. Ref. Data* **13**, 695 (1984).
- J.E. DelBene, *J. Comput. Chem.* **6**, 296 (1985).
- D.J. DeFrees and A.D. McLean, *J. Chem. Phys.* **82**, 333 (1985).