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AB INITIO STUDY OF DEHALOGENATION REACTION OF 2-HALO-2,3-DIHYDROPHOSPHININE**H. Shirani Il Beigi¹, M. Nikbakht², P. Ghanbar pour²**¹Young Researchers Club, Najaf Abad Branch, Islamic Azad University, Najaf Abad, Isfahan, Iran
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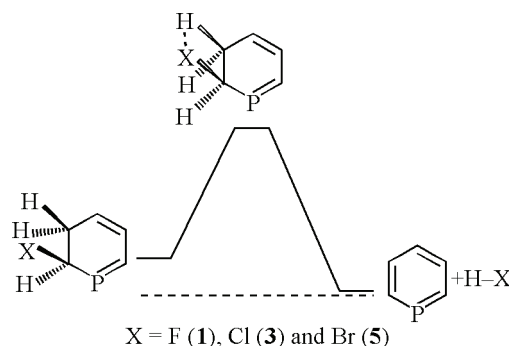
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Decomposition of 2-fluoro-2,3-dihydrophosphinine (**1**), 2-chloro-2,3-dihydrophosphinine (**3**), 2-bromo-2,3-dihydrophosphinine (**5**) to phosphinine was investigated using Molecular orbital and density functional theory. Study on the B3LYP/6-311+G** level of theory revealed that the required energy for the decomposition of compounds **1**, **3** and **5** to phosphinine is 30.56, 28.23 and 24.03 kcal·mol⁻¹, respectively. HF/6-311+G**//B3LYP/6-311+G** calculated barrier height for the decomposition of compound **1**, **3** and **5** to phosphinine is 57.56, 37.26 and 30.77 kcal·mol⁻¹, respectively. Also, MP2/6-311+G**//B3LYP/6-311+G** results indicated that the barrier height for the decomposition of compound **1**, **3** and **5** to phosphinine is 46.59, 47.28 and 42.57 kcal·mol⁻¹, respectively. Natural bond orbital (NBO) population analysis and nuclear independent chemical shift (NICS) results showed that, reactants are non-aromatic but products of elimination reaction are aromatic, C—H and C—X bonds are broken and H—X bond is appear.

Keywords: *ab initio*, NBO, NICS, 2-halo-2,3-dihydrophosphinines.

INTRODUCTION

Decomposition mechanism of 2-halo-2,3-dihydrophosphinines to phosphinine was investigated using *ab initio* molecular orbital (MO) and density functional theory (DFT). The experimental study of the kinetic of dissociation process of 2-halo-2,3-dihydropyridinies, showed that the decomposition reaction of 2-halo-2,3-dihydropyridinie is a unimolecular process (Scheme 1) [1].



Scheme 1

In this work, *ab initio* molecular orbital (MO), [2—6] DFT (B3LYP) methods [7, 8] and NBO analysis [9—11] were performed for the investigation of the pyrolysis reactions of 2-fluoro-2,3-dihydrophosphinine (**1**), 2-chloro-2,3-dihydrophosphinine (**3**) and 2-bromo-2,3-dihydrophosphinine (**5**) to phosphinine.

THEORETICAL METHODS

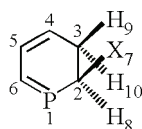
Ab initio calculations were carried out using B3LYP/6-311+G**, HF/6-311+G**//B3LYP/6-311+G**, and MP2/6-311+G**//B3LYP/6-311+G** levels of theory with the GAUSSIAN 98 package of programs [6, 12] implemented on a Pentium-PC computer with a 7300 MHz processor. Initial estimation of the structural geometry of the compound **1**, **3** and **5** were obtained by a molecular mechanic program PCMODEL (88.0) [13] and for further optimization of geometry, we used the PM3 method of the MOPAC 7.0 computer program [14, 15]. The GAUSSIAN 98 package of programs were finally used to perform *ab initio* calculations at the B3LYP/6-311+G** level. Energy-minimum molecular geometries were located by minimizing energy, with respect to all geometrical coordinates without imposing any symmetrical constraints. The nature of the stationary points for compound **1**, **3** and **5** and transition state structures has been fixed by means of the number of imaginary frequencies. For minimum state structure, only real frequency values, and in the transition-state, only single imaginary frequency values were accepted. Procedure (keyword SADDLE 0.10) these geometry structures were reoptimized by the QST2 subroutine at the B3LYP/6-311+G** level. For further optimization, TS subroutine was used. The vibrational frequencies of ground states and transition states were calculated by FREQ subroutine.

RESULTS AND DISCUSSIONS

Zero Point Energy (*ZPE*) and total electronic energies ($E_{el} = E_0 - ZPE$) for the energy minimum and energy maximum geometries of the decomposition of compound **1**, **3** and **5** to phosphinine were calculated on the B3LYP/6-311+G**//B3LYP/6-311+G** level of theory. For single-point energy calculations, both HF/6-311+G**//B3LYP/6-311+G** and MP2/6-311+G**//B3LYP/6-311+G** methods were used and are given in Table 1. Studies on the B3LYP/6-311+G**, HF/6-311+G**//B3LYP/6-311+G**, and MP2/6-311+G**//B3LYP/6-311+G** of theory show that the barrier height of the decomposition of the compound **1** to phosphinine and HF (reaction 1) is 30.57, 57.56 and 46.59 kcal·mol⁻¹, respectively. These calculation results for compound **2** revealed that the barrier height of reaction 2 is 23.33, 37.26 and 47.29 kcal·mol⁻¹, respectively. Also, barrier height of reaction 3 is 24.03, 30.77 and 42.57 kcal·mol⁻¹, respectively (Fig. 1).

It is well known that the strength of C—X bonds decreases, while the bond length increases with the size of halide atom. The lengths of C—F, C—Cl and C—Br bonds determined were found to be 1.33, 1.73 and 2.14 Å, respectively, in agreement with energetic behavior and other experimental data [16, 17].

C₂—C₃ bond lengths in reactants are greater than transition states and products in reactions 1—3 that showed that C=C double bond formed in products, see Table 2. The natural bond orbital (NBO) data revealed that electron population of C—C bond in reactants is similar to single bond but in products is double bond, see Table 3.



Scheme 2

In order to understand the reason for the lower barrier height of reaction 3 in comparison to reaction 1 and 2, we have carried out natural charge (from NBO calculations) distribution for the ground

Table 1

Calculated total energies (E), zero-point energies ZPE, and relative energies ΔE (E_h in Hartree) for the energy minima structures of compounds **1**–**6** and transition structures of reactions 1–3

Geometry	Method									
	B3LYP/6-311+G**				HF/6-311+G**/B3LYP/6-311+G**			MP2/6-311+G**/B3LYP/6-311+G**		
	ZPE	E_{el}	E_0	ΔE_0	E_{elc}	E_0	ΔE_0	E_{el}	E_0	ΔE_0
1	0.103	-348.800	-348.697	0.000 (0.000) ^b	-346.773	-346.671	0.000 (0.000) ^b	-347.848	-347.746	0.000 (0.000) ^b
2	0.101	-348.856	-348.754	-0.057 (-36.033) ^b	-346.820	-346.719	-0.048 (-30.290) ^b	-347.908	-347.807	-0.061 (-38.245) ^b
[1 → 2] [#]	0.097	-348.742	-348.645	0.052 (37.561) ^b	-346.684	-346.588	0.083 (57.560) ^b	-347.776	-347.680	0.066 (46.590) ^b
3	0.101	-709.153	-709.052	0.000 (0.000) ^b	-706.814	-706.713	0.000 (0.000) ^b	-707.828	-707.727	0.000 (0.000) ^b
4	0.971	-709.201	-709.104	-0.052 (-32.654) ^b	-706.855	-706.757	-0.044 (-27.806) ^b	-707.896	-707.772	-0.045 (-28.183) ^b
[3 → 4] [#]	0.096	-709.111	-709.014	0.037 (23.33) ^b	-706.759	-706.662	0.050 (31.721) ^b	-707.756	-707.660	0.066 (41.769) ^b
5	0.110	-2823.075	-2822.974	0.000 (0.000) ^b	-2819.675	-2819.574	0.000 (0.000) ^b	-2820.676	-2820.575	0.000 (0.000) ^b
6	0.099	-2823.122	-2823.023	-0.049 (-30.731) ^b	-2819.718	-2819.620	-0.045 (-28.446) ^b	-2820.713	-2820.615	-0.040 (-24.982) ^b
[5 → 6] [#]	0.096	-2823.038	-2822.942	0.032 (24.032) ^b	-2819.629	-2819.533	0.041 (25.866) ^b	-2820.612	-2820.516	0.592 (42.572) ^b

^b Numbers in parenthesis are the corresponding ΔE values in kcal·mol⁻¹.

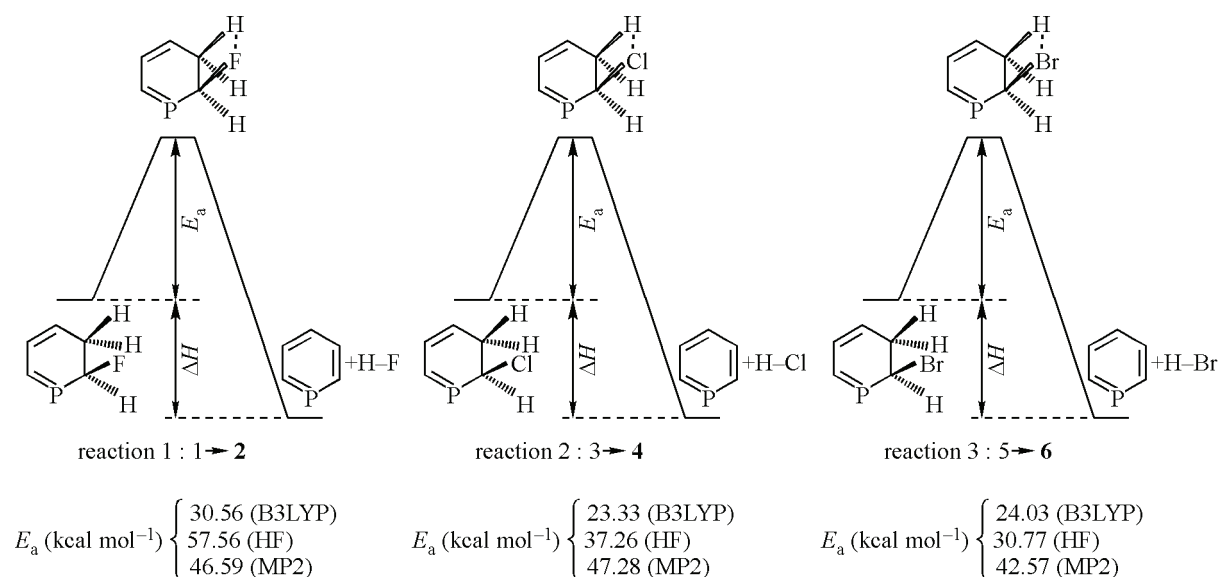


Fig. 1. B3LYP, HF and MP2 energy diagram of decomposition of compounds **1**, **3** and **5**

Table 2

*Selected B3LYP/6-31+G** calculated bond lengths in angstrom for the energy minima structures of compounds 1–6 and transition structures of reactions 1–3*

Bonds	1 [1 → 2] 2			3 [3 → 4] 4			5 [5 → 6] 6		
	C2—X7	1.487	1.853	—	1.951	2.526	—	2.136	2.744
C3—H9	1.043	1.217	—	1.102	1.153	—	1.182	1.146	—
C2—C3	1.621	1.475	1.391	1.621	1.465	1.391	1.410	1.563	1.482

Table 3

*Selected B3LYP/6-31+G** calculated bond populations for the energy minima structures of compounds 1–6 and transition structures of reactions 1–3*

Selected bonds	Occupancy		
	Reactant	Transition state	Product
C2—F7	1.980 (σ)	—	—
C2—C3	1.976 (σ)	1.963 (σ)	1.974(σ) & 1.635 (π)
C3—H9	1.955 (σ)	1.721 (σ)	—
C2—CL7	1.964 (σ)	—	—
C2—C3	1.976 (σ)	1.971 (σ)	1.973(σ) & 1.615(π)
C3—H9	1.959 (σ)	1.810 (σ)	—
C2—Br7	1.954 (σ)	—	—
C2—C3	1.976 (σ)	1.973 (σ)	1.971(σ) & 1.615(π)
C3—H9	1.960 (σ)	1.816 (δ)	—

state structures of compounds **1**, **3**, **5** and the transition state structures of reactions 1–3. Consequently, for such a drastic change in the charge distribution of halide and hydrogen atoms in the transition state structures of reactions 1, 2 and 3, the formation of the transition structure of reaction 3 is more favorable than reaction 1, 2 because of the larger variation of the charge distribution of Br atom in the transition state structure of reaction 3. According to the Natural charge distribution results, the hydrogen atom charge in the ground state structure of compound **5** and **6** is 0.18 and 0.18 respectively, while in the transition state structure of reaction 3 is 0.21 (Table 4).

Value of C₂—C₃—H₉—X₇ dihedral angles in transition state showed the planar structure for transition state. This form is the best structure for H—X dissociation. Internal dihedral angles in the heterocycle structures of reactants and products revealed that reactants are non-planar (non-aromatic) but products are planar and aromatic, see Table 2. Natural bond orbital (NBO) population analysis and

Table 4

*Selected B3LYP/6-31+G** calculated atomic charge for the energy minima structures of compounds 1–6 and transition structures of reactions 1–3*

Selected atoms	Natural charge			Selected atoms	Natural charge			Selected atoms	Natural charge		
	Reactant	Transition state	Product		Reactant	Transition state	Product		Reactant	Transition state	Product
C2	0.461	0.321	0.086	C2	0.013	0.370	0.079	C2	-0.151	0.359	0.123
C3	-0.586	-0.582	-0.237	C3	-0.471	-0.704	-0.334	C3	-0.475	-0.605	-0.234
F7	-0.807	-0.619	-0.611	Cl	-0.113	-0.588	-0.415	Br	-0.087	-0.661	-0.694
H9	0.218	0.440	0.546	H9	0.249	0.480	0.298	H9	0.250	0.264	0.390

nuclear independent chemical shift (NICS) [18] results have a good agreement with calculated structural parameters.

At this point, it seems useful to remember some useful aspects concerning the NBO analysis, which was effectively used in this work. In the NBO analysis, the electronic wave functions are interpreted in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbitals. The delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals corresponds to a stabilizing donor—acceptor interaction, which is taken into consideration by examining all possible interactions between filled (donor) and empty (acceptor) orbitals and then evaluating their energies by second order perturbation theory.

Accordingly, the delocalization effects (or donor—acceptor charge transfers) can be estimated from the presence of offdiagonal elements of the Fock matrix in the NBO basis. NBOs closely correspond to the picture of localized bonds and lone pairs as basic units of the molecular structure, so that it is possible to conveniently interpret *ab initio* wavefunctions in terms of the classical Lewis structure concepts by transforming these functions to NBO form [9]. The interactions due to electron delocalization are generally analyzed by selecting a number of bonding and antibonding NBOs, namely, those relevant to the analysis of donor and acceptor properties. As a result, the NBO program searches for an optimal natural Lewis structure, which has the maximum occupancy of its occupied NBOs, and in general agrees with the pattern of bonds and lone pairs of the standard structural Lewis formula. However, these orbitals suffer from small departures from the idealized Lewis structure, caused by interactions among them, which are known as hyperconjugative or stereoelectronic interactions. Therefore, the new orbitals are more stable than pure Lewis orbitals, stabilizing the wave function and giving a set of molecular orbitals equivalent to canonical molecular orbitals.

For each donor NBO (*i*) and acceptor NBO (*j*), the stabilization energy (E_2) associated with $i \rightarrow j$ delocalization is explicitly estimated by the following equation:

$$E_2 = \Delta E_{ij} = q_i \frac{F_{(i,j)}^2}{\varepsilon_j - \varepsilon_i}.$$

Where q_i is the *i*th donor orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies), and $F_{(i,j)}$ are off-diagonal elements, respectively, associated with the NBO Fock matrix. The NBO analysis of donor—acceptor interactions showed that the resonance energy $\pi_{C2-C3} \rightarrow \pi_{C4-C5}^*$ and $\pi_{C2-C3} \rightarrow \pi_{N1-C6}^*$ delocalization in phosphinine as product are 22.74 and 17.22 kcal·mol⁻¹, respectively. These electronic transitions disappear in reactant, therefore C—C bond in reactant is a single bond.

Nuclear independent chemical shift (NICS) results at GIAO/B3LYP/6-311+G** level of theory revealed that phosphinine cycle is aromatic but all reactants are non-aromatic.

NICS values in ring center, 0.5 and 1 angstrom upper than ring center are 2.59, 0.31 and -1.32 for compound **1** and -7.13, -9.45 and -10.21 for compound **2** (phosphinine), respectively (Table 5).

Table 5

Calculated NICS values at GIAO/B3LYP/6-311+G** and magnetic susceptibilities at CSGT/B3LYP/6-311+G** level of theory for the energy minima structures of compounds **1—6** and transition structures of reactions 1—3

Compounds	X=F			X=Cl			X=Br		
	1	1→2	2	3	3→4	4	5	5→6	6
NICS(0)	2.145	0.123	-7.136	2.534	4.362	-7.316	2.681	7.379	-7.838
NICS(0.5)	1.246	-3.967	-10.454	1.734	1.475	-9.319	1.901	2.588	-9.129
NICS(1)	-1.427	-6.054	-10.213	-2.811	-2.101	-10.317	-2.743	-1.746	-11.348
χ	-49.068	-48.45	-53.58	-58.096	-46.77	-94.89	-57.253	-71.65	-89.21

CONCLUSION

Ab initio HF, MP2, and B3LYP density functional-theory calculations provide a picture from structural, energetic, and natural charge distributions points of view for the decomposition mechanism of compound **1**, **3** and **5** to phosphinine and HX (X = F, Cl, Br). B3LYP/6-311+G**//B3LYP/6-311+G**, HF/6-311+G**//B3LYP/6-311+G**, and MP2/6-311+G**//B3LYP/6-311+G** results reveal that a lower barrier height for reaction 3 than that of reactions 1 and 2. These results are justified by natural charge distribution values, calculated structural parameters and NBO results analysis in the ground-state structure of compounds **1,3** and **5** and transition state structures of reactions 1–3. NBO analysis revealed that resonance energies in products are greater than reactants. Therefore, the number of conjugated π bond increased in products.

Also, NICS results showed that reactants are non-aromatic but products are aromatic compounds. Consequently, the calculated data could be considered as fairly acceptable and useful information from the QSAR point of view in the corresponding organic compounds, which are further confirmed by the corresponding energetic and structural results generated by the NBO analysis and NICS results.

REFERENCES

1. Liu B. // J. Chem. Phys. – 1984. – **80**. – P. 581.
2. Becke A.D. // J. Chem. Phys. – 1993. – **98**. – P. 5648.
3. Lee C., Yang W., Parr R.G. // Phys. Rev. – 1988. – **37**. – P. 785.
4. Hehre W.J., Radom L., Schleyer P.V.R., Pople J.A. *Ab initio* molecular orbital theory. – New York: Wiley, 1986.
5. Seminario J.M., Politzer P. / Eds. Modern density functional theory. A Tool for Chemistry, Elsevier, Amsterdam, 1995.
6. Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Zakrzewski V.G., Montgomery J.A. Jr., Stratmann R.E., Burant J.C., Dapprich S., Millam J.M., Daniels A.D., Kudin K.N., Strain M.C., Farkas O., Tomasi J., Barone V., Cossi M., Cammi R., Mennucci B., Adamo C., Clifford S., Ochterski J., Petersson G.A., Ayala P.Y., Cui Q., Morokuma K., Malick D.K., Rabuck A.D., Raghavachar K., Foresman J.B., Cioslowski J., Ortiz J.V., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Gomperts R., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Gonzalez C., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Andres J.L., Head-Gordon M., Replogle E.S. Gaussian 98 (Revision A3), Gaussian Inc., Pittsburgh, PA, 1998.
7. Molder U., Burk P., Koppel I.A. // J. Mol. Struct. (THEOCHEM). – 2004. – **712**. – P. 81 – 89.
8. Freeman F., Phormvoranunt A., Hehre W.J. // J. Phys. Org. Chem. – 1998. – **11**. – P. 831 – 839.
9. Glendening E.D., Reed A.E., Carpenter J.E., Weinhold F. NBO Version 3.1.
10. Reed A.E., Curtiss L.A., Weinhold F. // Chem. Rev. – 1988. – **88**. – P. 899 – 926.
11. Foster J.P., Weinhold F. // J. Amer. Chem. Soc. – 1980. – **102**. – P. 7211; Reed A.E., Curtiss L.A., Weinhold F. // Chem. Rev. – 1988. – **88**. – P. 899; Weinhold F. Natural bond orbital methods, in, P. Schleyer, N.L. Allinger, T. Clark, J. Gasteiger, P.A. Kollman (eds.), Encyclopedia of Computational Chemistry. – Wiley, Chichester, UK, 1998. – Vol. 3, pp. 1792 – 1811.
12. Alkorta I., Elguero J. // Struct. Chem. – 2005. – **16**. – P. 77 – 79.
13. Serena Software, Box 3076, Bloomington, IN, USA.
14. Dewar M.J.S., Zeobisch E.G., Healy E.F., Stewart J.J.P. // J. Amer. Chem. Soc. – 1985. – **107**. – P. 3902.
15. Stewart J.J.P. QCPE 581, Department of Chemistry, Indiana University, Bloomington, IN, USA.
16. Rahaman A., Raff L.M. // J. Phys. Chem. A. – 2001. – **105**. – P. 2156.
17. Kuns_agi-M_at_e S., V_egh E., Nagy G., Koll_ar L. // J. Phys. Chem. A. – 2002. – **106**. – P. 6319.
18. Schleyer P.V.R., Maerker C., Dransfeld A., Jiao H., Hommes N.J.R.E. // J. Amer. Chem. Soc. – 1996. – **118**. – P. 6317.