

MODELING THE FRAGMENTATION OF 2,5-DIKETOPIPERAZINE IONS

A. Basalae¹, V. Kuz'michev¹, M. Panov¹, A. Petrov², O. Smirnov¹

1 Ioffe Institute, St Petersburg, Russia

2 Institute of Chemistry, St. Petersburg State University, St. Petersburg, Russia

kuzmichevv@mail.ru

I. INTRODUCTION

Cyclic dipeptides, often found in nature, are formed by linking amino-terminus of a linear dipeptide to its carboxyl - terminus by amide bond. All of them are derivatives of 2,5-diketopiperazine (DKP) or cyclo-Diglycine with the molecular formula $C_4H_6N_2O_2$.

II. METHODS

To calculate the optimized geometry of molecules (Figure 1) and singly charged ions, as well as their total energies, the DFT method was used, using Dmol³ module from the Materials Studio software package. We used B3LYP functional and the all-electron atomic basis DNP (ver.3.5) with unrestricted spin polarization [1, 2]. The energy convergence was less than $1 \cdot 10^{-5}$ Ha and geometry convergence was less than $5 \cdot 10^{-3}$ Å.

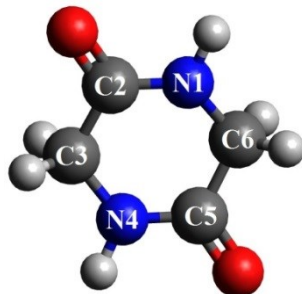


Figure 1. Structure of the DKP molecule

At the first stage we optimized geometry of molecules and ions with molecular mechanics using COMPASS II force field to minimize the interatomic interactions. The second stage includes DFT calculation of electronic structure with total geometry optimization. The calculated total energies of molecules and ions were used for further analysis. These data of the total energies make it possible to calculate the reaction energies for the channels of fragmentation of the formed ions. For the simulation, we chose the DKP ion fragmentation processes for which were observed experimentally the largest cross sections.

In the experiment DKP ionization occurred as a result of the capture of one electron by He^{2+} ions with an energy of 4 keV/u. The formed molecular ions were analyzed by mass and charge using a time-of-flight analyzer. Analysis of the measured mass spectra makes it possible to obtain the values of the relative cross sections the fragment ions formation. The fragments identification in our work was based on the assumption that the formation of compounds of mass m requires a minimum number of broken bonds and a minimum rearrangement of atoms between the formed ion and neutral fragments. It should be borne in mind that in the process of fragmentation, the processes of migration of hydrogen atoms are likely.

III. RESULTS AND DISCUSSION

It was shown that the largest cross section has the process of DKP^+ ion formation ($\sigma=180$ rel.u.). The most probable mechanisms of the major cross-sectional channels for the DKP^+ ion fragmentation were considered. (Table 1). The reaction energy (E_r) was determined as the difference between the total energies of the fragments and the parent ion (Figure 2). The most intense fragment $m=30$ (u) in the mass spectrum is formed when the C2—N1 and C5—C6 bonds (or symmetric to them) are broken and the hydrogen atom migrates to the charged fragment from the residue which was considered as four isomers. Ions with masses 42 and 72 (u) are formed upon cleavage of C2(5)—N1(4) and C3(6)—N4(1) bonds, and with masses 41 and 73 (u) upon cleavage of bonds N1(4)—C2(5) and C6(3)—C5(2). The charge with the same probability remains with either the light or the heavy fragment. It is also possible to form fragments with masses 28 and 86 (u), which are formed upon cleavage of the C2(5)—C3(6) and C2(5)—N1(4) bonds.

Table 1. Energy and relative cross section of the main channels of DKP^+ ion fragmentation

| Ion [m (u)] | Neutral fragment [m (u)] | E_r (eV) | σ (rel. u.) |
|---|---|-------------|--------------------|
| CH_4N [30] | $\text{C}_3\text{H}_2\text{NO}_2$ [84] | 2.07 – 2.36 | 100 |
| $\text{C}_2\text{H}_2\text{O}$ [42] | $\text{C}_2\text{H}_4\text{N}_2\text{O}$ [72] | 4.68 | 28.6 |
| $\text{C}_2\text{H}_4\text{N}_2\text{O}$ [72] | $\text{C}_2\text{H}_2\text{O}$ [42] | 3.19 | 20.0 |
| CHNO [43] | $\text{C}_3\text{H}_5\text{NO}$ [71] | 4.11 | 42.9 |
| $\text{C}_3\text{H}_5\text{NO}$ [71] | CHNO [43] | 1.78 | 37.9 |
| CO [28] | $\text{C}_3\text{H}_6\text{N}_2\text{O}$ [86] | 7.22 | 49.2 |
| $\text{C}_3\text{H}_6\text{N}_2\text{O}$ [86] | CO [28] | 0.89 | 8.1 |

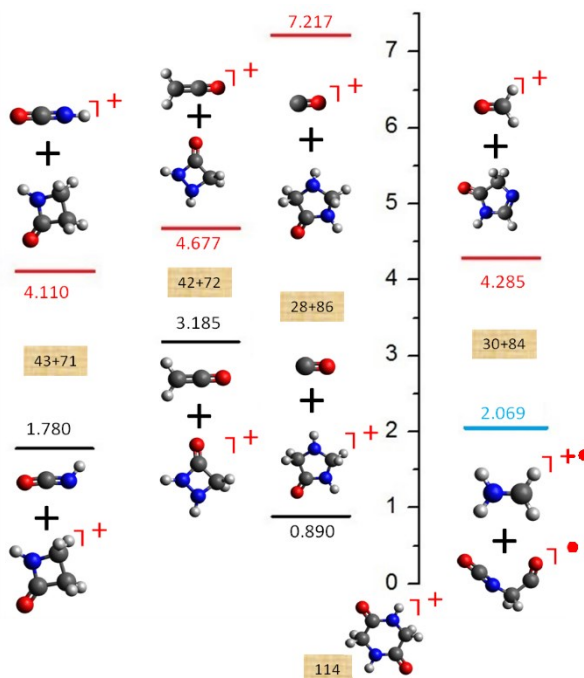


Figure 2. Energy diagram of E_r (eV) DKP^+ fragmentation reactions. The filled rectangles show the masses of the fragments formed during the fragmentation of the initial molecular ion, from the energy of which E_r is counted. The segments correspond to E_r (eV) for the considered reactions

IV. CONCLUSIONS

Quantum chemical calculations performed for the cyclo-Diglycine molecules showed that there is a correlation between the probability of the bond rupture and its length variation.

ACKNOWLEDGMENTS

The calculations were carried out using the computing resources of the RC "Computing Center of St. Petersburg State University" (<http://cc.spbu.ru>).

REFERENCES

- [1] B. Delley. "An all-electron numerical method for solving the local density functional for polyatomic molecules" J. Chem. Phys, Vol. 92, pp. 508-517, 1990.
- [2] B. Delley. "From molecules to solids with the DMol³ approach" J. Chem. Phys, Vol. 113, pp. 7756-7764, 2000.