250 Chinese Chemical Letters Vol. 15, No. 2, pp 250 – 252, 2004
http://www.imm.ac.cn/journal/ccl.html

Three Novel Isomers of FCH_2CP System

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Abstract: Three new isomers of FCH_2CP system, F(H)CCPH (**1**), F-cCPC-H(H) (**2**) and F-cCC(H)P-H (**3**), are predicted by means of B3LYP and CCSD(T) (single-point) methods with 6-311++G(d,p) and 6-311++G(2df,2p) basis sets, respectively. The three calculated isomers can isomerize into thermodynamically the most stable species F-cPC(H)C-H, which has been suggested in previous theoretical studies, with relatively higher reaction barriers. In view of their higher thermodynamic and kinetic stability, we believe that the three species can be detected in future experiments.

Keywords: FCH_2CP system, stability, isomer.

Investigation of unstable and metastable compounds is a basis for the development of many highpriority branches of modern chemistry, among which the recent emergence of the chemistry of doubly and triply bonded trivalent phosphorus is found to be an attractive topic[1]. Phosphaalkyne is a species that contains a triple bond between phosphorus and carbon. The synthesis of phosphaalkynes with small substituents is a huge challenge to experiment chemistry for their extreme instability. Up to now, only several phosphaalkyne molecules with simple organic functional group or heteroatom, such as $HC\equiv P$[2], $CH_3C\equiv P$[3,4], $FC\equiv P$[5], and $ClC\equiv P$[5], have been experimentally identified, but they only can be kept stably at low temperature. The $C\equiv P$ triple bond is often stabilized by bulky substituents, and many phosphaalkyne compounds with bulky substituents have been synthesized and can exist stably at ordinary temperature[6,7]. In this letter, we select FCH_2CP system for the following two reasons. The first is that CH_3CP molecule has been experimentally observed in previous studies[3,4], but to our knowledge, no any experimental information about halogen-substituted XCH_2CP compounds is available. And the other is that the selected system has been theoretically studied[8-10], and in predicted six isomers the cyclic isomer F-cPC(H)C-H was found to be the most stable species thermodynamically. But based on analyzing the bonding regularity, we think that some thermodynamic stable isomers may be omitted in these theoretical studies[8-10]. These possible species may be F(H)CCPH (**1**), F-cCPC-H(H) (**2**) and F-cCC(H)P-H (**3**) in terms of our analysis. Therefore, herein, we report a detailed

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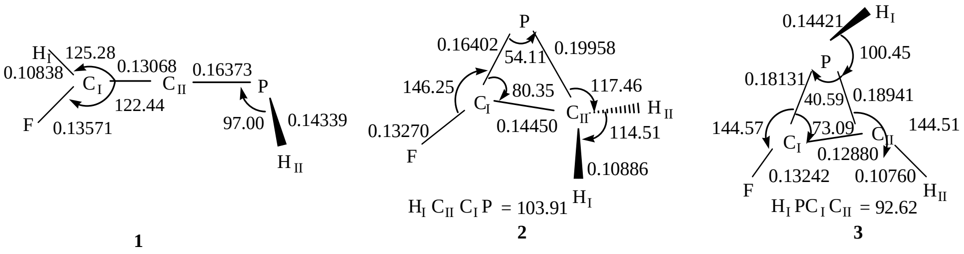
computational study using quantum chemistry methods on isomers **1**, **2**, and **3** with an attempt to predict their structural stability and the nature of bonding.

All computations are carried out with Gaussian98 program package running on the SGI/Origin300 server. The geometries (shown in **Figure 1**) of all stationary points and zero-point energies are obtained at the B3LYP/6-311++(d,p) level of theory. Intrinsic reaction coordinate (IRC) calculations are carried out at the same level. All energies used in the letter are at the CCSD(T)/6-311++G(2df,2p)//B3LYP/6-311++G(d,p) level with zero-point energies correction.

The isomer **1** lies 120.24 kJ/mol higher in energy than thermodynamically the most stable isomer F-cPC(H)C-H (C_s) which has been suggested in previous studies[8]. In **1**, the C-C (0.13068 nm) and C-P (0.16373 nm) bonds can be regarded as double bond for the normal C=C and C=P double bond lengths 0.13288 nm and 0.16713 nm in species CH_2CH_2 and CH_2PH, respectively, at the B3LYP/6-311++(d,p) level. The calculated result show that isomer **1** is a P = C = C phosphaallene structure, and can isomerize into the most stable isomer F-cPC(H)C-H (C_s) *via* a reaction pathway including several isomerizations. Because the reaction barrier (302.58 kJ/mol) is very higher, the transition reaction along the channel hardly happens in thermochemistry system. Furthermore, the dissociation energies of several fragment channels are also very high. Therefore, species **1** can be considered as a kinetically stable isomer.

Figure 1 Predicted three isomers of FCH_2CP system at the B3LYP/6-311++(d,p) level of theory



Bond lengths are in nanometers, and bond angles in degrees

Isomer **2** with C_s symmetry has a CPC three-membered ring with exocyclic C-F and two identical C-H bonding, and is higher in energy than thermodynamically the most stable isomer F-cPC(H)C-H (C_s) by 123.24 kJ/mol. The C_I-P bond distance is 0.16402 nm, which indicates that it is a normal double bond, while the C_{II}-P bond (0.19958 nm) should be considered as a weak single bond in terms of the normal 0.18780 nm C-P single bond length in species $CH_3P(H)H$ at the B3LYP/6-311++(d,p) level. The C-C bond (0.14450 nm) may be regarded as an intermediate between single and double bond because the distances of normal C-C single and C=C double bond are 0.15304 nm and 0.13288 nm (at the B3LYP/6-311++(d,p) level) in ethane (CH_3CH_3) and ethylene (CH_2CH_2), respectively. Theoretical results in the present study show that isomer **2** can also isomerize into the most stable isomer F-cPC(H)C-H (C_s) along a reaction pathway including several isomerizations. Because the highest reaction barrier is 237.25 kJ/mol, and the dissociation energies of several possible fragment channels are somewhat higher than the isomerization barriers, we can consider isomer **2** to be a kinetically stable species.

The isomers **3**, which has also a PCC three-membered ring with exocyclic P-H, C-F, and C-H bonding, lies 158.65 kJ/mol higher than thermodynamically the most stable isomer F-cPC(H)C-H (C_s). The C-C bond distance 0.12880 nm in isomer **3** suggests that it is a slightly weak double bond structure. The C_I-P and C_{II}-P bonds should be considered as single bond for the 0.18131 nm and 0.18941 nm bond lengths, respectively. The IRC computations indicated that isomer **3** can isomerize into an chain species $FPC_2H(H)$ (C_s), which has been predicted by Nguyen[8] and coworkers, *via* a coinstantaneous hydrogen and fluorine shift channel followed by the isomerization to thermodynamically the most stable isomer F-cPC(H)C-H (C_s). The reaction barriers are 251.91 kJ/mol and 270.32 kJ/mol, respectively, which are too high to make the transition process happen in thermochemistry system. Furthermore, the dissociation limits of **3** are higher than the isomerization barriers, so we can safely say that isomer **3** is a kinetically stable species.

As discussed above, species F(H)CCPH (**1**), F-cCPC-H(H) (**2**), and F-cCC(H)P-H (**3**) have higher thermodynamic and kinetic stability, we hope that the three isomers can be observed in future experiments.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Nos. 20171016, 20271019), the Scinece Foundation for Excellent Youth of Heilongjiang University (J200106), the Doctoral Start-up Foundation of Heilongjiang University (2002), and the Science Foundation for Young Scholar of Heilongjiang University (Q200242).

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Received 11 February, 2003