Theoretical Study on Mechanism for the Reaction of 2-propargyl radical (C_3H_3) with Isocyanic acid (HNCO) by Means of Quantum Chemistry

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Abstract

The reaction mechanism of the C_3H_3 + HNCO system has been studied by the Density Functional Theory (DFT) using the B3LYP functional in conjunction with the 6-311++G(3df,2p) basis sets. The potential energy surface (PES) for the C_3H_3 + HNCO reaction has been also established. Calculations show that the reaction has taken place according to two main entrance channels: H-abstraction from HNCO and additional reactions. There are two H-abstraction and six additional reaction pathways creating 11 intermediate states, 17 transition states and 10 products. All of the above products are possible to be formed. In which the formation of (H_2CCCH_2 + NCO) is the most favorable.

Keywords: *Reaction mechanism, propargyl radical, HNCO, basis sets, DFT, PES*
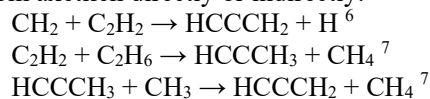
1. Introduction

Study structures of substances and reaction mechanisms occuring between substances has been a necessity for chemists. It not only helps to clarify nature of reaction processes, but also helps experimental chemistry save time and money in navigating reaction products in the most optimal way.

With help of the information technology industry, the emergence of computational software based quantum-chemistry making these processes are quickly and efficiently implemented. The obtained results are well matched with the experimental data.[1] Among the occurred reactions, much attention is paid to the reaction mechanism in the gas phase, typically the radical C_3H_3.[2] In nature, propargyl radicals are formed during the combustion of fuels, especially those that are high in fat.[3,4]

It is found in the combustion process, in addition to the formation of polycyclic aromatic hydrocarbons and soot, the presence of propargyl radical (C_3H_3)[5] occurs. Though formation of C_3H_3 as a non-durable intermediate, it plays an important role in determining the reaction mechanism and products.

In addition, propargyl radicals are formed primarily from axetilen directly or indirectly.

$$CH_2 + C_2H_2 \rightarrow HCCCH_2 + H \; ^6$$
$$C_2H_2 + C_2H_6 \rightarrow HCCCH_3 + CH_4 \; ^7$$
$$HCCCH_3 + CH_3 \rightarrow HCCCH_2 + CH_4 \; ^7$$

In laboratory, C_3H_3 was created by performing photolysis. A 248nm laser was used to separate the oxalyl chloride compound into chlorine and CO:[8]

$$(CClO)_2 \rightarrow 2Cl + 2CO$$
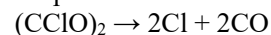
After that, chlorine atoms interact with propyne molecule to form propargyl radical and release HCl molecule.

$$Cl + C_3H_4 \rightarrow C_3H_3 + HCl$$
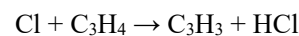
Structurally, C_3H_3 is a free radical with a single electron, so it is highly reactive, which can react with many free radicals and molecules in the gas phase. In particular, the recombinant reaction between the two propargyl radicals will produce a number of aromatic ring products, such as benzene or phenyl radical, which are important intermediates in the preparation of aromatic hydrocarbon compounds.

Besides, isocyanic acid is an organic compound with the formula HNCO, discovered in 1830 by Liebig and Wohler.[9] This colourless substance is volatile and poisonous, with a boiling point of 23.5°C. Isocyanic acid is the simplest stable compound that contains carbon, hydrogen, nitrogen, and oxygen, the four most commonly found elements in organic chemistry and biology.

Therefore, research on the reaction between propargyl radical and HNCO to find the reaction mechanism in the formation of beneficial products to the environment is very necessary.

2. Computational methods

The geometry of the reactants, intermediates, transition states and products are optimized by the density function theory at B3LYP/6-311++G(3df,2p).[1] In which, the correct transition states are verified by analyzing the oscillation frequencies, intrinsic reaction coordinates (IRC) of the system. From the results obtained will determine structures, energies, thermodynamic parameters and the potential energy surface of the system. Calculations are made by Gaussian 09 software.[10]

3. Results and discussion

3.1 Geometric structures and Potential energy surface

On the potential energy surface of the C_3H_3 + HNCO system (Fig. 2), reactants are denoted RA; 10 products are denoted as PRi (i = 1÷10); 11 intermediate structures are denoted as ISj (j = 1÷11) and 17 transition states are denoted Tx/y. Where x and y are intermediate structures, reactants and reaction products.

3.2 Analysis of reaction pathways

Results of the zero-point vibrational energy and single-point energy calculations help us to determine the relative energy levels of structures compared to the energy level of the initial reactants C_3H_3 + HNCO (RA), which is given as zero.

From the potential energy surface (PES), between the radical C_3H_3 and HNCO can occur reaction in the direction of separation of H atom from HNCO molecule to C_3H_3 or in the direction of addition between the two substances together.

Reaction in the direction of H atom separation. There are two possibilities to separate the H atom from the HNCO molecule. The first possibility is that when the head of the propargyl radical strikes the H atom in the HNCO molecule through the T0/1 transition state with an energy barrier of 18.91 kcal/mol, the direct product PR1 (H_2CCCH_2 + NCO) for the correlative energy of 19.77 kcal/mol will be formed.

In the T0/1 structure, the H atom attached to the N atom is separated for a bond length of 1.43 Å, and the bond between this atom and the CH group of the C_3H_3 radical is being formed at a distance of 1.21 Å. In order to facilitate the formation of a new bond

between the CH group and the H atom, the ∠HCC bond angle decreased from 180° to 130° in line with the sp^2 hybridization of the carbon atom in the C_3H_4 molecule.

Similarly, in the second cleavage, when two substances come together through T0/P2 transition state with an energy barrier of 20.67 kcal/mol, the product PR2 (H_3CCCH + NCO) with an energy level of 22.01 kcal/mol will be created. In the structure of T0/P2, the H atom is separated out at 1.47 Å and it is slowly forming a new bond H_2C-H at 1.21 Å. This gap is shortened to 1.091 Å in the H_3CCCH molecule. Contemporary, the ∠HCC bond angle in the T0/P2 structure is 110° is perfectly consistent with the sp^3 hybridization and the tetrahedral structure of C_3 carbon atom in the H_3CCCH molecule.

Thus, in terms of energy, in the first separation, passing through the T0/P1 transition state (18.91 kcal/mol), it will be more advantageous than the second separation passing through transition state T0/P2 (20.67 kcal/mol). On the thermodynamic side, the PR1 product (19.77 kcal/mol) produced by the first separation is also more stable than the PR2 product (22.01 kcal/mol) created by the second separation.

Reaction in the direction of addition. C_3H_3 and HNCO can be combined in 6 different directions through transition states T0/1, T0/2, T0/3, T0/4, T0/7 and T0/8 to form intermediate states such as IS1, IS2, IS3, IS4, IS7 and IS8 with relative energies 12.65, 12.35, 11.16, 21.69, 38.57 and 42.26 kcal/mol, respectively. Where IS1, H_2C=C=CH-NH=C=O, is generated by bond between carbon atom C1 of propargyl radical with the N atom of the HNCO molecule through T0/1 (22.9 kcal/mol). IS2, H_2C=C=CH-C(O)=NH, was formed by combination of C atom in HNCO with the CH group of C_3H_3 via transition state T0/2 (22.47 kcal/mol). Similarly, IS3 and IS4 have structures of HC=C=CH$_2$-NH=C=O and HC=C=CH$_2$-C(O)=NH, respectively, due to the bonding of N and C at HNCO with the CH$_2$ group in the C_3H_3 radical passes through the corresponding transition states T0/3 (23.74 kcal/mol) and T0/4 (25.51 kcal/mol). The remaining structures of IS7 (H_2C=C=CH-OCNH) and IS8 (HC=C=CH$_2$-OCNH) are generated by attacking of O at CH and CH$_2$ through two transition states T0/7 (92.94 kcal/mol) and T0/8 (98.06 kcal/mol), respectively. Of the six structures mentioned above, IS1 and IS2 are easier to be created, while IS7 and IS8 are less likely to be

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created than the rest due to pass through transition states T0/7 and T0/8.

As a result, the two reaction paths that make up IS7 and IS8 only stop there without further consideration because they are not feasible in terms of energy. From IS1, there are many different ways of forming products. Product PR3 (H_2CCCHNCO + H) with energy of 32.86 kcal/mol is produced through the T1/P3 transition state (80.54 kcal/mol) corresponding to separation of H atom from the NH group with the bonding distance of 1.62 Å. Therefore, the transition from IS1 to PR3 product passes through the quite high energy barrier, so PR3 product is difficult to form when the two substances react to each other. In terms of thermodynamics, PR3 product is less sustainable.

Product PR4 (HCCCHNCO + H_2) with energy level of 11.94 kcal/mol can also be generated from IS1 through the transition state T1/P4 (69.65 kcal/ mol). This is a H-cleavage process from groups CH_2 and NH with bond lengths of 1.33 Å and 1.4 Å, respectively. Here the angle $\angle$C1C2C3 decreases from 148° to 125°, and the angle $\angle$CCN also reduces from 123° to 114° so that two atoms H can easily approach each other at a distance of 0.98 Å. Two remaining reaction pathways from IS1 produce two intermediate products, IS5 (H_2CCCHNCOH) and IS6 (H_2CCCNHCOH), with relative energy of 23.94 and 40.51 kcal/mol, respectively. Where IS5 is generated when IS1 passes through the transition state T1/5 (63.3 kcal/mol) corresponding to an H-shift process from atom N to atom O. IS6 is created when IS1 goes via transitional state T1/6 (50.47 kcal/mol) corresponding to a transition of H atom from the CH group to the O atom. In comparison to enerswgies, IS6 is easier to be produced than IS5 due to the barrier energy T1/6 is lower than that of T1/5. From IS5 and IS6, PR9 (H_2CCCHN + COH) and PR8 (H_2CCCNH + COH), are formed with energy levels of 146.6 and 78.63 kcal/mol, respectively. Both of these products, however, are processes that directly cut off bonds without passing through any transition state. Both are exothermic reactions, so they are very difficult to occur in normal conditions.

IS2 continues to form two reaction pathways that produce two intermediates, IS9 (H_2CCC(OH)-NH) and IS10 (H_2CCC(O)-NH_2), corresponding to 5.83 and 20.9 kcal/mol. Where IS9 is formed through the transition state T2/9 (51.97 kcal/mol) corresponding to a H-shift process from the CH group to the O atom. Similarly, the transposition of H from the CH

group to the NH group via the transition state T2/10 (42.27 kcal/mol) will give the intermediate structure IS10. In terms of energy, IS10 is easier to be created than IS9. Two products of PR6 (H_2CCCCN + H_2O) and PR7 (H_2CCCCO + NH_2) are formed from the two intermediates mentioned above. If PR6 is formed through T9/P6 (60.75 kcal/mol), PR7 is formed directly from IS10 without passing through any transition state. Both processes are exothermic with heat output of 4.74 and 37.28 kcal/mol, respectively. The PR6 product is also the most stable thermodynamic product compared to others. IS3 (HCCCH$_2$NHCO) has formed directly PR10 (HCCCH$_2$NH + CO) by cutting off the N-C bond. That is an exothermic process with ΔH = + 29.7 kcal/mol. Finally, PR5 (HCCCHCN + H_2O) is produced when IS4 passes through two transition states of T4/11 (51.79 kcal/mol) and T11/P5 (61.64 kcal/mol). In which T4/11 corresponds to the process of transferring H atom from the CH_2 group to the O atom at distances of 1.32 and 1.35 Å, respectively. In addition, T11/P5 is a process of transferring H atom from the NH group to the OH group and severing the C-O bond to form molecule of water.
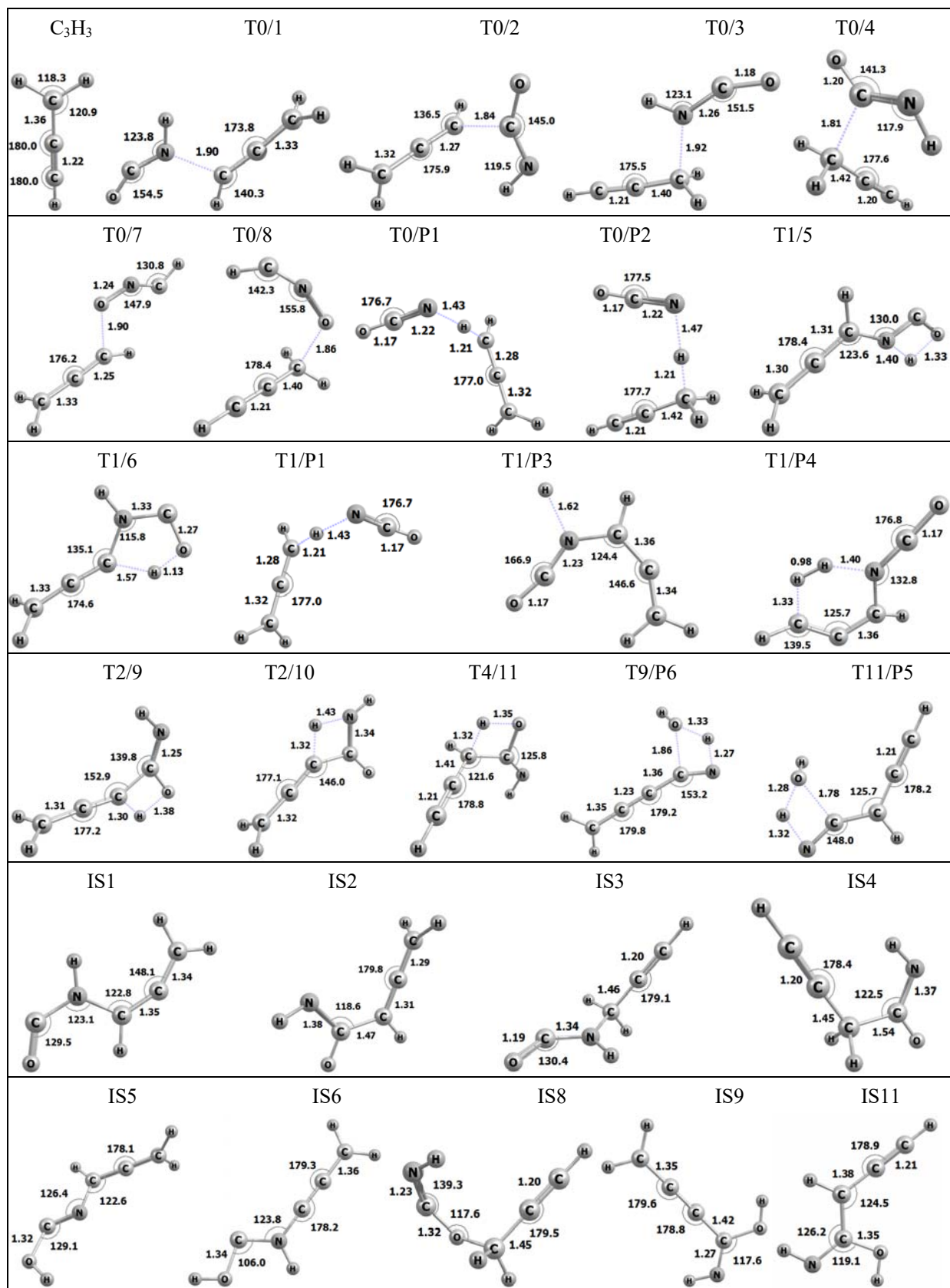
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Fig. 1: Some of intermediate states, transition states of the reaction system C_3H_3 + HNCO
[Bond lengths (Å), bond angles (°)]

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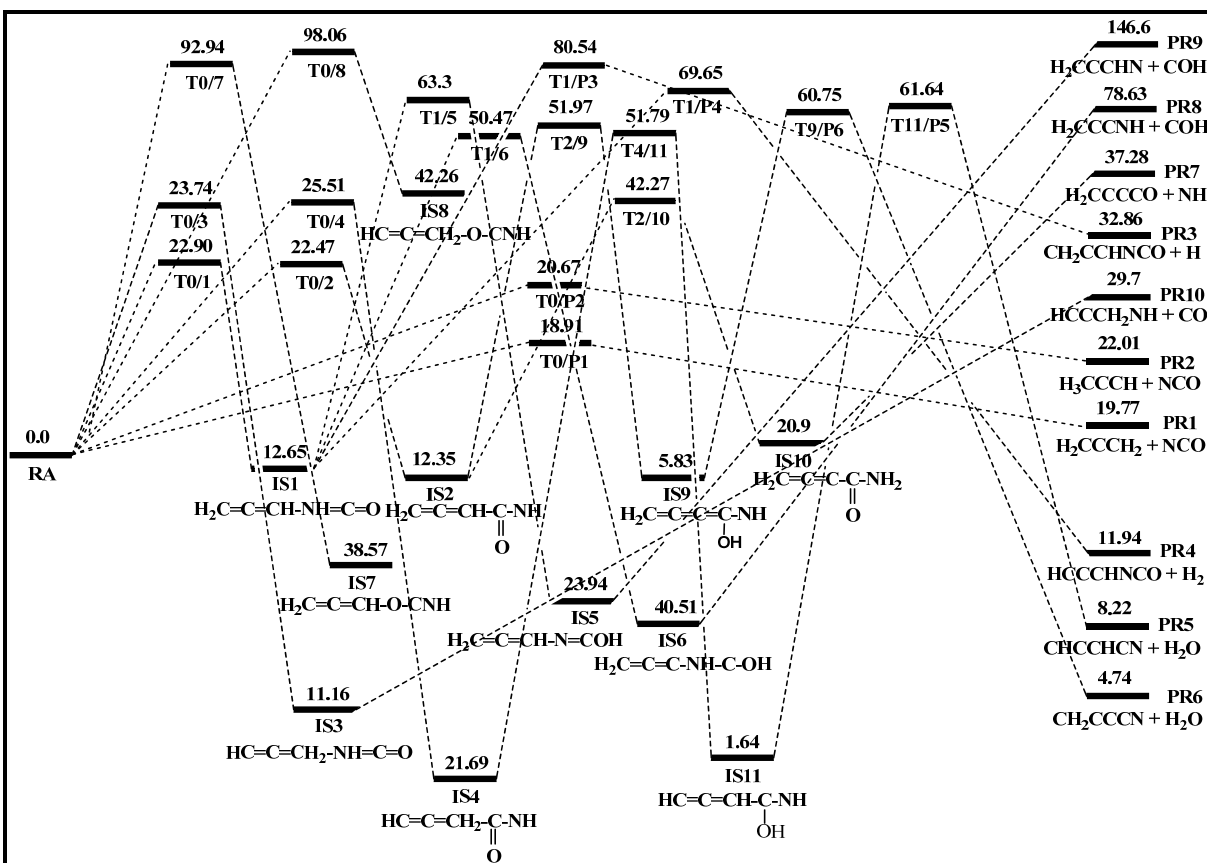*ISSN: 2395-3470*
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Fig. 2: The potential energy surface in detail of the C_3H_3 + HNCO system

Table 1: Thermodynamic values of the reaction system C_3H_3 + HNCO

Reaction paths	ΔG^o_{298}, kcal/mol	ΔS^o_{298}, cal/mol.K	ΔH^o_{298}, kcal/mol	ΔH^o_{298}, kcal/mol Reference [11]
PR1 (H_2CCCH_2 + NCO)	20.12	-2.70	19.31	18.33 ± 1
PR2 (H_3CCCH + NCO)	22.31	-2.30	21.64	21.02 ± 1
PR3 ($H_2CCCHNCO$ + H)	36.44	-12.0	32.97	----
PR4 (HCCCHNCO + H_2)	14.96	-7.50	12.73	----
PR5 (HCCCHCN + H_2O)	8.70	-0.30	8.62	----
PR6 (H_2CCCCN + H_2O)	5.44	-0.30	5.35	----
PR7 (H_2CCCCO + NH_2)	37.25	2.20	37.90	----
PR8 (H_2CCCNH + COH)	78.09	2.30	78.76	----
PR9 (H_2CCCHN + COH)	146.0	1.40	146.4	----
PR10 ($HCCCH_2NH$ + CO)	29.39	1.60	29.86	----

The thermodynamic parameters of the reaction paths are calculated by the density function theory and their values are presented in Table 1. In which the standard enthalpies of formation of some reactions are also compared with the results calculated from NIST data, namely NCO (128 kJ/mol), C_3H_3 (346-349 ± 8 kJ/mol, 352.2±1.0 kJ/mol), $H_2C=C=CH_2$ (190.92 kJ/mol), H_3CCCH (184.9 kJ/mol), and HNCO (-118.6 kJ/mol).[11]

The table shows that the standard enthalpies of formation of two paths are quite close to the experimental data. Thus, it can be seen that the results obtained from theoretical calculations are reliable. PR6 product has the lowest thermal effect. Hence, in terms of thermodynamics it is most favorable, which is consistent with the results from the above potential energy analysis.

4. Conclusion

By applying the DFT, we have optimized geometry structures of the reactants, intermediates, transitions and products of the reaction system between C_3H_3 and HNCO. The potential energy surface has been established and the reaction mechanism of the system has been explained. The above analysis shows that all 10 product groups from PR1 to PR10 have $\Delta G > 0$, so it is possible to predict that this reaction system is difficult to occur at normal conditions.

Through the potential energy surface we find that the reaction path producing PR9 is the most difficult to occur due to formation of product needing large power supply. The reaction path that forms the PR6 product is the most favorable in terms of energy as well as thermodynamics. Heat formations of some reaction paths are very consistent with previous published data, which suggests that the results are very reliable. The results of this study may be references to empirical processes or as inputs to later theoretical calculations.

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