Theoretical Study on Reaction Mechanism of HNCO with HX and XCH$_2$OH

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DFT calculations have been performed on complexes of isocyanic acid (HNCO) with HX and XCH$_2$OH. Vibrational analysis is carried out to confirm its identity as a transition structure. The method of intrinsic reaction coordinate is used to search the minimum energy pathway. The calculated results show that seven reactions belong to exothermic reactions. There are one σ bond and one π bond broken and two new σ bonds formed in the reactions. There is a four-member ring formed in transition state. Due to the difference in electronegativities of the atoms and molecules, the geometries of the four-member ring of the transition states are different. The transition state is characterized by the transfer of H atom.

Keywords: Isocyanic acid, Halogen acid, Vibrational analysis, Transition state, Intrinsic reaction coordinate.
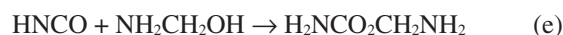
INTRODUCTION

As we know, C, H, N, O are four essential elements in atmosphere and isocyanic acid is the simplest molecule containing all four of the elements (H, C, N and O) of the biosphere. It is among more than 100 molecules presently identified in the gas phase in the interstellar medium [1,2]. Isocyanic acid (HNCO) and some other molecules was discovered in space more through the IR space based observation, such as H$_2$O, CO, NH$_3$, HF and CH$_3$OH [1,3]. Previous scientists have done many excellent investigations on the evolvement and reactive mechanism of these molecules [4-11]. Because diisocyanate and glycol can react to generate polyurethane which plays an important role in industry, thus these issue become so academic [12,13]. Halogen acid is the important industrial material but the halogen acid gas is one basal source of air pollution. As to the reaction of HNCO and halogen acid, people have done many research by means of theory and experiment, such as the polymerization pathway of reaction and photodissociation reaction of HNCO [14,15], the thermal reaction activity of the HNCO with ice-water [16], the vibration modes identity and IR spectrum intensity of solid HNCO [17]. Based on the research results of some predecessors and the industrial value of HNCO, it is very meaningful to study the reaction of HNCO with halogen acid and alcohol derivatives. In this paper the reaction mechanism of HNCO with halogen acid and methanol derivatives have been analyzed clearly and compared the effect on reaction with different substituents, illustrating the microscopic mechanism on molecular level.

EXPERIMENTAL

The full geometry optimization of structures HNCO with HX (X = F, Cl, Br) and XCH$_2$OH (X = CH$_3$, NH$_2$, OH, F) on the potential energy surface were performed at the 6-31++G(d,p) level using density functional theory B3LYP method. Vibration frequency analysis had been performed to confirm their identities as transition states and the intrinsic reaction coordinate (IRC) [18,19] method had also been performed to search the minimum energy path (MEP). Furthermore, we got the similar results with the HF and MP2 methods at the same level. All computations were carried out using the Gaussian 03 package [20].

RESULTS AND DISCUSSION

Seven chemical reactions to be studied are as follows:

$$HNCO + HF \rightarrow H_2NCOF \qquad (a)$$

$$HNCO + HCl \rightarrow H_2NCOCl \qquad (b)$$

$$HNCO + HBr \rightarrow H_2NCOBr \qquad (c)$$

$$HNCO + CH_3CH_2OH \rightarrow H_2NCO_2CH_2CH_3 \qquad (d)$$

$$HNCO + NH_2CH_2OH \rightarrow H_2NCO_2CH_2NH_2 \qquad (e)$$

$$HNCO + OHCH_2OH \rightarrow H_2NCO_2CH_2OH \qquad (f)$$

$$HNCO + FCH_2OH \rightarrow H_2NCO_2CH_2F \qquad (g)$$

The two stable structures of HNCO are presented in Fig. 1. One is linear structure with the energy -442898.55 kJ/mol and the other is nonlinear structure with the energy -442915.88

kJ/mol. The latter one is energitically more stable than the former one. Meanwhile, the bond parameters match the reported results well with previous reports [20,21]. So the latter one is chosen to search the transition states of these seven reactions.
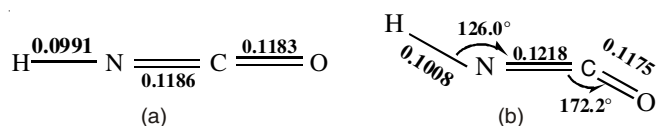

Fig. 1. Two stable structures of HNCO (a) linear structure; (b) non-linear structure [bond length (nm), bond angle (°)]

Fig. 2 shows the structures of seven transition states. There is only one imaginary frequency in each transition state and the corresponding vibration connected the reactant and product structures. There are two double bonds of HNCO: C=O and C=N and the additon reaction occurs on the C=N bond. As to the reactions (a), (b) and (c), the structures of reactants HNCO and the halogen acid change gradually along during the whole reaction, the bond X-H became longer while the bonds X6–C3 and N1–H5 were shortened. At the transition state point, the atoms of H5, X6, N1 and C3 form a four-member ring and the corresponding bond length and bond angles (Fig. 2) shows that all the six atoms of reactants are in the same plane and the atom H5 tends to leave the atom X6 for the atom N1. The transition structures prefigures the formation of bonds C3-X6 and H5–N1 and the fracture of bond H5–X6.

The transition state structures in Fig. 2 show some interesting trends. From reactions (a), (b) to (c), the bond length of both R_{H5-F6} and R_{X6-C3} increase, while that of R_{N1-C3} and R_{N1-H5} decrease. Similarly, from reactions (a), (b) to (c), the bond

angles of $D_{N1-C3-O4}$, $D_{H5-N1-C3}$ and $D_{N1-H5-X6}$ increase, while $D_{H2-N1-C3}$, $D_{H5-X6-C3}$ and $D_{N1-C3-X6}$ decrease. The increase of R_{N1-H5} indicates that the transfer of the atom H5 from HX to HNCO occurs more readily from reactions (a) to (c). Compared with Cl and Br, the F has the highest electronegativity, thus the distance between H5 and F6 is the shortest among these H5–X6 bonds. Combining Fig. 2 with the analysis of bond distances of H5–X6 and C3–X6, it can be deduced that the reaction mechanism of these three reaction is different. The reaction mechanism of (a) is the transfer of the atom H5 from the atom F6 to the atom N1 accompanied by the movement of F6 toward the atom C3, but the reaction (b) or (c) is the transfer of atom H5 from atom X6 to atom N1 and then a reaction takes place between the atom X and the H$_2$NCO group.

As for the transition states of reactions of (d), (e), (f), (g) in Fig. 2, due to the similar mechanism, our discussion is focused on the reaction (d) HNCO + CH$_3$CH$_2$OH → H$_2$NCO$_2$CH$_2$CH$_3$. The calculations show that the four-membered ring (N1-C3-H5-O6) is formed at the transition state point. The bond length of transtion states is between the reactant bond length and the product bond length. In the process of the change from the reactant to the transition state, the distance between N1 and C3 of HNCO increases from 0.1218 to 0.1311 nm and the bond H5-O6 of ethanol increases from 0.0973 to 0.1196 nm. At the same time two new bonds are formed between the ethanol and isocyanic acid, they are C3-O6 and N1-H5, respectively. In the change from the transition state to the product, the bond length of N1-C3 and H5-O6 increased gradually until the bond H5-O6 is broken, so the double bond N1=C3 changes to a single bond and two new bonds C3-O6 and N1-H5 are formed, the bond length are 0.1351nm and 0.1012nm, respectively.
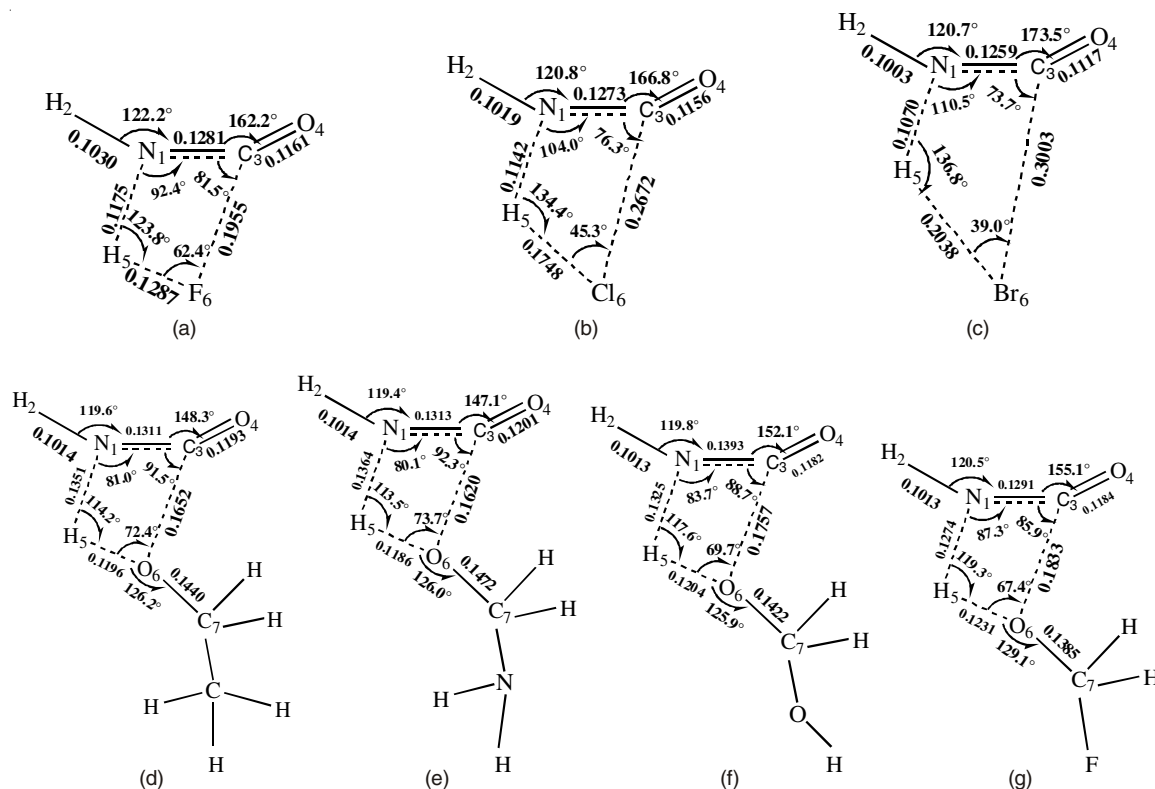

Fig. 2. Optimized geometry of transition state structures of HNCO reactions with HF (a), HCl (b), HBr (c), CH$_3$CH$_2$OH (d), NH$_2$CH$_2$OH (e), OHCH$_2$OH (f), FCH$_2$OH (g) [bond length (nm), bond angle (°)]

The change of bond length and angles are as follows: from these four transition state structures we can find the bond N1-H5 is getting shorter and shorter, which indicates the transfer of H atom occurs before the formation of C3-O6 bond, due to the different electronegativities of atoms C, N, O, F, Cl and Br.

The bond angles of $D_{H2-N1-C3}$ are almost equal in these seven reactions, because the atom H2 is not the atom of the four-member ring thus the substituent has little effect on it. All the above change trends accord with the order of C, N, O, F, Cl and Br in the Periodic Table of elements and the change of their electronegativities. In order to clarify the charge-transfer rule in the reaction process, we have calculated the charge of every atom not only in transition state but also in the whole reaction. The charge data are presented in Table-1.

From Table-1, it is inferred that the atom N1 captures electrons but the atom C3 loses clectrons in the process from the reactant to the transition state in reaction (a). On the other hand, the atom N1 loses electrons and atom C3 captures electrons in reaction (b) and (c). The negative charge of atom F6 slightly increases, but the negative charge of Cl6 and Br6 increase significantly, in agreement with the above result: reaction (a) has different mechanism to (b) and (c). The positive charge of atom H5 increases in all these three reactions. From the reactant to the product, it is concluded that the direction of charge transfer is as follows: in reaction (b) and (c), due to the long distance of bonds Cl6-C3 and Br6-C3, there is no charge transfer between the atom X6 (X = Cl or Br) and atom C3. When the atom H5 moving away from the atom X6 (X = Cl or Br) and getting close to the atom N1, it would transfer most of its charge to atom X6 and then capture electrons from HNCO, hence the negative charge obviously increased of atom Cl and Br. The net charge of atom Cl increases from -0.171 to -0.485, which of atom Br increases form -0.210 to -0.540. In reaction (b), the net charge of group HNCO increases from 0 to -0.241,

while in reaction (c), it increases from 0 to -0.255. The charge transfer between group HNCO and HF is relatively less *i.e.*, only 0.086. From Fig. 2, the atom Cl and Br is far from the group H₂NCO, so we supposed that there should be two parts being contained in the transition state structure of these two reactions: one is X atom with negative charge, the other is group H₂NCO with positive charge. In the process of the transition to the product, the charges of atoms Cl and Br also changed greatly, the negative charge of atom Cl reduces from -0.485 to -0.033, that of atom Br reduces from -0.540 to -0.127. As for the reactions (b) and (c) there are ion reactions between the negative atom X and the positive group H₂NCO in the process from the transition state to the product. But in reaction (a), the charge transfer of aom F is not so obvious, considering the whole reaction, HF is a capturing electron group in reaction (a), but in reactions (b) and (c), the group HX is a losing electron group. So the reaction mechanism of reaction (a) is different from (b) and (c).

As for the reaction (d) in the transition state, the net charge of ethanol is +0.272 and that of isocyanic acid is -0.272, which indicates there are 0.272 electrons transfered from the ethnol to HNCO. Thus, the reaction is a nucleophilic addition reaction, in which the ethanol is electron donor and the HNCO is electron acceptor. The charges of O6, N1,C3 and H5 are -0.411, -0.631, 0.510 and 0.424, respectively.

The electrostatic interaction plays an important role between the electronegative atoms (O6, N1) and the electro-positive atoms (C3, H5). Although the reactions (e), (f) and (g) have similar mechanism, because of the different electron-egativity, the charges transferred between the product molecules are different.

The variety of bond length curves along with the reaction coordinate are plotted, R_{N1-H5}, R_{X6-C3} and R_{X6-H5} changed a lot, but R_{N1-C3} just change slightly, dues to the rupture of π bond. With the whole reaction carried through, the double bond of

TABLE-1									
CALCULATED CHARGES FOR VARIOUS SPECIES IN THE HX (XCH₂OH) + HNCO REACTION									
HX (XCH₂OH) + HNCO	N1	H2	C3	O4	H5	X6 (O6)	HX (XCH₂OH)	HNCO	C7
Reactant (HF)	-0.505	0.331	0.612	-0.438	0.396	-0.396	0	0	–
Transition state	-0.590	0.350	0.678	-0.352	0.474	-0.560	0.086	0.086	–
Product	-0.587	0.330	0.707	-0.317	0.343	-0.475	0.132	0.132	–
Reactant (HCl)	-0.505	0.331	0.612	-0.438	0.171	-0.171	0	0	–
Transition state	-0.373	0.362	0.566	-0.314	0.244	-0.485	0.241	0.241	–
Product	-0.487	0.343	0.244	-0.384	0.317	-0.033	0.284	-0.284	–
Reactant (HBr)	-0.505	0.331	0.612	-0.438	0.210	-0.210	0	0	–
Transition state	-0.415	0.359	0.609	-0.298	0.285	-0.540	0.255	0.255	–
Product	-0.480	0.330	0.321	-0.378	0.334	-0.127	0.207	-0.207	–
Reactant (CH₃CH₂OH)	-0.505	0.331	0.612	-0.438	0.338	-0.468	0	0	-0.144
Transition state	-0.631	0.314	0.510	-0.465	0.424	-0.441	0.272	-0.272	-0.134
Product	-0.544	0.337	0.483	-0.524	0.319	-0.355	0.248	-0.248	-0.078
Reactant (NH₂CH₂OH)	-0.505	0.331	0.612	-0.438	0.334	-0.472	0	0	-0.206
Transition state	-0.622	0.311	0.493	-0.477	0.451	-0.443	0.295	-0.295	-0.185
Product	-0.540	0.339	0.517	-0.557	0.319	-0.375	0.241	-0.241	-0.310
Reactant (OHCH₂OH)	-0.505	0.331	0.612	-0.438	0.342	-0.481	0	0	-0.023
Transition state	-0.643	0.324	0.605	-0.441	0.447	-0.520	0.155	-0.155	0.001
Product	-0.553	0.345	0.521	-0.521	0.321	-0.398	0.208	-0.208	0.054
Reactant (FCH₂OH)	-0.505	0.331	0.612	-0.438	0.357	-0.464	0	0	0.156
Transition state	-0.625	0.337	0.600	-0.414	0.454	-0.537	0.102	-0.102	0.202
Product	-0.558	0.350	0.524	-0.514	0.325	-0.373	0.198	-0.198	0.253

Reaction	$E_{reactant}$	$E_{transition\ state}$	$E_{product}$	$E_{activation}$	$\Delta E_{(product-reactant)}$
HF + HNCO	-706581.15	-706462.79	-706633.29	116.71	-52.14
HCl + HNCO	-1652727.76	-1652626.39	-1652761.11	101.37	-33.35
HBr + HNCO	-7196732.13	-7196649.98	-7196777.29	82.18	-45.13
CH_3CH_2OH + HNCO	-850002.00	-849876.27	-850104.61	126.73	-101.56
NH_2CH_2OH + HNCO	-892121.27	-891994.75	-892227.08	126.52	-105.79
$OHCH_2OH$ + HNCO	-944271.58	-944142.78	-944369.25	128.80	-97.60
FCH_2OH + HNCO	-1007346.59	-1007198.09	-1007429.55	148.50	-82.94

N1=C3 changes into a single bond gradually. The curve R13 indicates this changing process relatively tempers. The rupturing bond H5-X6 (O6) elongated obviously, at the same time, the distance between the atom H5 and atom N1 (R_{N1-H5}) decreases gradually. The changing process of these two bonds is the process of atom H transfer. Curve R63 represents the formation of bond X6-C3. The bond distance of R_{F6-C3}, R_{C16-C3}, R_{Br6-C3} are 0.185, 0.257 and 0.276 nm, respectively at this position. The slope of curve R56 and curve R15 represent the transfer velocity of H atom. The slope become relatively large indicating the transfer velocity of H atom is fast. Combining the whole process of reaction with the transition state sturctures, from the reaction (a), (b) to (c), the transfer of H atom occurres earlier and earlier than the formation of bond X6-C3 and the higher atomic number the element X(in the same main group) is, the earlier the transfer of H atom is occurred than the formation of bond X6-C3. In summary, for these seven reactions, the characteristic of reaction in transition state is the transfer of H atom from atom 6 to atom 1 and the occured time associates with the electronegativity of atom X.

The varieties of the relative energy along with the reaction coordinate of each reaction are presented in Fig. 3. For convenient discussions, the energies of reactants are set to be zero for reference. Fig. 3 showed that all the reactions are exothermic. The energies of reactants, transiton states, products including the zero point energy are presented in Table-2. The results show reaction (c) has the lowest activation energy, viewed from the dynamics and is easy to proceed. Similarly, the reaction (g) is difficult to proceed.
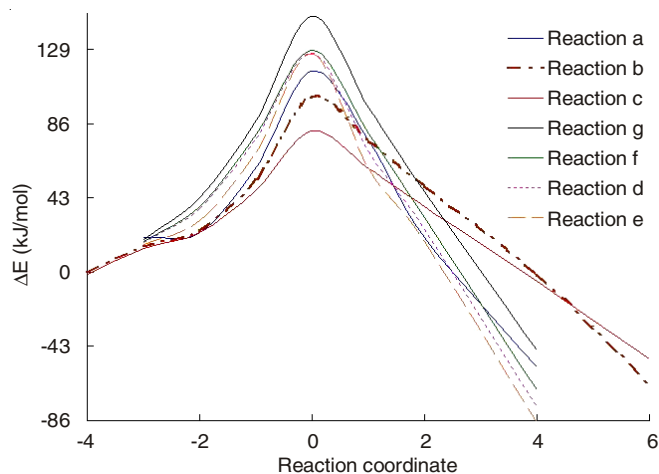

Fig. 3. Varieties of relative energy along with the reaction coordinate of each reaction (kJ/mol)

Conclusion

By studying and combining the seven transition states with reaction pathways, it is concluded that the most significant characteristics of transition state is the transfer of H atom from atom 6 to atom 1 in the addition reaction. Due to the different electronegativities, the charges transferred between the product molecules and the transition state structures are different. Generally, the reactions with one σ bond and one π bond broken and two new σ bonds formed belong to exothermic reactions. In the reactions of forming four-member ring transition state structure, different elements in the same periodic element group formed different four-member ring due to the increment of atomic number in the substituents, the amount of charge transfer of the atoms in the four-member ring are obviously different in the process of reaction.

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