Articles and Statements

Purification of the Toxic Gaseous HCN Emissions by Oxidation in O2 Atmosphere in the Gas Phase: Quantum Chemical Modeling

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Abstract

HCN oxidation has been conducted in oxygen atoms, whereas the higher availability of oxygen in the atmosphere increases the HCN purification. However, this study was studied theoretically using density functional theory (DFT) method. The present work aims to evaluate the oxidation behaviour of HCN emissions in O_2 atmosphere. A detailed chemical kinetic mechanism for HCN combustion was evaluated. According to the proposed kinetic mechanism, in the ambient conditions, the oxidation of HCN proceeds mostly through the following sequence: $HCN+O \rightarrow NCO+H$ and CO_2+NH. The present modeling shows that these oxidations are preferred kinetically and energetically and are spontaneously possible in the atmosphere.

Keywords: HCN, kinetics, combustion, oxidation, theoretically.

1. Introduction

In addition to plastic waste, most solid fuels contain organic nitrogen. HCN is apparently produced from the pyrolysis of these materials. However, hydrogen cyanide (HCN) is very important in many areas of chemistry and is of major interest to experimental and theoretical chemists (Benallou, 2016; Tian et al., 2007; Benallou, 2017). Moreover, HCN vapor is released into the air from various anthropogenic sources, including the coal chemical industry (Tian et al., 2007), metal mining, synthetic fiber processing (Rahaman et al., 2007), disposal processes NO_x (Baum et al., 2007; Karlsson, 2004), rubber industries (Zhao et al., 2015). Additionally, hydrogen cyanide (HCN) plays a key role in a variety of gasoline combustion systems, and this fuel-based fossil fuel has contributed to more than 80 % of the world's energy expenditure (EEA, 2006), so hydrogen cyanide (HCN) is formed intermediately during their combustion as long as the released HCN is a function of many parameters among which must be mentioned the nature of the solid fuel; the chemical structures present in the fuel, the heating rate conditions and residence time (Glarborg et al., 2003; Potila et al., 2004; Demirbas et al., 2004). Furthermore, according to recent

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studies, biomass combustion provides the main source of tropospheric HCN (1.4-2.9TgN/yr), while reactions with hydroxyl (OH) radicals and oceans uptake are responsible for its elimination (Li et al., 2000). Traces of HCN have also been measured in passenger vehicles exhausts, probably resulting from catalytic NO_x reduction reactions (Karlsson et al., 2004). In the stratosphere, HCN is oxidized by reaction with atomic oxygen and hydroxyl radicals (Kleinbohl et al., 2006).

Importantly, HCN is a very toxic gas in which 20 times more toxic than carbon monoxide (CO) and is one of the acutely toxic chemical species, HCN is extremely harmful to both health and life environment. It has been recommended by the National Institute for Occupational Safety and Health (NIOSH) that the short-term exposure limits for HCN is 4.7ppm averaged over 15 min (Chang et al., 2005). So with the cumulating emissions of HCN, it is urgent to remove the unconventional pollutant HCN in industrial waste gases.

Several treatment technologies for HCN removal have been reported (Oliver et al., 2005; Ye et al., 2009; Giménez-López et al., 2010). The sorption and catalytic oxidation are the widely used methods for the removal of HCN (Rastegar et al., 2013; Zhao et al., 2014; Shi et al., 2015). The presence of HCN gas in the atmosphere and their oxidation hypothesis by oxygen atoms in the stratosphere lead us to thinking about a possibility to purification this toxic gas by oxidation proceeds in low temperature in the gas phase, due to the lack of studies at these specific operating conditions and the increasing importance of the oxy-fuel combustion processes that represents the main source of HCN gas, while this latter can oxidize to other species not or less toxic in presence of atomic oxygen that is in excess of atmosphere. At this end, this paper will concentrate on the oxidation modeling of HCN in combustion process with the oxygen atoms in the gas phase.

2. Material and Methods

The geometry optimizations of stationary points were performed using the density functional formalism with the B3LYP exchange-correlation energy functional (Becke et al., 1993; Lee et al., 1988). All the calculations were realized with GAUSSIAN G09 program package (Frisch et al., 2009) and visualization of the output files is performed using the Gauss-View 5.0.8 software. The surface mapping was determined using a 6-311G** basis set level and the critical points (minima and transition states) were optimized and checked by calculating the intrinsic reaction coordinates (IRCs) with this basis set. All energies have been corrected for zero-point energy (ZPE) contributions calculated at the same level.

3. Results and discussion

3.1. Mechanisms studies characterization

In this paragraph, the mechanism reaction analyzing of HCN oxidation in air combustion (oxygen) to other gas not or less toxic is terminated, the HCN oxidation is carried out by one or two oxygen atoms in the gas phase, thus the relative energies of the minima and TSs are showed in Figures 3 and 4. CO, NH, CO_2, HNO, CN, NCO, OH formation were shown to be formed from HCN oxidation after a series of transformations, rearrangement, and rotation, the detailed step-by-step mechanism for the oxidation of gaseous HCN in space is depicted in Figure 1.
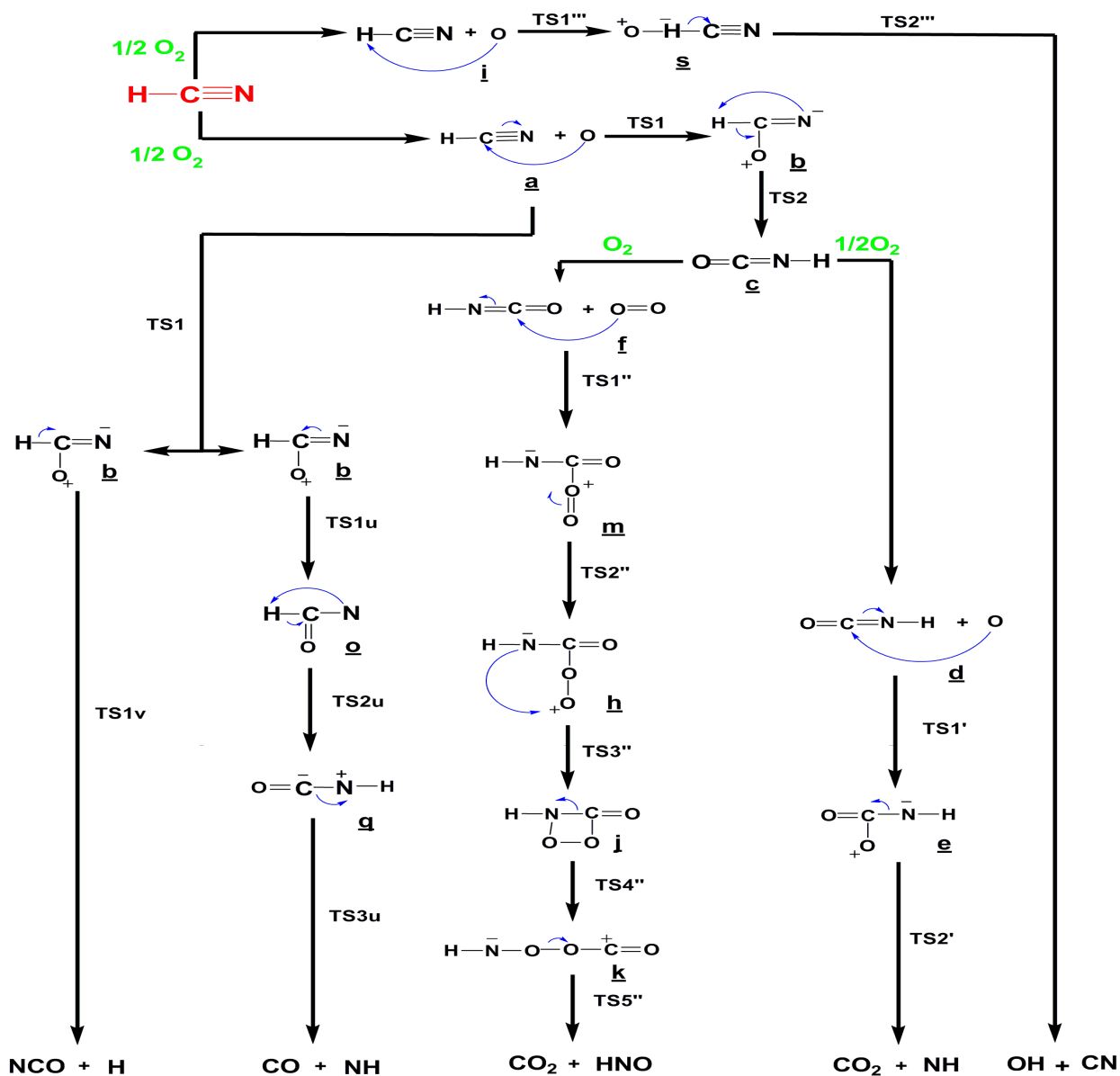
Fig. 1. Oxidation mechanisms of gaseous HCN by oxygen atoms.

Taking into account the structures mentioned in Figure 1, the minima and transition state of each complex is calculated at DFT method and 6-311G(d,p) basis set level, each TS species resulting from HCN oxidation in the gas phase are evaluated by imaginary frequency in the Hessian matrix. The distance and angle parameters of different TSs and minima are drawn and presented in figures 2 and 3.
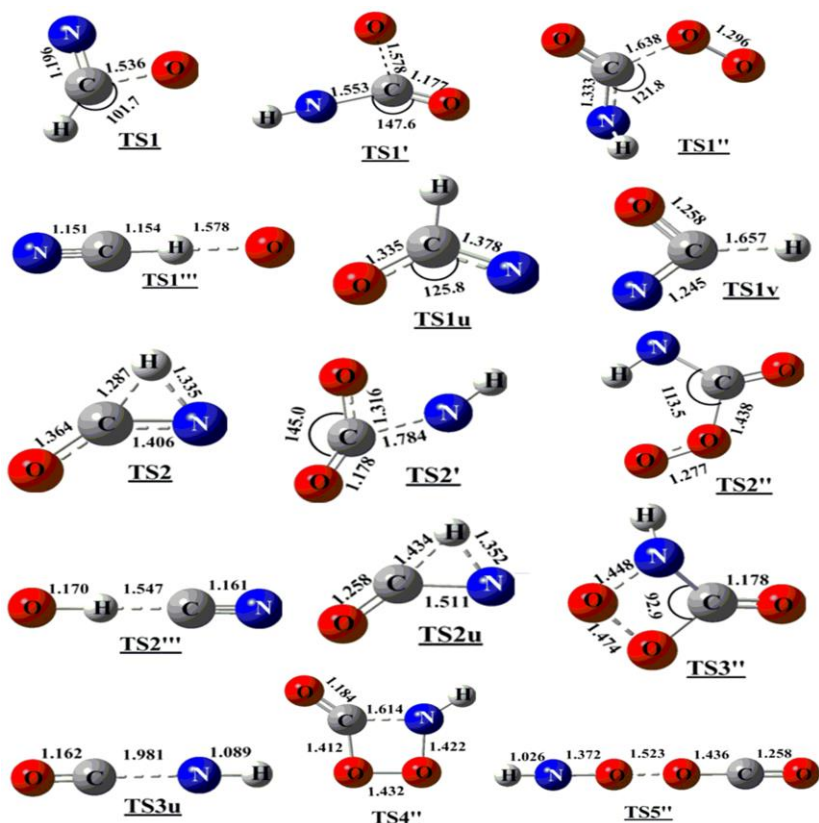
Fig. 2. Geometric structures of selected transition states of HCN oxidation optimized from DFT methods. All the transition states are planar. The distances are in Å and the angles are in degrees
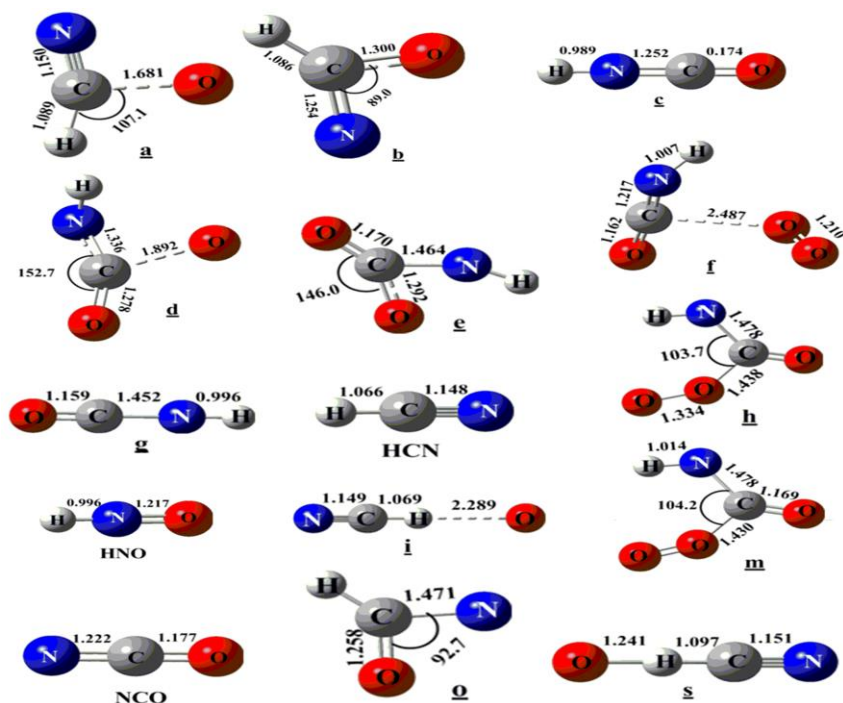

Fig. 3. Structures of the lowest-energy products of HCN oxidation optimized from DFT methods. All the minima are planar. The distances are in Å and the angles are in degrees

3.2. Barrier energy determination

The main energetic features of the oxidation of HCN is presented in this section, after mechanism pathway characterization of CO, NH, CO_2, HNO, CN, NCO, OH formation from gaseous HCN emissions in air combustion, whereas each step of oxidation process is identified energetically as well as the relative energies of different complexes (minima and transition state) shown in figures 1, 2 and 3 are determined and represented in figures 4, 5, 6, 7, 8 and 9.
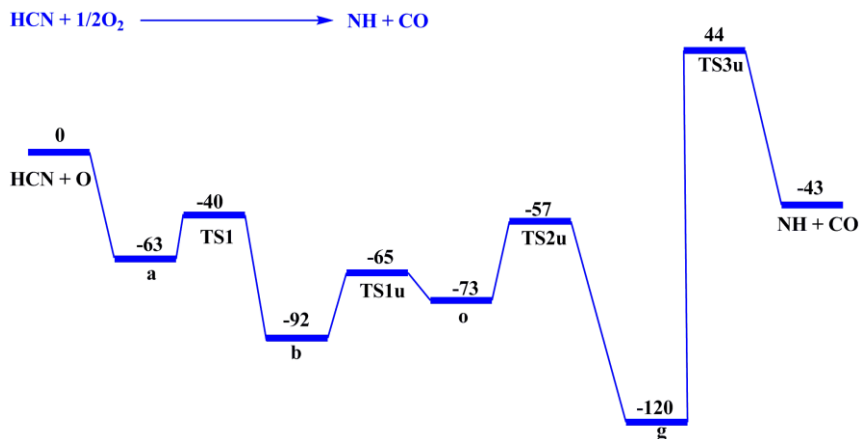
Fig. 4. DFT/6-311G(d,p) values correspond to the relative energies in kcal/mol for NH and CO formation from HCN oxidation in one atom of oxygen
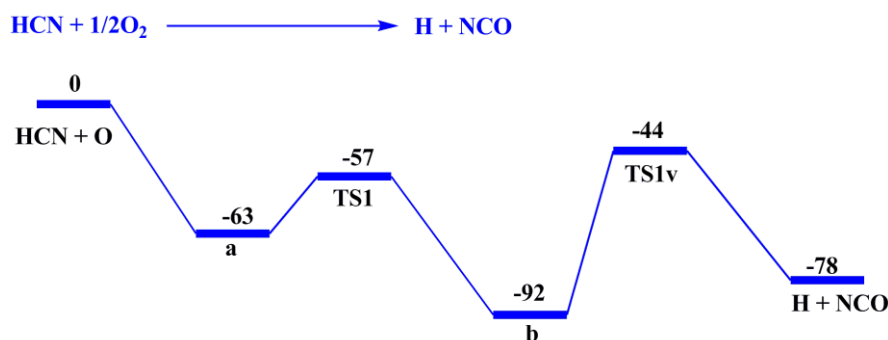
Fig. 5. DFT/6-311G(d,p) values correspond to the relative energies in kcal/mol for H and NCO formation from HCN oxidation in one atom of oxygen
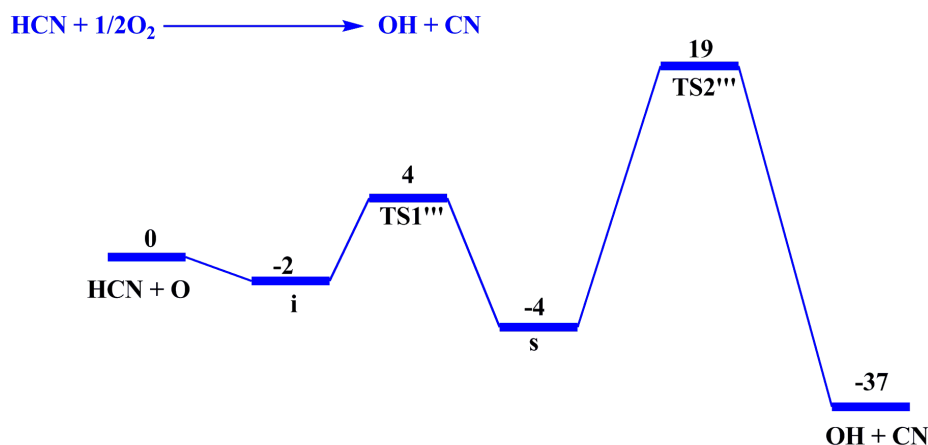
Fig. 6. DFT/6-311G(d,p) values correspond to the relative energies in kcal/mol for OH and CN formation from HCN oxidation in one atom of oxygen

Fig. 7. DFT/6-311G(d,p) values correspond to the relative energies in kcal/mol for HNCO formation from HCN oxidation in one atom of oxygen

Fig. 8. DFT/6-311G(d,p) values correspond to the relative energies in kcal/mol for NHO and CO₂ formation from HCNO oxidation in two atoms of oxygen
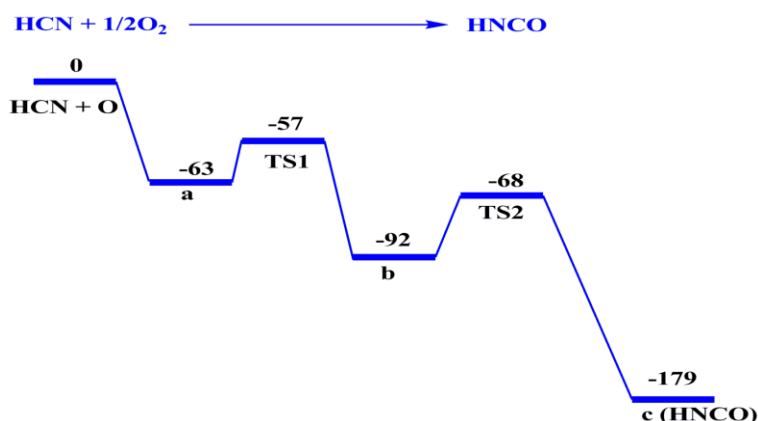

Fig. 9. DFT/6-311G(d,p) values correspond to the relative energies in kcal/mol for NHO and CO₂ formation from HCNO oxidation in one atom of oxygen
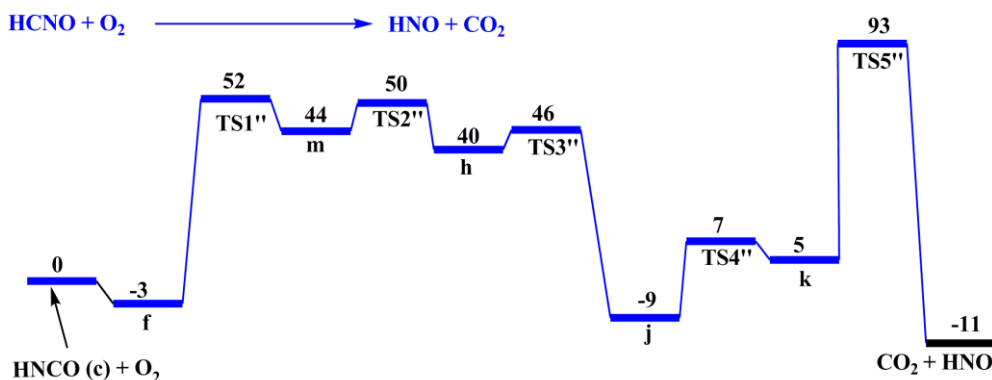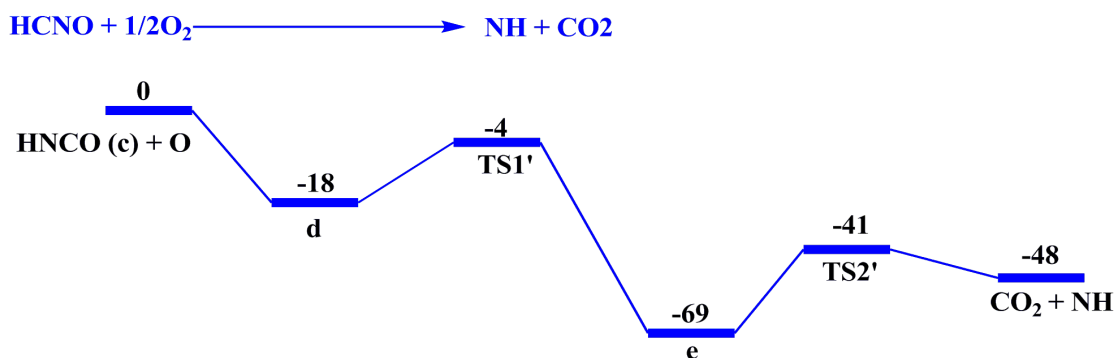
3.3. Discussion

The oxidation of HCN was studied in 1.0 atmospheric pressure and at 298K temperature, thus. Chemical kinetic reaction mechanisms of the different pathway have been proposed to represent the available data on the kinetics of HCN oxidation. However, these chemical kinetic reaction mechanisms where not certainly usable for simulating experiments over a wider range of conditions than originally tested, demonstrating the need for a more robust kinetic scheme. Although, the oxidation of HCN by O_2 or O oxygen atoms in ambient conditions and in the gas phase have been studied successfully in this paper. In this context, analyzing energetic diagrams and oxidation mechanisms lead us to conclude that HNCO, H and radical NCO are the most probable products of HCN oxidation by $\frac{1}{2}O_2$ in the gas phase because are represents the lowest

activation energies and shortest pathway processes, then they necessity less energetic contribution to started, in which need -44 and -57kcal/mol for NCO+H and HNCO formation respectively. So these oxidation reactions are endothermic and can occur spontaneously in efficiency in atmospheric space. In contrary, the other species formation OH+CN and NH+CO from gaseous HCN oxidation in one atom of oxygen, we have concluded that: on the one hand, the energetic activation is more higher in which 44 and 19kcal/mol for NH+CO and OH + CN formation respectively, and on the other hand these species are not sufficiently stables compared to the NCO+H and HNCO formation in which have values of -43kcal/mol (NH+CO), -37kcal/mol (OH+CN) versus -78kcal/mol (NCO+H) and -179kcal/mol for HNCO, therefore OH+CN and NH+CO compounds should not occur efficiently in the gas phase in atmosphere by oxidation in lonely oxygen atom but that being more likely if have a contribution for external source.

Due to stability of HNCO (-179kcal/mol) species and their high toxicity in human health, we are think to reburn this compound in lonely and twice oxygen atoms in same conditions in gas phase, so the results show that HNCO oxidation in one atom oxygen is energetically and kinetically more favourable to compare with HNCO oxidation in O_2 molecules, because this last require passing by the highest energetic activation pathway mechanism that represents the rate limiting step to be 93kcal/mol of TS5" (figure 8) for forming $HNO+CO_2$ gases. Subsequently, $HCN+1/2O_2 \rightarrow HNCO+1/2O_2 \rightarrow CO_2+NH$ and $HCN+1/2O_2 \rightarrow H+NCO$ are the most accepted mechanisms oxidation of HCN in the atmospheric gas. Since the proposed kinetic mechanisms for the oxidation of HCN were validated, a more comprehensive modeling has been needed.

Moreover, reactions burner of HCN is confirmed by calculating the enthalpy of reaction ΔHr of different compounds formation in combustion processes, this study was conducted in the same conditions of temperature and pressure, thus the results of such reaction is given below:

$HCN+1/2O_2 \rightarrow$ H+NCO; ΔHr=-94.125kcal/mol
$HCN+1/2O_2 \rightarrow$ NH+CO; ΔHr=-42.670kcal/mol
$HCN+1/2O_2 \rightarrow$ OH+CN; ΔHr=-37.022kcal/mol
$HCN+1/2O_2 \rightarrow$ HNCO; ΔHr=-181.347 kcal/mol
$HCNO+1/2O_2 \rightarrow CO_2+NH$; ΔHr=-54.593 kcal/mol
$HCNO+O_2 \rightarrow CO_2+HNO$; ΔHr=-7.530 kcal/mol
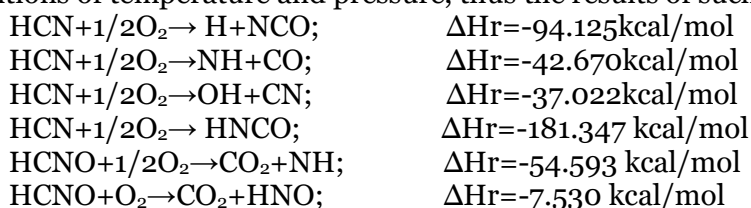
The found enthalpies energies ΔHr of oxidation reaction show that HCN oxidizes yielding H, NCO, NH, CO, OH, CN, HNCO via a complex reaction, in addition this pathway oxidation is extensively exothermic mainly of NCO and HNCO yielding to be -94.125kcal/mol and -181.347kcal/mol respectively. Thus, HCN consumption still occurs via reaction with O atoms, forming especially NCO and HNCO species in the normal conditions. However, these species can reburning in oxygen atoms to produce other products.

According to the currently accepted mechanisms, we have conclude that HCN combustion in oxygen atom is widely possible in the atmospheric conditions, can give the named gas of NCO, CO_2 and NH ($HNCO+O= CO_2+NH$) spontaneously in the gas phase.

4. Conclusion

A comprehensive detailed chemical kinetic modeling of the oxidation and combustion of HCN was performed by DFT theoretical methods. The main products formation of HCN oxidation in one or two atom oxygen's in the normal conditions are NCO, CO_2 and NH, these species are the feeble toxicity and can occur efficiently and spontaneously in the gas phase in the atmosphere of Earth. Although, the kinetic and energetic investigation show that the overall activation barrier of HCN oxidation to NCO+H and CO_2+NH is -44kcal/mol and -4kcal/mol respectively and they are more suitable for barrier activation. Therefore, the main accepted reaction paths involved in the oxidation of HCN is verified.

References

Benallou, 2016 – *Benallou A.* (2016). Understanding the most favourable dimer of HCN for the oligomerization process in the gas phase of interstellar clouds. *Comp. Theor. Chem.* 1097, 79–82.

Tian et al., 2007 – *Tian F.J., Yu J.L., McKenzie L.J., Hayashi J., Li C.Z.* (2007). Conversion of fuel-N into HCN and NH3 during the pyrolysis and gasification in steam: a comparative study of coal and biomass. *Energy. Fuel.* 21, 517–521.

Benallou, 2017 – *Benallou A.* (2017). The mechanism determination of trimer and tetramer HCN for adenine formation in the gas phase of interstellar space. *Comp. Theor. Chem.* 1101, 68–73.

Rahaman et al., 2007 – *Rahaman M.S.A., Ismail A.F., Mustafa A.* (2007). A review of heat treatment on polyacrylonitrile fiber. *Polym. Degrad. Stab.* 92, 1421–1432.

Baum et al., 2007 – *Baum M.M., Moss J.A., Pastel S.H., Poskrebyshev A.G.A.* (2007). Hydrogen cyanide exhaust emissions from in-use motor vehicles. *Environ. Sci. Technol.* 41, 857–862.

Karlsson, 2004 – *Karlsson H.L.* (2004). Ammonia, nitrous oxide and hydrogen cyanide emissions from five passenger vehicles. *Sci. Total. Environ.* 334, 125–132.

Zhao et al., 2015 – *Zhao Q., Tian S.L., Yan L.X., Zhang Q.L., Ning P.* (2015). Novel HCN sorbents based on layered double hydroxides: Sorption mechanism and performance. *J. Hazard. Mater.* 285, 250–258.

EEA, 2006 – EEA. Total energy consumption by fuel (CSI 029), assessment. Copenhagen, DK: *European Environment Agengy*, April 2006.

Glarborg et al., 2003 – *Glarborg P., Jensen A.D., Johnsson J.E.* (2003). Fuel nitrogen conversion in solid fuel fired systems. *Prog. Energy. Combust. Sci.* 29, 89–113.

Potila et al., 2004 – *Potila H., Sarjala T.* (2004). Seasonal fluctuation in microbial biomass and activity along a natural nitrogen gradient in a drained peatland. *Soil. Biol. Biochem.* 36, 1047–1055.

Demirbas et al 2004 – *Demirbas A.* (2004). Combustion characteristics of different biomass fuels. *Progr. Energy. Combust. Sci.* 30, 219–230.

Li et al., 2000 – *Li Q., Jacob D.J., Bey I., Yantosca R.M., Zhao Y., Kondo Y.* (2000). Atmospheric. Hydrogen. Cyanide. (HCN): Biomass. Burning. Source, Ocean Sink. *Geophys. Res. Lett.* 27, 357–60.

Karlsson et al., 2004 – *Karlsson H.L.* (2004). Ammonia, nitrous oxide and hydrogen cyanide emissions from five passenger vehicles. *Sci. Total. Environ.* 334–335, 125–132.

Kleinbohl et al., 2006 – *Kleinbohl A., Toon G.C., Sen B., Blavier J.F.L., Weisenstein D.K., Strekowski R.S.* (2006). Measurement of. HCN in the middle atmosphere by EOS MLS. *Geophys. Res. Lett.* 33, 11.

Chang et al., 2005 – *Chang L.P., Feng Z.H., Xie K.C.* (2005). Effect of Coal Properties on HCN and NH 3 Release During Coal Pyrolysis. *Energy. Sourc.* 27, 1399–1407.

Oliver et al., 2005 – *Oliver T.M., Jugoslav K., Aleksandar P., Nikola D.* (2005). Synthetic activated carbons for the removal of hydrogen cyanide from air. *Chem. Eng. Process.* 44, 1181–1187.

Ye et al., 2009 – *Ye P.W., Luan Z.Q., Li K., Yu L.Q., Zhang J.C.* (2009). The use of a combination of activated carbon and nickel microfibers in the removal of hydrogen cyanide from air. *Carbon.* 47, 1799–1805.

Giménez-López et al., 2010 – *Giménez-López J., Millera A., Bilbao R., Alzueta M.U.* (2010). HCN oxidation in an O2/CO2 atmosphere: An experimental and kinetic modeling study. Original research article. *Combust. Flame.* 157, 267–276.

Rastegar et al., 2013 – *Rastegar S.F., Peyghan A.A., Hadipour N.L.* (2013). Response of Si- and Al-doped graphenes toward HCN: A computational study. *Appl. Surf. Sci.* 265, 412–417.

Zhao et al., 2014 – *Zhao M., Yang F., Xue Y., Xiao D., Guo Y.* (2014). Adsorption of HCN on reduced graphene oxides: a first–principles study. *J. Mol. Model.* 20, 2214–2218.

Shi et al., 2015 – *Shi LB., Wang Y., Dong H.K.* (2015). First-principle study of structural, electronic, vibrational and magnetic properties of HCN adsorbed graphene doped with Cr, Mn and Fe. *Appl. Surf. Sci.* 329, 330–336.

Becke et al., 1993 – *Becke A.D.* (1993). Densityfunctional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 98, 1372–1377.

Lee et al., 1988 – *Lee C., Yang W., Parr R.G.* (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B.* 37, 785–789.

Frisch et al., 2009 – *Frisch M.J. et al.*, GAUSSIAN 09, revision A. 02, GAUSSIAN Inc., Wallingford, CT. 2009.