

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/239159885>

Theoretical studies on C 2H+NO reactions: mechanism for HCN+CO and HCO+CN formation

ARTICLE *in* CHEMICAL PHYSICS LETTERS · JANUARY 1998

Impact Factor: 1.9 · DOI: 10.1016/S0009-2614(97)01298-0

CITATIONS

19

READS

34

3 AUTHORS, INCLUDING:



Jozef Peeters

University of Leuven

205 PUBLICATIONS 4,431 CITATIONS

SEE PROFILE



Minh Tho Nguyen

University of Leuven

748 PUBLICATIONS 10,363 CITATIONS

SEE PROFILE

Theoretical studies on $C_2H + NO$ reactions: mechanism for $HCN + CO$ and $HCO + CN$ formation

Debasis Sengupta, Jozef Peeters¹, Minh Tho Nguyen

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

Received 4 September 1997; in final form 10 November 1997

Abstract

In order to investigate $HCN + CO$ and/or $HCO + CN$ formation during the reaction of the ethynyl radical with nitric oxide we explore the potential energy surface of $[C_2HNO]$ isomers via density functional theory. Product formation takes place via several isomerization steps after the initial adduct formation. We identified one reaction pathway resulting in fragmentation that is accessible without activation of the initial reactants; this path forms $HCN + CO$ and involves a four-membered cyclic structure. Other pathways, involving formyl cyanide and leading to $HCN + CO$ and/or $HCO + CN$, require initial activation. Wherever possible, our calculated energies are compared with higher level ab initio results. The heat of formation of formyl cyanide is calculated to be 14.4 kcal/mol which compares reasonably well with the reported value of 11.6 kcal/mol at the G2 level of theory. © 1998 Elsevier Science B.V.

1. Introduction

Reactions of the oxides of nitrogen NO_x , have continued to attract experimental as well as theoretical chemists due to their roles in atmospheric chemistry. The simplest among the oxides of nitrogen, nitric oxide (NO) plays a major role in the destruction of the stratospheric ozone layer and is well known as the precursor of tropospheric oxidants and acid rain. Hence, considerable research efforts are being devoted on how to control combustion-generated emissions of this toxic pollutant. However, ethynyl radicals (C_2H), besides having been detected in interstellar space and in planetary atmospheres, are also known to play a major role in hydrocarbon combustion. The reaction of C_2H with NO is of

potential relevance to the “reburn” technology which is an efficient method for reducing NO emissions in combustion. Recently, Peeters et al. [1] reported an experimental investigation of the $C_2H + NO$ reaction using a pulse laser photolysis–chemiluminescence technique, where C_2H radicals were generated by 193 nm photodissociation of C_2H_2 and their real-time decay was monitored by the chemiluminescence of $CH(A^2\Delta)$ produced by their reaction with O_2 , present in large excess. The rate coefficient, determined over the $T = 295$ – 440 K range, could be represented by $k(T) = (1.0 \pm 0.2) \times 10^{-10} \exp[-(287 \pm 65)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; the $k(T = 295 \text{ K})$ value of $(3.9 \pm 0.5) \times 10^{-11}$ was found to be independent of pressure. The high and pressure-independent value of the rate coefficient led the authors to conclude that the $C_2H + NO$ reaction proceeds by an association–elimination mechanism;

¹ Corresponding author.

Fig. 1. The overall profile of the potential energy surface for the $[C_2, H, N, O]$ system calculated at the B3LYP/6-311 + + G(d,p) level of theory.

ble with those from conventional ab initio calculations in order to check the reliability of the DFT results. Moreover, we also report the heats of formation of several isomers involved in the $C_2H + NO$ reaction.

2. Computational details

All calculations were performed using the GAUSSIAN 94 [9] program. Geometry optimizations of all the stationary points of the potential energy surface have been carried out using Schlegel's method, to better than 0.001 \AA for bond lengths and 0.1 degree for angles with a self-consistent field convergence of at least 10^{-9} on the density matrix. Initial geometry optimizations in the DFT calculations have been carried out with the 6-31G(d,p) basis sets using the B3LYP exchange-correlation functional. Geometries were further refined with 6-311++G(d,p) basis sets using the same exchange-correlation functional (hereafter referred to as B3LYP/6-311++G(d,p)). Vibrational wavenumbers are also

calculated at the B3LYP/6-311++G(d,p) level of theory. While equilibrium structures were characterized by the all-positive eigenvalues of the hessian, the transition structures were confirmed by one negative eigenvalue of the hessian for which the eigenvector corresponds to the desired reaction coordinate.

3. Results and discussion

A schematic representation of the potential energy surface for the $C_2H + NO$ reactions is shown in Fig. 1. In Fig. 2, unimolecular reactions arising from formyl cyanide, $HC(O)CN$ are schematically presented. Table 1 displays the total, zero-point vibrational and relative energies of all the stationary points presented in Figs. 1 and 2. Three different adducts can be formed in the association of C_2H and NO , depending upon the center of attack by NO . Among these, **3** is found to be the most stable isomer, 63 kcal/mol below the reactants; it is formed when the nitrogen end of NO combines with the radical center of C_2H . This process is found to be a

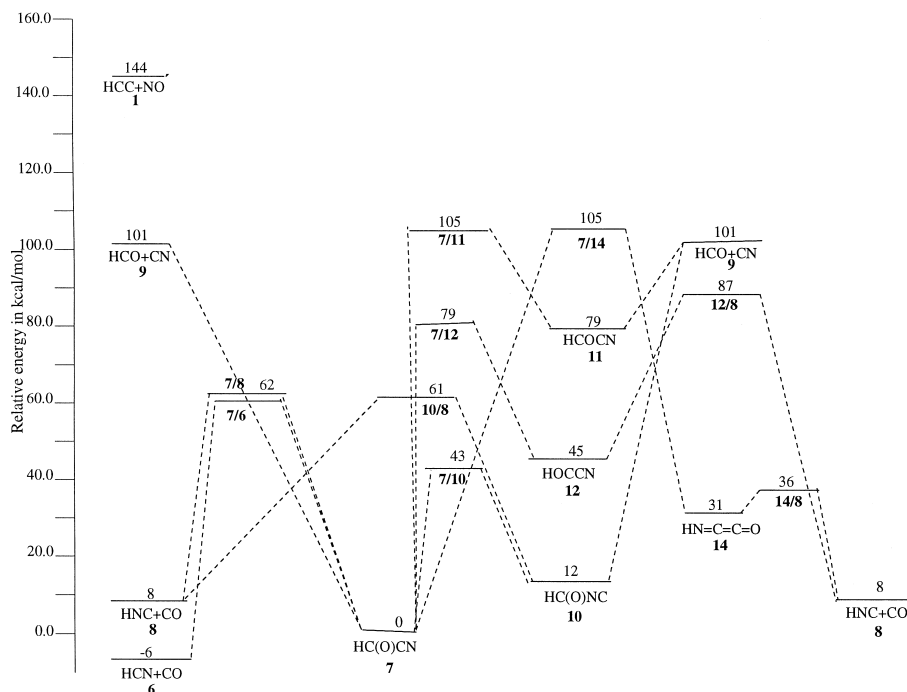


Fig. 2. The B3LYP/6-311++G** potential energy surface for the unimolecular decomposition of formylcyanide.

Table 1

Total (in hartree), zero-point vibrational (in kcal/mol) and relative (in kcal/mol) energies at the B3LYP/6-311 + + G(d,p) level of various stationary points shown in Figs. 1 and 2. E , ZPE and E_{rel} refer to total, zero-point vibrational and relative energies, respectively

Molecule	E	ZPE	E_{rel}	Molecule	E	ZPE	E_{rel}
HCC + NO 1	−206.5626028	11.7	143.6	2 /4	−206.5908083	14.1	128.3
ONCCH 2	−206.6293024	16.0	106.1	3 /4 (H)	−206.5959797	12.1	123.1
ONCCH 3	−206.6672411	15.1	81.4	3 /4 (NO)	−206.5920946	13.6	127.0
ONCHC 4	−206.6036238	14.0	120.2	4 /5	−206.5765715	14.4	137.6
ONCHC 5	−206.6064052	15.5	120.0	5 /6	−206.5893779	13.6	128.7
HCN + CO 6	−206.8035556	13.5	−5.8	3 /7	−206.5511508	13.9	153.0
HC(O)CN 7	−206.7993173	16.6	0.0	7 /6	−206.6948638	13.3	62.2
HNC + CO 8	−206.7806043	13.0	8.1	7 /8	−206.6940168	12.6	62.1
HCO + CN 9	−206.6301818	11.2	100.7	7 /10	−206.7285913	15.1	42.9
HC(O)NC 10	−206.7797414	16.3	12.0	7 /11	−206.6285155	14.0	104.6
HC-O-CN 11	−206.6719321	15.5	78.8	7 /12	−206.6674506	12.7	78.8
HOCCN 12	−206.7275389	16.6	45.0	7 /14	−206.6254034	12.9	105.4
HOC + CN 13	−206.5631387	11.4	143.0	10 /8	−206.6965780	12.8	60.7
HNCCO 14	−206.7484951	15.9	31.2	12 /8	−206.6530659	11.7	86.9
				14 /8	−206.7388656	14.4	35.7

barrierless association. The cyclic isomer **2** is formed via a [2 + 1] cycloaddition process. This isomer is found to be 26 kcal/mol less stable than **3**. We are unable to locate an optimized transition structure for this cycloaddition process. However, we carried out energy calculations at the B3LYP/6-31G(d,p) level as a function of the distance between the N atom and the center of C–C bond, in a perpendicular approach. We found a maximum in energy which is 55 kcal/mol higher than the energy of $\text{C}_2\text{H} + \text{NO}$ at the B3LYP/6-31G(d,p) level. Even though we do not associate much importance to the magnitude of this energy barrier, it gives an indication that $\mathbf{1} \rightarrow \mathbf{2}$ is not a barrierless process. The least stable isomer **4** is formed by the addition of the nitrogen end of NO to the carbon bonded to the hydrogen. This process is found to be barrierless.

Fig. 1 shows how **2** and **3** can be transformed to the 4-membered cyclic structure **5** via **4**. While the $\mathbf{3} \rightarrow \mathbf{4}$ transformation can take place via a 1,2 shift of either the NO group or the H atom, $\mathbf{2} \rightarrow \mathbf{4}$ conversion is possible simply through ring-opening. The $\mathbf{3} \rightarrow \mathbf{4}$ transformation via a 1,2-hydrogen shift requires 4 kcal/mol less activation energy than that via NO transfer. The four-membered cyclic isomer **5**, the precursor for HCN formation, can be formed via ring-closure of **4** with an activation barrier of 18 kcal/mol. Breaking of the N–O bond is followed promptly by the rupture of the C–C bond, as NCHCO is not a local minimum on the surface; this

process gives rise to HCN + CO. Most importantly, as shown in Fig. 1, the position of all transition structures for the isomerisation and dissociation steps from **3** and **4** to **6** lie below the energy of $\text{C}_2\text{H} + \text{NO}$. Since the initial adducts **3** and **4** are formed from C_2H and NO without a barrier, it follows that HCN + CO can be formed from the reactants without activation energy. On the other hand, HCN formation via the three-membered cyclic compound **2**, is possible at higher temperatures due to the existence of a finite activation barrier of the entrance channel. The most stable isomer **7**, is formed via 1,3 migration of the oxygen atom from the N-end to the C-end of **3**. This process is found to have a transition structure higher in energy than that of all other isomerisation steps; its position in the energy scale is about 9 kcal/mol higher than that of $\text{C}_2\text{H} + \text{NO}$. This essentially means that at higher temperatures the $\mathbf{3} \rightarrow \mathbf{7}$ isomerization can take place, thereby producing **7** with 153 kcal/mol of internal energy. This energy can rapidly be distributed into the appropriate vibrational modes to produce the dissociation products HCN + CO and HNC + CO via low-lying transition states connecting **6** and **8** to **7**. Figs. 1 and 2 show that HCO + CN **9**, can only be formed via isomer **7**. This means that HCO + CN formation can take place at higher temperatures. Once **7** is formed from **3** with an internal energy of 153 kcal/mol, it can undergo all the processes shown in Fig. 2.

At this stage it interesting to compare the calcu-

lated heats of reaction with experimentally obtained values, to check the reliability of DFT using the B3LYP functional. While the experimental heats of reaction at 0 K for $\text{C}_2\text{H} + \text{NO} \rightarrow \text{HCN} + \text{CO}$ and $\text{C}_2\text{H} + \text{NO} \rightarrow \text{HCO} + \text{CN}$ are -151 and -43 kcal/mol, respectively [10], the theoretically calculated values are -149.4 and -42.9 kcal/mol, respectively. The agreement between theory and experiment shows that the B3LYP/6-311++G(d,p) energies are quite reliable.

Fig. 2 shows that several dissociation and isomerization paths are available to **7**. Isomerization of **7** to formyl isocyanide **10** is found to have a lower barrier than the other isomerization steps. Dissociations of **7** into $\text{HCN} + \text{CO}$ and $\text{HNC} + \text{CO}$ have almost the same activation energy. These results are in agreement with the earlier ab initio calculation of Fang et al. [7] at the MP4/6-31G(d,p)//HF/6-31G(d,p) level. These authors found that the activation barrier is close to 71 kcal/mol. However, more recent ab initio calculations at the QCISD(T) level [6] show that the barrier for $\text{HCN} + \text{CO}$ formation is 2 kcal/mol higher than that for HNC formation; the reported activation barriers for $\text{HCN} + \text{CO}$ and $\text{HNC} + \text{CO}$ are 64 and 62 kcal/mol, which are close to the values obtained by us. Formation of HNC can also take place through a two-step mechanism: **7** \rightarrow **10** isomerization followed by 1,1 elimination of HNC . The barrier height for this elimination is 49 kcal/mol which compares well with the recent higher level ab initio calculation [6]. The position of the **TS10/8** is almost the same as that of **TS7/8** which clearly indicates that formation of HNC via the two-step mechanism can be competitive. It should be pointed out that HNC can arise with sufficient internal energy to isomerize promptly to the more stable isomer HCN . The activation barrier for $\text{HNC} \rightarrow \text{HCN}$ is calculated to be 30 kcal/mol, which is less than the energy it can acquire during its formation from $\text{C}_2\text{H} + \text{NO}$. It can be seen from Fig. 2 that $\text{HCO} + \text{CN}$, the other products of the $\text{C}_2\text{H} + \text{NO}$ reaction, can be formed either by direct dissociation of **7** or isomerization of **7** into **10** followed by its dissociation. The path **7** \rightarrow **11** followed by the dissociation of **11** into $\text{HCO} + \text{CN}$ is less likely due to the larger activation barrier for the **7** \rightarrow **11** step.

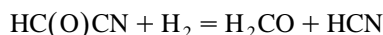
We now estimate the heats of reaction for various isomers involved in the $\text{C}_2\text{H} + \text{NO}$ reaction. To

Table 2

Heats of formation (in kcal/mol) of several $[\text{C}_2, \text{H}, \text{N}, \text{O}]$ isomers at 0 K

Molecule	ΔH_f°
ONCCH 2	120.5
ONCCH 3	95.8
ONCHC 4	134.6
ONCHC 5	134.4
HC(O)CN 7	14.4
HC(O)NC 10	26.4
HC–O–CN 11	93.2

calculate the heat of formation for formyl cyanide, **7**, we use the following isodesmic equation,



given the heats of formation at 0K of HCN , CH_2O and H_2 as 32.4, -25.0 and 0.0 kcal/mol, respectively [10], along with the heat of reaction of -7.0 kcal/mol calculated at the B3LYP/6-311++G(d,p) + ZPE level. This yields a heat of formation at 0K for formyl cyanide of 14.4 kcal/mol, which is in fair agreement with the reported value of 11.6 kcal/mol by Horwitz et al. [11] using the G2 method. The heats of formation of the other isomers were calculated using $\Delta H_f(\text{HC(O)CN})$ and the heats of reaction of the corresponding isomerization processes. The values obtained are shown in Table 2.

4. Conclusions

The potential energy surface, for the various reactions channels of the $\text{C}_2\text{H} + \text{NO}$ reaction system, has been explored via density functional theory using the B3LYP exchange correlation functional in conjunction with a 6-311++G(d,p) basis set. Calculations show that the formation of $\text{HC} \equiv \text{C}-\text{NO}$ **3**, and $\text{ON}-\text{CH}=\text{C}$ **4**, from the $\text{C}_2\text{H} + \text{NO}$ reaction are barrierless processes. The energetically most favourable reaction path is the formation of $\text{HCN} + \text{CO}$ via a four-membered cyclic structure **5** that is connected to **3** and **4** via transition structures lying below the $\text{C}_2\text{H} + \text{NO}$ level. However, at higher temperatures several other reaction pathways forming $\text{HCN} + \text{CO}$, $\text{HNC} + \text{CO}$ and $\text{HCO} + \text{CN}$ and involving the most stable $[\text{C}_2, \text{H}, \text{N}, \text{O}]$ isomer HC(O)CN **7**, also become accessible. The calculated PES and the

identified reaction paths are in full agreement with the conclusions from an experimental study [1] that the fast $C_2H + NO$ reaction is an association/fragmentation process.

Acknowledgements

We wish to thank the Fund for Scientific Research (FWO) and KU Leuven (GOA) for financial support and the Laboratory of Quantum Chemistry for providing us excellent computer facilities.

References

- [1] J. Peeters, H. Van Look, B. Ceursters, *J. Phys. Chem.* 100 (1996) 15124.
- [2] I.R. Sims, I.W.M. Smith, *J. Chem. Soc. Faraday Trans. 2* 84 (1988) 527.
- [3] I.R. Sims, I.W.M. Smith, *J. Chem. Soc. Faraday Trans. 2* 89 (1993) 1.
- [4] J. March, *Advanced Organic Chemistry*, Wiley, New York, 1985.
- [5] W. Lewis-Bevan, R.D. Gaston, J. Tyrell, W.D. Stork, G.L. Salmon, *J. Am. Chem. Soc.* 114 (1992) 1933.
- [6] N-Y. Chang, C-H. Yu, *Chem. Phys. Lett.* 242 (1995) 232.
- [7] W-H. Fang, R-Z. Liu, X-Z. You, *Chem. Phys. Lett.* 226 (1994) 453.
- [8] R. Flammang, Y.V. Haverbeke, S. Laurent, M.B. Flammang, M.W. Wong, C. Wentrup, *J. Phys. Chem.* 98 (1994) 5801.
- [9] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. DeFrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, *GAUSSIAN 94*, Revision C.3, Gaussian, Inc., Pittsburgh PA, 1995.
- [10] S.E. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.P. Levin, W.G. Mallard, *J. Phys. Chem. Ref. Data* 17 (1988) Suppl. 1.
- [11] R.J. Horwitz, J.S. Francisco, J.A. Guest, *J. Phys. Chem.* 101 (1997) 1231.