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Quantum chemical study of mechanisms of dissociation and isomerization reactions in some molecules and radicals of astrophysical significance: Cyanides and related molecules

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Abstract. A theoretical study of the mechanism of photodecomposition in carbonyl cyanide, diethynyl ketone, acetyl cyanide and formyl cyanide has been conducted using density functional and MP2 theories. A complete analysis of the electronic spectra of these molecules in terms of nature, energy and intensity of electronic transitions has been provided by time-dependent density functional theory. Mixing coefficients and main configurations of the electronic states have been used to identify the states leading to the photodecomposition process. While the Rydberg state ^{1}(n,3s) is involved in the dissociation of formyl cyanide and acetyl cyanide, the π^*_{CC}/π^*_{CN} states are involved in the case of carbonyl cyanide and diethynyl ketone. In all cases, however, stepwise decomposition process is preferred over the concerted reaction process. Based on potential energy curves for bond dissociation and the transition state and IRC studies, it is found that besides the direct dissociation of carbonyl cyanide, a photoisomerization process through a non-planar transition state may also occur resulting in the formation of a stable and planar isomer CNC(O)CN. A complete vibrational analysis of the higher energy isomer has been conducted and several new fundamental bands are predicted. Some of the earlier experimental results on the photodecomposition mechanism and energies of photofragments in carbonyl cyanide and acetyl cyanide have also been rationalized.

1. Introduction

Study of dissociation mechanism in molecules of the type AB_2 (where A and B may represent molecular or atomic species) has received considerable attention recently [1–7]. A few studies of this type have been reported for acetone $CO(CH_3)_2$ [2,3], azomethane $N_2(CH_3)_2$ [4,5] and halomethanes CF_2I_2 [6,7]. In a study of photodecomposition in a similar system, i.e. carbonyl cyanide $CO(CN)_2$ by photofragment

translational spectroscopy, Furlan *et al* [1] detected the presence of OCCN radical which further decomposed into CO and CN$^\bullet$. However, in a related study on acetyl cyanide [8], no OCCN radical could be detected. The prevalence of carbonyl and cyano compounds in the interstellar medium [9] also suggests the likelihood of molecules containing these groups to be of astrophysical importance. An attempt is, therefore, being made to understand at a theoretical level the mechanism of molecular dissociation and rearrangement in the short-lived carbonyl cyanide molecule and to correlate the photodecomposition process with its electronic, spectral and structural characteristics. Some of the experimental findings on the mechanisms and products of dissociation in carbonyl cyanide and acetyl cyanide are being rationalized from a theoretical point of view. Studies are also being reported on other short-lived molecules and molecular ions such as diethynyl ketone, acetyl cyanide, formyl cyanide and CH_3CO radical. An attempt is being made to identify the electronic states involved in the molecular dissociation processes and to find the possibilities of different transition states involved in dissociation or photoisomerisation processes. Calculations on energy, transition states, intrinsic reaction coordinates and electronic transitions in the molecules and ions are being used for the purpose.

2. Theoretical methods

Restricted and unrestricted density functional theory using B3LYP functionals and HF theory with second-order Moller-Plesset (MP2) corrections have been used in the present computations. Geometrical parameters were fully optimized using basis sets 6-311++G (2df,2p), 6-311+G* and 6-31G*, which were also used to compute electronic energies, harmonic vibrational frequencies and zero-point vibrational energies (ZPE). Geometry optimizations were carried out to better than 0.001 Å for bond lengths and 0.1° for bond angles with a self-consistent field convergence of at least 10^{-9} on the density matrix and with a residual r.m.s. force of less than 10^{-4} a.u. In order to understand bond dissociation mechanism, potential energy surface scans were conducted using unrestricted B3LYP/6-31G* and unrestricted MP2/6-31G* methods as the character of the wavefunction may change from a closed shell singlet to an open shell singlet along the reaction course. A search for the transition state structure was carried out by the STQN (QST2) procedure suggested by Peng *et al* [10]. The transition state was characterized by harmonic frequency analysis. Intrinsic reaction coordinate (IRC) studies were conducted by MP2 and DFT methods to analyze the reaction pathways from the transition states. Electronic transitions were calculated using time-dependent density functional (TD-DFT) theory with BLYP functionals and 6-311++G(2df,2p) basis set. All the calculations were performed using the computer software, Gaussian 98W [1].

3. Results and discussion

3.1 *Decomposition process*

The three-body photodecomposition event in a molecule may proceed either via sequential steps such as
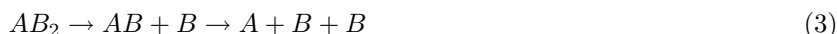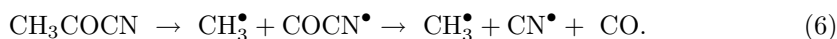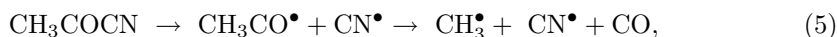
Dissociation mechanisms in molecules of the type AB_2

$$ABC + h\nu \rightarrow AB + C, \tag{1a}$$

$$AB + C \rightarrow A + B + C \tag{1b}$$

or by concerted reaction

$$ABC + h\nu \rightarrow A + B + C. \tag{2}$$

Accordingly, photodecomposition in molecules of the type AB_2 such as $CO(CN)_2$ and $CO(CCH)_2$ [A=CO, B=CN, CCH] may follow a sequential route

$$AB_2 \rightarrow AB + B \rightarrow A + B + B \tag{3}$$

or the concerted route

$$AB_2 \rightarrow A + B + B. \tag{4}$$

In the case of acetyl cyanide CH_3COCN [A=CH$_3$, B=CO, C=CN], the possible routes in accordance with the above equations are

$$CH_3COCN \;\rightarrow\; CH_3CO^\bullet + CN^\bullet \rightarrow\; CH_3^\bullet + \; CN^\bullet + CO, \tag{5}$$

$$CH_3COCN \;\rightarrow\; CH_3^\bullet + COCN^\bullet \rightarrow\; CH_3^\bullet + CN^\bullet + \; CO. \tag{6}$$

In the present study, the decomposition process is being analyzed from energy considerations as well as from potential energy curves.

In order to understand from energy considerations whether the photodecomposition follows a sequential or concerted process, the electronic energies ($E_{\text{elec.}}$), zero-point energies (ZPE) and total energies of the parent molecules, i.e. carbonyl cyanide $CO(CN)_2$, acetyl cyanide (CH_3COCN), formyl cyanide (HCOCN) and diethynyl ketone $CO(CCH)_2$ and their possible radicals such as $CN^\bullet$, $COCN^\bullet$, $CH_3CO^\bullet$, $CH_3^\bullet$, $COH^\bullet$, $COOCH^\bullet$ and $CCH^\bullet$ were obtained from restricted and unrestricted DFT theories in basis set 6-311++G(2df,2p). These are given in table 1. The table also contains energies for carbonyl cyanide, $COCN^\bullet$ and $CN^\bullet$ based on MP2 calculations as described above. Dissociation energies of these molecules and radicals after zero-point energy corrections together with the lengths of the C–CN/C–CCH bonds that break during the dissociation process are given in table 2.

It follows from tables 1 and 2 that stepwise decomposition of $CO(CN)_2$ into $COCN^\bullet + CN^\bullet$, in accordance with eq. (3), requires 97.2 kcal/mol of energy, after accounting for the zero-point energy corrections in B3LYP/6-311++G(2df,2p) calculations. Lower basis MP2/6-31G(d) calculations, however, predict a much higher value of 126.0 kcal/mol. After taking into account exit barrier for α-cleavage of about 13 kcal/mol [8], the dissociation energies should be about 110 kcal/mol (DFT) and 139 kcal/mol (MP2). Based on the photofragment translational spectroscopy, Furlan *et al* [1] suggested the upper limit for dissociation energy of carbonyl cyanide to be between 102.8 and 114.8 kcal/mol. Our B3LYP/6-311++G(2df,2p) value of about 110 kcal/mol therefore, agrees with the

Table 1. Electronic, zero-point and total energies of carbonyl cyanide and related molecules and radicals in B3LYP/6-311++G(2df,2p) and MP2/6-31G*.

Molecule	$E_{\text{elect.}}$ (kcal/mol)	ZPE (kcal/mol)	E_{total} (kcal/mol)
$CO(CN)_2$	−187722.8	15.9	−187706.9
$CO(CN)_2$ (MP2)	−187159.9	15.2	−187144.6
$COCN^{\bullet}$	−129406.2	8.7	−129397.6
$COCN^{\bullet}$ (MP2)	−129012.1	10.3	−129001.7
CO	−71152.8	3.2	−71149.6
$CN^{\bullet}$	−58215.2	3.1	−58212.1
$CN^{\bullet}$ (MP2)	−58020.9	4.1	−58016.8
CH_3COCN	−154511.0	34.1	−154476.9
$CH_3CO^{\bullet}$	−96189.0	27.0	−96162.0
$CH_3^{\bullet}$	−25018.8	18.6	−25000.1
HCOCN	−129815.2	16.6	−129800.5
$COH^{\bullet}$	−71493.3	8.1	−71485.1
$CO(CCH)_2$	−167525.4	29.4	−167496.0
$COCCH^{\bullet}$	−119309.2	15.0	−119294.2
$CCH^{\bullet}$	−48104.2	8.8	−48095.4

Table 2. C–CN/C–CCH bond lengths and dissociation energies of carbonyl cyanide and related molecules and radicals in DFT/6-311++G(2df,2p) and MP2/6-31G* after including ZPE corrections.

Molecule	Bond length		Dissociation energy (kcal/mol) (eq. (3))	Literature (kcal/mol)
	Calc.	Expt.		
$CO(CN)_2$	1.4623 (DFT)	–	97.2 (DFT)	108.8 ± 6.0^a
	1.4691 (MP2)		126.0 (MP2)	
CH_3COCN	1.4816	1.483^b	$79.2^{\dagger}$ (DFT)	101.9^b
		1.477 ± 0.008^c	102.8^* (DFT)	104.9^e
HCOCN	1.4687	1.473^b	102.9 (DFT)	102.9^b,
				118.7^d
$CO(C{\equiv}CH)_2$	1.4479	1.453 $^{\#}$	106.4 (DFT)	–
$CH_3CO^{\bullet}$	–	–	12.2 (DFT)	–
$COCN^{\bullet}$	–	–	35.8 (DFT)	$\sim 30.1^a$
$COCCH^{\bullet}$	–	–	49.1 (DFT)	$\sim 35.9^b$

^{a}Estimated upper limit, ref. [1]; ^{b}ref. [8]; ^{c}ref. [10]; ^{d}ref. [12]; ^{e}ref. [18]. *Reaction path $CH_3COCN \rightarrow CH_3CO^{\bullet} + CN^{\bullet}$; †reaction path $CH_3COCN \rightarrow CH_3^{\bullet} + COCN^{\bullet}$; $^{\#}$in propynal (HCOCCH), ref. [13].

experimental value suggested by Furlan *et al* [1] and supports a step-wise dissociation mechanism for the molecule. In contrast, the concerted mechanism (eq. (4)) requires at least 133.0 kcal/mol energy. Further, the calculated value of the

dissociation energy for COCN$^\bullet$ → CO + CN$^\bullet$ is found to be 35.8 kcal/mol (DFT) (table 2) which is close to the estimated experimental value of 35.9 kcal/mol [1]. Horwitz *et al* [8], however, reported a much lower value of 30.1 kcal/mol from RHF *ab initio* calculations using G2 theory.

Present calculations further tend to rationalize some of the findings of Furlan *et al* [1] on photodecomposition in CO(CN)$_2$ and Horwitz *et al* [8] in CH$_3$COCN by 193 nm radiation. Since the photon energy of 193 nm radiation is 148.2 kcal/mol, the available energy in photodecomposition experiment of Furlan *et al* [1] in a sequential reaction is 51.0 kcal/mol. This available energy is significantly higher than the bond dissociation energy of 35.8 kcal/mol for COCN$^\bullet$ → CO + CN$^\bullet$ and may, therefore, give rise to the secondary dissociation process observed by them leading to the formation of the CN radical.

In the case of acetyl cyanide, the photodissociation process may follow either eq. (5) or eq. (6). It follows from table 2 that the photodecomposition of acetyl cyanide to CH$_3^\bullet$ + OCCN$^\bullet$ (eq. (6)) requires only 79.2 kcal/mol of energy as against 102.8 kcal/mol required for dissociation to CH$_3$CO$^\bullet$ + CN$^\bullet$ (eq. (5)). Thus the pathway through decomposition to the OCCN$^\bullet$ radical may be preferred over the one through the CN$^\bullet$ radical (eq. (5)). Even after discounting for a 13 kcal/mol exit barrier for α-cleavage of simple first row gas phase carbonyls [8], photoirradiation through a 193 nm (148.2 kcal/mol) radiation may thus cause the cleavage of acetyl cyanide into CH$_3^\bullet$ + COCN$^\bullet$ with available energy ($E_{\text{avl.}}$) of 56.0 kcal/mol which is sufficient to further decompose the COCN$^\bullet$ radical into CO + CN$^\bullet$ requiring only 35.8 kcal/mol energy. Photodecomposition in acetyl cyanide may then follow a sequential pathway. In contrast, based on *ab initio* calculations, Horwitz *et al* [8] suggested that photo-dissociation path is primarily through the formation of CH$_3$CO and CN radicals with dissociation energy of 101.9 kcal/mol, followed by decomposition of the acetyl radical into CH$_3^\bullet$ and CO. This proposition is not supported by our results. Horwitz *et al* [8], however, do not exclude the possibility of an alternative α-cleavage pathway to CH$_3^\bullet$ + COCN$^\bullet$ as a possible source of COCN radical. Similarly, the non-detection of COCN$^\bullet$ in the photodecomposition of acetyl cyanide, as against carbonyl cyanide where it is present in upto 75% concentration, may be explained by the fact that the available energy of this radical in acetyl cyanide is 68.9 kcal/mol in contrast to 51.0 kcal/mol in carbonyl cyanide. The higher available energy of the COCN$^\bullet$ radical facilitates its decomposition into CO and CN$^\bullet$ radical.

Owing to structural similarities in carbonyl cyanide and diethynyl ketone, which are isoelectronic, it is expected that the dissociation processes in the two molecules may also be similar. It follows from tables 1 and 2 that an energy of 106.4 kcal/mol is required to dissociate diethynyl ketone into COCCH and CCH radicals. This value is close to the dissociation energy of carbonyl cyanide (97.2 kcal/mol). No experimental data is, however, available for diethynyl ketone. An energy of 49.1 kcal/mol is required to further dissociate the COCCH radical into CO + CCH$^\bullet$. This energy is much higher than that required for similar decomposition of the COCN radical. On photodecomposition of diethynyl ketone by 193 nm radiation, COCCH radical may have an available energy of 28.8 kcal/mol, after discounting for the exit barrier of about 13 kcal/mol for α-cleavage [8]. Since this energy is much less than the dissociation energy, a further decomposition of the COCCH

radical is not expected.

3.2 *Potential energy curve for bond dissociation in carbonyl cyanide*

In order to understand C–CN bond rupture process in carbonyl cyanide, potential energy surface scans were performed by UMP2/6-31G* and UB3LYP/6-31G* methods by increasing the C–CN bond length from 1.10 to 3.90 Å in intervals of 0.01 Å. A plot of bond distance versus relative energy with respect to the energy minima in the two cases is given in figure 1. Both the methods give almost identical curves, particularly near the equilibrium position. Total energies at equilibrium in DFT and MP2 calculations are found to be -187657.7 and -187159.9 kcal/mol, respectively (figure 1). In the DFT curve the dissociation process starts at C–CN bond length of 3.8355 Å whereas in MP2 it starts at a bond length of 3.8400 Å. Total energies at these points in DFT and MP2 calculations are found to be -187544.1 and -187037.9 kcal/mol, respectively, and give an estimate of dissociation energy in the two cases to be 113.5 kcal/mol and 122.0 kcal/mol, respectively. These values are close to the experimental value which is 108.8 ± 6.0 kcal/mol [1]. However, it may be mentioned that although the potential energy curves are effective in finding
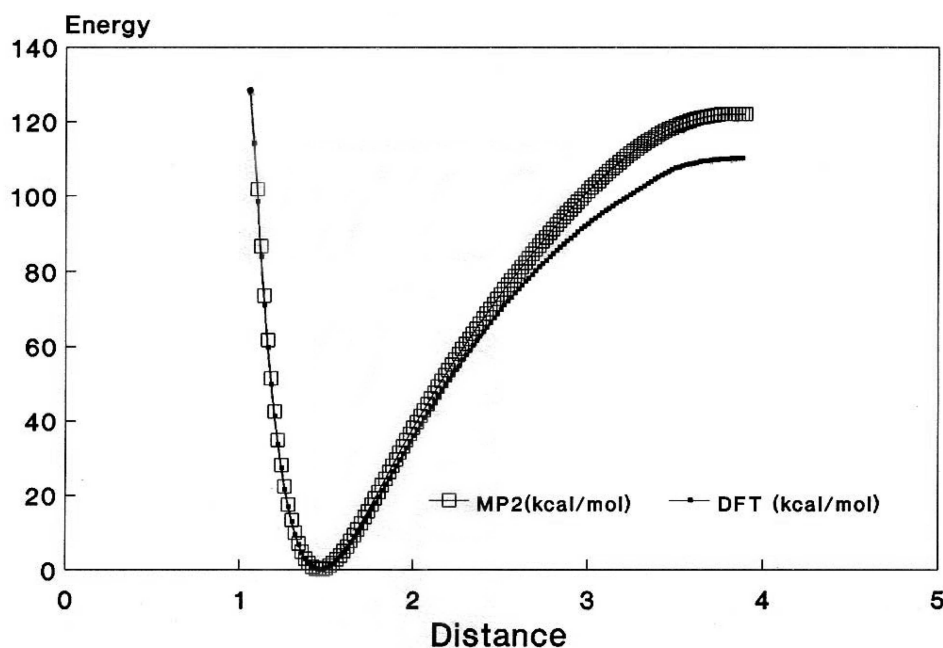

Figure 1. Potential energy curves for C–CN bond dissociation in B3LYP/6-31G* (-•-) and MP2/6-31G* (-□-) in carbonyl cyanide. The abscissa is the C–CN bond length in Å and ordinates are energies in kcal/mol relative to the energy minima which are -187159.9 and -187657.7 kcal/mol in MP2 and DFT, respectively.
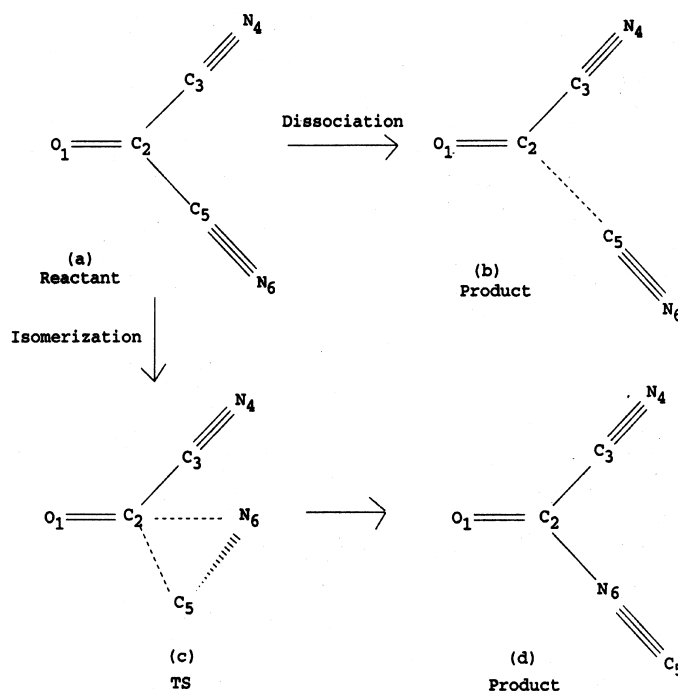
Figure 2. Molecular geometries at main points on dissociation and isomerization pathways of carbonyl cyanide. (**a**) Reactant, (**b**) dissociation product, (**c**) transition state (TS) in photoisomerization and (**d**) isomerization product (CN–C(O)–CN).

the trend of a process, they provide only an estimate of the dissociation energies. More accurate values are obtained from single point energy calculations using larger basis sets and zero-point vibrational energy corrections. These are listed in table 2.

The molecular geometries of the reactant (carbonyl cyanide) and the dissociation product (figure 2), as obtained from MP2/6-31G* and B3LYP/6-31G* calculations are given in table 3. It may be seen from this table that at the point of dissociation the C$_2$–C$_5$ bond length is 3.8400 Å in MP2 and 3.8355 Å in DFT. An increase in the C–CN bond length, which ultimately results in molecular dissociation causes an increase in the C=O bond length. Further, the bond angle CCN decreases from 180° (MP2) in carbonyl cyanide to about 171.34° (MP2) in the COCN group of the product. Also, the angle C$_2$C$_5$N$_6$ decreases from 180° to 178.79° (MP2) in the dissociation product thereby removing linearity of the C–C and C–N bonds in the reactant.

It follows from table 2 that an inverse relationship exists between the C–CN/ C–CCH bond lengths and the dissociation energies, as obtained from eq. (3), in diethynyl ketone, carbonyl cyanide and acetyl cyanide. Thus, for bond lengths 1.4479, 1.4623 and 1.4816 Å of the C–CN/C–CCH bonds, the dissociation energies in these molecules are 106.4, 97.2 and 79.2 kcal/mol, respectively. A similar relationship was suggested by Horwitz *et al* [8] in formyl cyanide and acetyl cyanide

V P Gupta and Archna Sharma

which is confirmed in table 2.

Table 3. Molecular geometries of reactants, transition state and products of carbonyl cyanide in dissociation and isomerization processes.

Coordinate	CO(CN)₂ Reactant MP2/6-31G*	DFT/6-31G*	COCN+CN Dissociation product MP2/6-31G*	DFT/6-31G*	CO(CN)₂ Reactant MP2/6-31G*	DFT/6-311+G*	COCN–CN TS MP2/6-31G*	DFT/6-311+G*	CNC(O)CN Isomerization product MP2/6-31G*	DFT/6-311+G*
$R(O_1C_2)$	1.2234	1.2091	1.2452	1.2333	1.2234	1.2016	1.1949	1.1735	1.2120	1.1944
$R(C_2C_3)$	1.4639	1.4655	1.4641	1.4478	1.4639	1.4634	1.4484	1.4410	1.4614	1.4609
$R(C_2C_5)$	1.4639	1.4655	3.8400	3.8355	1.4639	1.4634	1.7570	1.8132	2.5974	2.5755
$R(C_2N_6)$	–	–	–	–	–	–	1.7778	1.8041	1.4003	1.3950
$R(C_3N_4)$	1.1840	1.1616	1.1921	1.1804	1.1840	1.1533	1.1838	1.1531	1.1832	1.1528
$R(C_5N_6)$	1.1840	1.1616	1.2018	1.1962	1.1840	1.1533	1.2071	1.1875	1.1972	1.1805
$A(O_1C_2C_3)$	122.51	122.67	118.50	122.79	122.51	122.70	127.39	128.15	123.69	123.28
$A(C_2C_3N_4)$	180.00	179.97	171.34	176.18	180.00	179.36	178.26	178.94	177.41	177.83
$A(C_2C_5N_6)$	180.00	179.97	178.81	178.69	180.00	179.36	70.96	70.42	–	–
$A(C_2N_6C_5)$	–	–	–	–	–	–	69.11	71.25	178.84	178.82
$A(O_1C_2C_5)$	122.51	122.68	113.81	109.56	122.51	122.70	120.80	120.31	–	–
$A(O_1C_2N_6)$	–								123.39	123.63
$D(O_1C_2C_3N_4)$	0.0	0.0	−179.96	0.0	0.0	0.0	2.84	11.92	0.0	0.0
$D(O_1C_2C_5N_6)$	0.0	0.0	0.0	180.0	0.0	0.0	99.79	99.55	–	–
$D(O_1C_2N_6C_5)$	–	–	–	–	–	–	−104.36	−103.25	0.0	0.0

3.3 *Isomerization studies in carbonyl cyanide*

A search for transition state structures using STQN(QST2) procedure in MP2/6-31G* and B3LYP/6-311+G* calculations in carbonyl cyanide shows that, besides the molecular dissociation process, there is also the possibility of a photoisomerization process through a non-planar transition state (TS). This is shown diagrammatically in figure 2. Intrinsic reaction coordinate (IRC) calculations starting from the above non-planar transition state lead to a planar and stable isomeric structure CNC(O)CN having total energy of -187140.4 kcal/mol in MP2/6-31G* and -187698.7 kcal/mol in B3LYP/6-311+G*. The energies of the reactant, transition state and the product from the above two methods are given in table 4. Thus, the activation barrier for the isomerization process is 53.6 kcal/mol in MP2 and 47.8 kcal/mol in DFT. A similar isomerization process has been reported by So [21] in acetyl cyanide from G2 theory with an activation barrier of 40.8 kcal/mol. The calculated values of the enthalpy difference between the higher energy isomer CNC(O)CN and the lower energy isomer NCC(O)CN in MP2/6-31G* and B3LYP/6-311+G* are 19.5 and 13.4 kcal/mol, respectively. Further, it follows from table 3 that a planar reactant $CO(CN)_2$ with C_{2v} symmetry gets transformed into another planar structure CNC(O)CN through a non-planar transition state in which the dihedral angle $O_1C_2C_5N_6$ is about 100°. The bond lengths C_2N_6 and C_5N_6 in the higher energy isomer are 1.4003 Å and 1.1972 Å in MP2 and 1.3950 Å and 1.1805 Å in DFT calculations and show that these bonds have an almost single-bond and triple-bond character. While the atoms C_2, C_3, N_4 and C_2, C_5, N_6 are collinear in carbonyl cyanide, the deviation from co-linearity in CNC(O)CN is about 2°.

3.4 *Vibrational assignments of the higher energy isomer*

In order to ascertain the stability of the higher energy isomer CNC(O)CN, frequency calculations were conducted by MP2/6-31G* and B3LYP/6-311+G* methods. It is

Table 4. Energy of carbonyl cyanide at main points on isomerization pathway.

Molecule	Method	Energy (kcal/mol)
Reactant	MP2/6-31G*	-187159.9
$CO(CN)_2$	B3LYP/6-311+G*	-187712.1
Transition state (TS)	MP2/6-31G*	-187106.3
	B3LYP/6-311+G*	-187664.3
Product	MP2/6-31G*	-187140.4
CNC(O)CN	B3LYP/6-311+G*	-187698.7
Activation energy	MP2/6-31G*	53.6
	B3LYP/6-311+G*	47.8
Enthalpy difference	MP2/6-31G*	19.5
(product–reactant)	B3LYP/6-311+G*	13.4

found that all the calculated frequencies are real and hence confirm its stability. The fundamental IR frequencies, intensities and assignments of carbonyl cyanide and its higher energy isomer along with the experimental frequencies of carbonyl cyanide reported by Miller *et al* [22] are given in table 5. Our assignments for carbonyl cyanide based on MP2 and DFT methods agree with those of Miller *et al* [22]. The replacement of one of the two CN bonds of carbonyl cyanide by an NC bond in the higher energy isomer CNC(O)CN changes the frequencies of some of the CN stretch and CCN deformation modes. Thus, instead of two close absorption bands at 2172 (22.31) and 2178 (133.85) cm^{-1}, in carbonyl cyanide, the MP2 calculations predict bands at 2189 (58.95) and 2123 (380.0) cm^{-1} in CNC(O)CN; the latter band corresponds to the isocyanide (NC) stretch mode. Also, the CNC(O)CN bands at 177 (8.74) and 218 (6.42) in MP2 may be assigned to the CNC out-of-plane and in-plane bending modes, respectively. The carbonyl stretch band in this isomer is predicted at a higher frequency of about 1772 (133.4) cm^{-1} as against 1700 (84.24) cm^{-1} in carbonyl cyanide. The higher frequency shift of this band correlates well with a lower value of 1.2120 Å of the C=O bond length in CNC(O)CN as compared to 1.2234 Å in carbonyl cyanide.

3.5 *Electronic transitions*

In order to understand the nature of electronic transitions in terms of their energies and oscillator strengths, *ab initio* calculations were performed on carbonyl cyanide, diethynyl ketone, acetonitrile and formyl cyanide by time-dependent density functional theory (TD-DFT) using BLYP functionals and 6-311++G(2df,2p) basis sets. These calculations are particularly useful in understanding and rationalizing some of the experimental findings about the photodissociation processes in acetyl cyanide [8,24] and carbonyl cyanide [1] for which experimental results are available. Such a study does not seem to exist in the literature. Configuration interaction between the singly excited states was considered and spectral assignments of transitions in the 3–8 eV range are made on the basis of mixing coefficients and molecular orbital coefficients of the involved electronic states. These are given in table 6.

It may be seen that the first virtual orbital in all the four molecules is primarily π_{CO}^* with smaller contributions by π_{CN}^*/π_{CC}^* in the case of carbonyl cyanide/diethynyl ketone. Thus, the lowest weak electronic transition at 365.2, 379.9, 340.1 and 349.2 nm in the case of carbonyl cyanide, diethynyl ketone, acetyl cyanide and formyl cyanide may be assigned to the forbidden n-π^* transition involving promotion of the lone pair of electrons to the π_{CO}^* orbital with a small perturbation by π_{CN}^* and π_{CC}^* in the case of carbonyl cyanide and diethynyl ketone, respectively. Judge *et al* [14] reported a weak band system in the 358–385 nm range in case of formyl cyanide and Furlan *et al* [1] reported a weak band near 340 nm in carbonyl cyanide. The assignment of these bands to n-π^* transitions is confirmed by the present calculations. Further, three strong transitions having oscillator strengths between 0.022 and 0.11 have been predicted in the 220–250 nm range in all the molecules. Two of these have been assigned to π-π^* transitions involving carbonyl and nitrile groups (table 6).

Table 5. Fundamental IR frequencies (in cm^{-1}) of carbonyl cyanide (NCC(O)CN) and its stable isomer (CNC(O)CN) calculated at MP2/6-31G* and B3LYP/6-311+G* levels. Figures in parenthesis correspond to intensities in KM/Mol.

S.No.	$\nu_{expt.}$	Symmetry	NCC(O)CN $\nu_{calculated}$			CNCOCN $\nu_{calculated}$		
			MP2/6-31G*	DFT/6-311+G*	Assignments	MP2/6-31G*	DFT/6-311+G*	Assignments
ν_1	2230(vs)	a_1	2172(22.31)	2341(10.90)	C≡N str.	2189(58.95)	2349(41.42)	C≡N str.
ν_2	1711(vs)	a_1	1700(84.24)	1761(177.41)	C=O str.	1772(133.4)	1800(281.62)	C=O str.
ν_3	712(s)	a_1	724(5.79)	728(3.84)	C–C str.	754(16.5)	756(14.55)	C–C/C–N str.
ν_4	553(m)	a_1	574(1.37)	594(6.37)	CCC Sc.	575(0.15)	595(1.09)	CNC/CCN i.p. bend
ν_5	127.5(s)	a_1	122(5.38)	133(5.29)	NCC bend	120(3.14)	125(2.34)	CCN/CNC i.p. bend
ν_6	307(w)	a_2	314(0.0)	319(0.0)	NCC bend	177(8.74)	174(8.22)	CNC o.p. bend
ν_7	712(s)	b_1	731(6.59)	753(8.13)	C=O wag	729(18.3)	748(20.10)	C=O wag
ν_8	208.2(s)	a_1	213(26.81)	222(29.45)	NCC bend	281(10.80)	284(11.38)	CCN o.p. bend
ν_9	2230(vs)	b_2	2178(133.85)	2237(91.91)	C≡N str.	2123(380.0)	2146(555.88)	N≡C str.
ν_{10}	1102(vs)	b_2	1154(210.71)	1111(239.07)	C–C str.	1157(334.25)	1129(360.31)	C–N/C–C str.
ν_{11}	≈550	b_2	548(2.36)	558(0.21)	C=O wag	548(8.12)	550(6.27)	C=O i.p. wag
ν_{12}	245.2(s)	b_2	238(9.93)	260(15.62)	NCC bend	218(6.42)	232(8.34)	CNC/NCC i.p. bend

Table 6. Calculated transition energies, oscillator strengths and assignments along with main configurations and mixing coefficients for singlet ground and excited states using TD-DFT/6-311++G(2df,2p).

	Symmetry	Assignment	Transition energy eV	Transition energy nm	Oscillator strength ($f \times 10^{-4}$)	Mixing coefficients and main configurations[a]
CO(CN)$_2$						
Ground state						
$E = -299.064512$[b]	$^1A_1$					1.000[22222/00000]
	X^{1}A$_2$	n_O–π^*_{CO}, π^*_{CN}	3.3946	365.2[c]	(0.0)	0.686[22221/10000]
	X^{1}B$_1$	π_{CN}–π^*_{CN}	4.9216	251.9	(19.0)	0.664[12222/10000]
	X^{1}B$_2$	π_{CN}–π^*_{CO}	5.3224	232.9[d]	(945.0)	0.635[21222/10000]
	X^{1}A$_1$	π_{CN}–$\pi^*_{CO,CN}$	5.6472	219.5	(706.0)	0.600[22122/10000]
	X^{1}B$_2$	n_O–3S$_O$, π^*_{CN}	5.9655	207.8	(230.0)	0.684[22221/01000]
	X^{1}B$_1$	n_O–π^*_{CN}	7.0713	175.3	(3.0)	0.700[22221/00100]
CO(C≡CH)$_2$						
Ground state						
$E = -266.887671$	$^1A_1$					1.000[22222/00000]
	X^{1}A$_2$	n_O–π^*_{CO}, π^*_{CC}	3.2635	379.9	(0.0)	0.688[22221/10000]
	X^{1}B$_1$	π_{CC}–π^*_{CC}	4.4710	277.3	(1.0)	0.704[12222/10000]
	X^{1}B$_2$	π_{CC}–π^*_{CO}	4.7338	261.9	(1098.0)	0.621[21222/10000]
	X^{1}A$_1$	π_{CC}–π^*_{CC}	5.1454	240.9	(668.0)	0.596[22122/10000]
	X^{1}B$_2$	n_O–3S$_O$, π^*_{CC}	5.4722	226.6	(508.0)	0.654[22221/01000]
	X^{1}B$_2$	n_O–π^*_{CC}	6.1694	200.9	(32.0)	0.701[22221/00010]
CH$_3$COCN						
Ground state						
$E = -246.154290$	$^1A'$					1.000[22222/00000]
	X^{1}A″	n_O–π^*_{CO}	3.6456	340.1	(4.0)	0.688[22221/10000]
	X^{1}A″	π_{CN}–π^*_{CO}	5.3033	233.8	(1.0)	0.703[22212/10000]
	X^{1}A′	π_{CN}–π^*_{CO}	5.9816	207.3	(392.0)	0.482[22122/10000] −0.456[22221/01000]
	X^{1}A′	n_O–3S$_O$	6.2593	198.1	(220.0)	0.638[22221/00100]
	X^{1}A′	n_O–π^*_{CN}	6.3994	193.7	(397.0)	0.428[22221/01000]
	X^{1}A″	n_O–σ^*_{CN}	7.1291	173.9	(22.0)	0.631[22221/00010]
HCOCN						
Ground state						
$E = -206.810947$	$^1A'$					1.000[22222/00000]
	X^{1}A″	n_O–π^*_{CO}	3.5504	349.2[e]	(5.0)	0.686[22221/10000]
	X^{1}A″	π_{CN}–π^*_{CO}	5.2060	238.1	(0.0)	0.703[22212/10000]
	X^{1}A′	π_{CN}–π^*_{CO}	6.0849	203.7	(661.0)	0.494[22122/10000] −0.423[22221/01000]
	X^{1}A′	n_O–3S$_O$	6.2831	197.3	(461.0)	0.554[22221/01000] 0.342[22122/10000]
	X^{1}A′	n_O–π^*_{CN}	6.8674	180.5	(286.0)	0.704[22221/00100]
	X^{1}A′	n_O–σ^*_{CN}	7.8612	157.7	(242.0)	0.702[22221/00010]

[a]Five higher energy occupied orbitals and five lower energy unoccupied orbitals have been listed; [b]energy in a.u.; [c]experimental value ∼340 nm (ref. [1]); [d]experimental value 230 nm (ref. [1]); [e]experimental range 358–385 (ref. [14]).

The calculated absorption bands at 207.8 (0.0230), 226.6 (0.0508), 198.1 (0.0220) and 197.3 (0.0461) nm (table 6) in carbonyl cyanide, diethynyl ketone, acetyl cyanide and formyl cyanide, respectively, may be assigned to Rydberg transitions ^{1}(n,3s) in the oxygen atom. The numbers in brackets show oscillator strength. In the case of carbonyl cyanide and diethynyl ketone, however, these have perturbations from transitions to π^*_{CN} and π^*_{CC} states. Our assignments to these bands as being primarily the Rydberg transitions are in conformity with those of Robin [15]

and Donaldson *et al* [16] in similar carbonyl compounds. These authors, however, suggested that molecules excited to these Rydberg states subsequently predissociate from a lower electronic surface. While these findings may be true for acetyl cyanide, as suggested by Horwitz *et al* [8] also in the case of carbonyl cyanide and diethynyl ketone a transfer to a lower energy π^*_{CN}/π^*_{CC} level is also possible due to appreciable interaction between the $3S_O$ and π^*_{CN}/π^*_{CC} states as suggested by their molecular orbital coefficients.

Furlan *et al* [1], have interpreted their data on photodissociation in carbonyl cyanide using photofragment translational energy spectroscopy on the premise that a band at 230 nm in the molecule corresponds to the Rydberg transition. However, based on the present calculations this band may be correlated with the strongest band in the spectrum at 232.9 (0.0945) nm and assigned to a π-π^* transition (table 6). The Rydberg transition in carbonyl cyanide is predicted as a strong band at 207.8 (0.0230) nm, which is close to similar strong transitions in acetyl cyanide (198.1 nm) and formyl cyanide (197.3 nm).

4. Conclusions

Energy analysis and transition state, IRC (intrinsic reaction coordinates) and electronic transition studies based on high level *ab initio* calculations rationalize some of the experimental findings of Furlan *et al* [1] and Horwitz *et al* [8] on photodecomposition mechanism and energies of photofragments in carbonyl cyanide and acetyl cyanide. Stepwise decomposition with 193 nm radiation takes precedence over the concerted reaction mechanism in carbonyl cyanide, diethynyl ketone and acetyl cyanide. Photodecomposition of acetyl cyanide to $CH_3^\bullet + COCN^\bullet$, even after discounting for the exit barrier for α-cleavage, requires lesser energy than that needed for its dissociation to $CH_3CO^\bullet + CN^\bullet$. Thus the pathway through decomposition to the $COCN^\bullet$ radical may be preferred over the one through $CN^\bullet$ radical. The higher available energy of the $COCN^\bullet$ radical in acetyl cyanide (and hence a greater probability for its further decomposition) than in carbonyl cyanide may explain its non-detection during the dissociation of this molecule. This is in contrast to the latter molecule where it is found in 75% concentration. It may also be suggested that further decomposition of $COCCH^\bullet$ radical in diethynyl ketone into CO and $CCH^\bullet$ may not be possible from energy considerations. Quantum chemical calculations in carbonyl cyanide, diethynyl ketone, acetyl cyanide and formyl cyanide have provided complete assignment to the electronic transitions in terms of frequency, oscillator strength, mixing coefficients and main configurations of the involved electronic states. These are helpful in identifying the electronic states that lead to the decomposition process. Calculations suggest a strong interaction between the Rydberg state ^{1}(n,3S) and the π^*_{CN} and π^*_{CC} states of carbonyl cyanide and diethynyl ketones, respectively, resulting in molecular dissociation from the π^*_{CN}/π^*_{CC} states. In formyl cyanide and acetyl cyanide, however, the dissociation process involves the Rydberg state ^{1}(n,3S). DFT- and MP2-based potential curves and transition state, and IRC studies suggest that, in addition to the direct photodecomposition process in carbonyl cyanide, a photoisomerization process through a non-planar transition state may also occur. This may result in the formation of a stable planar isomer CNC(O)CN. Indications for the existence of such a non-planar

transition state have been reported [23] from FT-IR matrix isolation spectroscopy. Calculated optimized geometry and harmonic frequencies confirm that CNC(O)CN is a stable molecule with appropriate cyanide and isocyanide group bond lengths and frequencies. A comparison of the vibrational spectra of carbonyl cyanide and its higher energy isomer having the isocyanide linkage, predict a strong absorption band due to N≡C stretch at 2123 cm^{-1} and weak bands due to CNC in-plane and out-of-plane deformation modes at 218 and 177 cm^{-1}, respectively.

Acknowledgements

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