Theoretical analysis of thermal isomerisation barrier of isocyanides into cyanides : A semiempirical approach

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Abstract : AM1 semiempirical calculations for reactions have been performed and the effect of different substituents on thermal isomerisation barrier has been studied. As AM1 semiempirical calculations need much less time as compared to ab initio calculations, they have been employed to study the thermal rearrangement of five aliphatic and seven aromatic isocyanide → cyanides. Variation in activation energy of isocyanide → cyanides has been explained on the basis of electron releasing or electron withdrawing effect of different substituent, present in the molecule.

Keywords : AM1 calculations, isocyanide → cyanide isomerisation, transition state, substituent effect.
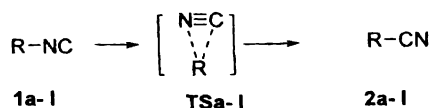
Introduction

During recent years the synthetic results have been supported by theoretical calculations, which have proven to be quite useful in predicting and understanding the structure and reactivity of various organic compounds[1-3].

Cyanides and isocyanides have widely been used as important precursors for the synthesis of carboxylic acids[4] as well as primary and secondary amines[5]. Cyanides are also well known as ligating agent[6,7] with various transitional and inner transitional metals. Isocyanide-cyanide isomerisation reactions are thermal rearrangement processes and no catalyst is required for these isomerisation reactions. Therefore the isomerisation of methyl and some other simple isocyanides proved to be excellent model reactions for testing kinetic theories of unimolecular gas phase reactions[8], thermal explosions[9,10] and vibrational energy transfer[11-13]. Survey of the literature reveals that though few isocyanide-cyanide thermal isomerisation reactions have been studied computationally using MNDO/2[14] and ab initio[15,16] methods, the effect of substituents on activation energy of isocyanide-cyanide thermal rearrangement has not been explored. Rabinovitch[17,18] experimentally studied the isocyanide → cyanide thermal isomerisation and found that for thermal rearrangement of simplest isocyanide i.e. methyl isocyanide into methyl cyanide, the temperature as high as 523-533 K is required. Although, the CN bond is more stable as compared to NC bond, the requirement of high temperature for thermal isomerisation and low yield of cyanides clearly indicates to a high energy barrier to break the C–NC bond. Therefore, to have a deep insight of the substitution effect on thermal isomerisation barrier of isocyanide-cyanide rearrangement, we carried out the present computational study. Affordable computational time required to perfom semiempirical calculations as compared to ab initio ones tempted us to perfom AM1 semiempirical study of five representative aliphatic and seven aromatic isocyanide-cyanide rearrangement reactions.

Results and discussion

In order to understand the electronic structures of cyanides, isocyanide and their corresponding transition states, AM1 semiempirical calculations of different aliphatic and aromatic isocyanides (1), cyanides (2) and their corresponding transition states (TS) (Scheme 1) have been carried out and their heat of formation (ΔH_f), zero point enegy (ZPE), total energy (E), relative energy (E_{rel}), core-core repulsion, ionization potential (IP) and dipole moment (μ), etc. have been determined. Energy barrier for each rearrangement reaction has been calculated from the heat of formation of isocyanide, cyanide and the corresponding transition state. The values thus obtained for total 36 systems are presented in Table 1.

$$R-NC \longrightarrow \left[\begin{array}{c} N\equiv C \\ \diagdown \diagup \\ R \end{array} \right] \longrightarrow R-CN$$

1a- l　　　　　**TSa- l**　　　　　**2a- l**

Scheme 1. Theoretically investigated isomerisation reaction (values of a-l given in Table 1).

Under present investigation, the activation energy for a variety of aliphatic and aromatic isocyanide-cyanide thermal rearrangements has been calculated using AM1 semi-empirical calculations. Experimentally obtained activation energy for $CH_3NC \rightarrow CH_3CN$ thermal isomerisation reac-

Table 1. Total energies (kcal/mol) and relative energies (kcal/mol) of isocyanides (**1**), cyanides (**2**) and the corresponding transition states (TS)

Molecular species	R/Ar	$\Delta H_f{}^a$	ZPE[b]	Total energy[c]	Relative energy[d]
1a	CH_3	50.38	28.32	78.70	0
TSa	CH_3	133.46	24.97	158.43	79.72
2a	CH_3	19.28	28.79	48.59	30.11
1b	C_2H_5	44.50	46.6	91.10	0
TSb	C_2H_5	125.29	42.92	168.21	77.11
2b	C_2H_5	13.02	48.05	60.07	31.03
1c	$(CH_3)_2CH$	42.43	64.22	106.65	0
TSc	$(CH_3)_2CH$	119.79	60.57	180.36	73.71
2c	$(CH_3)_2CH$	8.47	64.87	73.34	33.31
1d	$CH_3CH_2CH_2$	37.87	64.79	102.66	0
TSd	$CH_3CH_2CH_2$	119.06	61.04	180.10	77.44
2d	$CH_3CH_2CH_2$	6.74	65.11	71.85	30.81
1e	$(CH_3)_2CHCH_2$	33.08	82.57	115.65	0
TSe	$(CH_3)_2CHCH_2$	14.94	78.92	193.86	78.20
2e	$(CH_3)_2CHCH_2$	2.35	82.91	85.26	30.39
1f	C_6H_5	83.57	63.75	147.32	0
TSf	C_6H_5	160.85	61.75	224.6	77.28
2f	C_6H_5	53.38	64.20	117.58	29.73
1g	$p\text{-}CH_3C_6H_4$	75.83	81.02	156.85	0
TSg	$p\text{-}CH_3C_6H_4$	152.78	78.12	230.90	74.05
2g	$p\text{-}CH_3C_6H_4$	45.55	81.51	127.06	29.79
1h	$p\text{-}H_2NC_6H_4$	81.73	74.63	156.36	0
TSh	$p\text{-}H_2NC_6H_4$	156.89	71.63	228.52	72.16
2h	$p\text{-}H_2NC_6H_4$	50.79	75.09	125.88	30.48
1i	$p\text{-}CH_2{=}CH\text{-}C_6H_4$	100.22	84.85	185.07	10
TSi	$p\text{-}CH_2{=}CH\text{-}C_6H_4$	177.32	81.95	259.27	74.2
2i	$p\text{-}CH_2{=}CH\text{-}C_6H_4$	70.05	85.22	155.27	29.80
1j	$p\text{-}O_2N\text{-}C_6H_4$	88.46	66.69	155.15	0
TSj	$p\text{-}O_2N\text{-}C_6H_4$	168.48	63.71	232.19	77.04
2j	$p\text{-}O_2N\text{-}C_6H_4$	59.21	67.18	126.39	28.76
1k	$p\text{-}H_3CO\text{-}C_6H_4$	45.78	84.66	130.45	0
TSk	$p\text{-}H_3CO\text{-}C_6H_4$	121.86	81.78	203.64	73.19
2k	$p\text{-}H_3CO\text{-}C_6H_4$	15.06	85.15	100.21	30.24
1l	$p\text{-}HO\text{-}C_6H_4$	39.54	66.58	106.12	0
TSl	$p\text{-}HO\text{-}C_6H_4$	115.75	63.78	179.53	73.42
2l	$p\text{-}HO\text{-}C_6H_4$	8.82	66.58	75.41	30.71

[a]ΔH_f = Enthalpy of formation obtained from geometry optimisation at AM1 level.

[b]ZPE = Zero point energy obtained from force calculation.

[c]Total energy = $^a\Delta H_f$ + ZPE.

[d]Relative energy for **TS** = Energy of activation (E_a) and energy of reaction (E_{rxn}) for $CH_3NC \rightarrow CH_3CN$ thermal isomerisation for **2**.

tion as obtained by Rabinovitch[17] is 38.4 kcal/mol. Moffat *et al.*[14] were the pioneer to make theoretical MNDO/2 semi-empirical calculation for $CH_3NC \rightarrow CH_3CN$ isomerisation at 323 K and calculated activation energy as 32.9 kcal/mol. The twelve thermal isomerisation reactions have been studied by us at AM1 level at 298 K, when the activation barrier for the simplest system, i.e. $CH_3NC \rightarrow CH_3CN$ isomerisation is obtained to be 79.78 kcal/mol.

A correlation has been made between the activation energy and the molar mass of different aliphatic and aromatic isocyanides. These studies reveal slight but interesting changes in the values of activation energy with the change of alkyl group (Fig. 1).
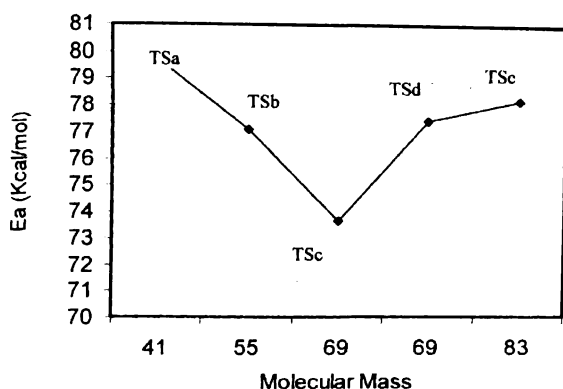

Fig. 1. Variation in activation barrier (kcal/mol) for aliphatic isocyanides relative to molar mass.

Activation barrier (E_a) for methyl isocyanides (79.73 kcal/mol) is higher than that for ethyl isocyanide (77.12 kcal/mol), which may be attributed to the stabilization of the transition state in latter due to larger electron releasing effect of ethyl group as compared to the methyl group. For the same reason the barrier in isopropyl isocyanides (E_a = 73.71 kcal/mol) is 3.41 kcal/mol less than the ethyl isocyanide. However, the fact that E_a of *n*-propyl isocyanides is slightly higher (by 3.73 kcal/mol) as compared to isopropyl isocyanide supports the greater electron releasing influence of isopropyl group than the isomeric *n*-propyl group.

Change in the values of activation energies for thermal isomerisation of aromatic isocyanides → cyanides is attributable to the nature of different substituents present at *para* position of phenyl group (Fig. 2). Activation barrier for phenyl isocyanides is 77.3 kcal/mol, which low-
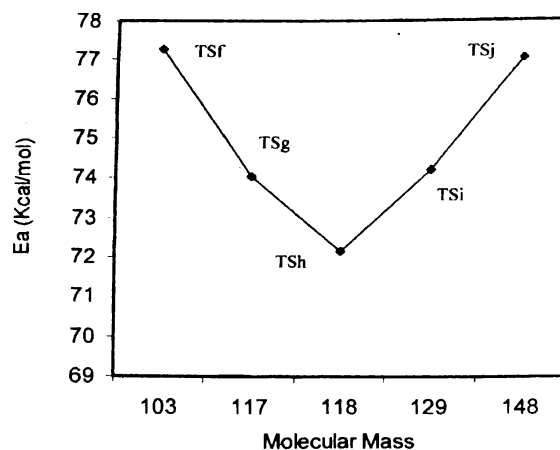

Fig. 2. Variation in activation barrier (kcal/mol) for aromatic isocyanides relative to molar mass.

ers down to 74.05 kcal/mol for *p*-tolyl isocyanides. This decrease in E_a value can be explained on the basis that the transition state is stabilized due to +M effect of CH_3 group present at *para* position of phenyl ring. Similar decreasing trend in E_a due to the +M effect of the substituent has been observed in the case of NH_2, OCH_3 and OH as well. At the same time, a higher barrier of 77.04 kcal/mol in case of the *p*-nitro substituent further indicates that the -M and electron withdrawing effect of NO_2 group destabilizes the transition state.

Computational methods :

Theoretical calculations were carried out at the restricted Hartree-Fock level (RHF) using AM1 semiemperical[19,20] SCF-MO methods as implemented in MOPAC 7.0 programme[21,22]. All structures were optimized to a gradient norm of <0.1 in the gas phase using the eigenvector method following (EF). The absolute entropies of all structures were calculated from a complete vibrational analysis. Entropies were corrected to free energies using calculated entropies. Initial estimates of all the structures were obtained by a molecular mechanics programme, followed by full optimization of all geometrical variables (bond length, bond angles and dihedral angles), without any symmetry constraints.

Acknowledgement

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