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A theoretical study of 1,3-dipolar cycloaddition of BNO with Acryl-nitrile

Mohammad R. Zardoost,* Seyyed Amir Siadati and Hoda Davoodi

Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr,Iran

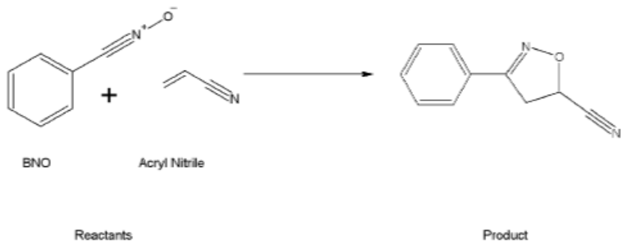
Abstract: A theoretical study of the kinetics and mechanism of Cycloaddition of Benzonitrile oxide, **BNO** with Acryl Nitrile in different solvents was performed using DFT methods at B3LYP level of theory using 6-311++G(d,p) basis sets at 298.15 K. Equilibrium molecular geometries and harmonic vibrational frequencies of the reactants, transition state and product were calculated. Effect of solvent dielectric on the kinetic parameters of 1,3-Dipolar cycloaddition, between BNO and Acryl nitrile was studied. The calculated rate constants and activation thermodynamic parameters showed good agreement with experimental results. These calculations showed that the reaction proceeds through a synchronous concerted mechanism.

Keywords: DFT, kinetics, benzonnitryl oxide (BNO), Acryl Nitrile, 1,3-Dipolar Cycloadditions (DC).

Introduction

Dipolar Cycloaddition, DC, reaction is an important method for designing different types of heterocyclic compounds. Products of DC reactions are numerous. They consist of compounds with different ring size and atoms. 1,3-DC is one type of dipolar cycloadditions that is applied to synthesize different five-member ring heterocycles. Usually in 1,3- DC reaction a carbon-carbon double bond reacts with a three member group of polar atoms.[1] 1,3-DC reaction is characterized by a concerted mechanism with an highly ordered transition state, a negative volume of activation and a high stereospecificity.

This reaction usually shows an inverse dependence of the reaction rate on the polarization of the medium, polar media makes the reaction slower [2-5]. Intermediate cases also have been known. DC process between norbornene and phenyl diazomethane is a sample for confirming this case. It was pointed that solvents have more or less effect on these types of reactions. The effect of various organic solvents on 1,3-dipolar cycloadditions is as characteristic as the one observed for Diels-Alder reactions : Usually, reaction rate constants hardly change on changing the solvent [6]. The small solvent effect seems to be dependent on the nature of the reactants, since reaction rate can either increase or decrease with increasing solvent polarization. This effect depends on the nature of reactant and TS. The kinetic parameters of this reaction had been studied in some of the organic solvents [7].



Scheme 1. 1,3-Dipolar Cycloaddition of BNO with acryl nitrile

Because of the importance of such reactions, they have been studied of different aspects [8-10]. In this work we performed a detailed study on the solvent effect on 1,3-dipolar cycloaddition of benzonitrile oxide with acryl nitrile.

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*Corresponding author. Tel: +(98) 911 253 5039, E-mail: m1605chemist@yahoo.com

Computational details

The structures corresponding to the reactants, TS, intermediate and product were optimized and the electronic structures and harmonic vibrational frequencies of all stationary points along the reaction pathway were calculated using Gaussian 03 computational package [11] with DFT methods.

Optimization of the geometries of the stationary points on the potential energy surfaces were performed using Beck's there-parameter hybrid exchange functional with the correlation functional of Lee ,Yang, Parr(B3LYP) [12-13] using 6-311++g** basis set [14-15]. The synchronous transit guided quasi Newton (STQN) method [16-17] was used to locate the TS. The intrinsic reaction coordinate (IRC) method [18-19] was also applied in order to check and obtain the profiles connecting the TS to the two associated minima of the proposed mechanism. The natural bond orbital (NBO) analysis [20-21] was also applied to determine the charge changes occurring in the studied process. To take the solvent into account, the calculations were done using the polarizable conductor calculation model (CPCM) [22]. All minimum and transition state structures are verified by vibrational frequency analysis.

The activation energies and Arrhenius factors were computed using eqns. (1) and (2), respectively, which were derived from the transition state theory [23- 26].

$$E_a = \Delta H^{\#} + mRT$$

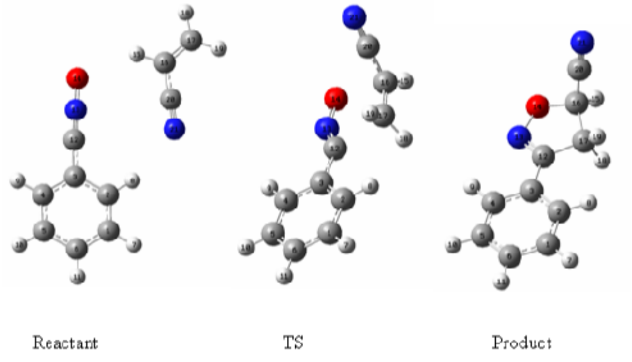
(1)

$$A = (ek_BT/h)\exp(\Delta S^{\#}(T)/R)$$

(2)

Result and discussion

Scheme **2** shows the optimized structures of reactants, TS, and product with the selected geometrical parameters at the B3LYP/6-311++g** (shown in Table **1**). Throughout this paper, all inter nuclear distances and angles are in angstroms and degrees, respectively.



Scheme 2. Optimized geometries of reactants, TS and product for the studied reaction at the B3LYP/6-311++G** level.

The concerted mechanism is initiated with the C16-C17 bond cleavage and C17-C12 and C16-O14 bond formation. The calculation shows that the C16-C17 bond is elongated and the C16-O14 bond shortened to form the TS. According to Table **1** the transition structure of 1,3-dipolar cycloaddition of BNO with acryl-nitrile has a breaking C16-C17 bond distance of 1.38 angstrom and forming C12-C17 and C16-O14 bond distances of 2.14 and 2.38 angstrom. The Pauling relation [27] was used to determine the related partial bond orders and the values of 0.126, 0.046, and 0.866 were obtained for C12-C17, C16-O14 and C16-C17, respectively. The obtained partial bond orders indicate that 13.4% of C16-C17 bond is broken, whereas C12-C17 and C16-O14 have only 12.6% and 4.6% reaching to the transition state, respectively. The extent of broken and formed bonds in transition state shows that a synchronous concerted mechanism has occurred for the 1,3-dipolar cycloaddition of BNO with acryl-nitrile. B3LYP/6-311++G** results for the reaction paths are shown in Fig. **1**. It demonstrates the energy as a function of the reaction coordinate, C16-C17, and represents the minimum energy paths which connect the reactant to the product through the saddle point.

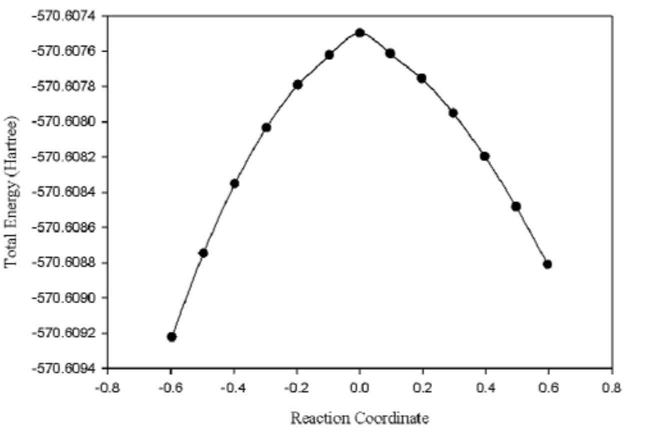


Fig. 1. Schematic energy profile of the potential energy surface for the studied reaction at B3LYP/6-311++G** level of theory.

Table **2** shows the charge distribution in the reactants, TS and the charge difference between TS and reactant (Δcharge) by means of NBO analysis. The results indicate that a small negative charge developed on C12, and C17 at the TS, which demonstrates that C12–C17 bond formation is faster than C16-O14 bond formation. In addition, the charge difference shows that electron donor groups at C12 and C17 accelerate the reaction while at C16 position opposite result is observed.

Table 1. Key geometrical parameters of reactants, TS, and product at the B3LYP/6-311++G(d,p) level of theory (the numbering of atoms is like that in Scheme **2**)

	Reactant	TS	Product
C12-N13	1.159	1.213	1.281
N13-O14	1.218	1.219	1.400
C16-C17	1.335	1.378	1.538
C12-C17	---	2.138	1.517
C16-O14	---	2.377	1.453

Table 2. Distributed NBO charges on the reactant and TS at the B3LYP/6-311++G (d, p) level of theory (the numbering of atoms is like that in Scheme **2**)

	C12	C16	C17	N13	O14
Reactant	0.2531	-0.3216	-0.2705	0.1755	-0.4445
TS	0.2358	-0.2763	-0.3994	0.1154	-0.3199
ΔCharge	0.0173	-0.0453	0.1289	0.0601	-0.1246

Table 3. Theoretical kinetic and activation parameters for 1,3-Dipolar Cycloaddition of BNO with Acryl-Nitrile in different solvents calculated B3LYP/6-311++G** at 298.15K. $\Delta G^{\circ,\#}$, $\Delta H^{\circ,\#}$, and E_a are in $Kcalmol^{-1}$ and $\Delta S^{\circ,\#}$ is in cal $mol^{-1}K^{-1}$.

	CH_2Cl_2	Heptane	DMSO	C_2H_5OH	Water
$\Delta G^{\circ,\#}$	19.22	22.71	21.30	18.93	19.08
$^a\Delta G^{\circ,\#}_{exp}$	20.48	----	19.51	19.98	19.53
$\Delta H^{\circ,\#}$	17.23	17.69	16.21	16.90	16.73
$\Delta S^{\circ,\#}$	-6.66	-16.83	-17.08	-6.83	-7.86
E_a	18.41	18.87	17.39	18.08	17.91
logA	11.77	9.55	9.49	11.73	11.51

The imaginary frequency for the transition structure was calculated to confirm the TS (-234.37 cm^{-1} at B3LYP++G**). In order to study solvent effect on the studied reaction, we performed the CPCM calculations in water, ethanol, DMSO, heptanes, and dichloromethane solvents in B3LYP/6-311++G** level of theory. Table **3** presents, $\Delta G^{\circ,\#}$, $\Delta H^{\circ,\#}$, $\Delta S^{\circ,\#}$, E_a, and Arrhenius factor for the reaction in different solvents. The Gibbs free energy barrier in water is 19.08 kcal mol^{-1} at B3LYP/6-311++G**, for the TS formation, which has a good agreement with experimental result.

The calculated value of $\Delta H^{\circ,\#}$ for this reaction is 16.73 kcal mol^{-1} indicates the reaction is exothermic. The calculated Gibbs free energies indicate that the reaction is not too slow and can be done at room temperature. As can be seen there is a good agreement between experimental and theoretical results. The good agreement between experimental and theoretical result, can help us to confirm this theoretical progress. According to Table **3** the least activation energy and Arrhenius factor is in DMSO.

Conclusion

1,3-dipolar cycloaddition of BNO with acryl-nitrile was studied by the Density Functional theory using 6-311++G** basis set in five different polar protic and aprotic solvents. The E_a calculated for the reaction in water by the B_3LYP/6-311++G** is 17.91 kcal mol^{-1} meaning formation is energetically feasible to occur.

The extent of broken and formed bonds in transition state shows that a synchronous concerted mechanism has occurred for the 1,3-dipolar cycloaddition of BNO with acryl-nitrile. The charge analysis shows that electron donor groups at C16 and C19 accelerate the reaction. However, at C1, C13, and C18 positions opposite result is observed. According to Table **3** the solvents have a small effect on this reaction which is resemble with Diels-Alder reactions. In going from nonpolar to polar solvents, the rate constants of 1,3-dipolar cycloadditions change, Which is in agreement with experiment [28-31].

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