A theoretical study on cycloaddition of norbornene and phenyl azide

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Abstract: A theoretical study of the kinetics and mechanism of second-order intermolecular Cycloaddition of Norbornene and Phenyl Azide was performed using DFT methods at B3LYP levels of theory with 6-311++G(d,p) and 6-311G(d,p) basis sets at 298.15K and 313.45 K. Equilibrium molecular geometries and harmonic vibrational frequencies of the reactants, transition state and product were calculated. Solvent effect on the kinetic and thermodynamic parameters of reaction of 1,3- Dipolar Cycloadditions of Norbornene and Phenyl Azide was investigated too. The calculated rate constants and activation thermodynamics parameters showed a good agreement with experimental results. These calculations indicated that the reaction proceeds through a synchronous concerted mechanism.

Keywords: DFT; kinetics; Activation energy; 1,3- Dipolar Cycloaddition; Norbornene; Phenyl Azide.

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 inverse dependence of the reaction rates on the polarization of the medium, polar media makes the reaction slower [2-4]. Intermediate cases also known. DC process between norbornene and phenyl diazomethane is a sample for confirming this case. These reactions have been studied in different aspects, experimentally and theoretically. For example, the Molecular Orbital Theory (MOT) has been used to explain many interesting aspects of different kinds of these reactions. Detailed kinetic studies by scheiner have confirmed the typical mechanistic features of a 1,3-dipolar cycloaddition for this reaction [5]. The activation energy of 1,3 dipolar cycloaddition of phenyl Azide with norbornene was investigated on HF and DFT (6-31g**) level of theory [6].

As we implied, azides are compounds that undergo 1,3-DC reaction. As we know these compounds are important precursors for the synthesis of heterocyclic organic compounds. They are considered to be important for, industrial and biological applications. Azide derivatives are applied in rubber, polymers, dyes and plastics technology, as well as in pharmaceuticals, pesticides and herbicides developments [7].

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 [8]. 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 [9]. In this work we wish to show solvent effect on 1,3-dipolar cycloadditions. The reaction of Norbornene and phenyl azide yields triazoline Product (see scheme 1).

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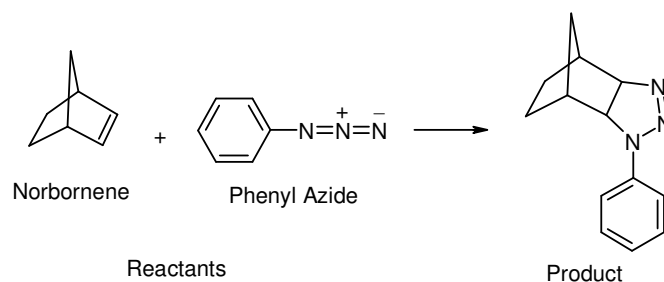
Scheme 1. The reaction of Norbornene with Phenyl Azide lead to triazine.

Computational details

The structures corresponding to the reactants, TS, 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 [10] 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) [11,12] using the 6-311g(d,p) and 6-311++g(d,p) basis sets [13,14]. The synchronous transit guided quasi Newton (STQN) method [15, 16] was used to locate the TS. The intrinsic reaction coordinate (IRC) method [17, 18] 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 [19, 20] was also applied to determine the charge changes occurring in the studied process. All minimum and transition state structures are verified byvibrational frequency analysis. To take the solvent into account, we performed our calculations using cosmo polarizable continuum model (CPCM) [21].

The activation energies and Arrhenius factors were computed using eqns. (1) and (2), respectively, which were derived from the transition state theory [22,23].

$$E_a = \Delta H^{\#} + RT \tag{1}$$

$$A = (ek_B T / h) \exp(\Delta S^{\#}(T) / R) \tag{2}$$

Result and discussions

Scheme (2) shows the optimized structures of reactants, TS, and product with the selected geometrical parameters at the B3LYP/6-311++G (d,p) shown in Table 1.

Reactants   **Transition State**   **Product**
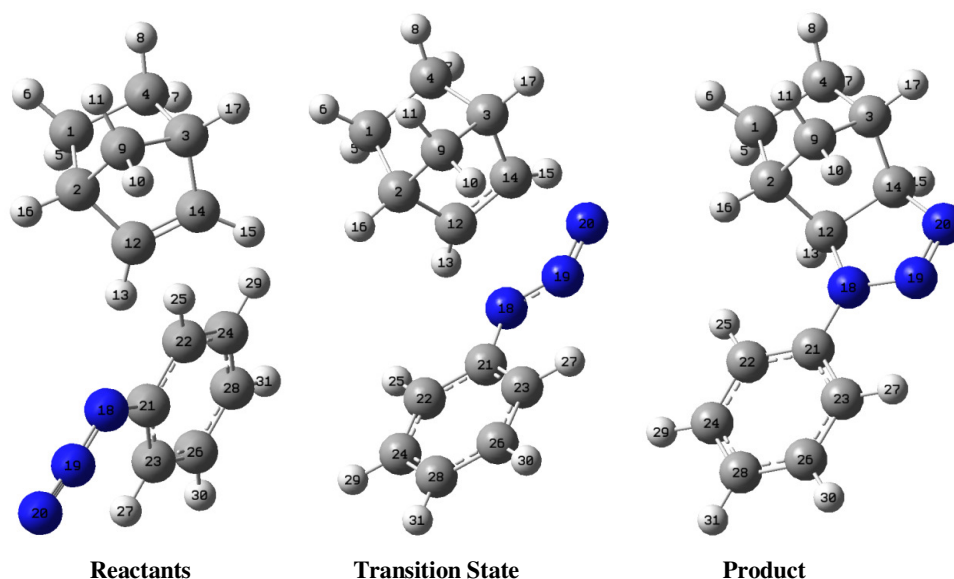
Scheme 2. Optimized geometries of reactants, TS, and product for the studied reaction at the B3LYP/6-311++G(d,p) level at 298.15 K.

The bond lengths and angles of the transition state, TS, were calculated using the B3LYP level of the theory using 6-311++G (d,p) basis set. Throughout this paper, all inter nuclear distances and angles are in angstroms and degrees, respectively.

The Concerted mechanism is initiated with the C12-C14 and N18-N19 π bond cleavage and C12-N18 and C14-N20 bond formation. According to Table 1 the transition structure of the reaction has a breaking C12-C14 and N18-N19 bond distance of 1.39 and 1.27 angstrom, respectively and a forming C12-N18 and C14-N20 bonds distance of 2.29 and 2.09 angstrom, respectively. The Pauling relation [24] was used to determine the related partial bond orders and values of 0.85 , 0.88, 0.065, and 0.131 were obtained for C12-

C14, N18-N19, and C12-N18 and C14-N20 , respectively. The obtained partial bond orders indicate that C12-C14 and N18-N19 bonds are broken 15% and 12%, respectively, whereas C12-N18 and C14-N20 have only 6.5% and 13% 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 Cycloaddition of norbornene to phenyl azide. B3LYP/6-311++G** results for the reaction path are shown in Fig 1. It demonstrates the energy as a function of the reaction coordinate, C20-N14, and represents the minimum energy path which connects the reactant to the product through the saddle point.
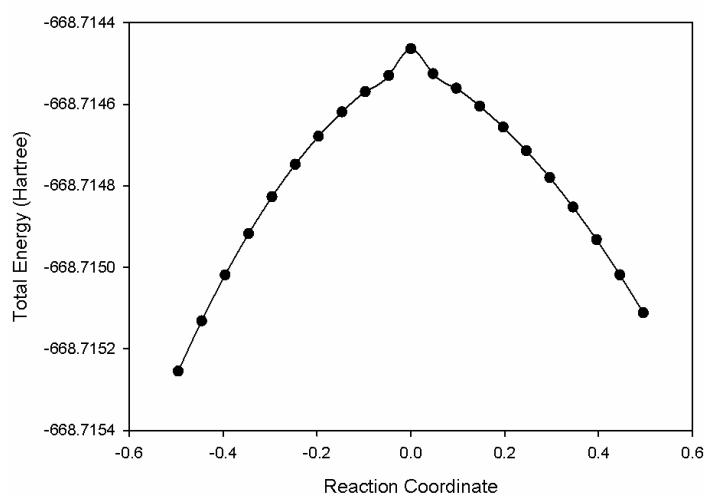

Fig. 1 Schematic energy profile of the potential energy surface for the studied reaction at B3LYP/6-311++G** level of theory.

Table 1. Key geometrical parameters of reactants, TS, and product at the B3LYP/6-311++G(d,p) level of theory

	Reactant	TS	Product
C12-C14	1.34	1.39	1.56
N18-N19	1.23	1.27	1.37
N19-N20	1.13	1.17	1.25
C12-N18	–	2.29	1.47
C14-N20	–	2.09	1.48
N18-C21	1.42	1.40	1.40

Table 2 shows the charge distribution in the reactant, 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 C14 at the TS, which demonstrates that C14–N20 bond

formation is faster than C12-N18 bond formation. In addition, the charge difference shows that electron donor groups at C12 and N18 accelerate the reaction while at C14 position opposite result is observed.

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	C14	C21	N18	N19	N20
Reactant	-0.1960	-0.1989	0.1194	-0.3294	0.2380	-0.0498
TS	-0.1033	-0.2208	0.1371	-0.3119	0.1322	-0.0856
ΔCharge	-0.0927	0.0219	-0.0177	-0.0175	0.1058	0.0358

The imaginary frequency for the transition structure was calculated to confirm the TS B3LYP++G**. Table 3 presents, $\Delta G^{\#}$, $\Delta H^{\#}$, $\Delta S^{\#}$, E_a, and rate constant for the reaction. In order to study solvent effect on the studied reaction, we performed the CPCM calculations in carbon tetrachloride, and n-heptane solvents. These calculations were performed in B3LYP/6-311G** and B3LYP/6-311++G** level of theory. It is clear from scheme 1 that the activated complex is not much more dipolar than the initial state, so it seems solvent have not much effect on this reaction.The Gibbs free energy barrier is 24.0 kcal mol^{-1} at B3LYP/6-311G**, for the TS formation. As can be seen in Table 3 the results are dependent on the basis sets, which means the

discrepancy found in the $\Delta G^{\#}$, comes from the reactants [25]. By comparing the calculated results and experimental values we see the solvents have a little effect on the reaction and the obtained results at B3LYP/6-311G** are closer to the experimental value. Using the most reliable energy barrier for this reaction calculated by the B3LYP/6-311++G (d, p) method, it is possible to estimate a TST rate coefficient of 6.29×10^{12} s^{-1} at 313.45 K in gas phase. The calculated rate constant indicates that the reaction is too fast and needs no catalyst or higher temperature. There was no experimental data about the reaction in gas phase but there were some, in liquid solutions (see Table 3).

Table 3 Theoretical kinetic and activation parameters for Cyclization of citronellal in gas phase at 313.45K. $\Delta G^{\#}$, $\Delta H^{\circ\#}$ and Ea are in $Kcalmol^{-1}$ and $\Delta S^{\circ\#}$, in cal mol^{-1}K^{-1}

Solvent	Basis set	$\Delta G^{\#}$	$G^{\#}(exp)^a \Delta$	logA	$\Delta H^{\#}$	$\Delta S^{\#}$	E_a
CCl$_4$	6-311g(d,p)	24.0	24.4	8.16	16.7	-23.3	17.3
	6-311++g(d,p)	22.0		10.10	17.4	-14.4	18.0
n-Heptane	6-311g(d,p)	23.3	24.5	8.64	16.7	-21.1	17.3
	6-311++g(d,p)	22.0		10.13	17.5	-14.3	18.1
Gas phase	6-311++g(d,p)	23.7	_	17.8	17.5	-20.8	18.7

^{a}from ref 9

Conclusion

Cycloaddition of Phenyl Azide to norbornene was studied by the Density Functional theory using B3LYP/6-311++G(d,p) and B3LYP/6-311G(d,p) basis sets. The calculated Gibbs free energy in gas phase is about 23.7 kcal mol^{-1} at 298.15 k. Because the experimental data of Gibbs free energy for this reaction was in carbon tetrachloride at 313.45 k (bout 24.4 kcal mol^{-1}), we studied this reaction in solvent too. There was a good agreement between experimental and

theoretical results that can confirm this theoretical study.

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