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ab initio Calculations and Mechanism of 1,3-Dipolar Additions on ethylene

P.K. ABDUL JALEEL and N.H. ZEINUL HUKUMAN*
Department of Chemistry, Sir Syed College, Taliparamba, Kannur-670 142, India
E-mail: zeinulhukuman@yahoo.com

ab initio calculations for the dipolar addition of ethylene with CNO, N_2O, ONO and O_3 have been carried out using hybrid density functional B3LYP and *moller plesset energy correlation* MP2 with aug-cc-PVDZ basis sets using Gaussian 03 suite of programmes. A cyclic Diels Alder type mechanism is suggested for N_2O and CNO and a fragmented one for ONO and O_3 using geometry optimization and harmonic vibrational frequencies. The shift in mechanism is due to difference in the ambivalent character of dienophiles.

Key Words: *Ab initio*, Basis sets, Dipolar addition.

INTRODUCTION

1,3-Dipolar compounds are found to be ambivalent compounds, which facilitate electrophilic and neucleophilic activity in 1 and 3 positions by virtue of the resonating structures[1]. Addition of 1,3-dipolar compounds to ethylene and its derivatives is very important as they provide 5-membered heterocyclic compounds.

Mechanism of addition of 1, 3-dipolar compounds with alkenes have been studied from various view points by many authors. The most notable among those are by Huisgen[2], with a formulation of thermally allowed 2+4 cycloaddition similar to Diels Alder ones. Experimentally they are stereospecific *cis* additions with respect to alkenes. Firestone[3] calculated thermodynamically the activation energies of these reactions and found it be close to those expected for the formation of a zwitter ion biradical intermediates. Houk and coworkers[4] suggested that modest energy barrier in the thermally allowed reaction is reasonable, because energy must be expended during the approach of reactants to accomplish distortion necessary before favourable HOMO-LUMO interactions to take effect.

The present study aims to performe optimization of reactants, products and transition states corresponding to concerted and biradical mechanism, harmonic vibrational frequency, charge density calculations and dihedral angle for CNO, N_2O ONO and O_3 to ethylene by using up to date density functional and Moller-Plesset calculations with a large basis set functions, thereby determining, computationally, the most possible fitting mechanism.

EXPERIMENTAL

Hybrid density functional B3LYP and moller-plesset energy correlation MP2, the Hartree-Fock(HF)6-311G, levels of calculations have been employed. Geometry optimization and harmonic vibrational frequencies were calculated by these methods using 6-311G and aug-cc-PVDZ basis sets. These calculations were performed using Gaussian 03 suite of programmes[5].

RESULTS AND DISCUSSION

The minimum energy values of optimized structures of the reactants, transition states and addition products are shown in Table-1. All these structures belong to C_1 point group. Calculated values of activation energies are given in Table-2. All the transition states are confirmed by one negative frequencies. The cyclic transition state can be further confirmed by the approximately zero values of dihedral angels and *ca.* 2 Å distance between end atoms (Tables 3 and 4).

TABLE-1
ab initio MINIMUM ENERGY GESMETRICS
(ZERO POINT CORRECTED)

Structure	Method and level of calculation		
	HF/6-311G	B3LYP aug.cc. PVDZ	MP2/aug.cc. PVDZ
N_2O + Ethylene reactants	- 261.5683386	- 263.2292050	- 262.5293084
N_2O + Ethylene Cyclic TS	- 261.5020129	- 263.1868332	- 262.4870720
N_2O + Ethylene Open TS	- 261.4342692	- 263.1094002	- 262.3703598
N_2O + Ethylene Product	- 261.5757536	- 263.2359991	- 262.5247239
CNO + Ethylene Reactants	- 244.9507092	- 246.4689029	- 245.6979451
CNO + Ethylene Cyclic TS	- 244.9061289	- 246.4447457	- 245.6738630
CNO + Ethylene Open TS	- 244.8386183	- 246.4234176	- 245.6525500
CNO + Ethylene Product	- 244.9103314	- 246.5117602	245.6786636
ONO + Ethylene Reactants	- 282.0380030	- 283.6512627	- 282.8963900
ONO + Ethylene Cyclic TS	- 281.9267089	- 283.6512586	- 282.8564615
ONO + Ethylene Open TS	- 281.9364733	- 283.6368941	- 282.8699017
ONO + Ethylene Product	- 281.9683836	- 283.6552723	- 282.9006848
O_3 + Ethylene Reactants	- 302.1763819	- 303.9939708	- 303.2360290
O_3 + Ethylene Cyclic TS	- 302.1761361	- 303.9713686	- 303.1776596
O_3 + Ethylene Open TS	- 302.1762870	- 303.9687152	- 303.1645250
O_3 + Ethylene Product	- 303.3100754	- 304.0631225	- 303.2959392

TABLE-2
ACTIVATION ENERGIES (Kcal)

Structure	Method and level of calculation		
	HF/6-311G	B3LYP aug.cc. PVDZ	MP2/aug.cc. PVDZ
N_2O + Ethylene Cyclic TS	41.62	26.590	26.50
N_2O + Ethylene Open TS	84.12	75.180	99.74
CNO + Ethylene Cyclic TS	27.97	15.160	15.11
CNO + Ethylene Open TS	70.34	28.540	28.48
ONO + Ethylene Cyclic TS	69.83	0.002	25.08
ONO + Ethylene Open TS	63.11	9.016	16.61
O_3 + Ethylene Cyclic TS	0.249	14.183	36.63
O_3 + Ethylene Open TS	0.053	15.850	44.79

TABLE-3
DISTANCE BETWEEN END ATOMS IN THE TRANSITION STATE (CYCLIC)

Structure	Method and level of calculation		
	HF/6-311G	B3LYP aug.cc. PVDZ	MP2/aug.cc. PVDZ
N_2O + Ethylene	2.04249	2.12448	1.93776
	2.07364	2.02708	1.97513
CNO + Ethylene	1.97180	2.27073	2.23589
	2.88861	2.12234	2.03634
ONO + Ethylene	3.93341	4.03720	1.88084
	3.93340	4.01350	2.23816
O_3 + Ethylene	3.95611	1.67675	2.47775
	3.95612	2.70560	2.42521

TABLE-4
DIHEDRAL ANGLES OF RING ATOMS IN THE CYCLIC TRANSITION STATE

Structure	Method and level of calculation		
	HF/6-311G	B3LYP aug.cc. PVDZ	MP2/aug.cc. PVDZ
N_2O + Ethylene	- 0.00398	0.04046	0
	- 0.01637	- 0.01961	0
CNO + Ethylene	- 0.12578	- 0.55634	0.039640
	0.02830	0.34123	0.014732
ONO + Ethylene	0	0	- 0.481070
	0	0	- 0.414420
O_3 + Ethylene	0	- 57.38224	- 46.90847
	0	- 31.24187	- 86.59832

The HF values are generally found to be higher than the other two methods. The high value can be attributed due to the comparatively low level of basis set. *ab initio* methods with small basis sets do not generally describe transition structures as accurately as they describe equilibrium geometries[6].

N_2O and CNO give two types of transition states, one corresponding to concerted and the other with open structures. A Diels-Alder type mechanism is suggested for the cyclic transition states for N_2O and CNO because the calculated activation energies are in the range of the one suggested for Diels-Alder value (20-30 K cals/mol)[7], which is lower than that for the open type transition structure.

Computed activation energy values for ONO and O_3 transition states shows that they have higher activation energies for cyclic transition states. In such circumstances only a fragmented mechanism can be suggested. 1,3-Dipolar addition of ozone to the double bond leads to the unstable primary ozonide which rapidly decomposes through retro 1,3-dipolar addition to a carbonyl compound and a carbonyl oxide. These two fragments then recombine in another 1, 3-dipolar addition to give ozonide. Fragmented structures are obtained in the open transition states of ONO and O_3.

In the cyclic transition state of ONO and ethylene, the DFT method gives a zero activation energy[8]. It is due to the fact that it is not a true transition state as evident from the distance between end atoms. Repeated attempts to optimize a cyclic transition state gives the structure which is very close to that of reactants itself. It is a further evidence for the fragmented pathway.

These view points are further supported by the energy difference between the HOMO's and LUMO's given in Table-5, as the reaction pathway favours lowest difference of HOMO's and LUMO's.

TABLE-5
ENERGIES OF HOMO AND LUMO

Structure	Method and level of calculation		
	HF/6-311G	B3LYP aug.cc.PVDZ	MP2/aug.cc.PVDZ
N_2O + Ethylene Reactants	0.38227 0.13242 **0.51469**	0.28013 0.03481 **0.24532**	0.37519 0.04080 **0.41599**
N_2O + Ethylene Cyclic TS	0.34742 0.04323 **0.44100**	0.28627 0.07924 **0.20703**	0.36985 0.03324 **0.36557**
N_2O + Ethylene Open TS	0.34742 0.04323 **0.39065**	0.21237 0.16237 **0.05000**	0.32145 0.03347 **0.36557**

Structure	Method and level of calculation		
	HF/6-311G	B3LYP aug.cc.PVDZ	MP2/aug.cc.PVDZ
CNO + Ethylene Reactants	0.38145	0.28118	0.37968
	0.01720	0.22425	0.01682
	0.39865	**0.05693**	**0.3965**
CNO + Ethylene Cyclic TS	0.37490	0.27022	0.35428
	0.04951	0.17478	0.02591
	0.42441	**0.09544**	**0.32837**
CNO + Ethylene Open TS	0.34688	0.24845	0.35580
	0.04515	0.11508	0.00755
	0.39203	**0.13337**	**0.34825**
CNO + Ethylene Product	0.38499	0.26145	0.37811
	0.00217	0.14033	0.02673
	0.38282	**0.12112**	**0.40484**
ONO + Ethylene Reactants	0.37685	0.27816	0.37969
	0.02069	0.16368	0.04020
	0.39754	**0.11448**	**0.33949**
ONO + Ethylene Cyclic TS	0.37685	0.27864	0.34997
	0.04581	0.16405	0.03006
	0.42266	**0.11459**	**0.38003**
ONO + Ethylene Open TS	0.39828	0.24511	0.36849
	0.08977	0.09880	0.03661
	0.48805	**0.146631**	**0.4051**
CNO + Ethylene Product	0.41359	0.20458	0.40476
	0.13531	0.05234	0.02989
	0.5489	**0.15224**	**0.37487**
O_3 + Ethylene Reactants	0.38276	0.28671	0.36900
	0.04648	0.17571	0.04421
	0.33628	**0.111**	**0.32479**
O_3 + Ethylene Cyclic TS	0.37454	0.24051	0.35732
	0.05539	0.15752	0.02562
	0.31915	**0.08299**	**0.3317**
O_3 + Ethylene Open TS	0.37848	0.2166	0.36010
	0.02019	0.1400	0.00924
	0.35829	**0.07666**	**0.35086**
O_3 + Ethylene Product	0.45693	0.24136	0.46020
	0.1370	0.02831	0.3121
	0.31993	**0.21305**	**0.49141**

The shift in mechanism from concerted to biradical may be attributed to the difference in ambivalent character of dienophiles. N_2O and CNO are more ambivalent than ONO and O_3 as evidenced from Table-6.

TABLE-6
CHARGE DENSITIES

Structure	Charge on atoms	
	B3LYP/aug.cc.PVDZ	MP2/aug.cc.PVDZ
N_2O	N -0.0369 N 0.3453 O -0.3823	N 0.2525 N 0.3178 O -0.5703
CNO	C -0.0491 N 0.3819 O -0.3329	C 0.1691 N 0.2363 O -0.4054
ONO	O -0.2481 N 0.4961 O -0.2481	O -0.3784 N 0.7568 O -0.3784
O_3	O -0.1352 O 0.2703 O -0.1351	O -0.1108 O -0.2214 O -0.1106

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