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QUANTUM MECHANICAL STUDIES OF THE KINETICS, MECHANISMS AND THERMODYNAMICS OF THE GAS-PHASE THERMAL DECOMPOSITION OF ETHYLVINYL ETHER.

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ABSTRACT

The thermal decomposition of Ethyl Vinyl Ether was studied using Austin Model (AMI), Re-parameterized Austin Model (RMI), Parameterized Model 3 (PM3) and Modified Neglect of Diatomic Overlap (MNDO) Hamiltonian in the Semi-Empirical method, Hartree – Fock at 3-21G,6-31G, 6-31G** level, and Density Functional method with Becke 3 Lee Yang Parr (B3LYP), 6-31G* in the Ab-initio method of calculation in Spartan'10. The geometric properties such as the bond length, dihedral, bond angles, heat of formation, atomic charges, and vibrational frequencies were obtained. The data were used to calculate the change in enthalpy* ΔH, *entropy* ΔS, *free energy* ΔG, *pre exponential factor A, Rate, k at 624K, and the variation of rate, k with temperatures at 498K - 773K at temperature interval of 25K. It was observed that the values obtained are in good agreement with experimental values for both semi-empirical and ab-initio methods and according to Arrhenius Theory, calculated rate k, increases with increase in temperature.*

KEYWORDS: Kinetics, ethyl vinyl ether, semi-empirical,ab-initio, transition state

RESUMO

A decomposição térmica do éter de etil vinila foi estudada usando os modelos Austin (AMI), Reparametrizado Austin (RMI), Parametrizado 3 (PM3) , Negligenciando a Superposição Molecular (MNDO), Hartree-Fock, Densidade Funcional Becke3 Lee Young Parr e o método Ab-initio em Spartan 10. Foram obtidos propriedades tais com comprimentos de ligações, ângulos, calor de formação, cargas atômicas e freqüência vibracional. Foram calculados parâmetros tais como a entalpia, energia livre, fator pré-exponencial A, velocidade, k à 624K. Os valores calculados concordaram com resultados experimentais.

PALAVRAS CHAVE: Cinética, éter de etil vinila , métodos semi-empíricos, ab-initio, estado de transição

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INTRODUCTION

Although there are numbersof experimental studies onthermal gas phase decomposition of aliphatic ethers and vinyl ethers but few work has been done on the kinetics,thermodynamics and mechanism using computational approach. However, semi empirical self –consistent field theory (SCF) molecular orbital method MNDO was used to study the kinetics of the pyrolysis of ethyl vinyl ether (Bamkole, 1990). The gas-phase thermal decomposition of alkylvinyl ethers proceeds through a retro–eneand in some cases through H-transfer molecular mechanism,through a six – membered cyclic transition state in which the $\beta - H$ atom,attracting the terminal vinyl carbon atoms is part of the six membered cyclic transition state which involves a C-H bond making, C-H and C-O bond breaking.

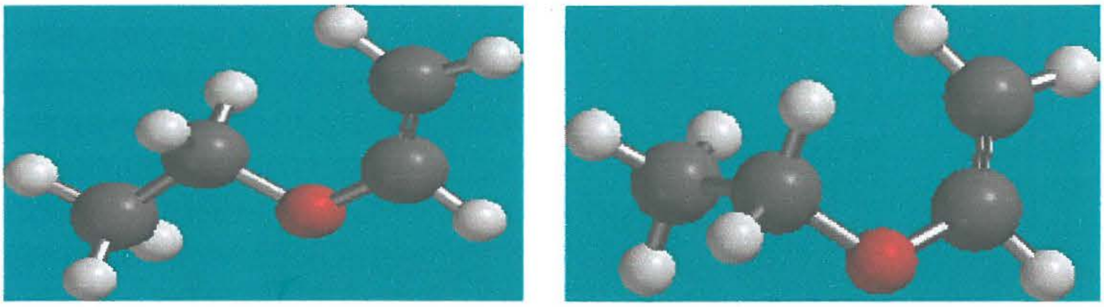
A large number of the gas- phase unimolecular reaction which have been studied, appeared to take place by way of 4-center and 6-center cyclic process (O' Neal and Benson, 1967). The thermal decomposition of ethyl vinyl ether gives acetaldehyde and acetylene as the products.

The aim of this study is to take a closer look through the computational method to study the kinetics, thermodynamics and mechanism of the thermal decomposition of ethyl vinyl ether through a procedure devised by Adejoro and Bamkole (2005) using semi –empirical and ab-initio method in Spartan '10.

COMPUTATIONAL METHOD

Conformational search was performed on the molecule to locate the structure with the lowestenergy. The conformational search was carried out using molecular mechanics force field (MMFF) which is quite successful in assigning low energy conformers and in providing quantitative estimates of conformational energy differences (Warren, J.Hehre, 2003). Using semi-empirical and ab initio methods the geometry of the lowest energy conformer in Spartan reactant was optimized. There are four different conformersand the heat of formation with AMI calculation is as shown in fig. 1 below:

Fig 1: CONFORMERS OF ETHYL VINYL ETHERS

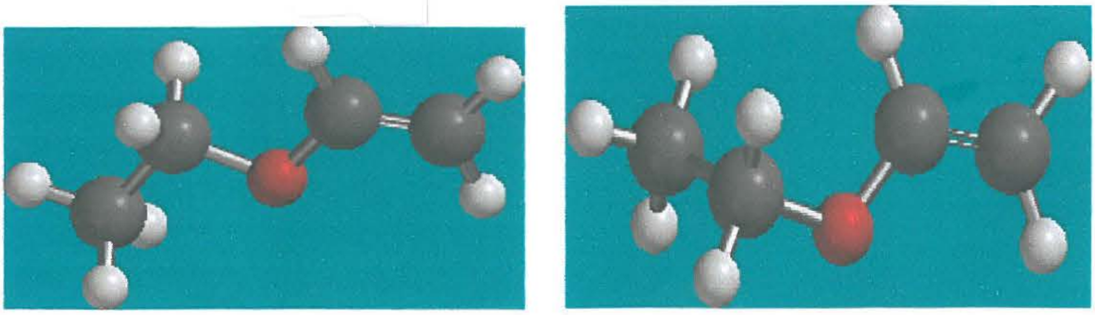


Energy = 16.384 **kJ/Mol**

HOF = -139.650 kJ/mol

Energy = 24.798 **kJ/Mol**

HOF = -139.282 kJ/mol



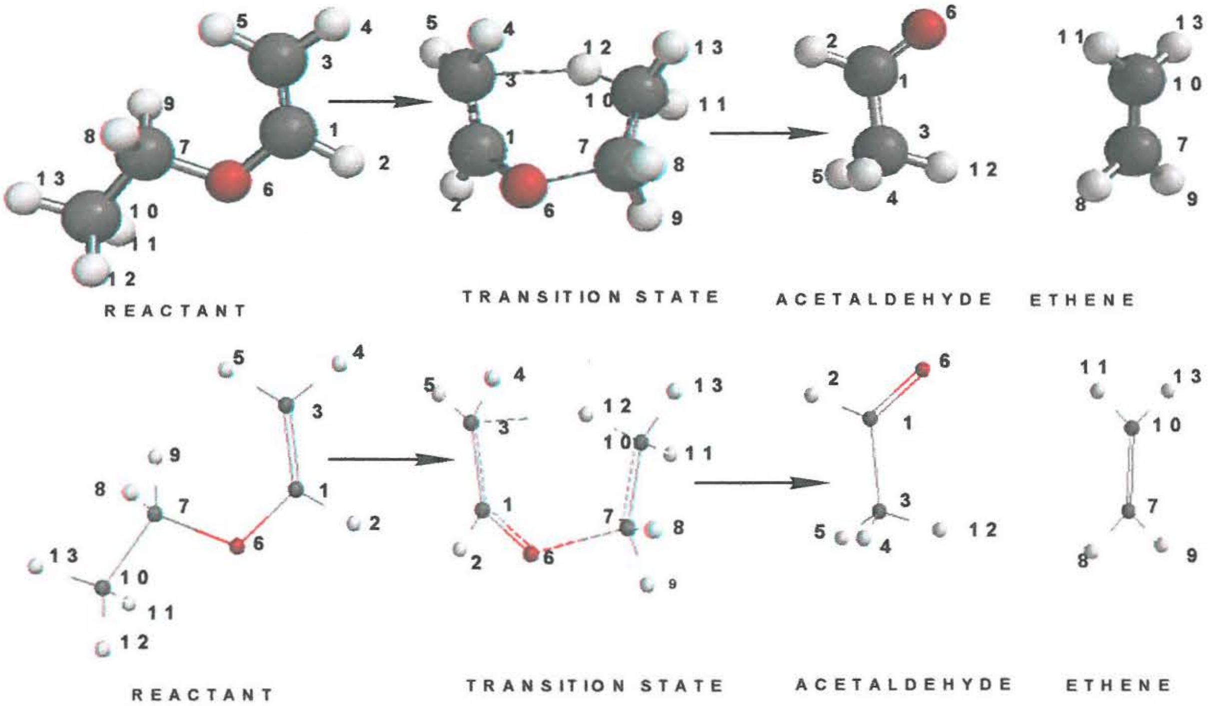
Energy = 25.189 **kJ/Mol**

HOF = -131.069 kJ/mol

Energy = 31.414 **kJ/Mol**

HOF = -133.733 kJ/mol

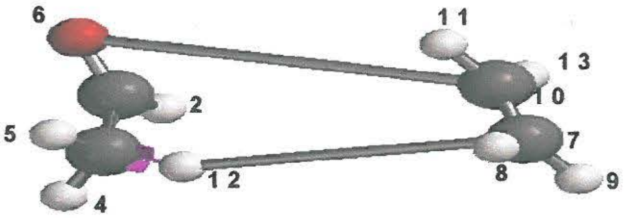
In the structure below H_{12} is the β -H atom to be eliminated from the alkyl part and the dihedral 6-7- 10-12(-59.91°) is acute negative.



Scheme 1: **REACTION SCHEME**

Reaction Path Study

Reaction path calculations were performed on the optimized geometry of each of the alkyl vinyl ether under study using $H_{12} - C_3$ as the reaction coordinate. The internal coordinate was varied from its initial distance in the stable reactants form to its value in the product molecule. For example, for ethyl vinyl ether, the initial distance between H_{12} and C_3 is 4.723Angstroms. This inter atomic distance is slowly altered throughout the reaction path calculation taking the value from 4.723 (initial value) to 1.09 Angstroms its approximate value in the stable product molecule in 20 steps. As reported in previous work, (Mclver, 1971) instead of the energy to pass smoothly through a maximum rose to a very high value and the geometry suddenly drop to a product with a drop in the heat of formation with the values approximately the same as the sum of the expected products (acetaldehyde and ethylene) as shown in figure 2 below:



REACTION PATH STUDY (ETHYL VINYL ETHER)

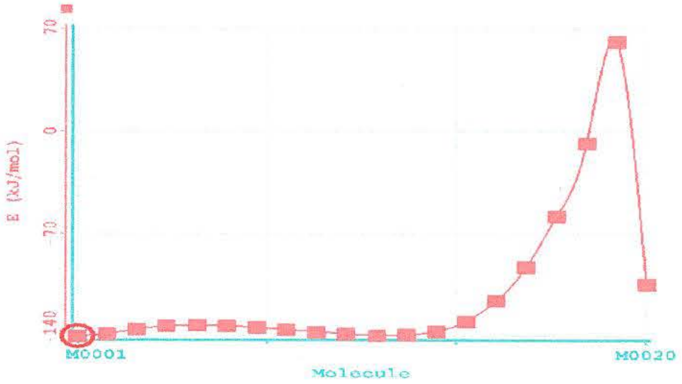


Fig 2: **A PLOT OF ENERGY AGAINST THE NUMBER OF MOLECULES TO DEPICT THE REACTION PATH STUDIES**

Transition State structure

Potential energy surfaces provide a basis for understanding the relationship between molecular structure and stability. Stable molecules correspond to energy minima along the reaction coordinate. Transition states correspond to the energy maxima. The problem is that the diagram cannot be constructed that is cannot bevisualized. However, the underlying principle is that stable molecules (energy minima) will be interconnected by smooth pathway passing through well – defined transition state remain the same. The only problem is to identify this special point (stable molecules/transition state).

Using the guess-transition state in Spartan on the suggested mechanism of the transition state structure was optimized and was subjected to the two tests needs to be performed in order to verify that a practical geometry corresponds to a saddle point (transition structure) and that this saddle point corresponds to the reactants and products. The tests are:

That the Hessian matrix of second – energy derivations with respect to coordinates yields one and only one imaginary frequency which will be in the range of 400-2000 cm^{-1} and the normal coordinates corresponds to the imaginary frequency smoothly corrects reactants and products. This could be achieved by animating the normal coordinate.

Intrinsic reaction Coordinate

The intrinsic reaction coordinates method was also used by optimizing the molecule subject to a fixed position along the reaction coordinate (Warren Hehre, 2003). The transition state was confirmed using the IRC method. Two IRC calculations were performed. The first one a positive perturbation was done by an initial perturbation on the atomic coordinates in the direction of the single negative frequency while the other one a negative perturbation performed along the same normal coordinates.

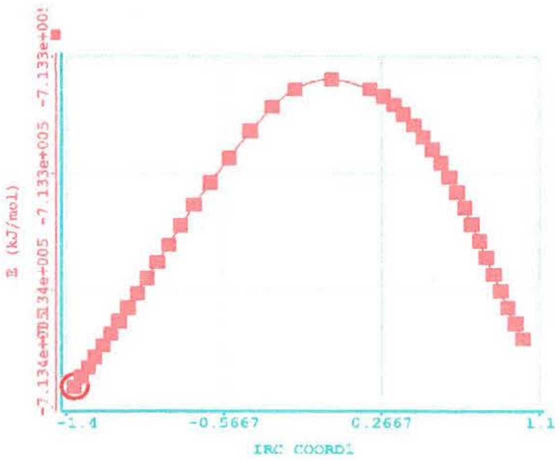
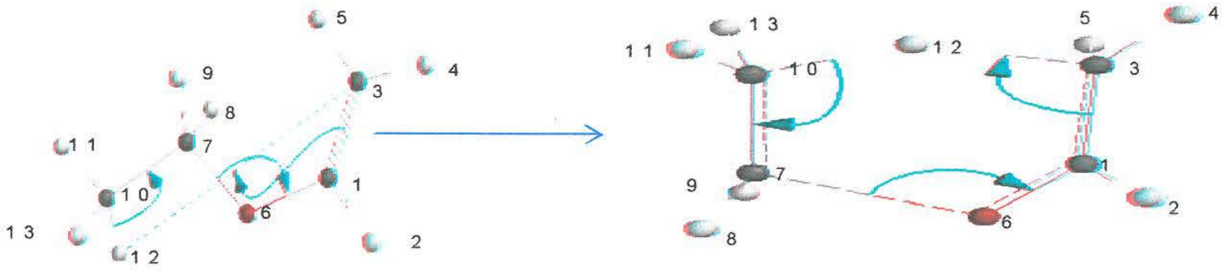


Fig 3: **A PLOT TO SHOW THE INTRINSIC REACTION COORDINATE**

Mechanismof decomposition of Alkyl Vinyl Ethers.

There are various studies on the thermal decomposition of aliphatic ethers in the gas phase but there are very few examples in the studies of vinyl ether with substituents on the vinyl carbon. (Flowers et al 1981 and Awan et al 1988) reported that the thermal decomposition of aliphatic ethers proceeds through a retro –ene molecular mechanism through a six – membered cyclic transition state in which the $\beta - H$ atom, attracting the terminal vinyl carbon atoms is part of the six member cyclic transition state which involves a C-H bond making, C-H and C-O bond breaking and according to experimental evidence, the C-O bond breaking is the rate-determining step (J.W. McIver Jr. and A. Kormonicki,1972)

In the kinetics study of the thermal gas phase decomposition of 2- butoxypropene at temperature range 640- 680K (Awan and Mahmood, 1999) states that acetone and 1-butene were the only products. Acetaldehyde and 1-butene were the only products in the pyrolysis of ethyl vinyl ether and the reaction proceeds through a six – membered cyclic transition state in which the $\beta - H$ atom, attracting the terminal vinyl carbon atoms is part of the six member cyclic transition state.



REACTANT TRANSITION STATE

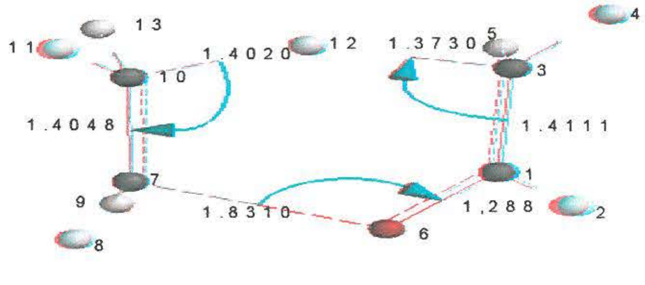


Fig 4: Reaction Mechanism

CALCULATION

The thermodynamic calculations were obtained for ethyl vinyl ether through calculation on the ground state GS, Transition state, TS and the product. The statistical mechanically calculated enthalpy and entropy was used which is not the true representative of the total energy of the molecule, knowing that the large portion of the enthalpy in a molecule is contained in its bonds and physical conformation hence the sum of the ground state energy (GSE) and the statistical mechanically calculated enthalpy are used to arrive at a closer approximation of the true energy of the molecule. With the said modified version of the heat of reaction the equation is given as shown below [Spartan guide]. The enthalpy of a species will be defined as:

$$\mathrm{H_i} = \mathrm{GSE}_i + \mathrm{H_i}^{\mathrm{sm}}$$

Where the superscript 'sm' is the statistical mechanically calculated enthalpy. Substitute this into the initial definition of the heat of reaction we have:

$$\Delta \mathrm{H_{Rxn}} = \left(\mathrm{GSE_{product}} + \mathrm{H^{sm}_{Product}}\right) - \left(\mathrm{GSE_{reactant}} + \mathrm{H^{sm}_{reactants}}\right)$$

The enthalpy of reaction was calculated at 624K.

Activation energy (Ea) was calculated according to the transition state theory for a unimolecular reaction at 624K.

$$\mathrm{Ea} = \Delta \mathrm{H} + \mathrm{RT}$$

The entropy of the reaction was calculated by taking the difference of product and reactant entropies that is

$$\Delta \mathrm{S_{reaction}} = \mathrm{S_{Product}} - \mathrm{S_{reactants}}$$

$$\text{And } \Delta S \text{ activated} = \mathrm{S_{\,transition}} - \mathrm{S_{\,reactant}}$$

The Gibbs free energy was calculated using the modified version of the heat of reaction equation. Knowing that $\mathrm{G} = \mathrm{H} - \mathrm{TS}$

$$\Delta \mathrm{G}^* = \Delta \mathrm{H}^* - \mathrm{T}\Delta \mathrm{S}.$$

The first order coefficient K (T) was calculated using transition State theory (TST) (Benson, 1960) assuming that the transition coefficient is unity as shown in the following equation

$$\mathrm{K(T)} = \frac{\mathrm{K'T}}{\mathrm{h}} \exp\left[\frac{-\Delta \mathrm{G}^*}{\mathrm{RT}}\right]$$

Where $\Delta \mathrm{G}^*$ is the Gibbs free energy change between the reactant and the transition state and $\mathrm{K'}$and h are the Boltzmann and Planck constants respectively.

Pre –exponential factor is given as $\mathrm{A} = \frac{\mathrm{K_B T}}{\mathrm{h}} \exp\left[\frac{-\Delta \mathrm{S}}{\mathrm{R}}\right]$

Arrhenius rate was obtained using the rate equation

$$K(T) = A \exp\left[\frac{-Ea}{RT}\right] \qquad [4]$$

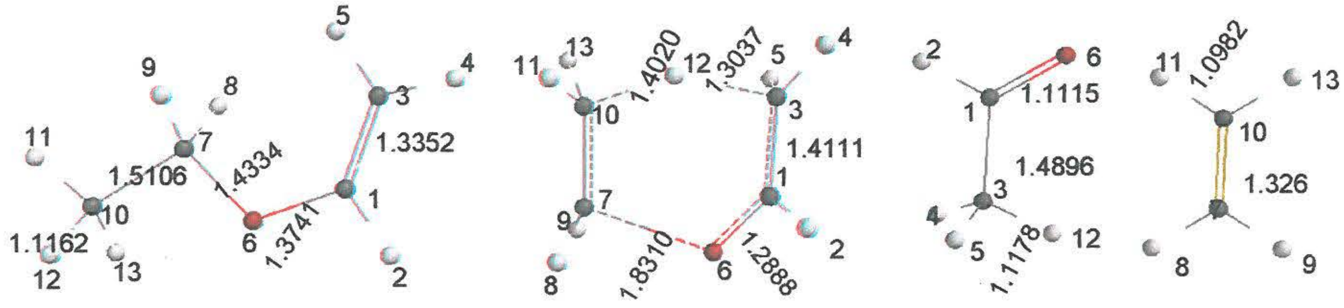
RESULTS AND DISCUSSION

The pyrolysis of ethyl vinyl ether gives acetaldehyde CH_3CHO and ethylene C_2H_4 in the structure (fig 1) H_{12} is the hydrogen attached to the β - carbon that is hydrogen eliminated from the alkyl group. The bond between C_3 and H_{12} is stretched with the bond length of 1.3730 (AM1), 1.4280 (RM1), 1.3910 (PM3), 1.2110 (MNDO) for semi empirical and the pyrolysis of ethyl vinyl ether gives acetaldehyde CH_3CHO and ethylene C_2H_4. The decomposition proceeds through a retro ene molecular mechanism through a six membered cyclic transition state as shown in fig (1) below which involves C – H bond making, C – H and C – O bond breaking as shown in fig 1 below. In the structure, $H_{12}$is the β – hydrogen to be eliminated from the alkyl group. In the transition state there is a stretch between $C_{10} - H_{12}$ bond with bond length 1.402 (AM1) 1.092 (RM1), 1.420 (PM3), 1.701 (MNDO) 1.400 (HF321G), 2.204 (HF631G*) 1.0761 (HF 631G**) and 1.0909 (DFT/B3LYP/631G*) as against the bond length of 1.1164 (AM1), 1.099 (RM1), 1.098 (PM3) 1.108 (MNDO), 1.082 (HF 321G), 1.0839 (HF 631G*), 1.0841 HF(631G*) and 1.095 (DFTB3LYP/631G*) at the ground state from the table 1 below, it is shown that both semi – empirical and ab initio method could predict the bond length effectively except for RM1 and DFT which has values lower compare with others. From the Table the (2) dotted lines shows the point where cleavage occurs that is between $O_6 - C_7$ also with a long stretch in the bond length in the transition state for all the methods and between $C_{10} - H_{12}$ while a bond is formed between $C_3 - H_{12}$ and also from the table, at the ground state the bond length is in the range of 4.7 to 4.9 transition state, in the range of 1.0 to 1.4 against the stable product bond length in the range of 1.07 to 1.09. The bond angles and dihedrals are shown in tables 1b and 1c below.

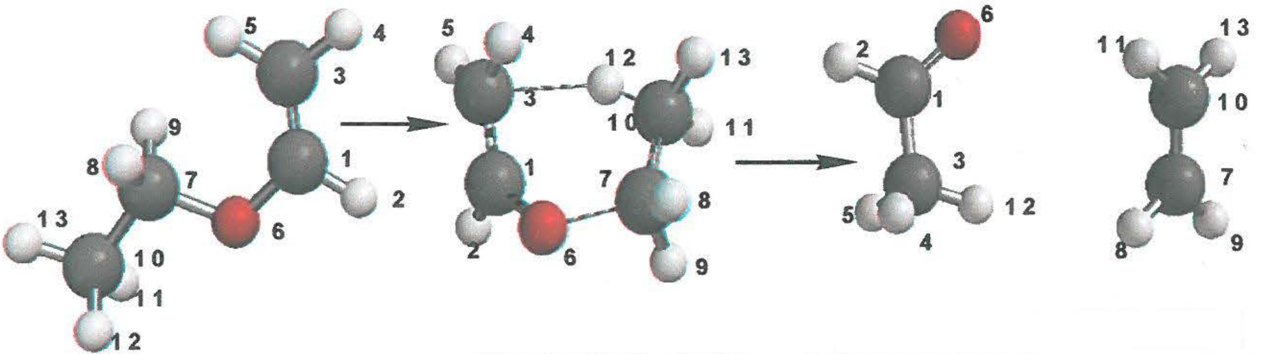
Atomic charges are shown in Mulliken. The Mullikencharges arepreferred because it gives simple and reasonable estimates of atomic charges. (Spartan guide). The formal charges in the TS: (table 1), show that H_{12} has the largest charge development while C_7 has the least (Lee et al 1987). The polarization of the $C_7 - O_6$ and $C_{10} - H_{12}$ bond cases positive charges on the carbon atoms C_1 and C_7 to increase and the C_{10} atom to become more negative (table 1d). the increase in the negative charge on C_{10} being much greater, cases much bond polarization of the $C_{10} - H_{12}$

places – considerable positive charge on the H_{12} atom, such that the positive charge is delocalized over the entire $O_6 - C_1 - C_3$ frame in the TS. In the TS, the $C_7 - C_{10} - H_{13}$ is electron demand and supply within the GS of ethyl vinyl ether, the vinyl carbon becomes (C_3) quite highly negative and β – Hydrogen, H_{12} becomes quite acidic, so that a fast proton transfer equilibrium takes place. The formation of an intermediate in which there is attack from the vinyl carbon on the β – Hydrogen, H_{12} takes place as a fast step followed by the rate determining step.

There is an assumption that the interaction and charge transmission C_7 and C_{10} is not efficient so that a sizable change on C_{10} is not efficiently transmitted to the electron deficient C_7, hence a double bond formation between C_7 and C_{10} takes place slowly. (Lee et al, 1987).



REACTANT TRANSITION STATE ACETALDEHYDE ETHYLENE



REACTANT TRANSITION STATE ACETALDEHYDE ETHENE

Table 1: BOND LENGTH FOR PYROLYSIS OF ETHYL VINYL ETHER

BOND		AMI	RMI	PM3	MNDO	HF/ 3-21G	HF/ 6-31G*	HF/ 6-31G**	DFT/ B3LYP 631G*
C_1-H_2	GS	1.1048	1.0965	1.0944	1.1013	1.0708	1.0743	1.0751	1.0871
	TS	1.1080	1.1016	1.0987	1.0990	1.0822	1.0940	1.0960	1.1065
	Prd	1.1142	1.1065	1.1024	1.1116	1.0868	1.0952	1.0971	1.1143
	Δd(TS-GS)	+0.0032	+0.0051	+0.0043	-0.0023	+0.0114	+0.0197	+0.0209	+0.0194
C_1-C_3	GS	1.3352	1.3310	1.3334	1.3486	1.3160	1.3206	1.3204	1.3371
	TS	1.4111	1.4000	1.4110	1.4525	1.3885	1.4990	1.4972	1.4010
	Prd	1.4896	1.5001	1.4985	1.5167	1.5070	1.5041	1.5030	1.5083
	Δd (TS-GS)	+0.0759	+0.069	+0.0776	+0.1039	+0.0725	+0.1784	+0.1768	+0.0639
C_1-O_6	GS	1.3741	1.3575	1.3619	1.3586	1.3693	1.3407	1.3406	1.3570
	TS	1.2888	1.2801	1.2737	1.3043	1.2721	1.1880	1.1880	1.2675
	Prd	1.1115	1.2146	1.2097	1.2214	1.2086	1.1876	1.1877	1.2105
	Δd (TS-GS)	-0.0853	-0.0774	-0.0882	-0.0543	-0.0972	-0.1527	-0.1526	-0.0895
C_3-H_4	GS	1.0958	1.0840	1.0846	1.0881	1.0705	1.0731	1.0733	1.0839
	TS	1.1018	1.0883	1.0887	1.1019	1.0733	1.0810	1.0821	1.0879
	Prd	1.1178	1.0997	1.0979	1.1090	1.0857	1.0866	1.0867	1.0924
	Δd (TS-GS)	+0.0060	+0.0043	+0.0041	+0.0138	+0.0028	+0.0079	+0.0088	+0.004
C_3-H_5	GS	1.0949	1.0821	1.0856	1.0860	1.0706	1.0729	1.0730	1.0836
	TS	1.1071	1.0903	1.0918	1.1065	1.0768	1.0830	1.0824	1.0883
	Prd	1.1169	1.0997	1.0979	1.1090	1.0857	1.0866	1.0867	1.0980
	Δd (TS-GS)	+0.0122	+0.0082	+0.0062	+0.0205	+0.0062	+0.0101	+0.0094	-0.0047
O_6-C_7	GS	1.4334	1.4133	1.4269	1.4056	1.4426	1.4059	1.4062	1.4275
	TS	1.8310	1.8880	1.8280	1.5060	1.9780	2.3670	2.3680	2.0600
	Prd	-	-	-	-	-	-	-	-
	Δd (TS-GS)	+0.3976	0.04747	+0.0401	+0.1004	+0.5354	+0.9611	+0.9618	+0.6325
C_7-H_8	GS	1.1221	1.1137	1.1071	1.1223	1.0833	1.0859	1.0869	1.0996
	TS	1.1037	1.0943	1.0949	1.1175	1.0694	1.0730	1.0736	1.0832
	Prd	1.0982	1.0858	1.0861	1.0891	1.0737	1.0761	1.0764	1.0876
	Δd (TS-GS)	0.01827	-0.0194	-0.0122	-0.0048	-0.0139	-0.0129	-0.0133	-0.0164
C_7-H_9	GS	1.1221	1.1137	1.1071	1.1223	1.0833	1.0859	1.0869	1.0996
	TS	1.1044	1.0941	1.0943	1.1166	1.0682	1.0710	1.0722	1.0827
	Prd	1.0982	1.0858	1.0861	1.0891	1.0737	1.0761	1.0764	1.0876
	Δd (TS-GS)	-0.0177	-0.0196	-0.0123	-0.0057	-0.0151	-0.0149	-0.0147	-0.0169
C_7-C_{10}	GS	1.5106	1.5247	1.5163	1.5406	1.5234	1.5150	1.5143	1.5186
	TS	1.4048	1.4164	1.4054	1.4521	1.3927	1.3140	1.3131	1.4055
	Prd	1.3260	1.3222	1.3220	1.3347	1.3151	1.3171	1.3165	1.3308
	Δd (TS-GS)	-0.1058	-0.1083	-0.1109	-0.0885	0.1307	-0.201	-0.2012	-0.1131
$C_{10}-H_{11}$	GS	1.1162	1.0994	1.0979	1.1081	1.0819	1.0839	1.0841	1.0946
	TS	1.1058	1.0926	1.0892	1.1089	1.0773	1.0760	1.0770	1.0760
	Prd	1.0982	1.0858	1.0861	1.0891	1.0737	1.0761	1.0767	1.0876
	Δd (TS-GS)	-0.0104	-0.0068	-0.0087	-0.0191	-0.0046	-0.0079	-0.0071	-0.0186
$C_{10}-H_{12}$	GS	1.1162	1.0994	1.0979	1.1081	1.0819	1.0839	1.0841	1.0946
	TS	1.4020	1.0926	1.4200	1.7010	1.4000	2.2040	1.0767	1.0909
	Prd	-	-	-	-	-	-	-	-
	Δd (TS-GS)	+0.2858	-0.0068	+0.3221	+0.5929	+0.3181	+1.1209	-0.0074	-0.0046
$C_{10}-H_{13}$	GS	1.1158	1.0989	1.0973	1.1095	1.0836	1.0854	1.0855	1.0955
	TS	1.1051	1.10927	1.0891	1.0883	1.0768	1.0750	1.0754	1.0906
	Prd	1.0982	1.0858	1.0861	1.0891	1.0737	1.0761	1.0767	1.0876
	Δd (TS-GS)	-0.0107	-0.0062	-0.0082	-0.0212	-0.0068	-0.0104	-0.0101	-0.0049
C_3-H_{12}	GS	4.7230	4.7400	4.7750	4.9130	4.7510	4.7360	4.7350	4.7630
	TS	1.3730	1.4280	1.3910	1.2110	1.4410	1.0770	1.0790	1.4980
	Prd	1.1178	1.0997	1.0977	1.1074	1.0804	1.0815	1.0816	1.0981
	Δd (TS-GS)	-3.3500	-3.3120	-3.3840	-3.7020	-3.310	-3.659	-3.6560	-3.2650

Table 2: SELECTED BOND ANGLE (0°) FOR ETHYL VINYL ETHER

BOND		AMI	RMI	PM3	MNDO	HF/ 3-21G	HF/ $6\ 31G^{*}$	HF/ $6\text{-}31G^{**}$	DFT/ B3LYP 631G*
$C_1-C_3-H_4$	GS	120.773	121.252	121.936	120.358	119.515	118.854	118.732	118.925
	TS	117.832	119.630	118.869	114.460	119.173	112.060	112.045	119.582
	Prd	109.531	110.919	110.065	109.575	109.888	109.807	109.713	110.499
$H_2-C_1-C_3$	GS	124.992	125.433	125.694	121.378	121.978	121.243	121.152	121.841
	TS	120.613	121.316	121.604	121.584	118.233	116.600	116.543	118.032
	Prd	115.258	115.910	116.637	114.022	114.306	115.317	115.295	114.800
$H_2-C_1-O_6$	GS	107.902	107.027	105.862	109.374	109.925	110.055	110.187	109.542
	TS	118.259	118.542	117.077	117.434	118.962	120.011	120.039	118.743
	Prd	121.214	122.101	119.944	121.016	120.897	120.281	120.325	120.495
$C_3-C_1-O_6$	GS	127.106	127.540	128.445	129.248	128.097	128.702	128.662	128.616
	TS	120.226	119.649	120.710	120.410	121.218	123.311	123.325	121.745
	Prd	123.528	121.990	123.419	124.962	124.796	121.805	124.380	124.705
$H_4-C_3-H_5$	GS	115.376	112.201	114.198	113.495	116.911	117.243	117.417	117.298
	TS	113.475	111.922	112.217	109.672	116.121	110.500	110.623	116.123
	Prd	108.508	107.112	107.544	108.185	107.632	107.199	107.194	109.999
$C_7-C_{10}-H_{11}$	GS	110.473	112.205	111.976	111.976	109.617	109.671	110.539	110.699
	TS	117.456	118.035	119.714	119.714	117.922	117.922	121.860	121.933
	Prd	122.720	123.700	123.191	123.191	121.896	121.896	121.746	117.250
$C_7-C_{10}-H_{13}$	GS	109.182	110.845	110.108	108.968	110.574	117.243	110.165	110.048
	TS	117.414	117.873	118.668	119.758	117.904	121.940	121.644	117.192
	Prd	122.720	123.700	113.805	123.191	121.896	121.805	121.746	121.933
$H_8-C_7-H_9$	GS	109.235	106.715	107.499	108.552	108.552	110.215	107.902	107.700
	TS	115.632	113.649	113.247	115.262	115.262	121.720	115.956	115.451
	Prd	114.560	112.599	123.098	116.208	116.208	121.805	116.538	116.134
$C_{10}-C_7-H_8$	GS	111.351	111.296	111.437	111.283	111.283	110.926	110.897	111.171
	TS	119.661	120.127	119.063	120.523	120.580	122.030	122.056	121.032
	Prd	122.720	123.700	123.098	121.896	121.896	121.805	121.731	121.933
$C_7-C_{10}-H_9$	GS	111.351	111.296	111.437	109.234	111.283	110.926	110.897	111.171
	TS	119.552	120.127	110.065	113.765	120.523	122.030	121.986	120.868
	Prd	122.720	123.700	123.098	123.191	121.890	121.805	121.731	121.933
$H_{11}-C_{10}-C_{13}$	GS	109.190	107.279	107.600	107.815	109.176	108.599	108.572	108.483
	TS	113.956	111.378	112.677	114.975	114.838	121.940	1116.501	116.134
	Prd	114.560	112.599	113.805	113.619	116.208	116.390	116.508	113.876
$C_1-C_3-H_5$	GS	123.851	126.547	124.866	126.147	123.574	123.903	123.851	123.777
	TS	118.385	121.016	119.869	116.745	117.632	112.060	110.494	118.421
	Prd	109.531	110.919	110.065	109.575	109.888	109.807	109.713	109.796

Table 3: SELECTED BOND DIHEDRALS OF ETHYL VINYL ETHERS

BOND		AMI	RMI	PM3	MNDO	HF/ 3-21G	HF/ 6-31G*	HF/ 6-31G**	DFT/ B3LYP 6 31G*
H_2–C_1 – C_3 –H_4	GS	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000
	TS	7.894	7.043	7.976	0.041	11.120	22.630	22.903	11.099
	Prd	59.448	-59.452	-59.182	-59.277	-59.129	-58.815	-58.756	180.000
H_2–C_1 – C_3 –H_5	GS	180.000	180.000	180.000	180.000	180.000	180.000	180.000	180.000
	TS	150.786	154.514	151.290	130.001	160.592	146.290	146.754	163.093
	Prd	-59.448	59.452	59.182	59.277	59.129	58.815	58.756	-58.492
H_4–C_3 – C_1 –O_6	GS	180.000	180.000	180.000	180.000	180.000	180.000	180.000	180.000
	TS	176.837	178.869	178.763	171.059	176.604	-160.800	-160.625	177.042
	Prd	-120.552	120.548	120.818	120.723	120.871	121.185	121.244	-0.000
H_5–C_3 – C_1 –O_6	GS	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000
	TS	-40.290	-33.660	-37.923	-58.898	-33.924	-37.140	-36.774	-30.965
	Prd	120.552	-120.548	120.723	120.723	120.871	-121.19	-121.244	121.508
H_8–C_7 – C_{10} –H_{11}	GS	-59.00	-60.466	-59.657	-60.993	-59.844	-60.024	-60.062	-59.922
	TS	-6.217	-5.452	-1.054	13.628	-5.488	-0.180	-0.200	180.00
	Prd	-0.000	-0.000	180.000	-0.000	-0.000	-0.000	-0.000	-0.000
H_8–C_7 – C_{10} –H_{13}	GS	61.090	-59.449	-60.040	58.187	60.605	59.981	59.933	59.988
	TS	-147.933	-143.938	-144.334	-138.782	-150.431	-179.680	-179.694	-150.154
	Prd	180.000	180.000	-180.000	180.000	180.000	180.000	180.000	180.000
H_9–C_7 – C_{10} –H_{13}	GS	-61.090	-59.449	-60.040	-58.187	-60.605	-59.981	-59.953	-59.988
	TS	5.594	6.842	1.518	-13.808	7.065	0.700	0.755	10.561
	Prd	-0.000	-0.000	180.000	-0.000	180.000	-0.000	-0.000	-0.000
H_9–C_7 – C_{10} –H_{11}	GS	178.820	-179.365	-179.736	-177.368	-178.946	-179.986	-179.927	179.898
	TS	147.309	144.799	144.799	138.602	152.008	-179.800	-179.760	151.500
	Prd	180.000	180.000	-0.000	-0.000	180.000	180.000	180.000	-0.000

Table 4: ATOMIC CHARGES (MULLIKEN) OF ETHYL VINYL ETHER

ATOMS		AMI	RMI	PM3	MNDO	HF/ 3-21G	HF/ 6 31G*	HF/ 6-31G**	DFT/ B3LYP 6 31G*
C_1	GS	-0.006	+0.068	+0.045	+0.099	+0.179	+0.216	+0.262	+0.158
	TS	+0.079	+0.170	+0.178	+0.097	+0.301	+0.301	+0.371	+0.227
	Prd	+0.180	+0.249	+0.278	+0.242	+0.340	+0.332	+0.379	+0.261
	Δq (TS-GS)	+0.073	+0.102	+0.133	-0.002	+0.122	+0.085	+0.109	+0.069
H_2	GS	+0.157	+0.127	+0.133	+0.081	+0.247	+0.194	+0.143	+0.140
	TS	+0.101	+0.075	+0.066	+0.063	+0.193	+0.301	+0.095	+0.097
	Prd	+0.083	+0.062	+0.041	+0.013	+0.183	+0.332	+0.090	+0.102
	Δq (TS-GS)	-0.056	-0.052	-0.047	-0.018	-0.054	-0.030	-0.048	-0.043
C_3	GS	-0.341	-0.345	-0.303	-0.186	-0.539	-0.505	-0.391	-0.402
	TS	-0.352	-0.404	-0.323	-0.047	-0.700	-0.597	-0.415	-0.456
	Prd	-0.289	-0.292	-0.196	-0.025	-0.726	-0.586	-0.434	-0.517
	Δq (TS-GS)	-0.011	-0.059	-0.020	-0.139	-0.161	-0.092	-0.024	-0.054
H_4	GS	+0.127	+0.111	+0.099	+0.053	+0.216	+0.180	+0.129	+0.140
	TS	+0.105	+0.099	+0.081	+0.021	+0.212	+0.176	+0.120	+0.147
	Prd	+0.103	+0.092	+0.062	+0.016	+0.234	+0.188	+0.140	+0.182
	Δq (TS-GS)	-0.022	-0.012	-0.018	-0.032	-0.004	-0.004	-0.009	+0.007
H_5	GS	+0.120	+0.111	+0.100	+0.050	+0.213	+0.179	+0.126	+0.140
	TS	+0.124	+0.118	+0.100	+0.038	+0.258	+0.219	+0.155	+0.180
	Prd	+0.103	+0.092	+0.062	+0.016	+0.234	+0.188	+0.140	+0.173
	Δq (TS-GS)	-0.004	+0.007	+0.000	-0.012	+0.045	+0.040	+0.029	+0.04
O_6	GS	-0.226	-0.246	-0.204	-0.288	-0.685	-0.606	-0.619	-0.445
	TS	-0.323	-0.377	-0.340	-0.258	-0.597	-0.604	-0.480	-0.458
	Prd	-0.287	-0.301	-0.315	-0.280	-0.516	-0.466	-0.475	-0.374
	Δq (TS-GS)	-0.097	-0.131	-0.136	+0.030	+0.088	+0.002	+0.139	-0.013
C_7	GS	-0.27	+0.040	+0.051	+0.166	-0.082	+0.001	+0.103	-0.029
	TS	-0.020	+0.111	+0.090	+0.172	-0.254	-0.292	-0.190	-0.160

	Prd	-0.218	-0.175	-0.153	-0.080	-0.425	-0.353	-0.254	-0.285
	Δq (TS-GS)	+0.007	+0.071	+0.039	+0.006	-0.172	-0.293	-0.293	-0.131
H_8	GS	+0.076	+0.054	+0.038	-0.006	+0.205	+0.158	+0.158	+0.141
	TS	+0.113	+0.082	+0.065	+0.018	+0.252	+0.212	+0.212	+0.183
	Prd	+0.109	+0.087	+0.076	+0.040	+0.213	+0.176	+0.176	+0.143
	Δq (TS-GS)	+0.037	+0.028	+0.027	+0.024	+0.047	+0.054	+0.022	+0.042
H_9	GS	+0.076	+0.054	+0.038	-0.006	+0.205	+0.158	+0.111	+0.141
	TS	+0.112	+0.090	+0.072	+0.021	+0.261	+0.212	+0.144	+0.184
	Prd	+0.109	+0.087	+0.076	+0.040	+0.213	+0.176	+0.127	+0.143
	Δq (TS-GS)	+0.046	+0.036	+0.034	+0.027	+0.056	+0.059	+0.033	+0.143
C_{10}	GS	-0.217	-0.191	-0.120	+0.024	-0.605	-0.492	-0.348	-0.456
	TS	-0.376	-0.394	-0.346	-0.075	-0.715	-0.606	-0.331	-0.471
	Prd	-0.218	-0.175	-0.153	-0.080	+0.425	-0.353	-0.254	-0.285
	Δq (TS-GS)	-0.159	-0.203	-0.226	-0.299	-0.110	-0.114	+0.017	-0.015
H_{11}	GS	+0.089	+0.075	+0.050	+0.009	+0.224	+0.177	+0.130	+0.162
	TS	+0.108	+0.103	+0.084	+0.037	+0.234	+0.245	+0.163	+0.184
	Prd	+0.109	+0.087	+0.076	+0.040	+0.213	+0.176	+0.127	+0.143
	Δq (TS-GS)	+0.019	+0.028	+0.034	+0.028	+0.010	+0.068	+0.033	+0.022
H_{12}	GS	+0.089	+0.075	+0.050	+0.009	+0.224	+0.177	+0.130	+0.162
	TS	+0.207	+0.221	+0.184	+0.071	+0.319	+0.185	+0.114	+0.171
	Prd	+0.107	+0.099	+0.067	+0.024	+0.250	+0.208	+0.160	+0.173
	Δq (TS-GS)	+0.118	+0.146	+0.134	+0.062	-0. 095	+0.008	-0. 016	+0.009
H_{13}	GS	+0.082	+0.075	+0.044	+0.003	+0.197	+0.161	+0.113	+0.148
	TS	+0.112	+0.106	+0.087	+0.042	+0.236	+0.188	+0.122	+0.173
	Prd	+0.109	+0.087	+0.076	+0.040	+0.213	+0.176	+0.127	+0.143
	Δq (TS-GS)	+0.030	+0.031	+0.043	+0.039	+0.039	+0.027	+0.009	+0.025

The calculated Arrhenius parameters as shown in table 5 below is in good agreement with the experimental value for instance ΔH calculated for AM1 (191.15), RM1 (191.21), PM3 (188.35). MNDO(193.94), HF/3 21G (190.55), HF/6 31G* (188.14), HF/ 6 31G**(194.56) and DFT/B3LYP 6 31G* (188.89) at 773K compare well with experimental data. Activation energy,Ea, log A and rate, k calculated are in perfect agreement with experimental data.

Table 5: ARRHENIUS PARAMETERS (624K)

	HOR	**ΔS $Jmol^{-1}K^{-1}$**	**ΔG $Jmol^{-1}$**	**ΔH $kJmol^{-1}$**	**E_a $kJmol^{-1}$**	**log A**	**$k(s^{-1})$**
EXPERIMENTAL	-	-	-	177.80 180.81 176.68	183.00 186.01 182.11	11.4 11.6 11.5	$1.3 X 10^{-4}$ (72) $1.1 X 10^{-4}$ (73) $1.7 X 10^{-4}$ (74)
AM1	31.30	11.29	-82.26	190.85	196.04	13.7	$2.0 X 10^{-3}$
RM1	31.01	11.79	-82.55	190.58	195.77	13.7	$2.2 X 10^{-3}$
PM3	33.99	14.49	-78.32	187.88	193.07	13.8	$5.2 X 10^{-3}$
MNDO	33.76	6.43	-81.81	193.13	198.33	13.5	$7.2 X 10^{-4}$
HF/3-21G	30.09	10.79	-64.22	190.05	195.24	13.7	$2.2 X 10^{-3}$
HF/6-21G*	29.62	13.46	-80.98	187.55	192.74	13.8	$4.9 X 10^{-3}$
HF/6-31G**	29.71	13.08	-87.60	189.25	194.44	13.8	$3.3 X 10^{-3}$
DFT/ B3LYP/6-31G*	32.45	13.88	-79.87	188.56	193.75	13.8	$3.9 X 10^{-3}$

The variation of rate, k with temperature from 498 to 773K at 25K interval as shown in table 6 shows that as the temperature increase, the rate of reaction also increases and at very high temperature the rate is at the maximum which in agreement with the Arrhenius theory(Bahl et al, 2004).

Table 6: Variation of Rate of Reaction (S^{-1}) with Temperature (K)

Temp (K)	AMI	RM1	PM3	MNDO	HF 3 21G	HF/6 31G*	HF/6 31G**	DFT
498	8.3x10^{-8}	9.1 X 10^{-8}	2.4 X 10^{-7}	2.9 X 10^{-8}	1.1 X 10^{-7}	2.61 X 10^{-7}	3.0 X 10^{-7}	1.84 X 10^{-7}
523	8.5 X 10^{-7}	9.3 X 10^{-7}	2.4 X 10^{-6}	3.1 X 10^{-7}	1.1 X 10^{-6}	2.58 X 10^{-6}	3.0 X 10^{-6}	1.85 X 10^{-6}
548	7.1 X 10^{-6}	7.8 X 10^{-6}	1.9 X 10^{-5}	2.6 X 10^{-6}	9.2 X 10^{-6}	2.07 X 10^{-5}	2.5 X 10^{-5}	1.51 X 10^{-5}
573	4.7 X 10^{-5}	5.4 X 10^{-5}	1.3 X 10^{-4}	1.8 X 10^{-5}	6.1 X 10^{-5}	1.39 X 10^{-4}	1.7 X 10^{-4}	1.01 X 10^{-4}
598	2.9 X 10^{-4}	3.2 X 10^{-4}	7.6 X 10^{-4}	1.1 X 10^{-4}	3.6 X 10^{-4}	8.39 X 10^{-4}	9.6 X 10^{-4}	6.06 X 10^{-4}
623	1.4 X 10^{-3}	1.6 X 10^{-3}	3.7 X 10^{-3}	5.9 X 10^{-4}	1.8 X 10^{-3}	4.02 X 10^{-3}	4.8 X 10^{-3}	2.95 X 10^{-3}
648	6.0 X 10^{-3}	7.4 X 10^{-3}	1.6 X 10^{-2}	2.8 X 10^{-3}	8.2 X 10^{-3}	1.78 X 10^{-2}	1.1 X 10^{-2}	1.32 X 10^{-2}
673	2.7 X 10^{-2}	2.9 X 10^{-2}	6.7 X 10^{-2}	1.1 X 10^{-2}	3.3 X 10^{-2}	7.10 X 10^{-2}	6.3 X 10^{-2}	5.22 X 10^{-2}
698	1.0 X 10^{-1}	1.1 X 10^{-1}	2.4 X 10^{-1}	4.3 X 10^{-2}	1.2 X 10^{-1}	2.55 X 10^{-1}	3.0 X 10^{-2}	1.89 X 10^{-1}
723	3.4 X 10^{-1}	3.6 X 10^{-1}	7.9 X 10^{-1}	1.4 X 10^{-1}	4.1 X 10^{-1}	8.39 X 10^{-1}	9.8 X 10^{-1}	6.23 X 10^{-1}
748	1.06	1.14	2.45	4.6 X10^{-1}	1.27	2.559	3.164	1.942
773	3.04	3.32	6.95	1.35	3.63	7.239	8.399	5.541

TABLE 7 : INFRA RED (CM^{-1})

	EXPERIMENTAL	AM1	RM1	PM3	MNDO	HF/ 321G	HF/ 6 31G*	HF/ 6 31G**	DFT/ B3LYP 631G*
REACTANT									
V(C-H)$_{BEND}$	N/A	1051 – 1393	1017 – 1357	1039 -1921	1068 - 1560	1038 – 1701	1069 – 1680	1066 – 1630	1066 – 1554
V(C=C) str	1660 -1675	1863	1822	1842	1849	1830	1862	1858	1715
V(C-O) str	1120	1411	1457	1274 - 1370	1560	1346	1372	1368	1254
V(C-H) str sp3	2870	3028 – 3162	2898 - 3087	2927 – 3090	3173 – 3448	3205 – 3292	3205 – 3294	3179 – 3276	3019 – 3140
V(C-H) str sp2	2975 - 3080	3179 - 3233	3119 - 15142	3152 – 3162	3355- 3448	3351 - 3430	3361 - 3442	3340 – 3427	3193 – 3278
PRODUCT1(Aldehyde)									
V(C-H)Bend	N/A	1036 – 1427	1061 – 1342	1053 -1401	1045 – 1481	1222 – 1646	1231 – 1616	1255 – 1600	1136 – 1500
V(C=O) str	1740 - 1690	2060	1947	.1985	2128	1925	2033	2031	1843
V(C-H) str	3100 - 3010	3058 – 3154	3026 – 3083	3082 – 3181	3245 – 3349	3157 - 3305	3206 – 3321	3185 – 3304	3043 – 3163
V(C-H) str (Aldehyde)	2720 - 2820		2922	2936			3151	3117	2900
PRODUCT 2(Ethene)									
V(C-H) $_{BEND}$	N/A	1056 – 1413	1035-1296	1054 – 1328	1099 – 1466	1115 – 1640	1095 – 1610	1093 – 1598	1068 – 1497
V(C=C) str	1680 – 1620	1827	1748	1829	1783	1842	1850	1852	1721
V(C-H) sp2	1470 -2925	3153 – 3217	3083 -3114	3128	3380 - 3433	3305 - 3402	3320 – 3420	3296 - 3400	3152 – 3247

SPECTRA OF ETHYL VINYL ETHER WITH AMI

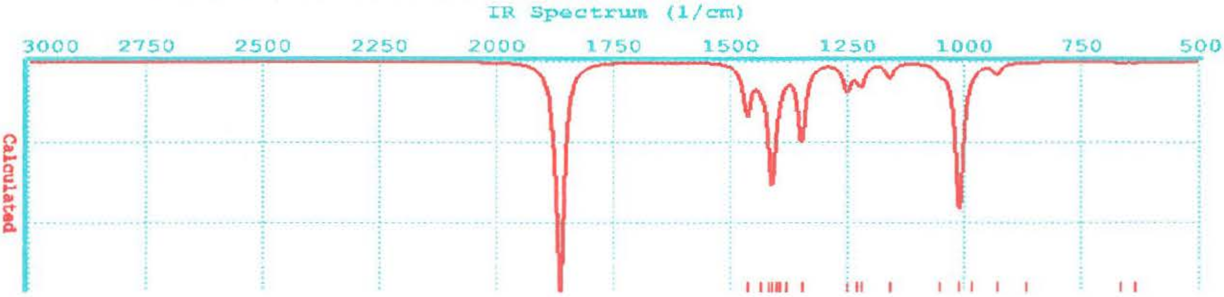


Fig 1: Ground state structure.

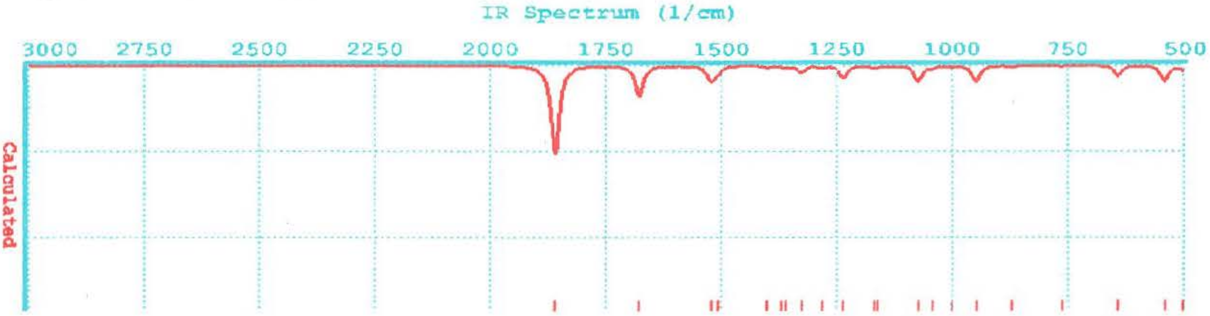


Fig 2: Transition State Structure.

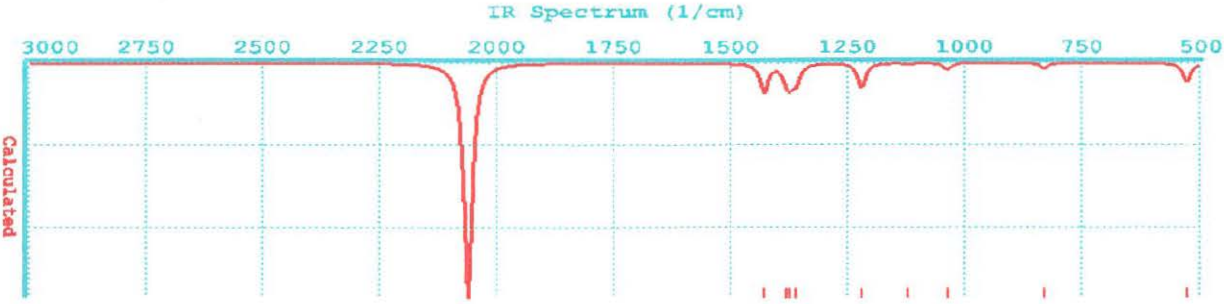


Fig 3: Product 1 (Acetaldehyde)

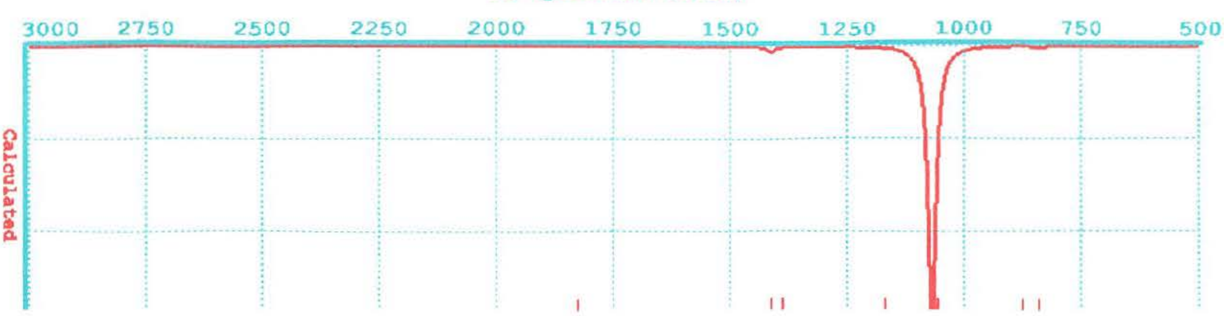
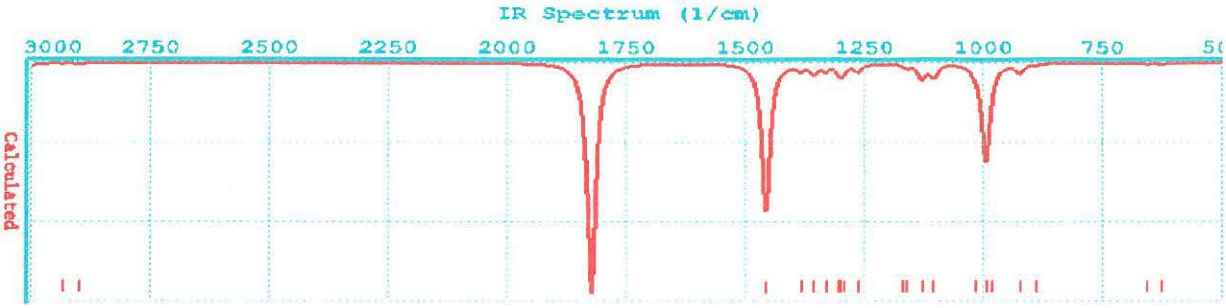


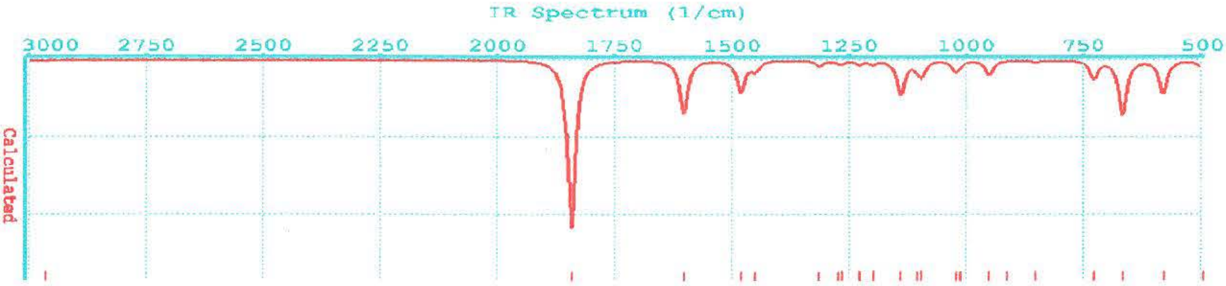
Fig 4 Product 2 (Ethene)

SPECTRA OF ETHYL VINYL ETHER WITH RMI

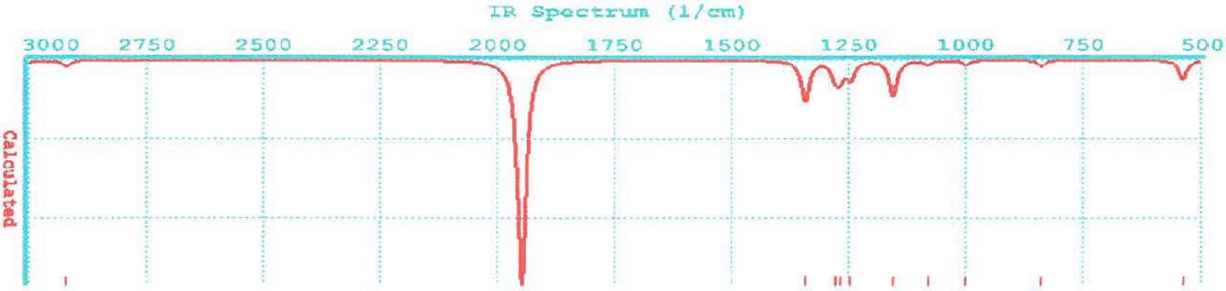
GROUND STATE SPECTRA



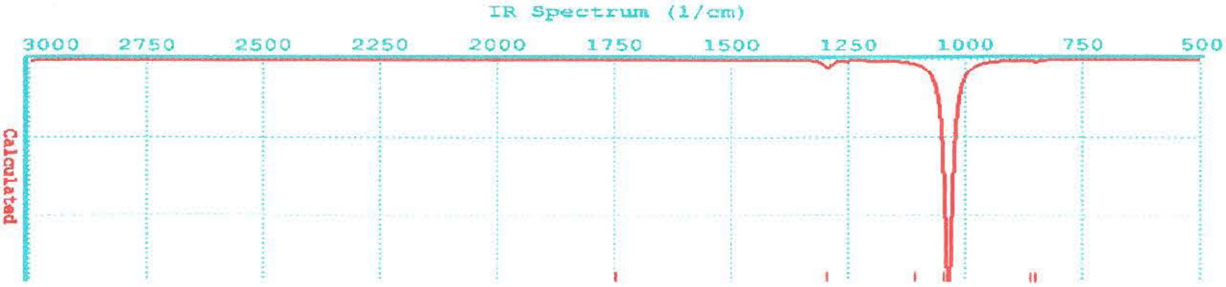
TRANSITION STATE



PRODUCT I (ACETALDEHYDE)

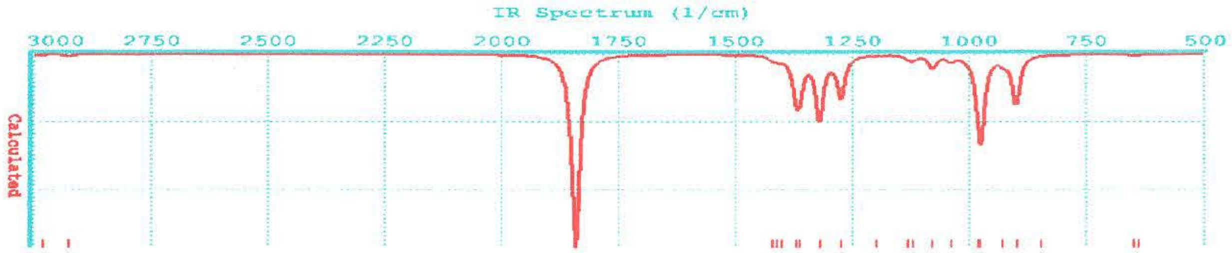


PRODUCT2 (ETHENE)

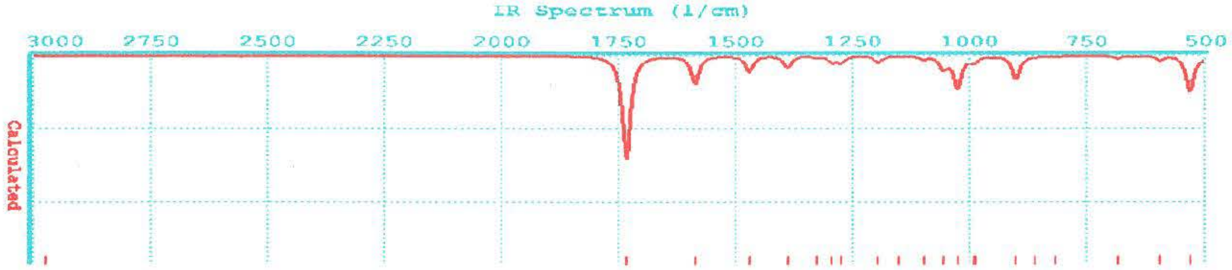


SPECTRA OF ETHYL VINYL ETHER WITH WITH PM3

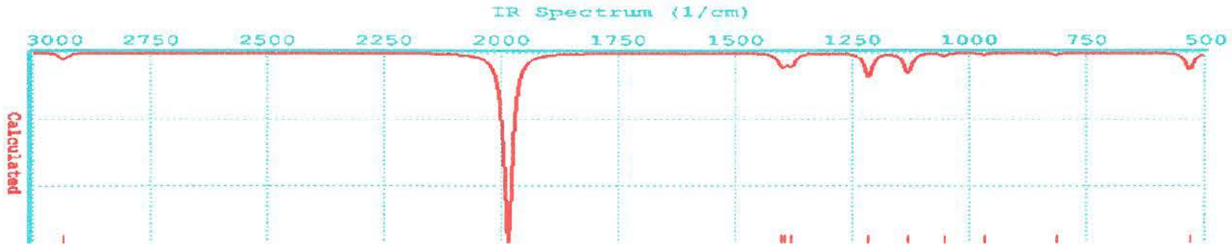
GROUND STATE SPECTRA



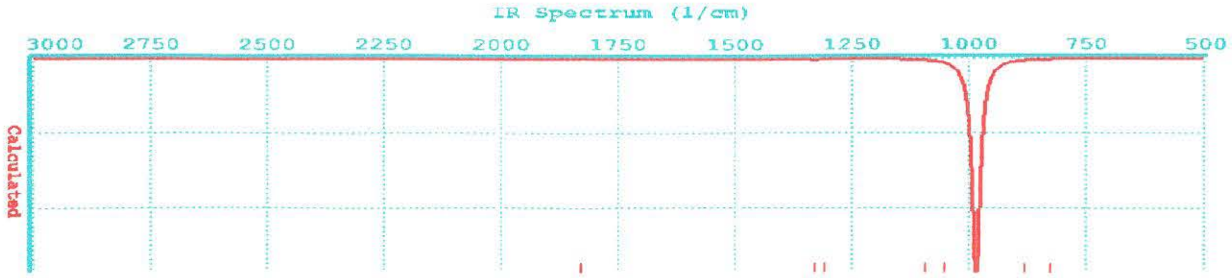
TRANSITION STATE



PRODUCT 1(PM3)

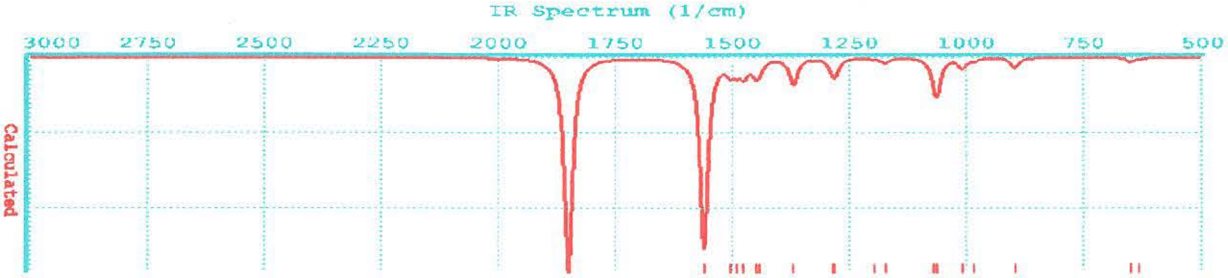


PRODUCT 2 (PM3)

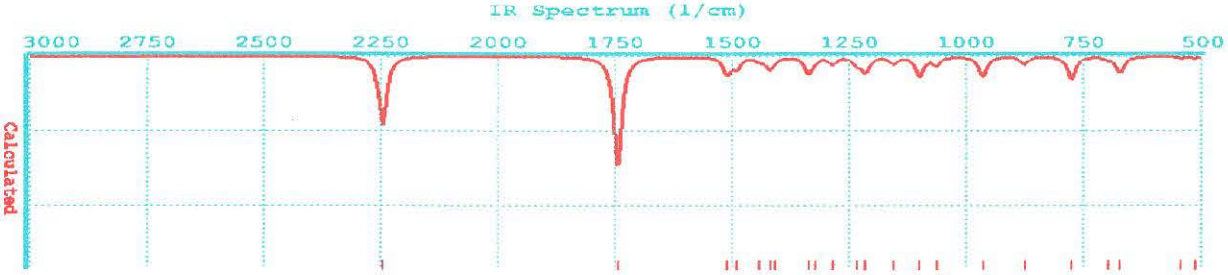


SPECTRA OF ETHYL VINYL ETHER WITH MNDO

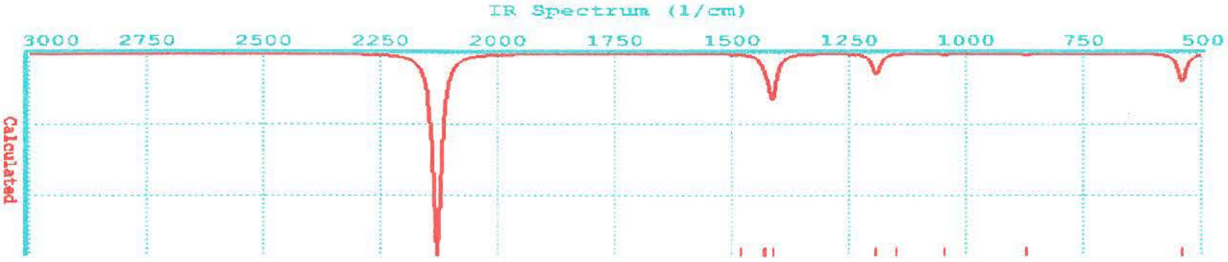
GROUND STATE SPECTRA



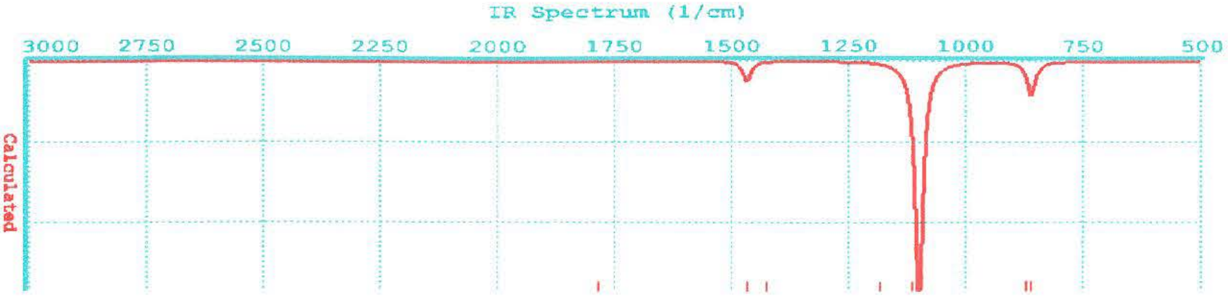
TRANSITION STATE WT (MNDO)



PRODUCT 1 MNDO



PRODUCT 2 MNDO



CONCLUSION

In conclusion, it is observed that both semi-empirical and ab-intio method in Spartan could be used effectively to study the kinetics, mechanism , thermodynamic and vibrational spectrosopy of ethyl vinyl ether.

ACKNOWLEDGEMENT

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