

Full Length Research Paper

Kinetics and mechanism of elimination of ethyl acetate in the gas phase: A theoretical study

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Using the PM3 semi-empirical quantum mechanical molecular orbital method, a procedure was devised to study the gas phase pyrolytic reaction of ethyl acetate in order to gain a deeper insight into both its kinetics and mechanism. By considering the involvement of formal charges and geometrical changes in the activation, a mechanism was proposed in which a pre-equilibrium of acidic proton transfer is followed by the rate limiting bond polarization of C-O bond in a cyclic transition state. The reactions involve a non-synchronous break in the β -carbon-hydrogen and the α -ether oxygen bonds through a six-centred transition state. The results obtained showed that the rate constant and the computed Arrhenius parameters compare well with the experimental values in the literature.

Key words: Kinetics, unimolecular elimination, semi-empirical calculation, MOPAC, transition state structure.

INTRODUCTION

The gas-phase elimination of esters of organic acids proceeds through a six-membered cyclic transition state type of mechanism as described in reaction Scheme 1. The presence of a C_{β} -H on the alkyl side of organic esters, such as acetates, leads to gas-phase elimination through a six-centered cyclic transition state type of mechanism.

A large number of gas-phase unimolecular reaction, which have been studied, appeared to take place by way of 4-centre and 6-centre cyclic activated complexes (O'Neal and Benson, 1967). The vast majority of the six-centre reactions are carboxylic acid eliminations from the alkyl acetates to produce olefins. The reactions involve a non-synchronous break in the β -carbon-hydrogen and the α -ether oxygen bonds through a six-centred transition state.

The aim of this study is to take a deeper look through computational approach at the kinetics and mechanism of pyrolytic elimination reaction of alkyl acetates by studying ethyl acetate as a representative, through a procedure devised by Adejoro and Bamkole (2005) for alkyl acetates.

COMPUTATIONAL PROCEDURE

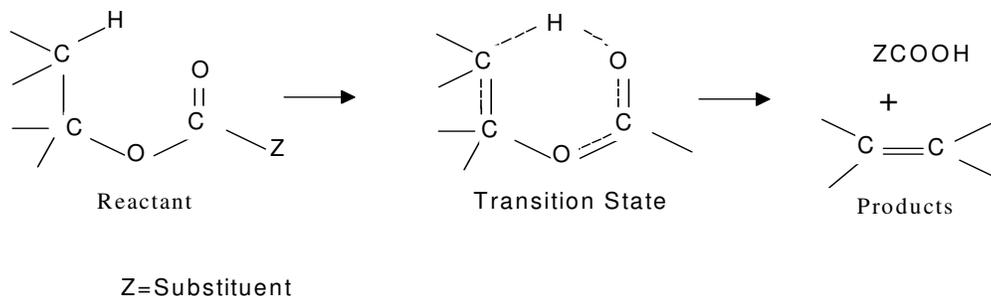
The semi-empirical PM3 method in MOPAC (Stewart, 1990) was used for the gas-phase elimination reaction of $CH_3COOC_2H_5$ into CH_3COOH and C_2H_4 . Geometries of the reactant (ground state, GS) and products were fully optimized. The transition state (TS) was located by the gradient norm minimization and was confirmed by the single negative eigenvalue in the Hessian matrix (Sizmadia, 1976). The geometry of the ethyl acetate is defined in Scheme 2.

H_{13} is the β -hydrogen to be eliminated and the dihedral angle 13-5-4-1 is acute and positive. The usual rules of geometry definition prescribed in MOPAC (Stewart, 1990) brochure are applied.

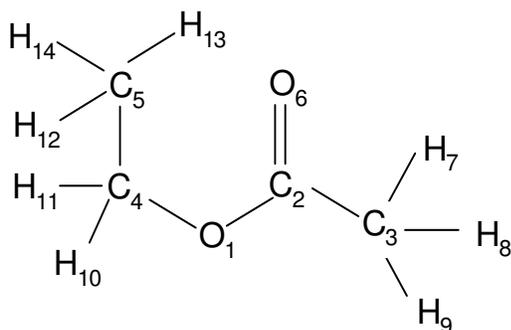
Reaction path study was performed for the substrate using $H_{13}-O_6$ as reaction coordinate. By decreasing this bond length systematically in many small steps from its initial value of 4.58\AA to the bond length in the product of about 0.96\AA , an approximate product structure was obtained and optimized. Other aspects of the procedure such as saddle calculation, etc, were carried out as previously described by Adejoro and Bamkole (2005).

The apparent enthalpy of activation was obtained for ethyl acetate through FORCE calculation on both the ground state and transition state, geometries subtracting the enthalpy of the reactant at 623K from the enthalpy of

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Scheme 1.



Scheme 2.

of transition state at 623K. The correction computed is subtracted from the apparent enthalpy of activation.

According to the Transition State Theory (TST), for a unimolecular reaction

$$E_a = \Delta H^* + RT$$

Where ΔH^* is the corrected enthalpy of activation, at 623K.

The apparent entropy ΔS^* was obtained from the FORCE calculation by subtracting the entropy of the substrate at 623k from the entropy of the transition state also at 623k.

The effect of internal rotation was obtained by making corrections, $(R \ln \sigma)$ for symmetry, where σ is the number of equivalent β -hydrogen atoms available for elimination. It is otherwise known as the reaction path degeneracy. This is added and not subtracted as it can only enhance reaction.

ΔS^* value was used to calculate Arrhenius pre-exponential factor using the relation.

$$A = \{e^m k' T/h \exp(\Delta S^*/R)\}$$

Where m is the molecularity of the reaction (that is, the number of reactant molecules involved in the reaction). The first-order rate coefficient $k(T)$ was calculated using TST (Benson, 1960) and assuming the transmission coefficient is equal to unity as expressed in the following equation:

$$k(T) = k' T/h \exp(-\Delta G^*/RT)$$

where ΔG^* is the Gibbs free energy change between the reactant and the transition state and k' and h are the Boltzmann and Planck constants, respectively. ΔG^* was calculated using the following relation:

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

RESULTS

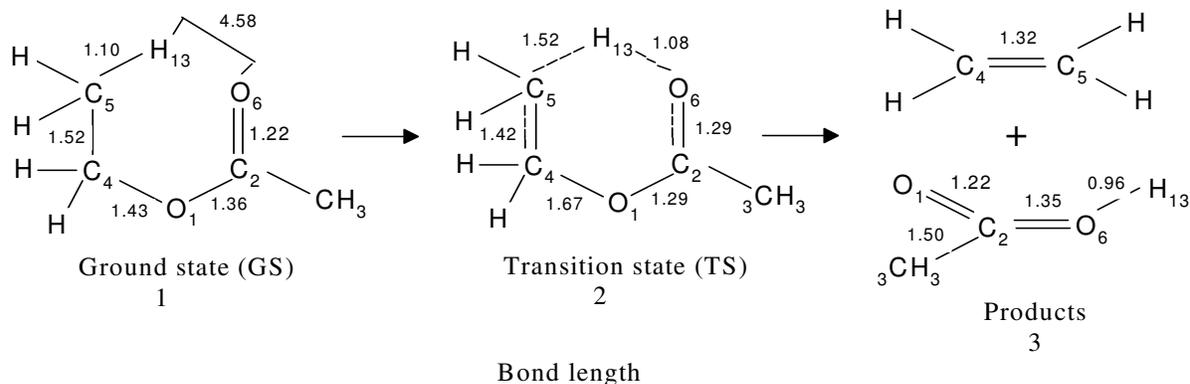
Using the PM3 Hamiltonian, the geometries of the reactant 1 and products 2 and 3 are predicted as shown in Scheme 3.

In the transition state, C_4-O_1 is stretched, whereas the C_5-H_{13} bond is now a long bond and virtually broken while the $H_{13}-O_6$ bond is almost fully formed showing that the gas-phase elimination reaction of $C_2H_5COOCH_3$ to give C_2H_4 and CH_3COOH occurs by a concerted non-synchronous mechanism. That is, processes that lead to the intermediate are concerted but the rate determining process is not synchronous but is delayed (Scheme 4).

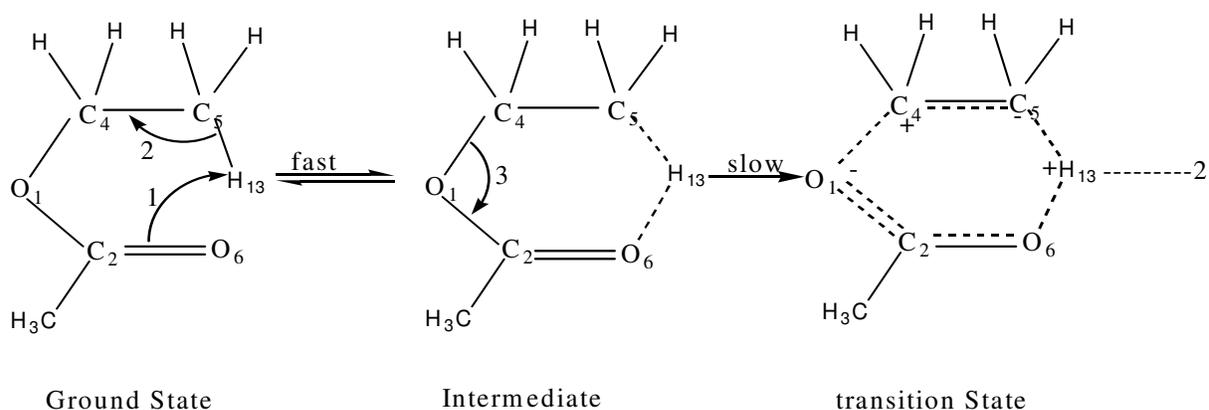
This is a two-stage reaction in which one is concerted but not synchronous. Some changes in bonding took place mainly before, and some mainly after the transition state.

Rotational barriers

The above values are the values of some dihedral angles in going from the ground state (GS) to the transition state (TS) through etacreat, the reactant structure obtained through IRC calculation (Table 1). For each rotation, the rotation for the heat of formation (ΔH , kJ/mol) with relevant dihedral angle (\angle) is recorded (Table 2), minimum on the first row, maximum on the next; the difference on the third row being the barriers encountered on a 360° cycle. Using the rotation about C_4-O_1 bond as an example, that is, for changes in dihedral angle 5-4-1-2, the following 3-part barrier is crossed. In a similar way, rotation about O_1-C_2 bond produced a 2-part barrier of which none is crossed. For the rotation of the C_4-C_5 bond, the dihedral 12-5-4-1 was used and out of the 3-part barrier obtained



Scheme 3.



Scheme 4.

Table 1. Variation of Dihedral angles (degrees, °) in going from ground state (GS) to Transition State (TS) through 'etacreac'.

Dihedral	GS	Etacreac	TS
4-1-2-3	179.37°	-175.51°	151.34°
5-4-1-2	-179.16°	-79.79°	11.77°
7-3-2-1	-178.74°	179.97°	151.64°
12-5-4-1	-177.75°	-170.13°	111.85°

Table 2. Variation of heat of formation (ΔH , kJ/mol) with the indicated dihedral angle (<, °), (here 5-4-1-2).

<	ΔH	<	ΔH	<	ΔH
-179.16°	-413.66	280	-415.08	80	-415.54
230.00	-411.11	360	-391.28	140	-411.02
	2.55		23.80		4.52 kJ

only the first two (10.88 kJ) are crossed. The barrier produced by C_2C_3 bond rotation (That is, the rotation of the methyl group on the acetyl functional group) is small

Table 3. Formal charges of species involved in elimination reaction (electronic charge unit).

Atom	GS	TS	Product	Δq (TS - GS)
1O	-0.27	-0.36	-0.40	-0.09
2C	0.37	0.43	0.38	+0.06
3C	-0.11	-0.14	-0.11	-0.03
4C	0.08	0.24	-0.14	+0.16
5C	-0.12	-0.65	-0.16	-0.53
6O	-0.38	-0.35	-0.32	+0.03
7H	0.07	0.07	0.06	0.00
8H	0.06	0.07	0.07	0.01
9H	0.06	0.07	0.06	0.01
10H	0.04	0.04	0.08	0.00
11H	0.04	0.04	0.08	0.00
12H	0.04	0.10	0.08	-0.03
13H	0.04	0.32	0.23	+0.28
14H	0.04	0.09	0.08	+0.05

and negligible. From the use of $H_{13}-O_6$ bond length as the reaction coordinate, only one barrier is encountered and the value is 3.26 kJ. Therefore, for ethylacetate, the sum

Table 5. Heats of formation of reactant (GS), transition state (TS) and products, and derived energetics, ΔE^\ddagger and ΔE_0 (kJ/mol).

GS	TS	Products	$\Delta E^\ddagger = E_{\text{trans}} - E_{\text{reac}}$	$\Delta E_0 = E_{\text{pdt}} - E_{\text{reac}}$
-413.80	-175.27	-364.30	238.53	49.50

Table 4. Ground state (GS), transition state (TS) and product atom distances.

Bond length	GS	TS	Product	Δd (TS-GS)
O ₁ -C ₂	1.36	1.29	1.22	-0.07
C ₂ -C ₃	1.50	1.50	1.50	0.00
O ₁ -C ₄	1.43	1.67	3.73	+0.24
C ₄ -C ₅	1.52	1.42	1.32	-0.01
C ₂ -O ₆	1.21	1.29	1.35	0.08
C ₃ -H ₇	1.10	1.10	1.10	0.00
C ₃ -H ₈	1.10	1.10	1.10	0.00
C ₃ -H ₉	1.10	1.10	1.10	0.00
C ₄ -H ₁₀	1.11	1.10	1.09	-0.01
C ₄ -H ₁₁	1.11	1.10	1.09	-0.01
C ₅ -H ₁₂	1.10	1.09	1.09	-0.01
C ₅ -H ₁₃	1.10	1.52	1.52	+0.42
C ₅ -H ₁₄	1.10	1.09	1.09	-0.01
O ₆ -H ₁₃	4.58	1.08	0.96	-3.50

of the relevant barriers (That is, 26.35 +10.88+3.26 =40.49 kJ) serves as correction to the apparent activation enthalpy. The geometric parameters shown in Tables 3 and 4 indicate a product-like transition state, while the energetics are shown in Table 5 for ethyl acetate.

The geometric parameters shown in Table 4 indicate a product-like transition state. Calculated activation parameters are in reasonable agreement with the experimental values. Calculated activation parameters are in reasonable agreement with the experimental values (Table 6) obtained by Blades (1954) and Blades and Gilderson (1960).

DISCUSSION

In the transition state, C₄-O₁ is stretched, whereas the C₅-H₁₃ bond is now a long bond and virtually broken while the H₁₃-O₆ bond is almost fully formed showing that the gas-phase elimination reaction of C₂H₅COOCH₃ to give C₂H₄ and CH₃COOH occurs by a concerted non-synchronous mechanism.

The transition state found is late in the reaction coordinate in the sense of the breaking of C₄-O₁ and C₅-H₁₃ bonds and the formation of H₁₃-O₆ bond.

Calculated activation parameters are shown in Table 6 and they are in reasonable agreement with experimental value. Blades (1954) and Blades and Gilderson (1960) First order rate coefficient is in perfect agreement with both the experimental and calculated values, thus corroborating our earlier submission (Adejoro and Bamkole,

2005) that, PM3 method perfectly predicts the gas-phase pyrolysis of alkyl acetates.

The formal charges in the TS (Table 4), shows that the C₅ has the greatest charge development while the least is on C₄. This is in agreement with findings of Ikchoon Lee et al. (1987). However it has been experimentally shown that the Hammett ρ values showed that C₄ has the largest charge development while C₅ has the least in the TS (Lee et al., 1987). This is not in agreement with the formal charges found theoretically in this work (Table 4). This apparent discrepancy has been rationalized as follows:

In the activation, polarization of the C₄-O₁ and C₅-H₁₃ bonds causes positive charges on the carbon atoms C₄ and C₂ to increase and the C₅ atom to become more negative (Table 3), the increase in the negative charge on the C₅ being much greater. Much greater bond polarization of the C₅-H₁₃ places considerable positive charge on the H₁₃ atom, so that the positive charge is delocalized over the entire O₁-C₂-O₆ frame in the TS. Originally in the TS, the C₄-C₅-H₁₃ frame was somewhat electron deficient and the O₁-C₂-O₆ frame electron rich.

As a result of electron demand and supply within the GS of ethyl acetate, the carbonyl oxygen, O₆, becomes highly negative and β -hydrogen, H₁₃, becomes quite acidic, so that a fast equilibrium, reminiscent of a fast proton transfer equilibrium, takes place.

The formation of an intermediate (scheme 4) in which an attack from the acyl oxygen on the β -hydrogen, H₁₃ takes place as a fast step followed by the rate-determining step. In the intermediate, the negative charge builds up on the C₅ atom, since double bond formation between C₄ and C₅ is delayed until the leading event, the C₄-C₅ polarization takes place in the rate-determining step. The processes that lead to the intermediate are concerted but the rate determining process is not synchronous but is delayed. The already built-up negative charge on C₅ makes further increase on the rate determining process small. Since the rate determining process is the leading event in the activation, the charge development will be largely reflected on C₄ (positive) and O₆ (negative). There is an assumption that the interaction and charge transmission between C₄ and C₅ is inefficient so that sizable charge on C₅ is not efficiently transmitted to the electron-deficient C₄ and consequently double bond formation between C₄ and C₅ takes place slowly at a later stage (Lee et al., 1987).

Conclusion

In conclusion the PM3 results are consistent with the TS where the C _{α} -O bond polarization is the rate determining

Table 6. Comparative theoretical and experimental activation parameter at (623k).

Method	Ea (kJmol ⁻¹)	ΔH* (kJmol ⁻¹)	ΔS* (kJmol ⁻¹)	ΔG* (kJmol ⁻¹)	Log A (s ⁻¹)	k ¹ 10 ⁻⁵ (s ⁻¹)	Ref.
PM3	203.51	198.32	-21.05	211.47	12.45	2.44	
Experimental	199.79	194.61	-20.54	207.40	12.48	5.36	9
	200.83	195.65	-18.41	207.13	12.59	5.65	10
Calculated	201.69	196.51	-18.28	207.89	12.60	4.88	9

step, which follows the pre-equilibrium involving the acidic hydrogen shift towards the carbonyl oxygen.

Also the negative entropy of activation shows that the mechanism involves a cyclic transition state (Hurd and Blunck, 1938). It is equally encouraging that the TS satisfy the four criteria prescribed by Kormonicki and McIver (1972).

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