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PM3 study of the effects of α-methylation on the gas-phase kinetics of thermal decomposition of ethyl acetates

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ABSTRACT

The effects of α-methylation on the gas-phase reaction kinetics and mechanism of the pyrolysis of ethyl acetates was studied theoretically at semi-empirical PM3 level. All the calculations showed that the thermal decomposition of these alkyl acetates is a concerted asynchronous process via a six-membered cyclic transition state. The overall result of the calculations shows that α-methyl substitution has a steric releasing effect in the transition state, hence it is rate enhancing. Also it is found that rate enhancement due to C_4-O_1 bond stretching in the formation of the T.S. is more significant as a rate determinant than the acidic nature of the β hydrogen eliminated. The first order rate coefficients and computed activation parameters predicted by PM3 method are in good agreement with the experimental results for the series studied.

KEYWORDS

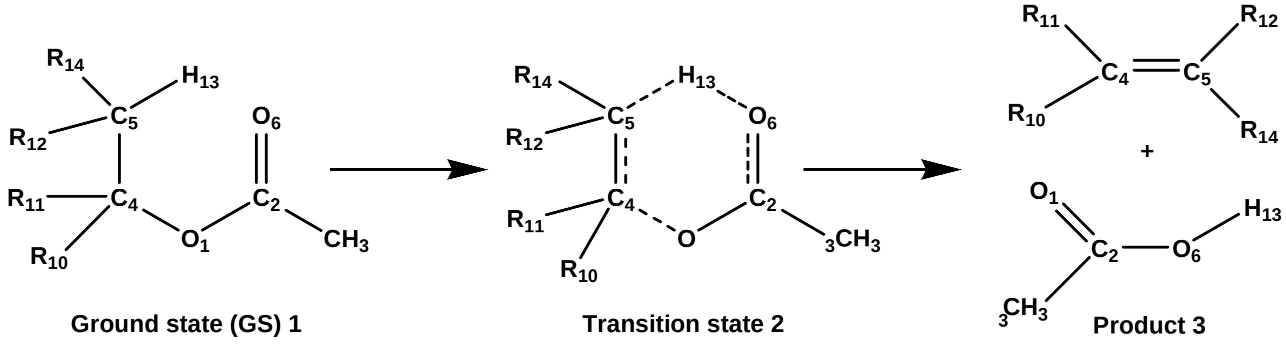
Kinetics;
Unimolecular elimination;
Semi-empirical calculation;
MOPAC;
Transition state structure;
α-methylation.

INTRODUCTION

Ester fragments to alkenes and carboxylic acids, often cleanly and in good yield, when passed through a heated tube at 400-450°C; with a contact time of a few seconds.Thermal decomposition of esters has been extensively studied experimentally and theoretically. For molecular elimination, 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 as described in reaction Scheme 1.

The vast majority of the six-centre reactions are carboxylic acid eliminations from the alkyl acetates to produce olefins. The reactions involve asynchronous break in the β-carbon-hydrogen and the α-ether oxygen bonds through a six-centred transition state.

In a previous work by Adejoro and Bamkole[1], we examined theoretically the calculation of Arrhenius parameters of some alkyl acetates and we equally carried out the PM3 study of the kinetics and mechanism of ethyl acetate[2]. As a part of continuing effort to understand the pyrolysis mechanism, we have carried out the PM3 studies of the pyrolysis reactivities of the α-methylated ethyl acetates. This study focuses on the effects of progressive methylation of ethyl acetate at the α-carbon on the kinetics and activation parameters, through a procedure devised by Adejoro and Bamkole[1] for alkyl acetates.

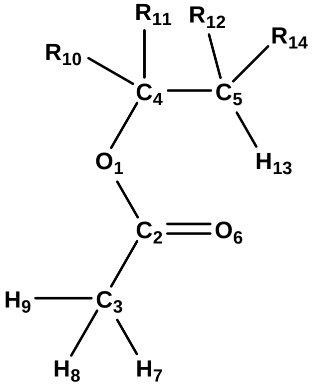


Scheme 1

COMPUTATIONAL METHOD AND MODEL

The semi-empirical PM3 method in MOPAC[3] was used throughout in this work. Geometries of the reactant (RE) 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[4]. Three esters investigated are given in TABLE 1. The geometry of the alkyl acetate is defined in Scheme 2 below.

Ethyl acetate is derived from the reactant geometry by regarding R_{10}, R_{11}, R_{12} and R_{14} as hydrogen atoms and iso-propyl acetate can be regarded as derivable from the alkyl acetate by the substitution of R_{10} or R_{11} on C_4 with a methyl group; while tert-butyl acetate can be regarded as derivable from ethyl acetate by the substitution of both R_{10} and R_{11} on C_4 by methyl groups (TABLE 1).



Reactant Geometry

Scheme 2

TABLE 1 : Esters studied in this work

Designation	Non-Hydrogen Sbstituent	Nomenclature
I	-	Ethyl acetate
II	R_{10} or R_{11}=CH_3	i-propyl acetate
III	R_{10} = R_{11}=CH_3	t-butyl acetate

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 brochure[3] are applied.

Reaction path study was performed for the reactant using H_{13}-O_6 as reaction coordinate. By decreasing this bond length systematically in many small steps from its initial value of 4.58A° (e.g. for ethyl acetate) to the bond length in the product (about 0.96A°), 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[1]. The apparent enthalpy of activation was obtained through FORCE calculation on both the ground state and transition state geometries by subtracting the enthalpy of the reactant at 623k from the enthalpy 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

$$Ea = \Delta H^* + RT,$$

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 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.

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

where m is the molecularity of the reaction.

The first-order rate coefficient k(T) was calculated using TST[5], and assuming the transmission coefficient is equal to unity as expressed in the following equation:

$$\mathbf{k(T)=k_{B}T/h \exp(-\Delta G^{*}/RT)}$$

where ΔG* is the Gibbs free energy change between the reactant and the transition state and k_B and h are the Boltzmann and Planck constants, respectively.

ΔG* was calculated using the following relation:

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

RESULTS

The experimental works reported by Arthur Blades[6], Arthur Blades and Gilderson[7], Emovon and Maccoll[8]; Rudy and Fugassi[9] suggested that the thermal decomposition of alkyl acetates passes through a six-membered ring transition state irrespective of substituents.

Using ethyl acetate as an example, the geometries of the reactant 1 and products 2 and 3 are predicted as shown in scheme 3 below:

The reaction pathway is depicted in scheme 3 in which the relevant atom numbering is also indicated.

Two bonds that are breaking i.e. C_4-O_1 and C_5-H_{13} are seen to stretch from 1.43A° and 1.10A° in the RE to 1.67A and 1.52A° respectively in the TS (TABLE 2). 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 alkyl acetate occurs by a concerted asynchronous mechanism. That is, processes that lead to the intermediate are concerted but the rate determining process is not synchronous but is delayed[2].

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.

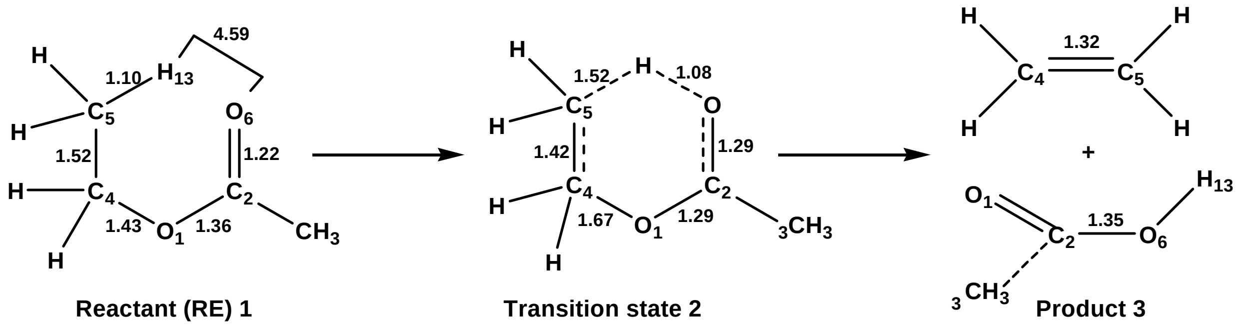
In the activation, polarization of the C_4-O_1 and C_5-H_{13} bonds causes positive charges of the carbon atoms C_4 and C_2 to increase and the C_5 atom to become more negative (TABLE 2). TABLES 2 and 3 are TABLES of selected optimized geometric parameters (bond lengths, bond angles and dihedral angles) of reactants, transition states and products. It reveals that the progresssive α-methylation i.e. I-II-III, leads to greater O_1-C_4 stretch in the TS.

For the six-membered ring TS, the PM3 optimized distance between atoms O_6 andH_{13} is in the range of 1.08-1.13 A°, becoming much shorter by about 3.53 A° than its length in the reactant, still not being close to that in the product (*ca.* 0.97 A°). In moving from I-III (TABLE 1), there is no significant change in bond lengths (TABLE 2), bond and dihedral angles (TABLE 3) thus showing clearly that α-methylation does not change the structure of reactants significantly.

TABLE 4 shows that methylation on C_4 decrease the activation energies in agreement with the rate increases found experimentally[6-9].

The lowering of the activation barrier accompanied by the α-methylation is evident from these energy component changes in TABLE 5.

TABLE 5 shows that both activation energies, ΔE^{*}



Reactant (RE) 1 Transition state 2 Product 3

Scheme 3

TABLE 2 : Formal charges (q) of atoms (in electronic charge unit) and bond length (d in A°) involved in activation and equilibrium processes for the elimination reaction*

Atom	Ethyl acetate				i-Propyl acetate				t-Butyl acetate			
	RE	**TS**	**PR**	**Δq^***	**RE**	**TS**	**PR**	**Δq^***	**RE**	**TS**	**PR**	**Δq^***
${}_1O$	-0.27	-0.36	-0.40	-0.09	-0.27	-0.37	-0.40	-0.10	-0.27	-0.39	-0.41	-0.12
${}_2C$	0.37	0.43	0.38	+0.06	0.37	0.43	0.38	+0.06	0.38	0.44	0.38	+0.06
${}_4C$	0.08	0.24	-0.14	+0.16	0.09	0.26	-0.12	+0.17	0.13	0.30	0.10	+0.17
${}_5C$	-0.12	-0.65	-0.16	-0.53	-0.12	-0.65	-0.17	-0.53	-0.12	-0.64	-0.20	-0.52
${}_6O$	-0.38	-0.35	-0.32	+0.03	-0.38	-0.37	-0.32	+0.01	-0.38	-0.38	-0.32	0.00
${}_{13}H$	0.04	0.32	0.23	+0.28	0.04	0.32	0.23	+0.28	0.05	0.33	0.24	+0.28
Bond	**RE**	**TS**	**PR**	**Δd^***	**RE**	**TS**	**PR**	**Δd^***	**RE**	**TS**	**PR**	**Δd^***
O_1-C_2	1.36	1.29	1.22	-0.07	1.36	1.29	1.21	-0.07	1.36	1.29	1.21	-0.07
C_2-C_3	1.50	1.50	1.50	0.00	1.50	1.50	1.49	0.00	1.51	1.51	1.50	0.00
O_1-C_4	1.43	1.67	3.73	+0.24	1.44	1.70	4.53	+0.26	1.45	1.74	3.81	+0.29
C_4-C_5	1.52	1.42	1.32	-0.10	1.53	1.43	1.33	-0.10	1.54	1.43	1.33	-0.11
C_2-O_6	1.21	1.29	1.35	0.08	1.22	1.28	1.35	+0.06	1.22	1.28	1.35	+0.06
C_5-H_{13}	1.10	1.52	2.58	+0.42	1.10	1.48	2.74	+0.38	1.10	1.44	2.43	+0.34
O_6-H_{13}	4.58	1.08	0.96	-3.50	4.24	1.10	0.96	-3.14	4.63	1.13	0.96	-3.5

$*\Delta q^* = q^{(TS)} - q^{(RE)}$, $\Delta d^* = d^{(TS)} - d^{(RE)}$

and energy changes of reaction, ΔE_o, decrease with α-methylation. Lowering of activation energies by the methylation is consistent with the experimentally found faster rate ester pyrolysis upon methylation on C_α atoms. The parallel decrease of ΔE^* and with ΔE_o, is however a manifestation of Bell-Evans-Polanyi (BEP) principle[10].

Activation energy correlation

Some very interesting and systematic substitution or methylation effects on the activation energy, E_a now become apparent (TABLE 4). Methyl substitution at the α-carbon position of the esters (i.e. the saturated carbon singly bonded to oxygen) as in the series ethyl, i-propyl and t-butyl acetates appears to lower the activation energy. The PM3 values of the activation energy (TABLE 4) show methyl substitution at the α-carbon position lowers the E_a by 10.29 and 24.4kJ/CH_3 thus showing that increase in the rate from i-propyl to t-butyl is greater that from ethyl acetate to i-propyl acetate. This implies that the replacement of α-hydrogen atom by a methyl group increases the rate of subsequent α-methyl substitution.

A Factor: In almost all cases, the agreement between PM3 (TABLE 4) and experimental A factors is good. And the increase in A factor can be attributed primarily to an increase in reaction path degeneracy, i.e. the number of equivalent β-hydrogen atoms available for elimination. This is in agreement with the estimated values of O'Neal, and Benson[11].

Entropy of activation: An interesting feature of this series of compounds is the negative value of the entropy of activation (TABLE 4), which is consistent with the formation of cyclic transition state suggested by Hurd and Blunck[12]; since three internal rotational degrees of freedom are converted to relatively inactive vibrations in the process of activation. The regular trend in the entropy of activation as successive methyl groups are added to the molecule is predictable on the basis of the increased number of β-hydrogen atoms available for the formation of the activated complex, and of the increased restriction of internal rotation in the normal molecule.

TABLE 3 : Optimized bond and dihedral angles for both reactants (RE) and transition states (TS) for α-smethylated alkyl acetates at PM3 level

(°)	Ethyl acetate		i-Propyl acetate		t-Butyl acetate	
	RE	**TS**	**RE**	**TS**	**RE**	**TS**
Bond angle						
$C_4O_1C_2$	118.59	120.33	119.87	120.78	123.15	121.14
$C_5C_4O_1$	106.33	111.57	105.48	110.01	102.46	108.27
$H_{12}C_5C_4$	109.96	118.04	110.13	117.41	110.41	117.03
$H_{13}O_6C_2$	52.36	109.76	56.22	109.46	46.64	109.52
Dihedral angle						
$C_4O_1C_2C_3$	179.82	151.23	175.98	-155.08	179.81	157.45
$C_5C_4O_1C_2$	179.85	11.81	-148.11	-5.30	-179.88	9.41
$H_{12}C_5C_4O_1$	-178.58	111.86	-179.50	104.70	-179.50	113.09
$H_{13}O_6C_2O_1$	14.28	25.45	13.81	-24.79	15.43	20.74

TABLE 4 : Comparative theoretical and experimental activation parameters for α-series at (623k)

Method	substrate	Ea ($kJmol^{-1}$)	log A(s^{-1})	ΔH* ($kJmol^{-1}$)	ΔG* ($kJmol^{-1}$)	ΔS* ($Jmol^{-1}K^{-1}$)	$k^1(s^{-1})$
PM3	Ethyl Acetate	203.51	12.45	198.32	211.47	-21.05	2.44×10^{-5}
	i-Propyl Acetate	193.22	12.97	188.04	194.88	-10.98	5.95×10^{-4}
	t-Butyl Acetate	168.82	13.07	163.64	169.30	-9.09	0.083
Observed	Ethyl Acetate	199.79	12.48	194.61	207.40	-20.54	5.36×10^{-5}
		200.83	12.59	195.65	207.13	-18.41	5.65×10^{-5}
	i-Propyl Acetate	188.28	13.00	183.10	189.60	-10.43	1.65×10^{-3}
		193.72	13.40	188.54	190.26	-2.76	1.45×10^{-3}
	t-Butyl Acetate	169.45	13.30	164.27	167.18	-4.67	0.125
		167.36	13.15	162.18	166.86	-7.51	0.133

TABLE 5 : Heats of formation of reactant (GS), transition state (TS) and products, and derived energetics, ΔE^* and ΔE_o (kJ/mol)

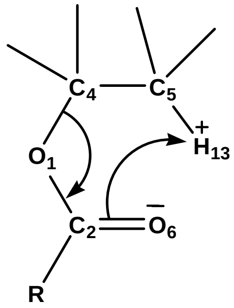
Substrate	GS	TS	Products	$\Delta E^*=E_{trans}-E_{reac}$	$\Delta E°=E_{pdt}-E_{reac}$
Ethyl Acetate	-413.80	-175.27	-364.30	238.53	49.50
i-Propyl Acetate	-436.27	-206.02	-409.53	230.25	26.74
t-Butyl Acetate	-452.21	-234.39	-448.86	217.82	3.35

DISCUSSION

The results presented must reflect the effect on the formation of the transition states of methyl substitution on C_4, particularly the effect on charge density and bond strengths of bonds joined to the sites of substitution. Thus α-methyl substitution will primarily reflect on the charge density on C_4 and the C_4-O_1 and C_4-C_5 bond lengths.

The results are better discussed in terms of the modified transition state of Maccoll[13] as depicted in Scheme 4.

Methyl group has a positive (electron-releasing) inductive effect, the C_5 of the methyl group being partially negative. Therefore, α-methyl substitution should facilitate electron movement from C_4-O_1 bond into O_1-C_2 bond as shown in Scheme 4. This is in consonance with the progressive increase in C_4-O_1 bond length in the T.S. as α-methyl substitution progresses starting from ethyl acetate. The effect on C_4-C_5 bond length is to lessen the developing double bond character. Overall, our calculations show rate enhancement with α-methyl substitution. This would suggest that the C_4-O_1 bond stretching is more significant as a rate-determinant than the development of double bond character in C_4-C_5 bond.



Scheme 4

This explanation of these substituent effects can be attributed to the polar transition state. Substituents which are able to stabilize the growing charge centres of the activated complex, effect reductions in the activated energies relative to the unsubstituted reactants, while substituents which destabilize the growing charge centres have the opposite effect. The effects of the α-carbon are consistent with the fact that stabilizations are more readily effected at the positive centres than at the negative centres.

The overall result of the calculations shows that α-methyl substitution is rate enhancing and it can therefore be concluded that rate enhancement due to C_4-O_1 bond stretching in the formation of the T.S. is more significant as a rate determinant than the acidic nature of the β hydrogen eliminated.

In general, we can discern that three factors come into play, namely, (i) the acidic nature (i.e. the tendency to depart as a proton) of the hydrogen to be eliminated, (ii) any factor that will favor the C_4-O_1 bond cleavage and (iii) the enhancement of the C_4-C_5 double bond development. The methyl group so far considered in this work affects reaction rate through making possible the heterolytic scission of the C_4-O_1 bond, particularly when in the α-position and the enhancement of the acidic nature of the hydrogen atom eliminated.

It can be concluded that α-methylation cause depression of activation barriers due to steric releasing in the TS.

The PM3 results are consistent with the TS where C_α-O bond polarisation is the rate-determining step, followed by pre-equilibrium involving the acidic hydrogen shift towards the carbonyl oxygen.

CONCLUSION

In conclusion the PM3 results are consistent with the TS where the C_α-O bond polarization is the rate determining 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. It is equally encouraging that the TS satisfies the four criteria prescribed by Kormonicki and McIver[14].

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