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Homogeneous and unimolecular gas-phase thermal decomposition kinetics of methyl benzoylformate: experimental and theoretical study

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The kinetics of the gas-phase thermal decomposition of the α -ketoester methyl benzoylformate was carried out in a static system with reaction vessel deactivated with allyl bromide, and in the presence of the free radical inhibitor propene. The rate coefficients were determined over the temperature range of 440–481 °C and pressures from 32 to 80 Torr. The reaction was found to be homogenous, unimolecular and obey a first-order rate law. The products are methyl benzoate and CO. The temperature dependence of the rate coefficient gives the following Arrhenius parameters: $\log_{10} k (s^{-1}) = 13.56 \pm 0.31$ and $E_a (kJ mol^{-1}) = 232.6 \pm 4.4$. Theoretical calculations of the kinetic and thermodynamic parameters are in good agreement with the experimental values using PBE1PBE/6-311++g(d,p). A theoretical Arrhenius plot was constructed at this level of theory, and the good agreement with the experimental Arrhenius plot suggests that this model of transition state may describe reasonably the elimination process. These results suggest a concerted non-synchronous semi-polar three-membered cyclic transition state type of mechanism. The most advanced coordinate is the bond breaking C^{$\delta+-...\delta-OCH_3$} with an evolution of 66.7%, implying this as the limiting factor of the elimination process. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: DFT calculations; gas-phase thermal decomposition; kinetic; mechanism; methyl benzoylformate

INTRODUCTION

The gas-phase elimination of esters of carboxylic acids is generally known to proceed through a six-membered cyclic transition state type of mechanism to give the corresponding acid and ole-fin [(reaction (1)].^[1,2] A C_β—H bond at the alkyl side of the ester is required for molecular elimination.



When a carbonyl group is interposed between substituent Z and the acid side of the alkyl ester, that is, alkyl esters of 2-oxoacids, interesting complex reactions have been found. In this respect, a work on the gas-phase thermal decomposition of an α -ketoester, methyl benzoylformate, was reported to yield benzaldehyde, formaldehyde and CO gas^[3] for which the Arrhenius expression was log k = 13.2–222.9 kJmol⁻¹(2.303RT)⁻¹. The mechanism of this reaction was believed to involve a fivemembered cyclic transition state as depicted in reaction (2).



An experimental and theoretical study of the elimination kinetics of methyl oxalyl chloride, ClCOCOOCH₃, found this compound to decarbonylate by chlorine migration through a three-membered cyclic transition state as shown in reaction (3).^[4] Semi-empirical PM3 and MP2/6-31G* level of theories gave good agreement with the experimental results.

$$\begin{array}{c} \begin{array}{c} 0 & 0 \\ \parallel & \parallel \\ \text{CI-C-C-OCH}_{3} \end{array} \end{array} \left[\begin{array}{c} \begin{array}{c} 0 & 0 \\ \parallel & 0 \\ C \end{array} \right] \stackrel{\dagger}{\underset{CI}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}}{\overset{\bullet}}{\overset{\bullet}}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}}{\overset{\bullet}{\overset{\bullet}}{\overset{\bullet}}$$

A year later, a few ethyl esters of 2-oxocarboxylic acids, ethyl oxamate and ethyl oxanilinate,^[5] were proposed to decarbonylate as the first step of the reaction. The corresponding ethyl ester in-

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termediate then went through a parallel decomposition as shown in reactions (4).



Since a parallel reaction of the gas-phase elimination kinetics of ethyl oxamate and ethyl oxanilinate^[5] was postulated, a theoretical study was undertaken to verify or support the above suggested mechanisms.^[6] In this respect, the quantum chemical calculations by using ab initio level of theory were limited to study two competitive mechanisms [(reaction (4) Steps 2 and 3] leading to ethylene and ethanol formation. The transition state for ethylene formation (Step 2) implied a non-planar six-membered cyclic structure, where the most important factor was the polarization of O₄---C₆ bond (breaking of ester bond). The process was proposed to be concerted and semi-polar, with the hydrogen being transferred located halfway between carbonyl oxygen O₅ and C₉ (Scheme 1). In the case of ethanol formation from ethyl oxamate and ethyl oxanilate seemed to occur through a planar four-membered cyclic transition state structure (Step 3). Calculations suggested this reaction to proceed in a concerted non-synchronous type of mechanism, where the dominating process was the breaking of N_1 — H_2 bond (**Step 3**). NBO charge analysis suggested the bond polarization of alkyl oxygen-carbon, in the sense $O_4 \xrightarrow{\delta^-}{-}C_6 \xrightarrow{\delta^+}$, as a determining factor **Step 2**, while N₁—H₂ bond breaking was considered the limiting process in Step 3. Activation parameters were found to be in reasonable agreement with experimental values at MP2/6-31G level of theory for these substrates.

Further investigation related to the gas-phase elimination of esters of 2-oxo-acids [reactions (3) and (4)]^[4,5] containing electron-withdrawing substituents (Cl, NH₂ and NHPh) was to change it to electron-releasing groups, i.e. methyl (ethyl-2-oxo-propionate) and isopropyl (3-methyl-2-oxo-butyrate).^[7] The thermal decomposition of these substrates underwent as in ethyl carboxylic acids^[1,2] through a concerted sixmembered cyclic transition state mechanism, producing the corresponding 2-oxo-acid and ethylene. Under the reaction conditions the oxo-acid intermediate decarboxylates, accord-

ing to the mechanism explained previously,^[8] to give the corresponding aldehyde product [reaction (5)].



Additional kinetic determination of the above-mentioned work^[7] was the inclusion of the compound of reference ethyl glyoxalate. The presence of H as a substituent gave a parallel decomposition where the predominant pathway originated formic acid, ethylene and CO_2 , through **Step 1** and **Step 2** of reaction (5). The small amount of decarbonylation as a parallel process occurred through a mechanism similar to reaction (4). The product intermediate ethyl formate was thought to undergo a slow decomposition, as depicted in reaction (1) to yield formic acid and ethylene.

A combined experimental and theoretical study in the elimination kinetic of methyl trifluoropyruvate^[9] was recently reported. The degree of polarization between the substituent at the acid side and the carbon of the C=O was considered important. The products of decomposition of methyl trifluorobutyrate are methyl trifluoroacetate and CO gas. Using DFT calculations with different basis sets led to a result in reasonable good agreement with the experimental values for a 1, 2-migration of the OCH₃ group rather than the F_3C substituent. The threemembered cyclic transition state shown in Scheme 2 suggested that the F_3C group, a strong electron-withdrawing substituent, appears to be weakly polarizable in the 2-oxo-ester. Consequently, it has a lesser migratory aptitude than the OCH₃ group.

Reyes *et al.*^[10] investigated the gas-phase elimination kinetics of several selected 2-oxo-esters. This investigation aimed at studying the effect of electron-withdrawing substituents Cl, piperidyl and phenyl in ethyl oxalyl chloride, ethyl piperidine glyoxylate and ethyl benzoylformate. Ethyl oxalyl chloride decomposed to ethyl chloroformate and CO gas, and the mechanism was thought to be along the same line as reaction (3). With regard to both ethyl piperidine glyoxylate and ethyl benzoyl formate they underwent to a parallel elimination of decarboxylation similar to the mechanism of reaction (5) (**Steps 1 and 2**).

The above-described investigations on the gas-phase elimination of ethyl ester of 2-oxo-acids indicate that the presence of H at the C_{β} —H bond at the alkyl side gives the corresponding 2oxo-acids and ethylene as delineated in organic esters [reaction



Scheme 1. Transition State for ethylene and ethanol formation

Scheme 2. Transition state of methoxy migration

(1)]. However, the absence of the β -hydrogen, that is, the replacement of ethyl group by a methyl group in carboxylic esters has rarely shown abstraction of α -H of the CH₃ group. In association with this fact, the work on the gas-phase elimination of methyl benzoylformate described in reaction (2)^[3] appeared to be give an interesting and different result when compared with the reported papers^[5–9] showing no abstraction of the α -H in the CH₃ group.

Our experimental conditions have been considered by Allinger *et al.*^[11] as true gas-phase reaction because, at subatmospheric pressures, deactivated reaction vessels and under the presence of free radical suppressors are employed. In this sense, the present work was initiated to determine a joint experimental and theoretical study on the homogeneous, molecular gas-phase elimination kinetics of methyl benzoylformate. In order to formulate a reasonable mechanism in the decomposition of this substrate, a theoretical study at DFT computational levels has been included and also to compare the kinetic and thermodynamic parameters of activation with those values obtained in the experiments. Another purpose of this research is whether to support or modify the mechanism formulated in the abovementioned work.^[3]

COMPUTATIONAL METHOD AND MODEL

The kinetic and mechanism of the gas-phase elimination of methyl benzoylformate have been examined as implemented in GAUSS-IAN 09 package^[12] and by means of the electronic structure calculations using density functional theory (DFT) methods. The calculations at this level of theory were PBE1PBE,[13] MPW1PW91,^[14,15] M06,^[16] M062X^[16] and WB97XD^[17] with 6-311++G(d,p) and 6-311G++(2d,2p) basis sets. For the optimization process, the Berny analytical gradient was employed. The convergence on the density matrix was 10^{-9} atomic units, the threshold value for maximum displacement was 0.0018 Å and maximum force was 0.00045 Hartree/Bohr. The optimized reactant and product structures in the lowest energy conformation were used to find the Transition State (TS) structure, using Quadratic Synchronous Transit (QST) protocol. The nature of stationary points was recognized by frequency calculations. The TS was identified and characterized by a unique imaginary frequency associated with the transition vector (TV). Intrinsic reaction coordinate (IRC) calculations were carried to verify that the transition state connected reactant and products.

Frequency calculations allow estimation of the thermodynamic quantities, such as zero point vibrational energy (ZPVE), temperature corrections (E(T)) and absolute entropies (S(T)) at temperatures of 440.9, 450.4, 459.8, 470.2 and 481.4 °C and pressure values within the experimental range. Scale factors and hindered rotors were not used. These frequency calculations at different temperatures allow constructing a theoretical Arrhenius plot in order to compare with the experimental Arrhenius plot.

The activation Gibbs free (ΔG^{\dagger}) and enthalpy (ΔH^{\dagger}) energy were assessed using the following equations 1 and 2.

$$\Delta G^{\dagger} = \Delta H^{\dagger} - T \Delta S^{\dagger} \tag{1}$$

$$\Delta H^{\dagger} = V^{\dagger} + \Delta ZPVE + \Delta E(T) \tag{2}$$

 V^{\ddagger} is the potential energy barrier, while $\Delta ZPVE$ and $\Delta E(T)$ are the differences of ZPVE and temperature corrections between the TS and the reactant, respectively.

RESULTS AND DISCUSSIONS

The gas-phase elimination of methyl benzoylformate produces methyl benzoate and CO gas. The reaction took place in a static system, with allyl bromide deactivated vessel and using propene as a free radical inhibitor [reaction (6)].

$$\bigcup_{O}^{O} CH_3 \longrightarrow \bigcup_{O}^{COOCH_3} + CO$$
(6)

The stoichiometry of reaction (6) requires that the final pressure, P_f , be twice the initial pressure, P_o . Experimentally, the average P_f/P_o value at three different temperatures and ten half-lives was 1.95 (Table 1).

Further examination of the stoichiometry of reaction (6) is shown in Table 2. The methyl benzoylformate, up to 55% reaction, gave a reasonable good agreement between the extent of decomposition of the substrate as predicted from pressure measurements and the chromatographic analyses of the product methyl benzoate.

To examine the effect of surface upon the rate of elimination, several runs under the presence of propene inhibitor were carried out in a vessel with a surface-to volume ratio of 6 relative to the normal vessel which equal to one (Table 3). The packed and unpacked clean Pyrex vessel showed a small effect on the rates. However, when the packed and unpacked are deactivated with the product decomposition with allyl bromide, no effect on the rate coefficients was obtained.

Kinetic runs were performed in the presence of propene to inhibit any possible radical reaction (Table 4). Consequently, the elimination reaction in deactivated vessel had to be carried out in the presence of at least twice the amount of the inhibitor. No induction period was observed.

The rate coefficients determined in deactivated vessels and in the presence of the inhibitor propene are independent of the initial pressure of the substrate, and the first-order plot is satisfactorily linear to at least 55% decomposition (Table 5). The rate coefficients are reproducible with a standard deviation not greater that \pm 5% at a given temperature.

The variations of the rate coefficient with temperature are listed in Table 6. The results shown in Table 6 lead, by using the least squares procedure and 90% confidence coefficients, to the shown Arrhenius expression [Fig. 1, in white circle (o)]. The theoretical plot in black squares (\blacksquare) is also depicted in Fig. 1, where a reasonable agreement was obtained between experimental and theoretical plots with nearly similar slope and intercept. This result suggests a good description of the elimination process by the PBE1PBE/6-311++G(d,p) level of theory explained in the methodology section. In this sense, the data of the kinetic and thermodynamic activations parameters described in Table 7

Table 1. Ratio of final (P_f) to initial pressure (P_0)					
Temperature (°C)	P ₀ (Torr)	P _f (Torr)	P _f /P ₀		
460.5	65.4	125.5	1.92		
470.5	64.5	127.0	1.97		
480.4	64.7	127.5	1.97		
$P_{a} = initial pressure, P_{f} = final pressure.$					

Table 2. Stoichiometry of the reaction at 459 °C (732 K)							
Parameter Value							
Time (min)	3	4	7	9	13		
Ester product (%) GLC)	15.8 18.4	23.1 25.5	35.5 37.1	45.0 48.5	55.8		

Table 3. Homogeneity	y of the reaction at 459.	5°C (732 K)
S/V (cm ⁻¹)	$10^4 k (s^{-1})^{(a)}$	$10^4 k (s^{-1})^{(b)}$
1 6	12.85 ± 0.49 11.65 ± 0.21	$\begin{array}{c} 10.02 \pm 0.28 \\ 10.45 \pm 0.49 \end{array}$
^a Clean Pyrex vessel. ^b Deactivated Pyrex ves	sel.	

Table 4. (733 K)	Effect of propene	inhibitor on r	ates at 460.1 °C
P _o (Torr)	P _i (Torr)	Pi/Po	$10^4 k_1 (s^{-1})$
79.7	0	0	22.60
70.4	66	1.1	10.50
70.6	131	1.9	9.69
68.2	136	2.0	10.10
42.1	120	2.9	10.40
30.0	130	4.3	10.30
P _o = press	ure of substrate. P _i =	pressure inhib	itor.



Figure 1. Arrhenius plots of gas-phase elimination of methyl benzoylformate, in white circles (o) experimental and in black squares (**■**) theoretical at PBE1PBE/6-311++G(d,p) level of theory

suggest an elimination process through a three-membered transition state (Scheme 3). These results allow the present work to approach to quantum chemical calculations for the consideration and interpretation of a rational mechanism of elimination of methyl benzoylformate depicted as in reaction (6).

THEORETICAL RESULTS

Kinetic and thermodynamic parameters

According to the experimental results of the gas phase elimination of methyl benzoylformate producing methyl benzoate and CO gas, this work aimed at examining by quantum chemical calculations the mechanism of this process. Based on reaction (7) the proposed mechanism through a three-membered cyclic

Table 5. Invariability of rate coefficient with initial pressure at 459.7 °C (732.9 K)						
Parameters Value						
P ₀ (Torr) 10 ⁴ k ₁ (s ⁻¹)	32.6 9.65 ± 0.19	46.2 9.81 ± 0.32	55.4 10.10±0.38	70.6 9.69±0.23	80.1 10.10±0.50	

Table 6. Experimental and theoretical temperatures dependence of the rate coefficients						
Parameters			Value			
Temp. (°C) (a) $10^4 k_1 (s^{-1})$ (b) $10^4 k_1 (s^{-1})$ Rate equation: (a) log	440.9 3.53 ± 0.06 2.44 $k_1 (s^{-1}) = (13.56 \pm 0.31)$	450.4 5.79±0.21 3.97) – (232.64±4.38) kJ r	459.8 10.02 ± 0.28 6.74 mol ⁻¹ (2.303RT) ⁻¹ (r = 0.	470.2 15.90 ± 0.65 11.27 9994).	481.4 29.20±0.71 19.54	
(b) log (a) Experimental; (b) 1	(b) log k_1 (s ⁻¹) = (13.30 ± 0.14) - (231.32 ± 2.01) kJ mol ⁻¹ (2.303RT) ⁻¹ (r = 0.9998). (a) Experimental; (b) theoretical by using the frequentials of PBE1PBE/6-311++G(d,p) level of theory.					

Table 7. Kinetic and thermodynamic parameters						
E _a (kJ/mol)	$Log A (s^{-1})$	ΔH [‡] (kJ/mol)	ΔS^{\ddagger} (J/mol K)	ΔG^{\ddagger} (kJ/mol)		
232.64	13.56	226.50	-1.07	227.30		
ΔH^{\dagger} , ΔS^{\dagger} and ΔG^{\dagger} were estimated at 459.8 °C.						

transition state structure was studied. Table 8 describes the thermodynamic and kinetic parameters that have been determined theoretically together with the experimental results.



We have obtained a reasonable agreement between experimental and theoretical results for calculated enthalpies of activation, and consequently the energies of activation with all DFT methods used. The calculated entropy of activation from M062x/6-311++G(2d,2p) was closer to the experimental value; however, the enthalpy of activation of PBE1PBE/6-311++G(d,p) gave better results when compared to experimental. For PBE1PBE/6-311++G(d,p), the departure in the calculated entropy of 2.41 J/mol K is an acceptable agreement considering the experimental error. PBE1PBE/6-311++G(d,p) was chosen for the subsequent analysis. Figure 2 shows the optimized structures for the Reactant (R), Transition State (TS) and Products (P) at PBE1PBE/6-311++G(d,p) level of theory.

Intrinsic reaction coordinate (IRC) calculations were carried out to verify the Transition State structures. Figure 3 shows the IRC reaction profile, illustrating how the transition state connects with reactant and products.

A theoretical Arrhenius was generated from the frequency calculations at PBE1PBE/6-311++G(d,p) level of theory at the five different temperature reported in the experimental work (Table 6). The



Scheme 3. Transition state of CO elimination

theoretical Arrhenius (Fig. 1, black squares) is parallel to the experimental line, resulting in the same energy of activation.

Transition state and mechanism

Structural parameters for R, TS and P are given in Table 9; atom numbers for discussion are shown in Scheme 3. Geometrical parameters demonstrate the breaking of O_1-C_2 bond is the most advanced coordinate in the elimination process, with change in atom distance from 1.325 Å to 1.870 Å from R to TS. The C_2-C_3 and C_3-C_4 bond distances show small increase from R to TS in the reaction path. The distance C_3-O_1 diminishes from 2.362 Å to 1.677 Å from R the TS. The imaginary frequency associate with the TS structure is 507.64 cm⁻¹, thus confirming the observation of a saddle point with the movement in the reaction coordinate.

NBO charges

The changes in electronic structures through the reaction path were examined using natural bond orbital (NBO) analysis. NBO analysis is based on a method for optimally transforming a given wave function into localized form. The NBO charges of atoms involved in the mechanisms are reported in Table 10. Atom numbers and the percent change in charges are given in Scheme 4.

The most important change in the charge distributions is observed for the methoxy oxygen atom O_1 , from -0.516 to -0.624 from R to TS, respectively. This result implies an increase in the negative charge by 20.9% in the TS. At carbon C_3 there is an increase in the positive charge of 11.0%. No significant change was observed in the atomic charge at C_2 (2.4%) (Scheme 4).

Natural bond orbital (NBO) analysis

NBO bond order calculations have been used to describe the reaction coordinate of the gas-phase thermal decomposition of methyl benzoylformate (Table 11).^[18–20] Wiberg bond indexes $B_i^{[21]}$ were

Table 8. Thermodynamic and Arrhenius parameters for the Gas phase elimination reaction of methyl benzoylformate at 460 °C						
Method	Ea (kJ/mol)	$\log A (s^{-1})$	ΔH^{\neq} (kJ/mol)	ΔS^{\neq} (J/mol K)	ΔG^{\neq} (kJ/mol)	
Experimental	232.64	13.56	226.50	-1.07	227.30	
PBE1PBE/6-311++G(d,p)	233.09	13.44	227.00	-3.48	229.55	
PBE1PBE/6-311++G (2d,2p)	233.93	13.44	227.84	-3.45	230.36	
MPW1PW91/6-311++G(d,p)	233.83	13.47	227.73	-2.93	229.88	
MPW1PW91/6-311++G(2d,2p)	234.84	13.49	228.75	-2.42	230.52	
M06/6-311++G(d,p)	229.96	13.18	223.87	-8.47	230.08	
M06/6-311++G(2d,2p)	229.77	13.04	223.67	-10.99	231.73	
M062x/6-311++G(d,p)	235.87	13.39	229.78	-4.42	233.02	
M062x/6-311++G(2d,2p)	237.63	13.55	231.53	-1.38	232.54	
WB97xd/6-311++G(d,p)	238.33	13.05	232.24	-10.96	240.27	
WB97xd/6-311++G(2d,2p)	239.23	12.97	233.14	-12.34	242.18	



Figure 2. Optimized structures for reactant (R), transition state (TS) and products (P) in the gas phase elimination of $C_6H_5COCOOCH_3$ at PBE1PBE/6-311 ++G(d,p) level of theory



Figure 3. IRC profile for CO formation from methyl benzoylformate at PBE1PBE/6-311++G(d,p) level of theory. T = $460 \text{ }^{\circ}\text{C}$

Table 9. Structural parameters of reactant (R), transition state (TS) and products (P) for CO elimination from methyl benzoylformate in gas phase at 460 °C, obtained from PBE1PBE/6-311++G(d,p) calculations

Atomic length (Å)						
	$O_1 - C_2$	$C_2 - C_3$	C ₃ —O ₁	$C_3 - C_4$		
R	1.325	1.534	2.362	1.481		
TS	1.870	1.596	1.677	1.493		
Р	5.043	4.400	1.341	1.485		
Imaginary frequency (cm ⁻¹): 507.64.						

Table 10. NBO charges of reactant (R), transition state (TS) and products (P) for CO elimination from methyl benzoylformate at PBE1PBE/6-311++G(d,p). $T = 460 \degree$ C					
NBO cha	arges				
	O ₁	C ₂	C3	C ₄	
R	-0.516	0.739	0.480	-0.167	
TS	-0.624	0.757	0.533	-0.130	
Р	-0.545	0.488	0.799	-0.167	

estimated for the reactant (R), transition state (TS) and products (P) by using the natural bond orbital (NBO) program^[22] as implemented in Gaussian 09.^[12] The synchronous character of concerted reaction mechanism can be accounted through the synchronicity (*Sy*) concept



Scheme 4. Charge percentage of atoms in methyl benzoylformate

Table 11. Wiberg bond index, B_{i} of reactant (R), transition state (TS) and products (P) and synchronicity (*Sy*) of CO elimination from methyl benzoylformate at PBE1PBE/6-311++G(d, p). T = 460 °C

	0 ₁ —C ₂	C ₂ —C ₃	C ₃ —O ₁	Sy
B_i^R	1.079	0.907	0.016	0.651
B_i^{TS}	0.359	0.791	0.500	
B_i^P	0.000	0.001	1.032	
%E _v	66.7	12.8	47.7	

proposed by Moyano *et al.*^[23]; the equations involved are described in the literature.^[5] The evaluated bonds were O_1 — C_2 , O_1 — C_2 and O_1 — C_2 .

The most advanced reaction coordinate is the O_1 — C_2 bond breaking (66.7%), followed by the C_3 — O_1 bond formation (47.7%). The synchronicity parameter defined by Moyano for concerted reactions varies from Sy=1 for synchronous reactions to $S_y=0$ for nonsynchronous processes. In this reaction, the *Sy* value of 0.651 implies a non-synchronous process for the mechanism describing the gasphase elimination process of methyl benzoylformate shown in reaction (7). These results are consonant with the previously reported thermal decomposition of methyl trifluoropyruvate^[9] where the decomposition products are methyl trifluoroacetate and CO gas (Scheme 2).

Our findings contrast with a previous study on the thermal decomposition of methyl benzoylformate reported in the literature,^[3] regarding product formation and the stoichiometry. The cited work reports three decomposition products, e.g. benzaldehyde, formaldehyde and carbon monoxide, while in this work two products are obtained: methyl benzoate and CO. To further investigate this issue, we carried out theoretical calculations of their above-reported mechanism (3) at PBE1PBE/6-311++G(d,p) level of theory. Compared to the reported experimental barrier 222.9 kJ/mol,^[3] the calculated parameter for reaction (2) was significantly higher, 308.0 kJ/mol. The discrepancy between the results described in (3)^[3] with ours may probably be due to the different conditions of experimental works. In the work reported in ref. 3, methyl benzoylformate was in a very dilute solution of acetonitrile in a 9-ml vacuum sealed uncoated tube, whereas our experiments were carried out using the substrate pure, under homogenous condition, in a static system at sub-atmospheric pressure, and which has been depicted in figures as reported in previous papers.^[26,27]

EXPERIMENTAL SECTION

The substrate methyl benzoylformate (98%) was bought from Aldrich. The purity of the substrate and product was determined by GC/MS/MS (Saturn 2000, Varian), capillary column DB—5MS, 30 mm \times 0.250 mm. id. 0.25 μ m. The quantitative chromatographic analysis of methyl benzoate was determined by using a Gas Chromatograph Hewlett Packard 5710-A with a column 3% Versamid 900/Chromosorb G, 3.5 mts. The identification of the product was made by comparing chromatogram of the reaction product with true authentic sample of methyl benzoate bought from Aldrich and in a GC–MS (Saturn 2000, Varian 3600X with a DB-5MS capillary column 30 m \times 0.25 mm. i.d., and 0.25 μ m).

Kinetics

The experiments were carried out in vessel seasoned or deactivated by the decomposition products of allyl bromide, in a static system^[24–27] and in the presence of the free radical suppressor propene (100%, Air Product Co.). The rate coefficients were determined manometrically (mercury manometer). The temperature was controlled within ± 0.2 °C with a SHINKO DIC-PS 23TR resistance thermometer controller with a calibrated Iron Constantan thermocouple. The reading temperature was within ± 0.1 °C with the Iron-Constantan thermocouple attached to a Digital Multimeter Omega 3465B. The reaction vessel showed no temperature gradient at different points, and the substrate was injected directly ($\approx 0.05-0.1$ ml) into the reaction vessel through a silicone rubber septum.

CONCLUSIONS

The kinetics and mechanism for the thermal decomposition of methyl benzoylformate in the gas phase were investigated both experimental and theoretically. The reaction was found to be homogenous, unimolecular and obeys a first-order rate law with Arrhenius equation $\log_{10} k (s^{-1}) = 13.56 \pm 0.31$ and $E_a (kJ mol^{-1}) = 232.6 \pm 4.4$. The products of methyl benzoylformate thermal decomposition are methyl benzoate and carbon monoxide. This observation diverges from previous work findings reporting benzaldehyde, formaldehyde and carbon monoxide product formation,^[3] and it may be attributed to the differences in the experimental conditions. To explain the product formation and to propose a reasonable mechanism for this reaction, we carried out theoretical calculations of the kinetics and thermodynamics parameters at several DFT levels. We obtained a reasonable agreement between experimental and theoretical results for calculated enthalpies of activation and consequently, energies of activation with all DFT methods used. With M062x/6-311++G(2d,2p) calculated entropy of activation was closer to the experimental value; however, for the enthalpy of activation PBE1PBE/6-311++G(d,p) gave better results, compared to experimental, and the departure in the calculated entropy of 2.41 J/mol K, which is an acceptable agreement taking into account the experimental error. A theoretical Arrhenius plot was generated at PBE1PBE/6-311++G(d,p) using the five temperatures reported in the experimental work, showing the calculated and experimental lines nearly parallel, with the result in the same energy of activation. Analysis of NBO charges, bond orders and synchronicity parameters

suggests a concerted non-synchronous semi-polar threemembered cyclic transition state type of mechanism. The most advanced coordinate is the bond breaking $C^{\delta+}$ --- $^{\delta-}$ OCH₃ with an evolution of 66.7%, implying this as the limiting factor of the elimination process.

Our initiative to estimate the theoretical Arrhenius by means of calculating the frequencies from the chosen PBE1PBE/6-311++G(d,p) level of theory at the five different temperature reported in the experimental work is described.

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