Kinetic and Mechanisms of the Homogeneous, Unimolecular Elimination of Phenyl Chloroformate and *p*-Tolyl Chloroformate in the Gas Phase

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ABSTRACT: The gas-phase elimination of phenyl chloroformate gives chlorobenzene, 2-chlorophenol, CO_2, and CO, whereas *p*-tolyl chloroformate produces *p*-chlorotoluene and 2-chloro-4-methylphenol CO_2 and CO. The kinetic determination of phenyl chloroformate (440–480°C, 60–110 Torr) and *p*-tolyl chloroformate (430–480°C, 60–137 Torr) carried out in a deactivated static vessel, with the free radical inhibitor toluene always present, is homogeneous, unimolecular and follows a first-order rate law. The rate coefficient is expressed by the following Arrhenius equations:

Phenyl chloroformate:

Formation of chlorobenzene, $\log k_{\text{I}} = (14.85 \pm 0.38) - (260.4 \pm 5.4)$ kJ mol^{-1} $(2.303RT)^{-1}$; $r = 0.9993$

Formation of 2-chlorophenol, $\log k_{\text{II}} = (12.76 \pm 0.40) - (237.4 \pm 5.6)$ kJ mol^{-1}$(2.303RT)^{-1}$; $r = 0.9993$

p-Tolyl chloroformate:

Formation of *p*-chlorotoluene: $\log k_{\text{I}} = (14.35 \pm 0.28) - (252.0 \pm 1.5)$ kJ mol^{-1} $(2.303RT)^{-1}$; $r = 0.9993$

Formation of 2-chloro-4-methylphenol, $\log k_{\text{II}} = (12.81 \pm 0.16) - (222.2 \pm 0.9)$ kJ mol^{-1}$(2.303RT)^{-1}$; $r = 0.9995$

The estimation of the k_{I} values, which is the decarboxylation process in both substrates, suggests a mechanism involving an intramolecular nucleophilic displacement of the chlorine atom

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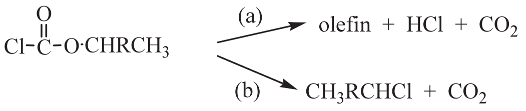
through a semipolar, concerted four-membered cyclic transition state structure; whereas the k_{II} values, the decarbonylation in both substrates, imply an unusual migration of the chlorine atom to the aromatic ring through a semipolar, concerted five-membered cyclic transition state type of mechanism. The bond polarization of the C–Cl, in the sense $C^{\delta+}\cdots Cl^{\delta-}$, appears to be the rate-determining step of these elimination reactions. © 2015 Wiley Periodicals, Inc. Int J Chem Kinet 47: 664–670, 2015

INTRODUCTION

The kinetics of the gas-phase elimination of alkyl chloroformates has been for years the subject of different mechanistic interpretations according to experimental conditions, structure of the substrates, and products formation [1–12]. In this sense, it is noteworthy to classify the several types of esters of chloroformic acid studied at high temperatures and at subatmospheric pressures according to structures: (a) presence of the C_β–H bond at the alkyl side of the chloroester; (b) absence of the C_β–H bond but the presence of a C_α–H bond at the alkyl side of the chloroester; (c) absence of both active C_β–H bond and C_α–H bond at the alkyl side of the chloroester.

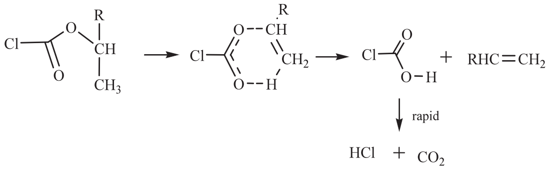
Presence of the C_β–H Bond at the Alkyl Side

Many works of alkyl chloroformates with the presence of a C_β–H bond resulted in several discrepancies in product formation ascribed to surface effects. Some types of these substrates were found to undergo parallel elimination reactions [9,11] as depicted in reaction (1).

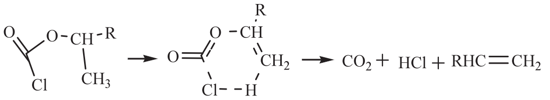


$$\mathrm{Cl{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{\cdot}CHRCH_3}\ \begin{cases}\xrightarrow{(a)}\ \text{olefin} + \mathrm{HCl} + \mathrm{CO_2}\\[4pt] \xrightarrow{(b)}\ \mathrm{CH_3RCHCl} + \mathrm{CO_2}\end{cases} \qquad (1)$$

This parallel elimination reaction (1) was thought that through via (a) to be homogeneous, whereas via (b) heterogeneous, yet both molecular in nature. Two different mechanisms were suggested to account for the formation of products: mechanism via (a), which is similar to the gas-phase elimination reaction of alkyl acetates [reaction (2)]; whereas mechanism via (b) is a concerted process with direct participation of the Cl atom [reaction (3)] [13,14],



Mechanism via (a)



Mechanism via (b)

Absence of the C_β–H Bond, but the Presence of the C_α–H Bond

The elimination kinetics of methyl chloroformate [10], lacking a C_β–H bond, under homogeneous and molecular conditions (425–480°C) yielded CH_3Cl and CO_2 gas ($\log k_1 = (14.26 \pm 0.20) - (251.0 \pm 2.0)$ kJ $\mathrm{mol^{-1}}(2.303RT)^{-1}$. The result of $\log A = 14.26$ suggested the reaction to proceed through a four-membered cyclic transition state type of mechanism.

A recent investigation of a chloroester without C_β–H, that is, the gas-phase thermal decomposition of benzyl chloroformate (475–523 K) [15] in deactivated reaction vessels and in the presence of a free-radical inhibitor, was found to be unimolecular homogeneous and obeys a first-order rate law: $\log k_1 = (13.30 \pm 0.38) - (152.9 \pm 3.6)$ kJ $\mathrm{mol^{-1}}$ $(2.303RT)^{-1}$; $r = 0.9989$. According to the results of the kinetic and thermodynamic parameters, the reaction was thought to proceeds through a concerted four-membered cyclic transition state to give benzyl chloride and CO_2 gas. Additionally, the homogeneous, unimolecular gas-phase elimination of neopentyl chloroformate (563–622 K, 37–70 Torr) [15] proceeded to a parallel reaction, where the formation of neopentyl chloride appears to be obtained through a polar four-membered cyclic transition state, whereas the mixture of olefins, 2-methyl-2-butene, and 2-methyl-1-butene is produced from a carbene intermediate. This intermediate supposed to be originated from a concerted five-membered cyclic transition state type of mechanism.

Absence of Both Active C_β–H Bond and C_α–H Bond

The gas-phase decomposition kinetics of trichloromethyl chloroformate [16] at 533–583 K was shown to be first order and homogeneous, except with some wall catalysis. The final products were two molecules of phosgene. Deactivation of the reaction vessel and the presence of a free radical inhibitor were not reported. The yield of phosgene, instead of the formation of CCl_4 and CO_2, is surprising.

With this background of information, the present work is addressed to examine the elimination kinetics of chloroesters of a special structure to bring about the possibility of a greater degree of polarizations in the transition state. Consequently, rearrangement, isomerization, intramolecular migrations, and probably other interesting mechanistic pathways may well be obtained. From the consideration that only a single information was reported in the chemical literature with regard to decomposition of substrates of the type (c), which is the absence of both active C_β–H bond and C_α–H bond at the alkyl side of the chloroester [16], this investigation aimed at studying the mechanisms of the gas-phase elimination kinetics of phenyl chloroformate and *p*-tolyl chloroformate under homogeneous and molecular conditions of the experiments

EXPERIMENTAL

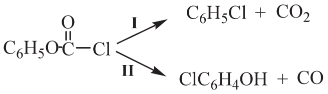
The starting materials phenyl chloroformate and *p*-tolyl chloroformates were bought from Aldrich, Milwaukee, Wisconsin, USA and used after distillation to better than 99.0% purity. Analyses of these substrates and products were carried out using a GC/MS (Saturn 2000, Varian 3600X), utilizing a DB–5MS capillary column, 30 mm ×0.250 mm. id. 0.25 μm. For quantitative analysis of phenyl chloroformate, chlorobenzene, and 2-chlorophenol was made by the use of *n*-propyl benzene as an internal standard. A Varian 3700 gas chromatograph with 15% OV-101, Chrom. G 100/120 mesh 3 m column was employed. The same column of 15% OV-101 was utilized for quantitative determination of *p*-tolyl chloroformate, *p*-chlorotoluene, and 2-chloro-4-methylphenol when using chlorobenzene as an internal standard. The quantitative analysis of CO_2 gas, with propene as an internal standard, was performed on a Varian 3600X chromatograph provided with a thermal conductivity detector, and the capillary column used was GS-Q, 30m, id.53 mm.

Kinetics

The kinetic measurements were performed in a static reaction system described in detail and with the figure of the apparatus as previously reported [17–20]. The wall of the Pyrex reaction vessel was deactivated with the products of decomposition of allyl bromide [21]. The reaction products were collected in a storage reservoir cooled in liquid nitrogen and retired at different reaction times. The rate coefficients were calculated from a pressure increase measured manometrically and by quantitative gas chromatograph analysis. The temperature was controlled by a SHINKO DIC-PS 23TR resistance thermometer controller, maintained to better than ± 0.2°C and measured with a calibrated iron constantan thermocouple. The temperature reading was measured within ± 0.1°C with a thermopar of iron constantan attached to a digital multimeter Omega 3465B. No temperature gradient was found at different points of the reaction vessel. The substrates were directly injected into the reaction vessel of approximately 250 mL with a syringe through a silicone rubber septum. The amount of reactant employed for each kinetic run was ≈0.05–0.1 mL.

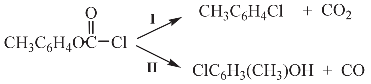
RESULTS AND DISCUSSION

The elimination reaction of both phenyl and *p*-tolyl chloroesters, in a static system, deactivated reaction vessel with allyl bromide, and in the presence of the free radical inhibitor toluene was determined over the temperature range of 430–480°C and the pressure range of 60–137 Torr. The products formed are described in reactions (4) and (5).



$$C_6H_5O\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{I} C_6H_5Cl + CO_2 \qquad C_6H_5O\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{II} ClC_6H_4OH + CO$$

(4)



$$CH_3C_6H_4O\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{I} CH_3C_6H_4Cl + CO_2 \qquad CH_3C_6H_4O\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{II} ClC_6H_3(CH_3)OH + CO$$

(5)

The theoretical stoichiometry based on reactions (4) and (5) required that, for long reaction times, $P_f = 2P_0$, where P_f and P_0 are the final and initial pressure, respectively. The average experimental P_f/P_0 values at five different temperatures and 10 half-lives was in both cases approximately 2.0 (Table I).

The homogeneity of these elimination reactions was determined by carrying out several runs in a vessel with a surface to volume ratio of 6.0 relative to that of the normal vessel which is equal to 1.0 (Table II). The packed and unpacked Pyrex vessels, deactivated with allyl bromide products of decomposition, had no effect on rates. However, the packed and unpacked clean Pyrex vessels caused a marked heterogeneous effect on the rate coefficients.

The effect of different proportions of the free radical suppressor toluene in the elimination process is shown in Table III. Apparently, these reactions proceed in a molecular nature; yet the experiments were carried out in the presence of at least equal amounts of the inhibitor toluene to prevent any possible radical reactions. No

Table I Rate of Final (P_f) to Initial (P_0) (Pressure)[a]

Substrate	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f / P_0	Average
Phenyl chloroformate	440.1	90	176	1.96	1.99 ± 0.06
	450.6	83	105	2.05	
	460.4	55	105	1.91	
	470.6	121	243	2.01	
	480.1	135	271	2.04	
p-Tolyl chloroformate	430.2	80	154	1.93	2.02 ± 0.06
	440.3	59	122	2.07	
	449.8	70	144	2.06	
	460.2	76	150	1.97	
	469.8	53	109	2.06	

[a] Reaction vessels deactivated with allyl bromide.

Table II Homogeneity of the Elimination Reactions

Substrate	S/V (cm^{-1})[a]	$\times 10^4\ k_1$ (s^{-1})[b]	$\times 10^4\ k_1$ (s^{-1})[c]
Phenyl chloroformate at 450.0°C	1	5.21 ± 1.17	1.15 ± 0.02
	6	12.49 ± 5.10	1.17 ± 0.03
p-Tolyl chloroformate at 440.3°C	1	11.49 ± 3.75	4.37 ± 0.09
	6	34.16 ± 7.16	4.32 ± 0.12

[a] S = surface area; V = Volume. [b] Clean Pyrex vessel. [c] Vessel deactivated with allyl bromide.

induction period was observed. The rate coefficients were reproducible with a relative standard deviation less ±5% at a given temperature.

The first-order rate coefficients of these chloroesters, calculated from $k_1 = (2.303/t)$ log $[2P_0/(3P_0 - P_t)$, were found to be independent of the initial pressures (Table IV). A plot of log $(3P_0 - P_t)$ against time t gave a good straight line up to 60% decomposition. The variations of the rate coefficients with temperature are given in Table V. The results given in Table V, led by using least-squares procedure and 90% confidence limits, to the shown Arrhenius equations (Figs. 1 and 2).

The results of the kinetic and thermodynamic parameters shown in Table VI demand a careful consideration for a reasonable interpretation in the elimination process of these substrates. The value of log A of 14.85 appears to be consistent with the idea that phenyl chloroformate decomposition may proceed through via I in concerted polar four-membered cyclic transition state. The positive value of $\Delta S^{\ddagger}$ of 23.5 J mol^{-1} K^{-1} (5.6 cal mol^{-1} K^{-1}) obtained for the formation of chlorobenzene indicates that the entropy of the transition state, $S^{\ddagger}$, is a little greater than the entropy of the reactant, S_r, suggesting a cyclic transition structure to be less ordered in comparison with the starting material; this means a more loose and polar in nature. The formation of the four-membered cyclic transition state requires the bonds to be very elongated, without breaking the $C^{\delta+}$—$Cl^{\delta-}$, diminishing the torsional stress and angles from electronic interactions. Consequently, the significant increase in the polarization generates gains in degree of translational freedom in

Table III Effect of Free Radical Inhibitor on Rates[a]

Substrate	Temperature (°C)	P_i/P_s	$\times 10^4\ k_I$ (s^{-1})	$\times\ 10^4\ k_{II}$ (s^{-1})
Phenyl chloroformate	470.6	—	3.52	1.16
		1.4	3.54	1.17
		1.6	3.45	1.18
		2.0	3.53	1.17
		2.5	3.04	1.10
p-Tolyl chloroformate	460.2	—	2.64	9.54
		0.8	2.59	9.51
		1.6	2.68	9.58
		2.8	2.68	9.43
		3.5	2.60	9.61

Vessel deactivated with allyl bromide. P_s = pressure substrate. P_i = pressure inhibitor.

[a] Toluene inhibitor.

Table IV Invariability of the Rate Coefficients with Initial Pressures

Phenyl chloroformate (450.6ºC)					
P_0 (mmHg)	60	85	96	107	110
k_I ($\times 10^4$ s^{-1})	1.18	1.17	1.15	1.14	1.10
k_{II} ($\times 10 \times 10^4$ s^{-1})	0.41	0.39	0.41	0.39	0.41
p-Tolyl chloroformate (460.2ºC)					
P_0 (mmHg)	63	84	98	120	137
k_I ($\times 10^4$ s^{-1})	2.56	2.64	2.63	2.59	2.62
k_{II} ($\times 10 \times 10^4$ s^{-1})	9.62	9.60	9.76	9.51	9.53

Table V Variation of the Rate Coefficients with Temperature

T (ºC)	k_{I} ($\times 10^4$ s^{-1})	k_{II} ($\times 10^4$ s^{-1})
Phenyl chloroformate		
440.1	0.61 ± 0.02	0.24 ± 0.01
450.6	1.15 ± 0.02	0.41 ± 0.02
460.4	1.94 ± 0.03	0.69 ± 0.01
470.6	3.54 ± 0.03	1.17 ± 0.03
480.1	6.42 ± 0.11	2.03 ± 0.02
$\log k_{\mathrm{I}} = (14.85 \pm 0.38) - (260.4 \pm 5.4)$ kJ mol^{-1} $(2.303RT)^{-1}$; $r = 0.9993$		
$\log k_{\mathrm{II}} = (12.76 \pm 0.40) - (237.4 \pm 5.6)$ kJ mol^{-1}$(2.303RT)^{-1}$; $r = 0.9993$		
p-Tolyl chloroformate		
430.1	0.43 ± 0.02	1.99 ± 0.06
440.7	0.77 ± 0.05	3.60 ± 0.12
449.8	1.43 ± 0.02	5.79 ± 0.09
460.2	2.62 ± 0.09	9.54 ± 0.26
470.6	4.28 ± 0.08	15.21 ± 0.13
480.6	7.68 ± 0.19	26.53 ± 0.15
$\log k_{\mathrm{I}} = (14.35 \pm 0.28) - (252.0 \pm 1.5)$ kJ mol^{-1} $(2.303RT)^{-1}$; $r = 0.9993$		
$\log k_{\mathrm{II}} = (12.81 \pm 0.16) - (222.2 \pm 0.9)$ kJ mol^{-1} $(2.303RT)^{-1}$; $r = 0.9995$		

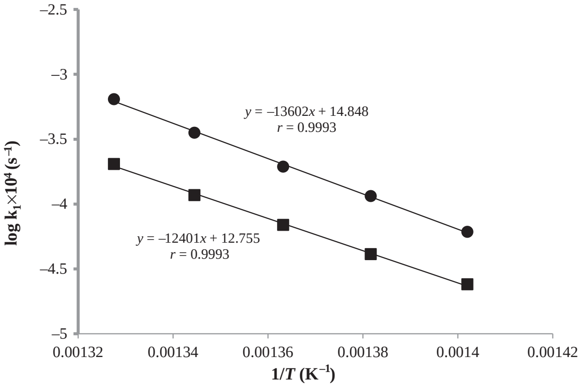


Figure 1 Arrhenius plot for the formation of (●) chlorobenzene and (■) 2-chlorophenol in the gas-phase elimination of phenyl chloroformate.

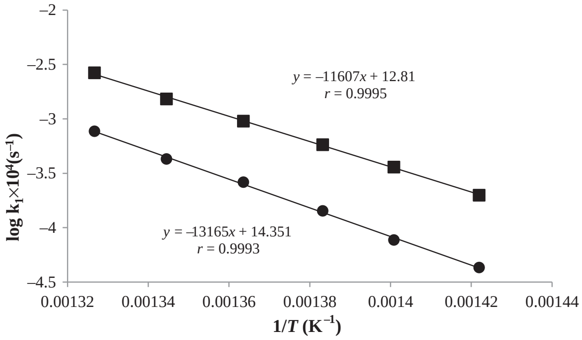


Figure 2 Arrhenius plot for the formation of (●) *p*-chlorotoluene and (■) 2-chloro-4-methylphenol in the gas-phase elimination of *p*-tolyl chloroformate.

some centers involved in the transition state when compared to the reactant. Likewise, we may well consider that this transition state has a late formation with respect to the reaction coordinate. With regard to via II, the formation of 2-chlorophenol $\Delta S^{\ddagger}$ of –15.4 J mol^{-1} K^{-1} (–3.7 cal mol^{-1} K^{-1}) indicates that $S^{\ddagger} < S_r$, suggesting a more rigid transition state close to planarity and with less bond polarization in comparison to via I. Also, there is a loss of degree of freedom arising from the restrictions of movements arising from the formation of the transition state. The value of log A of 12.82 implies the reaction to occur through the formation of a five-membered cyclic transition state in agreement with the $\Delta S^{\ddagger}$ value.

In the case of *p*-tolyl chloroformate, the results of log A and $\Delta S^{\ddagger}$ obtained for both reaction pathway suggest the transition state to be with similar geometry described for phenyl chloroformate.

According to products formation and the results of the kinetic and thermodynamic parameters of these aryl chloroformates elimination (Fig. 3), the polarization of the C–Cl bond of both substrates, in the direction of

Table VI Kinetic and Thermodynamic Parameters

Product	$\times 10^4$ k (s^{-1})	E_a (kJ mol^{-1})	log A	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
Phenyl chloroformate (460.4ºC)						
Chlorobenzene	1.99	260.4 ± 5.4	14.85 ± 0.38	23.5	254.3	237.1
2-Chlorophenol	0.81	237.4 ± 5.6	12.82 ± 0.40	-15.4	231.3	242.6
p-Tolyl chloroformate (460.2ºC)						
p-Chlorotoluene	2.50	252.0 ± 1.5	14.35 ± 0.28	13.9	245.9	235.7
2-Chloro-4-methylphenol	9.56	222.2 ± 0.9	12.81 ± 0.16	-15.6	216.1	227.5

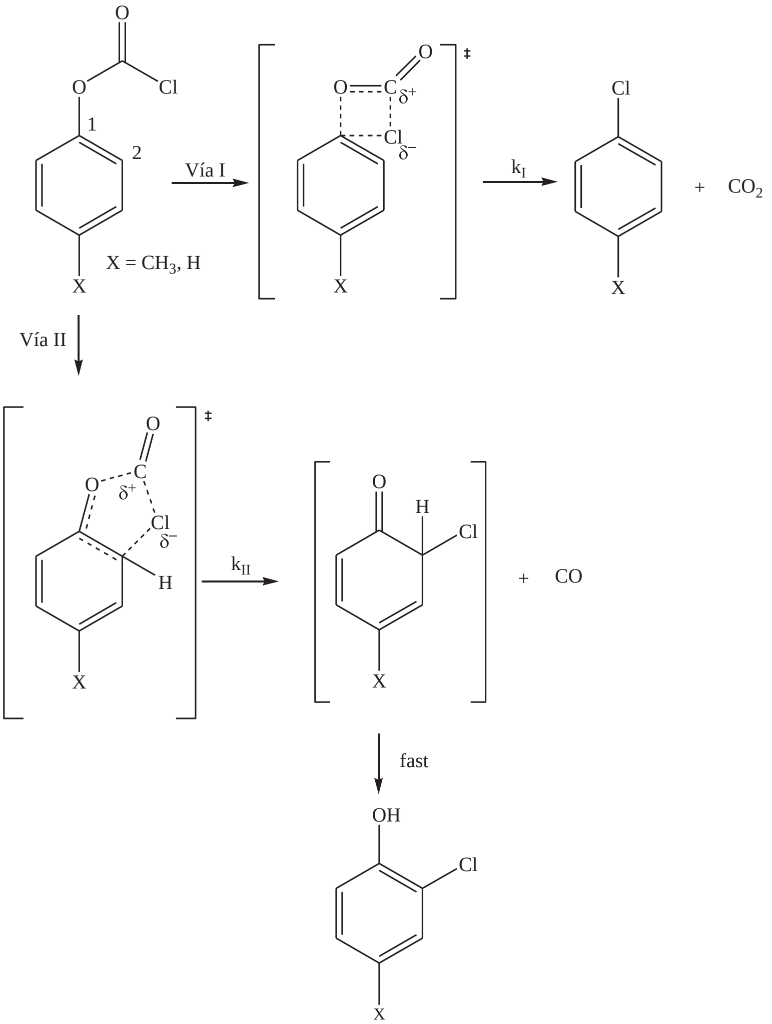


Figure 3 Mechanistic consideration for the gas-phase elimination of aryl chloroformates.

$C^{\delta+}\cdots Cl^{\delta-}$, appears to be the rate-determining step. Moreover, the consideration of a reasonable mechanism of via I suggests that the chlorine atom undergoes in both cases an intramolecular substitution at positions 1 and 2 of the benzene ring, where decarboxylation occurs through a four-membered cyclic transition state, whereas decarbonylation by way of a five-membered cyclic transition state takes place through via II.

Because of a more complex interpretation is required for *p*-tolyl chloroformate, it was thought to be first discussed. Consequently, this substrate undergoes through via I to produce about 20.7% *p*-chlorotoluene and 79.1% by via II with the formation of 2-chloro-4-methylphenol. This result suggests an intramolecular competition of aromatic migration by the chlorine atom. A difference in the energy of activation of $\approx$30 kJ mol^{-1} lower in the 2-chloro-4-methylphenol formation, implies a more favorably process than via I; additionally, a smaller value of $\Delta G^{\ddagger}$ means a faster reaction rate. Moreover, formation of a five-membered cyclic transition state is more favored when compared to that of a four-membered cyclic transition state, since an augmentation in the size of the cyclic structure there is a relative decrease in the stress. In addition to these facts, chlorine migration at the position 2 of the aromatic ring appears to be favored by electron release (+I) of the methyl group present at the para position of the benzene ring. The above argument may explain the difference in reactivity with respect to phenyl chloroformate. The products formations are different, that is, 71.1% of chlorobenzene vía I, and 28.9% of 2-chlorophenol vía II. Apparently, the most important process appears to be through four-membered cyclic structure. In this case, there is less stabilization on the carbonyl carbon adjacent to the electron-withdrawing chlorine atom, which may be the absence of the electron release of the CH_3 substituent at the para position of the ClCOO substituent.

CONCLUSIONS

The gas-phase elimination of aryl chloroformates undergoes a homogeneous, unimolecular reaction and follows a first-order rate law. The aryl chloroformates appears to undergo through a mechanisms involving two competitive intramolecular reactions, where decarboxylation occurs on the one side and decarbonylation on the other side. The proposed mechanisms were considered to proceed through a concerted, polar four- and five-membered cyclic transition states. The bond polarization of the C–Cl, in the sense $C^{\delta+}\cdots Cl^{\delta-}$, appears to be the rate-determining step of these elimination reactions.

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