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Experimental and theoretical study of the homogeneous, unimolecular gas-phase elimination kinetics of methyl oxalyl chloride

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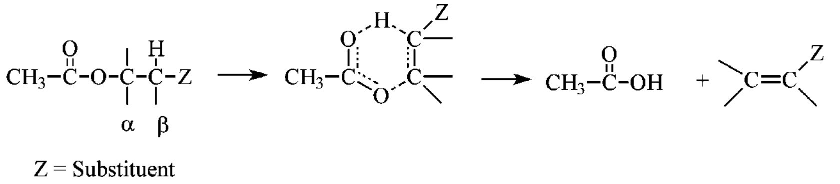
ABSTRACT: The products of the gas-phase elimination of methyl oxalyl chloride are methyl chloroformate and carbon monoxide. The kinetics were determined in a static system over the temperature range 280.3–320.7 °C and pressure range 56–140.4 Torr. The reaction, in vessels seasoned with allyl bromide and in the presence of the free-radical inhibitor cyclohexene, is homogeneous, unimolecular and follows a first-order rate law. The rate coefficients are given by the Arrhenius equation: $\log[k_1\,(\mathrm{s}^{-1})] = (12.73 \pm 0.58) - (174.3 \pm 6.3)\,\mathrm{kJ\,mol}^{-1}\,(2.303\,RT)^{-1}$. Theoretical studies of the mechanism at the semi-empirical PM3 and MP2/6–31G* levels imply a concerted non-synchronous process. Analysis of the three-membered ring transition state suggests that polarization of the Cl—C(═O) bond is rate limiting in the elimination process. The kinetics and thermodynamic parameters are in good agreement with the experimental values. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: kinetics; unimolecular elimination; pyrolysis; methyl oxalyl chloride; semi-empirical and *ab initio* calculations; reaction mechanism; transition-state structure

INTRODUCTION

The presence of a C_β—H bond on the alkyl side of an organic ester, such as acetates, leads to a gas-phase pyrolytic elimination through a six-membered cyclic transition state type of mechanism as described in reaction (1):[1,2]

However, methyl esters without a C_β—H bond generally decompose by way of complex concurrent molecular–radical mechanisms and at very high temperatures. Contrary to this rule, the gas-phase pyrolysis of methyl chloroformate was reported to give methyl chloride and carbon dioxide at 299–491 °C.[3] A similar process of decarboxylation was described in the decomposition of methyl bromoformate in the gas phase.[4] An additional investigation on methyl chloroformate, under homogeneous conditions and in the presence of the free-radical inhibitor propene, was reported to eliminate methyl chloride and CO_2 at 425–480 °C.[5] [reaction (2), step 2].



(1)

$$\mathrm{ClCOCOOCH_3} \xrightarrow[\mathbf{1}]{-\,\mathrm{CO}} \mathrm{ClCOOCH_3} \xrightarrow[\mathbf{2}]{-\,\mathrm{CO_2}} \mathrm{CH_3Cl} \qquad (2)$$

A curious organic molecule with which to investigate the elimination kinetics in the gas phase is methyl oxalyl chloride (methyl chlorooxoacetate). The thermal decomposition of this substrate may proceed vià a consecutive reaction, where methyl oxalyl chloride, as an acyl chloride, may decarbonylate [reaction (2), step 1], while the intermediate methyl chloroformate decarboxylates [reaction (2), step 2] to yield methyl chloride [reaction

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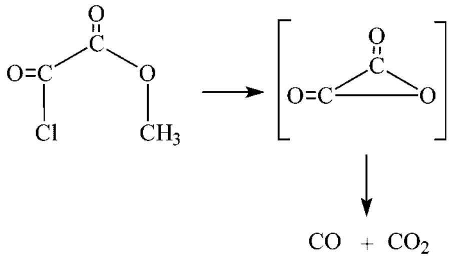
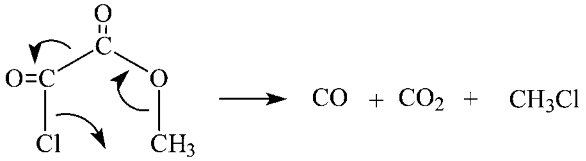
(2)]. An alternative mechanistic process for the decomposition of the above-mentioned substrate may be thought to proceed through a five-membered cyclic structure to methyl chloride and an assumed unstable intermediate C_2O_3 [reaction (3)]. A extremely rapid simultaneous fragmentation to methyl chloride, CO and CO_2 may be another process of elimination [reaction (4)].



(3)



(4)

In order to achieve a reliable interpretation concerning the mechanistic elimination of the assumed reactions (2), (3) and (4), this investigation was aimed at examining the elimination kinetics of methyl oxalyl chloride and to perform a combination of kinetic experiments and theoretical studies of the said substrate. The intention was to obtain the kinetic parameters and the characterization of the potential energy surface (PES) in order to elucidate the nature of the molecular mechanism for the elimination process.

COMPUTATIONAL METHOD AND MODEL

The kinetics for the gas-phase elimination reaction of $ClCOCOOCH_3$ into CO and $ClCOOCH_3$ suggest a concerted mechanism. Theoretical calculations using the semi-empirical PM3 method and the MP2 level of theory with the 6–31G* basis set[6,7] were performed with the Gaussian 94 W program. The Berny analytical gradient optimization routines were used for optimization.[8,9] A transition-state search was performed using the Quadratic Synchronous Transit method. The nature of stationary points was established by calculating and diagonalizing the force constant matrix to determine the number of imaginary frequencies.[10] Intrinsic reaction coordinate (IRC) calculations were performed to verify transition-state structures.[11] Frequency calculations provided thermodynamic quantities such as zero-point vibrational energy (*ZPVE*), temperature corrections and absolute entropies, and consequently the rate coefficient can be estimated assuming that the transmission coefficient is equal to unity. Temperature corrections and absolute entropies were obtained assuming ideal gas behavior, from the harmonic frequencies and moments of inertia by standard methods[12] for a temperature of 300 °C and 1 atm pressure.

The first-order rate coefficient $k(T)$ was calculated using the TST[13] and assuming that the transmission coefficient is equal to unity, as expressed in the following relation:

$$k(T) = (KT/h)\exp(-\Delta G^{\ddagger}/RT) \tag{5}$$

where $\Delta G^{\ddagger}$ is the Gibbs free energy change between the reactant and the transition state and K and h are the Boltzmann and Plank constants, respectively. $\Delta G^{\ddagger}$ was calculated using the following relations:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{6}$$

and

$$\Delta H^{\ddagger} = V^{\ddagger} + \Delta ZPVE + \Delta E(T) + PV \tag{7}$$

where $V^{\ddagger}$ is the potential energy barrier and $\Delta ZPVE$ and $\Delta E(T)$ are the differences in $ZPVE$ and temperature corrections between the transition state and the reactant, respectively. $\Delta S^{\ddagger}$ values were obtained from the difference between the reactant and the corresponding transition-state entropies directly from the Gaussian output. $\Delta S^{\ddagger}$ values were used to calculate Arrhenius pre-exponential factor using the relation

$$A = (e^m kT/h)\exp(\Delta S^{\ddagger}/R) \tag{8}$$

where m is the molecularity of the reaction.

RESULTS AND DISCUSSION

The elimination process of methyl oxalyl chloride, in a static system, seasoned with allyl bromide and in the presence of the free-radical suppressor cyclohexene, was determined over the temperature range 280–320 °C and the pressure range 56–140 Torr (1 Torr = 133.3 Pa). The stoichiometry based on reaction (9) demands that, for long reaction times, $P_f = 2P_0$, where P_f and P_0 are the final and initial pressure, respectively. The experimental P_f/P_0 value at four different temperatures and 10 half-lives was 1.94.

$$ClCOCOOCH_3 \rightarrow ClCOOCH_3 + CO \tag{9}$$

The yields of pyrolysis products within the range of rate determination, that is, up to 65% reaction, were methyl chloroformate and CO gas [reaction (9)]. Methyl chloroformate did not decompose further, since the experimental working temperature is less than the 425 °C of the investigation reported previously.[5]

The homogeneity of the elimination was examined by using a reaction vessel with a different surface-to-volume

Table 1. Homogeneity of the reaction

Substrate	Temperature (°C)	S/V (cm^{-1})[a]	$10^4\,k_1$ (s^{-1})[b]	$10^4\,k_1$ (s^{-1})[c]
Methyl oxalyl chloride	311.5	1	17.62[d]	14.65
		6	29.62[d]	14.91

[a] S = surface area (cm^2); V = volume (cm^3).
[b] Clean Pyrex vessel.
[c] Vessel seasoned with allyl bromide.
[d] Average k values.

Table 2. Effect of the free radical inhibitor cyclohexene on rates

Substrate	Temperature (°C)	P_s (Torr)[a]	P_i (Torr)[a]	P_i/P_s	$10^4\,k_1$ (s^{-1})
Methyl oxalyl chloride[b]	320.7	95.5	—	—	27.33
		120.5	122	0.6	26.05
		102	169	1.7	25.66
		102.5	262.5	2.6	25.72

[a] P_s = pressure of the substrate; P_i = pressure of the inhibitor. Vessel seasoned with allyl bromide.
[b] Inhibitor cyclohexene.

ratio. That is, the packed vessel has a 6.0 times greater surface-to-volume ratio than the unpacked vessel (Table 1). The packed and unpacked clean Pyrex vessels had a significant effect on the rates. However, the packed and unpacked Pyrex vessels seasoned with allyl bromide had no effect on rates. The methyl oxalyl chloride reaction, in seasoned vessels, had to be carried out in the presence of at least twice the amount of the inhibitor cyclohexene in order to prevent any radical reaction (Table 2). No induction period was observed and the rates were reproducible with a standard deviation not greater than 10% at a given temperature.

The rate coefficient of this elimination was found to be independent of the initial pressure (Table 3), and the first-order rate was calculated from $k_1 = (2.303/t)\ \log P_0/(2P_0 - P_t)$. A plot of $\log(2P_0 - P_t)$ against time t gave a good straight line up to 65% reaction. The variation of the rate coefficients with temperature and the corresponding Arrhenius equation is given in Table 4 (90% confidence coefficient from least-squares procedure).

Table 3. Invariability of the rate coefficients with initial pressure[a,b]

Substrate	Temperature (°C)	Parameter	Value			
Methyl oxalyl chloride	320.7	P_0 (Torr)	53	102	120.5	140.5
		$10^4\,k_1$ (s^{-1})	25.79	25.66	25.85	25.73

[a] Vessel seasoned with allyl bromide.
[b] In the presence of the inhibitor cyclohexene.

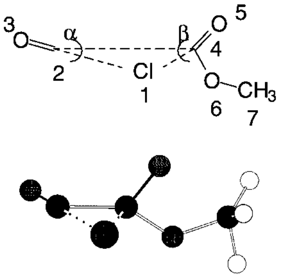


Figure 1. The transition state for this reaction is a three-membered ring structure showing a very large C2—C4 distance as well as a large Cl1—C2 distance. Also, chlorine is closer to C4 in the transition state. Angles α and β are also shown. Below is the transition state as a three-dimensional molecule. The transition state is late in the reaction coordinate; the new Cl—C4 bond is almost completely formed in addition to a C—O triple bond in CO

With these results and to establish the most adequate mechanism for the gas-phase elimination of methyl oxalyl chloride, a theoretical study was carried out.

THEORETICAL RESULTS

Theoretical studies suggest that the gas-phase elimination reaction of methyl oxalyl chloride to give methyl chloroformate and carbon monoxide occurs by a concerted non-synchronous mechanism. The transitions state found is late in the reaction coordinate in the sense of the

Table 5. Transition-state (TS) atom distances (Å)

TS atoms	PM3 distance	MP2/6–31G* distance
Cl1—C2	3.77	4.10
C2—O3	1.13	1.13
C2—C4	5.20	5.64
C4—O5	1.21	1.18
C4—Cl1	1.73	1.84
C4—O6	1.36	1.36

Table 6. TS bond angles (°)

	PM3	MP2/6–31G*
α $\angle C_4Cl1C_2$	12.7	11.9
β $\angle C_2Cl1C_4$	28.53	27.58

Table 4. Variation of rate coefficients with temperature[a]

Substrate	Parameters	Value				
Methyl oxalyl chloride	Temperature (°C)	280.3	290.2	300.2	311.5	320.7
	$10^4\,k_1$ (s^{-1})	1.96	3.74	7.05	14.62	25.97

[a] Rate equation: $\log k_1\ (\mathrm{s}^{-1}) = (12.73 \pm 0.58) - (174.3 \pm 6.3)\ \mathrm{kJ\,mol^{-1}}\ (2.303\ RT)^{-1}$; $r = 0.9980$.

Table 7. Comparative theoretical and experimental activation parameters at 300 °C

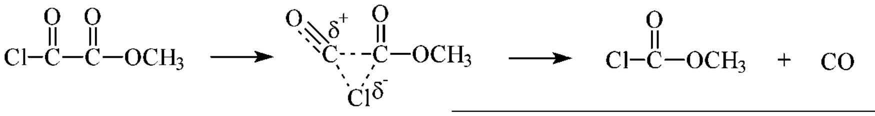
Method	E_a (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})	Log [A (s^{-1})]	10^4 k_1 (s^{-1})
PM3	174.6	169.8	−16.7	179.4	12.64	5.29
MP2/6–3G*	173.2	168.5	−14.0	176.5	12.78	9.81
Experimental	174.3	169.5	−14.9	178.1	12.73	6.94

breaking of Cl1—C2 and C2—C4 bonds and the formation of a Cl1—C4 bond. The transition-state geometry is shown in Fig. 1. The geometric parameters shown in Tables 5 and 6 indicate a product-like transition state.

Calculated activation parameters are in reasonable agreement with the experimental values (Table 7). First-order rate coefficients are of the same order of magnitude as the experimental value.

CONCLUSIONS

Results from theoretical calculations combined with experimental shows that the reaction proceeds in a concerted, rather polar mechanism [reaction (10)], the transition state being product-like or late in the sense of the reaction progress. The activation parameters are satisfactory and first-order reaction rate coefficients are of the same order of magnitude. Semi-empirical PM3 calculations are in slightly better agreement with experiment than MP2/6–31G* calculations. Analysis and comparison of the results suggest the validity of the methods used.



(10)

EXPERIMENTAL

Methyl oxalyl chloride (methyl chlorooxoacetate). This compound (Aldrich) was distilled several times (b.p. 114–115 °C at 633 Torr) to better than 98.8% purity (GC: Porapak Q, 80–100 mesh, 2 min). The decomposition products methyl chloroformate was determing using a 10% SP 1200–1% H_3PO_4 Chromosorb W AW DMCS (80–100 mesh) column. The verification of the substrate and identification of the product were carried out by gas chromatography–mass spectrometry (Saturn 2000, Varian) using a DB–5MS capillary column (30 × 0.25 mm. i.d., 0.25 μm film thickness).

Kinetic studies. The kinetic experiments were performed in a static reaction system as previously reported[14,15] with an Omega DP41-TC/DP41-RTD high-temperature performance digital temperature controller. The rate coefficients were determined manometrically. The temperature was controlled by a Shinko DC-PS resistance thermometer controller and an Omega Model SSR280A55 solid-state relay maintained within ± 0.2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was found along the reaction vessel. The substrate was injected (0.05–0.1 ml) directly into the reaction vessel with a syringe through a silicone-rubber septum.

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