

Mechanisms of the homogeneous, unimolecular gas-phase elimination kinetics of triethyl orthoacetate and triethyl orthopropionate

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Triethyl orthoacetate and triethyl orthopropionate were pyrolyzed in a static system over the temperature range of 291–351°C and pressure range of 80–170 Torr. The elimination reactions of these orthoesters in seasoned vessels are homogeneous, unimolecular, and follow a first-order rate law. The reaction products are ethanol, ethylene and the corresponding ethyl ester. The Arrhenius expressions of these eliminations were found as follow: for triethyl orthoacetate, $\log k_1 \text{ (s}^{-1}\text{)} = (13.76 \pm 0.09) - (187.6 \pm 1.1) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}$ ($r = 0.9993$), and for triethyl orthopropionate, $\log k_1 \text{ (s}^{-1}\text{)} = (13.63 \pm 0.07) - (193.3 \pm 1.8) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}$ ($r = 0.9992$). A reasonable mechanism of these elimination is to consider that the C—OCH₂CH₃ bond, as C^{δ+}...^{δ-}OCH₂CH₃ in the TS, is the rate-determining step. The nucleophilicity of the oxygen atom of OCH₂CH₃ may abstract the hydrogen of the adjacent C—H bond for a four-membered cyclic structure to give the corresponding unsaturated ketal. The unstable ketal intermediate decomposes, in a six-membered cyclic transition state, into ethylene and the corresponding ethyl ester. Copyright © 2008 John Wiley & Sons, Ltd.

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INTRODUCTION

The chemical literature does not describe the pyrolysis kinetics of orthoesters in the gas phase. However, it seemed interesting to find some related works of thermal decomposition carried out under different conditions. In 1922, Staudinger and Rathsam^[1] carried out the pyrolysis of some triethyl orthoesters in the presence of nickel at 250–260°C to produce ethyl ether and the corresponding ethyl ester. They also pyrolyzed triethyl orthophenylacetate with the simultaneous formation of ethyl phenyl acetate and corresponding phenylketene acetal after distillation. No ethyl ether was detected as a final product. These authors proved that pure phenylketene diethyl acetal when heated in a bomb at 260–270°C yielded mainly ethyl phenylacetate, presumably ethylene gas, and an unidentified solid.

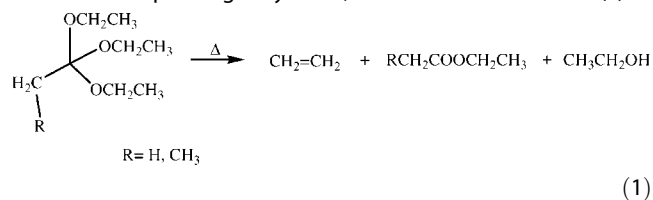
Diethylbenzyl orthoacetate^[2] in the glass liner of a steel bomb were electrically heated at 200°C for several hours. This reaction was found to give *o*-tolylacetate from the rearrangement of the ketene ethylbenzylacetal intermediate. In the case of triethyl orthobenzoate, which has no α -hydrogen, gave the normal ester and diethyl ether on pyrolysis.

The substrate triethyl orthophenyl acetate through slow distillation gave phenylketene diethyl acetal and ethyl phenylacetate.^[3] Otherwise, when trimethyl orthophenyl acetate was heated at 250–260°C yielded phenylketene dimethyl acetal and methyl phenylacetate in a better yield than ethyl phenylacetate. Moreover, the vigorous evolution of methanol formation in the pyrolysis of the latter orthoester led to believe the interaction of two molecules of trimethyl orthophenyl acetate.

In view of the interesting reactions undergone by different methods of pyrolysis of orthoesters as described above,^[1–3] the present work aimed at studying the kinetics of this type of compounds in the gas phase, especially under homogeneous and molecular conditions. In this respect, this investigation examines the gas-phase elimination kinetics of triethyl orthoacetate and triethyl orthopropionate.

RESULTS

The gas-phase elimination of triethyl orthoacetate and triethyl orthopropionate at the temperature range of 291–351°C and pressure range of 80–170 Torr were found to give ethanol, ethylene, and the corresponding ethyl ester, as described in reaction (1).



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Table 1. Ratio of final (P_f) to initial pressure P_o of the substrate

Substrate	T ($^{\circ}\text{C}$)	P_o (Torr)	P_f (Torr)	P_f/P_o	Average
Triethyl orthoacetate	301.8	90	262	2.9	2.9
	310.6	102	298	2.9	
	320.2	107	318	3.0	
	330.5	80	230	2.9	
	340.7	60	176	2.9	
Triethyl orthopropionate	301.8	75	218	2.9	2.9
	312.3	90	262	2.9	
	323.3	98	286	2.9	
	331.3	80	236	3.0	
	341.4	70	205	2.9	

Stoichiometry (1) demands that, for long reaction times, $P_f = 3P_o$, where P_f and P_o are the final and initial pressure, respectively. The average experimental results for P_f/P_o values at five different temperatures and 10 half-lives were 2.9 for both triethyl orthoacetate and triethyl orthopropionate (Table 1). Further confirmation of the above stoichiometry (1) was made by comparing the per cent decomposition of the orthoester substrate from pressure measurements against the quantitative chromatographic analyses of the product ethylene gas (Table 2).

The homogeneity of this elimination was examined by using a packed reaction vessel with a surface-to-volume ratio six times greater than that of the unpacked vessel (Table 3). The rates were unaffected by the packed and unpacked seasoned vessels, whereas a marked heterogeneous effect was obtained with the packed and unpacked clean Pyrex vessels. The absence of a free radical chain reaction was verified by carrying out several runs in the presence of different proportions of toluene as inhibitor (Table 4). No induction period was observed. The rates are reproducible with a standard deviation not greater than 5% at a given temperature.

The rate coefficients for the orthoesters calculated from $k_1 = (2.303/t) \log [2P_o/(3P_o - P_f)]$ were found to be independent of the initial pressure (Table 5). A plot of $\log (3P_o - P_f)$ against time t gave a good straight line up to 60% reaction. The temperature dependence of the rate coefficients and the corresponding Arrhenius equation are given in Table 6 and Fig. 1 (95% confidence coefficients from a least-squares method). Therefore,

Table 2. Stoichiometry of the reactions

Substrate	T ($^{\circ}\text{C}$)	Time (min)	Reacción (pressure) (%)	Ethylene (GC) (%)
Triethyl orthoacetate	301.8	3	5.6	5.7
		10	17.5	17.8
		15	25.1	25.3
		18	29.3	29.5
		25	38.2	38.5
		35	49.0	49.2
		48	60.3	60.8
		2	3.3	3.4
Triethyl orthopropionate	312.3	5	8.0	8.4
		10	15.4	15.5
		15	22.2	22.7
		25	34.1	34.3
		35	44.2	44.5
		45	52.8	53.0
		55	60.0	61.0

these reactions carried out in seasoned vessels are homogeneous, unimolecular, and follow a first-order rate law. The rate coefficient is expressed by the following Arrhenius equations:

$$\begin{aligned} \text{Triethyl orthoacetate, } \log k_1(\text{s}^{-1}) &= (13.76 \pm 0.09) \\ &- (187.6 \pm 1.1) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1} \\ &\times (r = 0.9993) \end{aligned}$$

$$\begin{aligned} \text{Triethyl orthopropionate, } \log k_1(\text{s}^{-1}) &= (13.63 \pm 0.07) \\ &- (193.3 \pm 1.8) \text{ kJ mol}^{-1} \\ &\times (2.303 \text{ RT})^{-1} (r = 0.9992) \end{aligned}$$

DISCUSSION

The data described in Table 7 shows, for both substrates, that the log of A value is greater than 13.2. Such value of $\log A > 13.2$ implies a four-membered cyclic structure in the transition state as postulated by Benson *et al.*^[4,5] Moreover, the positive values of the entropy of activations suggest a very polar concerted cyclic transition state. Consequently, a reasonable explanation of the

Table 3. Homogeneity of the elimination reaction

Substrate	Temperature ($^{\circ}\text{C}$)	S/V (cm^{-1})	$10^4 k$ (s^{-1}) ^a	$10^4 k$ (s^{-1}) ^b
Triethyl orthoacetate	301.8	1	51.60 ± 3.10	5.20 ± 0.20
		6	79.20 ± 10.10	5.25 ± 0.10
Triethyl orthopropionate	312.3	1	31.12 ± 6.40	3.31 ± 0.30
		6	61.12 ± 12.10	3.35 ± 0.12

^aClean pyrex vessel.
^bVessel seasoned with allyl bromide.

Table 4. Effect of the free radical chain suppressor on rates

Substrate	Temperature (°C)	P_0 (Torr)	P_1 (Torr)	P_1/P_0	$10^4 k$ (s ⁻¹)
Triethyl orthoacetate	301.8	80	0	0	5.28 ± 0.20
		86	88	1	5.22 ± 0.15
		82	120	1.5	5.21 ± 0.17
		60	150	2.5	5.20 ± 0.30
Triethyl orthopropionate	312.3	80	0	0	3.31 ± 0.33
		70	106	1.5	3.37 ± 0.32
		86	170	2	3.39 ± 0.35
		80	180	3	3.35 ± 0.28

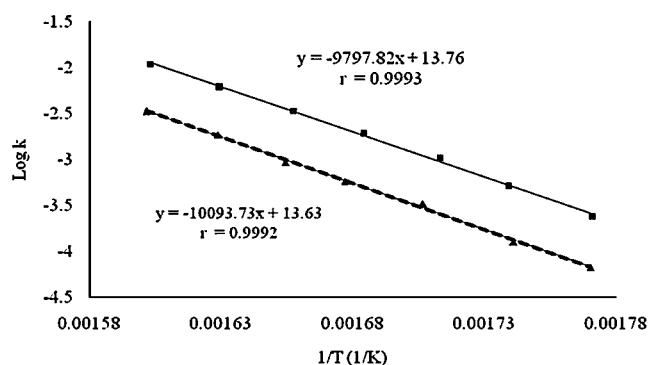
Table 5. The invariability of the rate constant with initial pressure

Substrate	Temperature (°C)	P_0 (mmHg)	$10^4 k_1$ (s ⁻¹)
Triethyl orthoacetate	301.8	80	5.25 ± 0.11
		95	5.30 ± 0.16
		115	5.32 ± 0.14
		125	5.27 ± 0.50
		170	5.23 ± 0.38
Triethyl orthopropionate	312.3	80	3.32 ± 0.33
		92	3.37 ± 0.51
		102	3.31 ± 0.25
		120	3.38 ± 0.23

Table 6. Variation of rate coefficient with temperature

Substrate	Temperature (°C)	$10^4 k_1$ (s ⁻¹)
Triethyl orthoacetate	291.5	2.40 ± 0.14
	301.8	5.23 ± 0.20
	310.6	1.05 ± 0.49
	320.2	18.9 ± 0.92
	330.5	34.00 ± 1.97
	340.7	61.20 ± 2.86
Triethyl orthopropionate	301.3	1.27 ± 0.22
	312.8	3.30 ± 0.30
	323.1	5.75 ± 0.50
	331.3	9.35 ± 0.25
	340.8	18.37 ± 0.35
	351.2	33.60 ± 0.55

mechanism in the elimination of these orthoesters is to consider that breakage of the C—OCH₂CH₃ bond, such as C^{δ+}...^{δ-}OCH₂CH₃ in the TS, is the rate-determining step [reaction (2), step 1]. The nucleophilicity of the oxygen atom of the OCH₂CH₃ will then abstract the hydrogen of the adjacent C—H bond for a four-membered cyclic structure to give the corresponding

**Figure 1.** Graphic representation of the Arrhenius plot for the gas-phase elimination of triethyl orthoacetate (—) and triethyl orthopropionate (----)

unsaturated ketal. This intermediate, under the reaction condition of temperature, rapidly decomposes into ethylene and the corresponding ethyl ester. To explain this latter mechanism of elimination, if one of the two OCH₂CH₃ of the unsaturated ketal is considered as any other substituent, then the corresponding ethyl vinyl ether decomposes through a six-membered cyclic transition state to give ethylene and the corresponding ethyl ester [reaction (2), step 2] as reported in the literature.^[6] Further data of the kinetic and thermodynamic

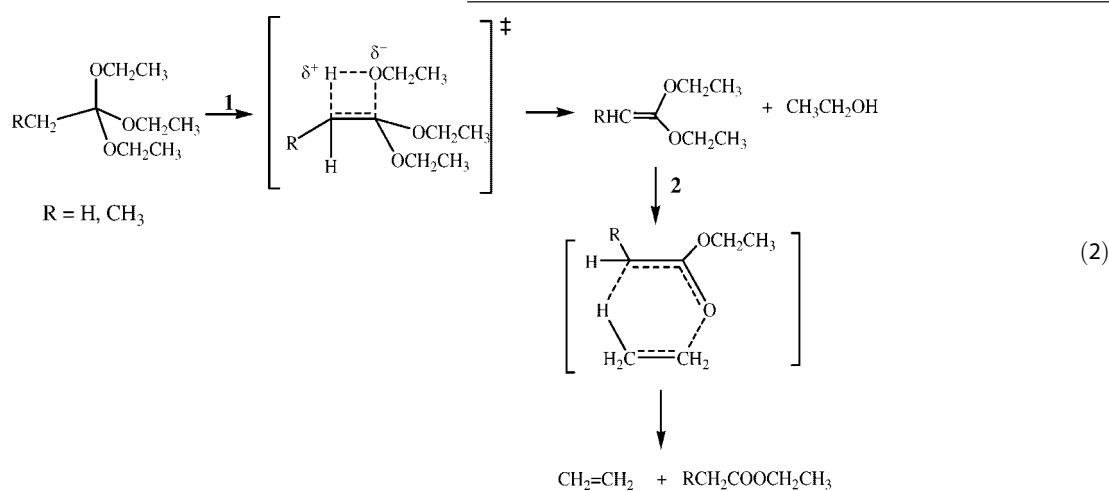
Table 7. Kinetic and thermodynamic parameters

Substrate	$10^4 k_1 \text{ (s}^{-1}\text{)}^a$	$E_a \text{ (kJ/mol)}$	$\log A \text{ (s}^{-1}\text{)}$	$\Delta H^\ddagger \text{ (kJ/mol)}$	$\Delta S^\ddagger \text{ (J/mol K)}$
Triethyl orthoacetate	10.05	187.6 ± 1.1	13.76 ± 0.09	182.8 ± 1.07	4.62 ± 0.64
Triethyl orthopropionate	2.06	193.3 ± 1.8	13.63 ± 0.07	188.5 ± 1.76	2.14 ± 0.25

^aAt 310°C.

parameters show that triethyl orthoacetate is about five times greater in elimination than triethyl orthopropionate. This difference may be rationalized from the fact that the abstraction of the adjacent hydrogen of the C—H bond by the nucleophilic OCH_2CH_3 is less acidic in the propionate than in the acetate.

SHINKO DIC-PS 23TR resistance thermometer controller with a calibrated Iron-Constantan thermocouple. The temperature reading was measured within $\pm 0.1^\circ\text{C}$ with a thermopar of Iron-Constantan attached to a Digital Multimeter Omega 3465B. The reaction vessel showed no temperature gradient at different



EXPERIMENTAL

Triethyl orthoformate (97%) and triethyl orthopropionate (97%) were bought from Aldrich. The purity of the substrates and products and their identifications were determined by GC/MS/MS (Saturn 2000, Varian). Capillary column DB-5MS, 30 mm $\times$ 0.250 mm, i.d. 0.25 μm . The olefin product ethylene was analyzed using a chromatograph Varian Star 3600 CX with a thermal conductivity detector (capillary column: GS-Q, 30 m long and 0.53 i.d., Helium gas carrier).

Kinetics

The kinetics determinations were carried out in a static reaction system as described before.^[7–9] The reaction vessel was deactivated with the product of decomposition of allyl bromide. The rate coefficients were determined manometrically. The temperature was found to be within $\pm 0.2^\circ\text{C}$ when controlled by a

points, and the substrate was injected directly into the reaction vessel through a silicone rubber septum. The volume of substrate used for each reaction was $\approx 0.05\text{--}0.1$ ml.

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