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Kinetics and Mechanisms of the Homogeneous, Unimolecular Gas-Phase Elimination of Trimethyl Orthoacetate and Trimethyl Orthobutyrate

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The gas-phase elimination kinetics of the title compounds have been examined over the temperature range of 310−369 °C and pressure range of 50−130 Torr. The reactions, in seasoned vessels, are homogeneous, unimolecular, and follow a first-order rate law. The products are methanol and the corresponding methyl ketene acetal. The rate coefficients are expressed by the Arrhenius equation: for trimethyl orthoacetate, log k_1 (s^{-1}) = [(13.58 ± 0.10) − (194.7 ± 1.2) (kJ mol^{-1})]$(2.303RT)^{-1}$$r$ = 0.9998; and for trimethyl orthobutyrate, log k_1(s^{-1}) = [(13.97 ± 0.37) − (195.3 ± 1.6) (kJ mol^{-1})]$(2.303RT)^{-1}$$r$ = 0.9997. These reactions are believed to proceed through a polar concerted four-membered cyclic transition state type of mechanism.

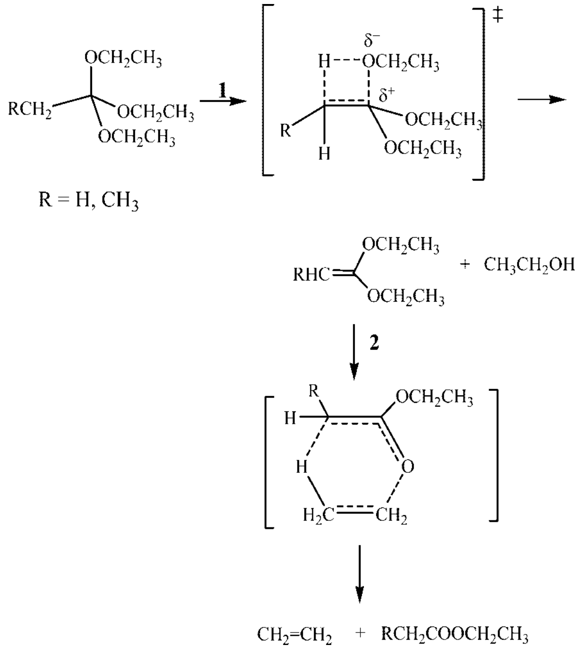
I. Introduction

Few pyrolyses of orthoesters have been reported. However, some related works on the thermal decomposition of these type of compounds were carried out under different conditions. The pyrolysis of several triethyl orthoesters in glass tubes and the presence of nickel on pumice stone at 250−260 °C was found to give ethyl ether and the corresponding ethyl ester.[1] Moreover, distillation of triethyl orthophenylacetate under reduced pressure yielded ethyl phenyl acetate and corresponding phenylketene acetal. No ethyl ether was detected as a final product. Twenty years later, the substrate benzyldiethyl orthoacetate[2] in the glass liner of a steel bomb heated at 200 °C produced *o*-tolylacetate by rearrangement of the benzylethylacetal intermediate. However, triethyl orthobenzoate heated under the same conditions showed the formation of ethyl benzoate and diethyl ether.

The work of triethyl orthophenylacetate was revisited by slow distillation[3] at atmospheric pressure, and produced as reported[1] similar products of phenylketene diethyl acetal and ethyl phenylacetate. Trimethyl orthophenylacetate heated at 250−260 °C gave phenylketene dimethyl acetal and methyl phenylacetate.

Recently, The gas-phase elimination kinetics of triethyl orthoacetate and orthopropionate was shown to be homogeneous, unimolecular, and obey a first-order rate law. The reaction products are ethanol and the corresponding ethyl ester.[4] The mechanism of these eliminations was rationalized in terms of a four-membered cyclic transition state as described in reaction 1.

Since little is known about the gas-phase elimination kinetics of orthoesters, and also with the possibility of considering a simultaneous six-membered cyclic transition state type of mechanism described in reaction 2, the present work aimed at finding some support for mechanism 1. In this respect, the kinetics of elimination of trimethyl orthoacetate and trimethyl orthobutyrate in the gas phase, where CH_3CH_2 was replaced by CH_3, were examined under homogeneous and molecular conditions.



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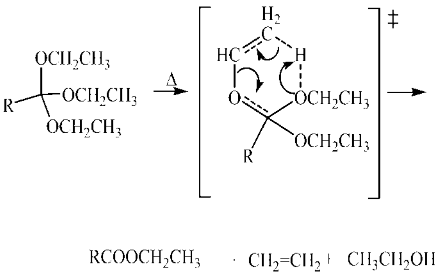

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II. Experimental Method

The substrates trimethyl orthoformate (98.7%) and trimethyl orthobutyrate (97%) were acquired 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 × 0.250 mm., i.d. 0.25 μm). A Varian Star 3600 CX chromatograph with a thermal conductivity detector (capillary column: GS-Q, 30 m long and 0.53 i.d., helium gas carrier) was used for the quantitative analysis of the products methanol and the corresponding methylketene acetal.

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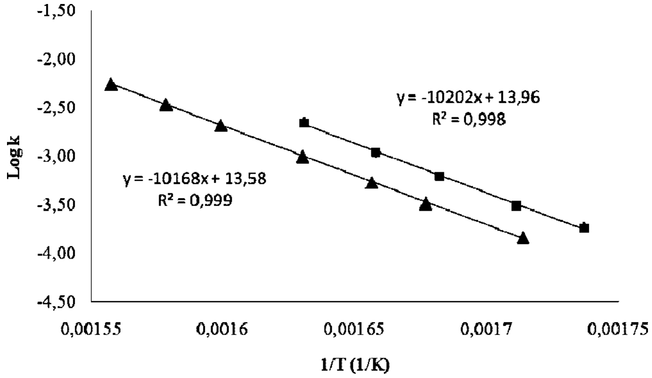


Figure 1. Graphic representation of the Arrhenius plots for the gas-phase elimination of trimethyl orthoacetate (▲) and trimethyl orthobutyrate (☐).

TABLE 1: Ratio of Final (P_f) to Initial (P_0) Pressure of the Substrates

substrate	temp (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	av
trimethyl orthoacetate	323.3	70	135	1.93	1.94±0.02
	330.5	102	200	1.96	
	340.2	88	172	1.95	
	352.2	130	250	1.92	
	360.4	60	114	1.90	
trimethyl orthobutyrate	322.9	70	135	1.93	1.95±0.02
	330.6	88	172	1.95	
	340.2	96	188	1.96	
	352.2	116	228	1.97	

TABLE 2: Stoichiometry of the Reactions

substrate	temp (°C)	time (min)	reaction (pressure) (%)	MeOH (GC) (%)
trimethyl orthoacetate	340.2	3	19.8	19.2
		5	27.1	26.7
		8	38.0	38.4
		11	47.3	46.8
		16	60.1	59.0
		20	70.2	68.0
trimethyl orthobutyrate	330.3	2	18.0	17.6
		5	28.1	27.4
		8	41.1	40.1
		10	48.3	47.4
		12	55.2	54.2

TABLE 3: Homogeneity of the Elimination Reactions

substrate	temp (°C)	S/V (cm^{-1})	10^4k (s^{-1})[a]	10^4k (s^{-1})[b]
trimethyl orthoacetate	340.2	1	41.60 ± 4.1	10.02 ± 0.18
		6	58.20 ± 6.8	9.98 ± 0.37
trimethyl orthobutyrate	330.2	1	28.52 ± 4.3	11.00 ± 0.36
		6	46.58 ± 5.2	10.93 ± 0.56

[a] Clean pyrex vessel, [b] Deactivated pyrex vessel with allyl bromide.

TABLE 4: Effect of the Free Radical Chain Suppressor Cyclohexene on Rates

substrate	temp (°C)	P_0 (Torr)[a]	P_i (Torr)[b]	P_i/P_0	10^4k (s^{-1})
trimethyl orthoacetate	340.2	85	0	0	9.98 ± 0.20
		86	88	1	10.05 ± 0.45
		82	140	1.7	10.12 ± 0.32
		58	160	2.8	9.96 ± 0.36
trimethyl orthobutyrate	330.2	85	0	0	10.80 ± 0.20
		88	86	1	10.98 ± 0.45
		86	160	1.8	10.92 ± 0.32
		50	160	3.2	11.00 ± 0.36

[a] P_0 = pressure of the substrate. [b] P_i = pressure of the inhibitor cyclohexene.

TABLE 5: Invariability of the Rate Coefficients with Initial Pressure

substrate	temp (°C)	P_0 (Torr)	10^4k_1 (s^{-1})
trimethyl orthoacetate	340.2	50	9.79 ± 0.18
		85	9.82 ± 0.25
		100	9.78 ± 0.30
		115	9.79 ± 0.20
trimethyl orthobutyrate	330.2	60	10.93 ± 0.32
		100	11.08 ± 0.36
		120	10.95 ± 0.21
		130	10.97 ± 0.41

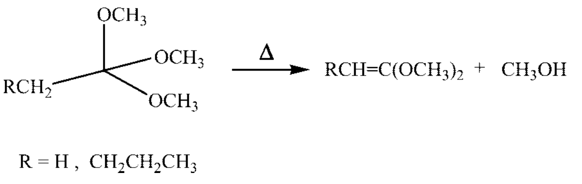
TABLE 6: Variation of Rate Coefficients with Temperature

substrate	temp (°C)	10^4k_1 (s^{-1})
trimethyl orthoacetate	310.3	1.40
	323.2	2.90
	330.5	5.18
	340.2	9.81
	352.2	16.50
	360.4	31.39
	368.9	50.90
trimethyl orthobutyrate	302.5	1.83
	311.2	3.11
	321.3	6.27
	330.1	11.00
	340.0	22.10

Kinetics. The reactions were carried out in seasoned or deactivated vessels by the products of decomposition of allyl bromide, in a static system,[5−7] and the kinetics were followed 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 temperature reading was measured within ±0.1 °C with a thermopar of iron−constantan attached to a Digital Multimeter Omega 3465B. The reaction vessel showed no temperature gradient at different points, and the substrates were injected directly into the reaction vessel through a silicone rubber septum. The volume of substrate used for each reaction was ca. 0.05−0.1 mL.

III. Results and Discussion

The products of gas-phase elimination of trimethyl orthoacetate and trimethyl orthobutyrate, in vessels deactivated with allyl bromide, were mainly methanol and the corresponding ketene methyl acetal (eq 3).



(3)

The stoichiometry based on reaction 3 would lead to a ratio of 2 for P_f/P_0, where P_f and P_0 are the final and initial pressure, respectively. Several measurements in the temperature range

TABLE 7: Kinetic and Thermodynamic Parameters at 330 °C

substrate	$10^4 k_1$ (s^{-1})	E_a (kJ/mol)	log A (s^{-1})	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/mol·K)	$\Delta G^{\ddagger}$ kJ/mol)
trimethyl orthoacetate	5.18	194.7 ± 1.2	13.58 ± 0.10	189.7 ± 1.2	0.13 ± 0.01	189.6 ± 1.21
trimethyl orthobutyrate	11.28	195.3 ± 1.6	13.97 ± 0.37	190.3 ± 1.6	8.36 ± 0.03	185.3 ± 1.62

322.9−360.4 °C and pressure range 60−130 Torr gave a mean value of 1.94 for trimethyl orthoacetate and of 1.95 for trimethyl orthobutyrate (Table 1). The stoichiometry was further verified by comparison of the percentage of decomposition from pressure measurements with that determined by the quantitative chromatographic analysis of the product methanol (Table 2).

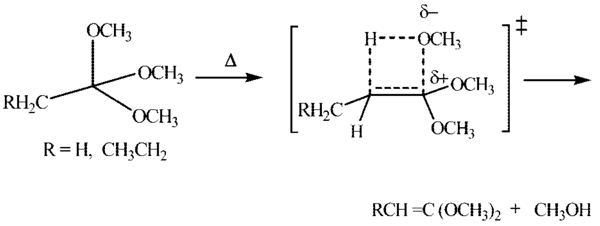
The homogeneity of the reaction was examined by using a vessel with surface-to-volume ratio of 6 relative to the normal vessel which had an $S/V = 1$ cm^{-1}. The rates were unaffected in a packed and unpacked seasoned Pyrex vessel, but some heterogeneous effect was found in the clean packed and unpacked Pyrex vessel (Table 3). The absence of a free radical reaction is indicated by the lack of effect of added cyclohexene, an effective free radical suppressor (Table 4), and no induction period was observed.

The rates of elimination calculated for trimethyl orthoacetate and trimethyl orthobutyrate from $k_1 = (2.303/t) \log[P_0/(2P_0 - P_t)]$ were found to be independent of the initial pressure (Table 5). Plots of $\log[(2P_0 - P_t)/P_0]$ vs time t gave a good straight line up to 60−70% reaction. The temperature dependence of the rate coefficients is given in Table 6 and Figure 1 (95% confidence coefficients from a least-squares method). The data in Table 6 were fitted to the Arrhenius equations

$$\text{trimethyl orthoacetate:}\quad \log k_1\ (\mathrm{s}^{-1}) = [(13.58 \pm 0.10) - (194.7 \pm 1.2)\ (\mathrm{kJ\ mol}^{-1})](2.303RT)^{-1} r = 0.9998$$

$$\text{trimethyl orthobutyrate:}\quad \log k_1\ (\mathrm{s}^{-1}) = [(13.97 \pm 0.37) - (195.3 \pm 1.6)\ (\mathrm{kJ\ mol}^{-1})](2.303RT)^{-1} r = 0.9997$$

An important result (Table 7), the frequency factor of log of the A value, is found to be greater than 13.2. Values of log A > 13.2 are consistent with, as postulated by Benson et al.,[8,9] a four-membered cyclic structure in the transition state that may be operating during the process of decomposition. The estimation of the entropy of activation from log A gives small positive values, which maybe assume a concerted transition state. In this respect, the mechanism for the elimination of these trimethyl orthoesters may be explained in terms of the elongation and subsequent bond polarization of the C−OR bond, in the direction of $C^{\delta+} \cdots {}^{\delta-}OR$, as the rate-determining step [reaction 4]. The presence of at least a hydrogen atom at the C−H bond adjacent to the $C(OCH_3)_3$ appears to assist the leaving methoxy group to produce methanol. This mechanism has the same path of decomposition as that reported for triethyl orthoesters [reaction 1].[4] Consideration of the alternate mechanism 2 seems unlikely to occur because by exchanging CH_3CH_2 for CH_3 in the alkoxy group a different mechanistic pathway does not occur.



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IV. Conclusion

The gas-phase elimination reactions of trimethyl orthoacetate and trimethyl orthobutyrate in seasoned vessels are homogeneous, unimolecular, and obey a first-order rate law. The mechanism of decomposition of these trimethyl orthoesters may be explained in terms of a concerted four-membered cyclic transition state structure. The presence of at least a hydrogen atom at the C−H bond adjacent to the $C(OCH_3)_3$ is necessary for molecular elimination.

References and Notes

(1) Staudinger, H.; Rathsam, G. *Helv. Chim. Acta* **1922**, *5*, 645–655.

(2) McElvain, S. M.; Anthes, H. I.; Shapiro, S. H. *J. Am. Chem. Soc.* **1942**, *64*, 2525–2531.

(3) McElvain, S. M.; Stevens, C. L. *J. Am. Chem. Soc.* **1946**, *68*, 1917–1961.

(4) Marquez, E.; Tosta, M.; Dominguez, R. M.; Herize, A.; Chuchani, G. *J. Phys. Org. Chem.* **2008**, *21*, 666–669.

(5) Maccoll, A. *J. Chem. Soc.* **1955**, *965*, 973.

(6) Swinbourne, E. S. *Aust. J. Chem.* **1958**, *11*, 314–330.

(7) Dominguez, R. M.; Herize, A.; Rotinov, A.; Alvarez-Aular, A.; Visbal, G.; Chuchani, G. *J. Phys. Org. Chem.* **2004**, *17*, 399–408.

(8) Benson, S.; O'Neal, W. *J. Phys. Chem.* **1967**, *71*, 2903–2921.

(9) Benson S. B. *Thermochemical Kinetics*; John Wiley & Sons: New York, 1968.

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