Anchimeric Assistance of the CO_2CH_3 Substituent in the Elimination Kinetics of 3-(Methoxycarbonyl)propyl Methanesulfonate in the Gas Phase

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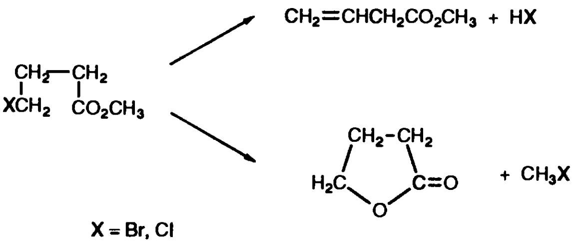
The elimination kinetics of 3-(methoxycarbonyl)propyl methanesulfonate have been determined in a static system over the temperature range of 289.3–329.8 °C and pressure range of 43–111 torr. The reaction, in vessels seasoned with allyl bromide and in the presence of at least an equal amount of the free radical suppressor toluene, is homogeneous, unimolecular and first-order kinetically. The rate coefficients follow the Arrhenius equation: $\log k_1 = (13.50 \pm 0.47) - (182.2 \pm 5.3)\ (2.303\ RT)^{-1}$. A very high extent of lactone formation suggests an unequivocal participation of the carbonyl oxygen of the CO_2CH_3 group. The partial rates for the parallel elimination towards the formation of butyrolactone and a small amount of methylbut-3-enoate have been estimated, reported, and discussed. The present results provide further evidence of intimate ion pair mechanisms in the gas phase pyrolyses of special types of organic molecules.

The lactonization of ethyl 4-bromobutyrate has been shown to be a reaction which involves neighbouring group participation and ionic intermediates in solvents of widely varying dielectric properties, except in the gas phase at all accessible temperatures.[1] However, further research along this line showed that the pyrolysis of the ethyl bromoester in the gas phase led to several parallel elimination paths, where a resonable amount of γ-butyrolactone was formed.[2,3] Replacing the $CO_2CH_2CH_3$ substituent by the CO_2CH_3 group in the 4-halocarboxylic ester in order to avoid elimination towards the C_β-H of the ethyl ester, the pyrolysis products of $XCH_2CH_2CH_2CO_2CH_3$ are shown in Scheme 1.[4,5]



Scheme 1

The results described in Scheme 1 suggested that the anchimeric assistance of the methoxycarbonyl substituent is important in the elimination process, where the dehydrohalogenation product and lactone formation arise from an intimate ion-pair type of mechanism.[4,5]

Since the proposed generalization for the occurrence of neighbouring group participation in gas phase reactions requires a highly polar transition state,[6] the CH_3SO_3 group is expected to be better assisted and eliminated than Br and Cl leaving groups. This consideration appears to be reasonable because of the greater stability of the negatively charged oxygen atom towards sulfur in the transition state. Consequently, the present work sought to examine the elimination kinetics of 3-(methoxycarbonyl)propyl methanesulfonate, $CH_3SO_3CH_2CH_2CH_2COOCH_3$, in the gas phase.

Experimental

Methyl 4-hydroxybutyrate was prepared by refluxing γ-butyrolactone (Aldrich) with Dowex 50(H^+) (BDH) and methanol (Aldrich) as reported[7] (b.p. 33–34 °C at 0.2 torr; b.p. lit.,[7] 33 °C at 0.2 torr). The reaction product was then treated with CH_3SO_2Cl in diethyl ether as described.[8] The resulting methoxycarbonyl methanesulfonate substrate decomposed on distillation, however, after removal of the solvents its purity was found to be greater than 98.5% as determined by NMR spectroscopy [δ 2.2 (t, 2 H), 3.0 (s, 3 H), 3.5 (m, 2 H), 3.7 (s, 3 H), 4.4 (t, 2 H)].

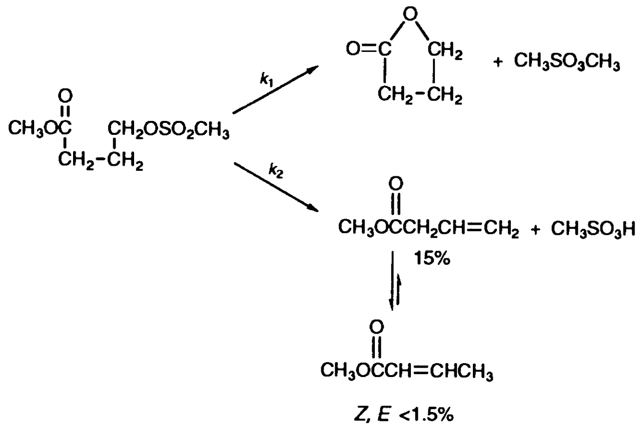
γ-Butyrolactone was acquired from Aldrich, while methyl 3-butenoate (b.p. 95 °C at 755 torr) and methyl crotonate (b.p. 65–66 °C at 100 torr) were prepared as reported.[9] The chromatographic column used for quantitative analyses of the products was Dinonyl Phthalate 20%-Chromosorb Q 80–100 mesh. The identities of substrate and products were further confirmed by mass spectrometry and by IR and NMR spectroscopy.

The kinetics were carried out in a static system,[10] seasoned with allyl bromide and in the presence of nearly equal amounts of the free radical inhibitor toluene and/or cyclohexene. The methanesulfonate reagent was injected directly into the reaction vessel with a syringe through a silicone rubber septum, and the rate coefficients were determined by pressure increase and/or by the overall chromatographic analyses of the reaction products. After a few pyrolysis runs with the methanesulfonate substrate, the reaction vessel was seasoned again with allyl bromide in order to obtain reproducible k values. No temperature gradient was found along the reaction vessel, and the temperature was controlled by a resistance thermometer controller type SHINKO DIC-PS 25RT maintained within ±0.2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple.

Results and Discussion

The products of the gas phase elimination of 3-(methoxycarbonyl)propyl methanesulfonate, in a seasoned static reaction vessel, are described in Scheme 2.

The theoretical stoichiometry based on Scheme 2 implies that for long reaction times $P_f/P_0 = 2$, where P_f and P_0 are the final and initial pressures, respectively. However, a series of reactions, at four different temperatures and ten half-lives, and maximum inhibition of the free radical suppressor toluene or cyclohexene, gave an average experimental value of $P_f/P_0 = 1.53$. The departure from $P_f = 2P_0$ is due to some polymerization of butyrolactone in the presence of CH_3SO_3H. The verification of the above stoichiometry was possible by comparing, up to 20%



Scheme 2

Table 1 Stoichiometry of the reaction at 289.3 °C

		Product formation (%)[b]	
Time/min	% Reaction[a]	γ-Butyrolactone	Methyl butenoates
5	9.9	9.8	1.0
10	17.0	15.6	2.6
15	25.0	25.0	5.0

[a] From pressure measurements. [b] From chromatography.

Table 2 Product distribution at different percentages of reaction. Temperature 289.3 °C

Reaction (%)	Butyrolactone (%)	Methylbut-3-enoate (%)	Methyl crotonate (%)
18.2	83.3	15.5	1.2
30.4	83.6	15.3	1.1
38.1	82.7	16.1	1.2
55.4	83.2	15.6	1.2
69.5	84.2	14.7	1.1

Table 3 Product distribution at different temperatures

Temperature/ °C	Butyrolactone (%)	Methylbut-3-enoate (%)	Methyl crotonate (%)
289.3	83.4	15.7	0.9
296.6	83.3	15.6	1.1
303.7	83.0	16.3	0.7
311.1	83.6	15.3	1.1

reaction, the percentage decomposition of the substrate from pressure measurements with the sum of the chromatographic analyses of butyrolactone and the methyl butenoates (Table 1).

In spite of the fact that the verification of the stoichiometry by pressure increase was only valid up to 20% decomposition of the methanesulfonate, it is noteworthy to point out that the overall rate coefficient of Scheme 2, estimated by the sum of the products, is reproducible up to 70% decomposition of the substrate at any given temperature.

The analyses of the elimination products of the methoxycarbonylpropyl methanesulfonate substrate, in seasoned vessels are shown in Tables 2 and 3. Within experimental error, the distribution of products does not vary as the reaction progresses at one working temperature, or at different temperatures. Apparently, the formation of butyrolactone and methyl butenoates proceeds under kinetic control.

Table 4 Homogeneity of the reaction

Temperature/°C	S/V/cm^{-1}	$k_1/10^{-4}$ s^{-1}[a]	$k_1/10^{-4}$ s^{-1}[b]
303.7	1	*c*	9.84
	6	*c*	9.42
296.6	1	*c*	6.50
	6	*c*	6.62

[a] Clean Pyrex vessel. [b] Vessel seasoned with allyl bromide. [c] The *k* values tend to decrease.

Table 5 Effect of the inhibitor toluene at 303.7 °C

P_s/torr[a]	P_i/torr[b]	P_i/P_s	$k_1/10^{-4}$ s^{-1}[c]	$k_1/10^{-4}$ s^{-1}[d]
107.0	—	—	10.00	9.91
111.0	85.0	0.8	9.84	9.79
66.5	110.0	1.7	9.91	9.89
43.0	203.0	4.7	9.80	9.82

[a] P_s = pressure of the substrate. [b] P_i = pressure of the inhibitor. [c] *k* values by pressure increase. [d] *k* values by the sum of chromatographic analyses of products.

Table 6 Invariance of rate coefficients with initial pressure at 303.7 °C

P_0/torr	$k_1/10^{-4}$ s^{-1}
43.0	9.82
66.5	9.89
83.0	9.92
107.0	9.91
111.0	9.79

Table 7 Temperature dependence of the rate coefficients

Temperature/°C	$k_1/10^{-4}$ s^{-1}
289.3	3.73
296.6	6.50
303.7	9.84
311.1	16.92
320.6	30.02
329.8	51.33

The effect of surface upon the rate of elimination of the substrate was examined by using a vessel packed with glass tubing in which the surface-to-volume ratio has been increased by a factor of 6 compared with the unpacked clean Pyrex vessel, which is equal to 1 (Table 4). Packed and unpacked clean Pyrex vessels gave irreproducible *k*-values, whether by pressure measurements or by quantitative analyses of products, suggesting some surface heterogeneous effect. With respect to the packed and unpacked vessels seasoned with allyl bromide, there was no effect on the rate coefficients. The relative standard deviation was not greater than 5% at each temperature.

Using different proportions of the free radical inhibitor toluene and/or cyclohexene (Table 5) does not affect the rate of elimination of the methanesulfonate substrate, and no induction period was observed.

The rate coefficients of the reactions were found to be independent of their initial pressure (Table 6), and the first-order plot gave a good straight line up to 70% of the methoxycarbonylpropyl methanesulfonate decomposition (*k* value estimated by the sum of product formation). The variation of the rate coefficient with temperature, in a seasoned vessel and in the presence of the inhibitor toluene, is shown in Table 7. These

Table 8 Comparative rates and Arrhenius parameters at 320.0 °C

Compound	$k_1/10^{-4}$ s^{-1}	E_a/kJ mol^{-1}	log(A/s^{-1})	Ref.
$CH_3CH_2OSO_2CH_3$	11.48	171.7 + 1.3	12.18 ± 0.12	11
$CH_3OCOCH_2CH_2CH_2OSO_2CH_3$	28.18	182.2 ± 5.3	13.50 ± 0.47	This work

Table 9 Variation with temperature of rate coefficient for formation of products from 3-(methoxycarbonyl)propyl methanesulfonate

	$k_1/10^{-4}$ s^{-1}	
Temperature/°C	Methyl butenoate[a]	γ-Butyrolactone
289.3	0.57	3.16
296.6	1.00	5.50
303.7	1.60	8.24
311.1	2.58	14.41
320.6	5.12	24.90
329.8	8.65	42.68

[a] Includes small yield of methyl crotonate.

Table 10 Arrhenius parameters and partial rates for the pyrolysis products of 3-(methoxycarbonyl)propyl methanesulfonate at 320.0 °C

Compound	$k_1/10^{-4}$ s^{-1}	E_a/kJ mol^{-1}	log(A/s^{-1})
Methylbut-3-enoate	4.79	189.6 ± 4.9	13.38 ± 0.44
γ-Butyrolactone	23.44	180.8 ± 6.3	13.30 ± 0.57

data were fitted to the Arrhenius equation shown [eqn. (1)], where 90% confidence coefficients from a least squares procedure are quoted.

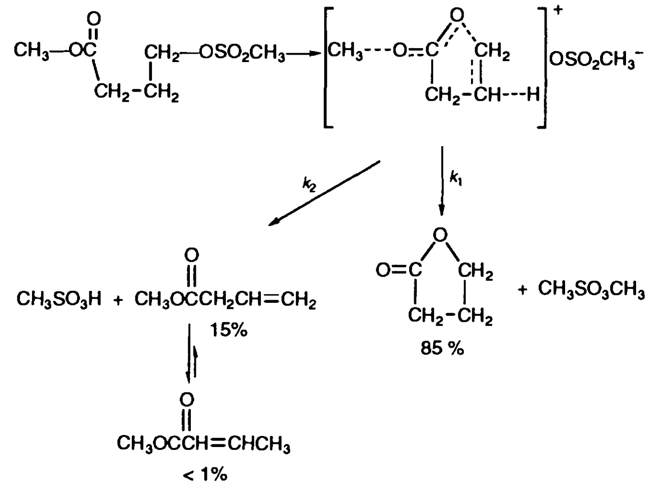
$$\log k_1 = (13.50 \pm 0.47) - (182.2 \pm 5.3)(2.303\,RT)^{-1} \quad (1)$$

The influence of the CO_2CH_3 group on the pyrolysis of the methoxycarbonylpropyl methanesulfonate relative to the reference compound ethyl methanesulfonate can be appreciated from Table 8. According to the present results, both the moderate increase in rate of elimination and the formation of the cyclic product, γ-butyrolactone in high yield, suggest an anchimeric assistance by the methoxy carbonyl substituent in the pyrolytis of the substrate. Consequently, the mechanism of this elimination reaction may be described in terms of an intimate ion-pair type of intermediate with the common feature of neighbouring CO_2CH_3 group participation and intramolecular solvation or autosolvation of the $CH_3SO_3^-$ ion which may proceed by two pathways (Scheme 3).

Additional evidence for anchimeric assistance in this elimination is obtained by plotting $Z = CH_2CO_2CH_3$ ($\sigma^* = 1.03$) in the correlation of log $ZCH_2CH_2OSO_2CH_3$ *vs.* Taft σ^* values.[11] The point for $CH_2CO_2CH_3$ falls far above the slope of the line, which is indicative of neighbouring group participation.

The partial rates for the formation of the primary product, as represented in Scheme 2, were determined up to 70% decomposition of the substrate by the quantitative chromatographic analyses of the methyl butenoate and γ-butyrolactone. The temperature dependence of the rate coefficients for the formation of these products (Table 9) gives, by the least-squares procedure and 90% confidence limits, the Arrhenius equations (2) and (3) for methyl butenoate and γ-butyrolactone formation respectively. The Arrhenius parameters and partial rates for each of the anchimerically assisted primary products are given in Table 10.

$$\log k_1 = (13.38 \pm 0.44) - (189.6 \pm 4.9)(2.303\,RT)^{-1} \quad (2)$$



Scheme 3

$$\log k_1 = (13.30 \pm 0.57) - (180.8 \pm 6.3)(2.303\,RT)^{-1} \quad (3)$$

The intimate ion-pair mechanism proposed for the formation of γ-butyrolactone in Scheme 3 is similar to those described for the gas phase elimination of methyl 4-chlorobutyrate[4] and methyl 4-bromobutyrate.[5] In this respect, it seemed interesting to compare the extent to which the leaving group departure (X = Cl, Br and CH_3SO_3) in $XCH_2CH_2CH_2COOCH_3$, is assisted by the methoxycarbonyl substituent in the pyrolytic elimination of this type of compound. Because of the greater stability of the negatively charged oxygen atom towards sulfur in the leaving methanesulfonate group, the transition state must be very polar. Therefore, a faster elimination rate is to be expected when compared to chloride and bromine leaving groups. The comparisons for the overall rates of the substrates $XCH_2CH_2CH_2COOCH_3$ and the partial rates towards the formation of γ-butyrolactone (Tables 11 and 12) appear to support previous generalization with regard to the occurrence of neighbouring group participation in gas phase reaction of organic molecules.[6] This phenomenon is believed to be most effective when the transition state is highly polar.

Acknowledgements

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Table 11 Effect of the CO_2CH_3 on leaving groups in the gas phase at 360.0 °C

Compound	$k_1/10^{-4}\ s^{-1}$	Rel. rate	E_a/kJ mol^{-1}	log(A/s^{-1})	Ref.
$CH_3OCOCH_2CH_2CH_2Cl$	0.050	1.0	226.8 ± 8.2	13.41 ± 0.60	4
$CH_3OCOCH_2CH_2CH_2Br$	0.32	6.4	216.7 ± 7.6	13.38 ± 0.59	5
$CH_3OCOCH_2CH_2CH_2OSO_2CH_3$	295.1	5902.0	182.2 ± 5.3	13.50 ± 0.47	*a*

[a] This work.

Table 12 Comparative partial rates in butyrolactone formation at 360.0 °C

Compound	$k_1/10^{-4}\ s^{-1}$	Rel. rate	E_a/kJ mol^{-1}	log(A/s^{-1})	Ref.
$CH_3OCOCH_2CH_2CH_2Cl$	0.026	1.0	223.0 ± 3.9	12.82 ± 0.29	4
$CH_3OCOCH_2CH_2CH_2Br$	0.16	6.4	210.8 ± 8.1	12.59 ± 0.63	5
$CH_3OCOCH_2CH_2CH_2OSO_2CH_3$	239.9	9227.0	180.8 ± 6.3	13.30 ± 0.57	*a*

[a] This work.

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