The Gas-Phase Elimination Kinetics of 3-Buten-1-Methanesulphonate and 3-Methyl-3-Buten-1-Methanesulphonate

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Abstract

The elimination kinetics of the title compounds were carried out in a static system over the temperature range of 290-330 °C and pressure range of 29.5-124 torr. The reactions, carried out in seasoned vessels with allyl bromide, obey first-order rate law, are homogeneous and unimolecular. The temperature dependence of the rate coefficients is given by the following Arrhenius equations: for 3-buten-1-methanesulphonate, $\log k_1(s^{-1}) = (12.95 \pm 0.53) - (175.3 \pm 5.9)$ kJ mol⁻¹ $(2.303RT)^{-1}$; and for 3-methyl-3-buten-1-methanesulphonate, $\log k_1(s^{-1}) = (12.98 \pm 0.40) - (174.7 \pm 4.5)$ kJ mol⁻¹ $(2.303RT)^{-1}$. The olefinic double bond appears to assist in the rate of pyrolysis. The mechanism is described in terms of an intimate ion-pair intermediate. © 1995 John Wiley & Sons, Inc.

Introduction

The Π -bond of the phenyl substituent at the 2-position of ethyl methanesulphonate suggested participation of the aromatic ring in the elimination process of CH₃SO₃H [1]. In view that olefinic double bond is more polar in nature than the conjugated Π -system of the benzene ring, and in association with the result obtained in the above-mentioned article, the present work aimed at examining, under homogeneous and molecular elimination, the pyrolysis kinetics of 3-buten-1-methanesulphonate and 3-methyl-3-buten-1-methanesulphonate.

Experimental

Both buten-1-yl-methanesulphonates substrates were prepared by treating the corresponding alcohols (Aldrich) with CH_3SO_2Cl in ether-pyridine mixture as reported [2]. The product 3-buten-1-methanesulphonate was distilled several times at 67°C at 1 torr. The purity of this substrate was found 97.8% as determined by gasliquid chromatography (Di-isodecyl phthalate 5%-Chromosorb G AW DMCS 60-80 mesh). 3-Methyl-3-buten-1-methanesulphonate exploded on distillation. However, this compound was purified in a high-vaccum system to at least 95% as estimated by nuclear magnetic resonance analysis. The product 1,3-butadiene (Matheson) was quantitatively analyzed in a column of Carbopack C-0.19% picric acid 80-100 mesh, while 2-methyl-1,3-butadiene (Merck) in a 2 meter column of Porapak R 80-100 mesh. The identities of the substrates and products were also verified with a mass spectrometer and by infrared and nuclear magnetic resonance spectroscopy.

International Journal of Chemical Kinetics, Vol. 27, 657–661 (1995) © 1995 John Wiley & Sons, Inc. CCC 0538-8066/95/070657-05 The sulphonates were pyrolyzed in a static reaction vessel seasoned with allyl bromide. The substrates were injected directly into the reaction vessel with a syringe through a silicone rubber septum, and the rate coefficients were determined by pressure increase. After few pyrolysis runs, it was necessary to season again the reactions vessels with allyl bromide for good reproducible *k*-values. This procedure was carried out, since the CH₃SO₃H product can not be quantitatively withdrawn from the system. Therefore, the small amount left in the vessel, which increased after a few runs, will act upon the seasoned wall and thus, a surface effect causes the changes on the rate coefficients. The temperature was controlled by a resistance thermometer controller type SHINKO DIC-PS 25RT maintained with ± 0.2 °C and measured with a calibrated platinum-platinum-13% rhodium thermocouple. The reaction vessel showed no temperature gradient at different points.

Result and Discussion

The elimination reaction of 3-buten-1-methanesulphonate and 3-methyl-3-buten-1methanesulphonate in the gas phase (Eq. (1)), in seasoned vessel with allyl bromide, showed up to 50-70% decomposition, a good agreement between the extent of pyrolysis predicted from pressure measurements and the quantitative chromatographic analyses of the corresponding olefin products (Table I).

Additional examination of the above stoichiometry (Eq. (1)) demands that the final pressure P_f be twice the initial pressure P_o . The average experimental results of P_f/P_o values at four different temperatures and ten half-lives are shown in Table II. The fact that $P_f/P_o < 2$ in both theoretical reactions was due to a small polymerization of the corresponding butadiene products in CH₃SO₃H present during the pyrolysis.

3-Buten-1-methanesulphonate at 300.2°C						
Time.min.	3	6	9	12		
Reaction, (%) press.	15.6	29.7	40.3	48.9		
Chrom. (%) olefin	16.3	28.1	38.0	47.8		
	3-Methyl-3-buten-1-m	ethanesulphonate at 3	310.0°C			
Time.min.	2	4	6	8		
Reaction, (%) press.	25.1	41.8	57.4	64.3		
Chrom. (%) olefin	24.2	41.0	55.4	62.3		

TABLE I. Pressure measurements versus olefin analyses.^a

^a Seasoned with allyl bromide.

Temp.,°C	P_o , torr	P_f , torr	P_f/P_o	av.
	3-But	en-1-methanesulphonate		
310.2	53.5	99.5	1.86	
315.2	95	177.5	1.87	1.90
320.9	62	117.5	1.90	
328.8	62.5	122	1.95	
	3-Methyl-3	3-buten-1-methanesulphor	nate	
300.2	80	141.5	1.77	
310.2	88.5	164.5	1.86	1.85
320.1	77.5	144.5	1.86	
330.0	68	130.5	1.92	

TABLE II. Ratio of final to initial pressure.^a

^a Seasoned vessel.

Examination of surface effect upon the rate of elimination, several runs were carried out in a vessel with a surface-to-volume ratio of 6 times that of the normal vessel (Table III). Only the packed and unpacked clean Pyrex vessel showed a significant heterogeneous effect on the pyrolysis rates of 3-methyl-3-buten-1-methanesulphonate.

The effect of different proportions of the free radical suppressor propene and/or toluene showed no effect in the rate of CH_3SO_3H elimination (Table IV).

The rate coefficients are found to be independent for initial pressures, and the first-order plots have a good straight line up to 50% decomposition of 3buten-1-methanesulphonate and up to 60–70% decomposition of 3-methyl-3-buten-1methanesulphonate (Table V). The rate coefficients are reproducible with a standard deviation not greater than $\pm 5\%$ at any of the working temperature. The temperature dependence of rate coefficients, in a seasoned vessel and in the presence of the freeradical inhibitor, is described in Table VI. The Arrhenius parameters obtained by the least-square procedure and with a confidence coefficient of a 0.90 are given by the following equations: for 3-buten-1-methanesulphonate, log $k_1(s^{-1}) = (12.95) \pm 0.53) - (175.3 \pm 5.9)$ kJ mol⁻¹ $(2.303RT)^{-1}$; for 3-methyl-3-buten-1-methanesulphonate, log $k_1(s^{-1}) = (12.98 \pm 0.40) - (174.7 \pm 4.5)$ kJ mol⁻¹ $(2.303RT)^{-1}$.

It is apparent from the comparative rates shown in Table VII, the olefinic double bond exert a small but a significant accelerating effect when compared with the corresponding unsaturated parent compound ethyl methanesulphonate (Z = H, Table VII).

$\rm S/V,~cm^{-1}$	$10^4 k_1, { m s}^{-1{ m a}}$	$10^4 k_1, \mathrm{s}^{-1\mathrm{b}}$
	3-Buten-1-methanesulphonate at 300.2°C ^c	
1	9.70	9.68
6	9.80	9.81
	3-Methyl-3-buten-1-methanesulphonate at 310.2°	C ^c
1	27.30 ^d	21.38
6	58.46 ^d	21.37

TABLE III. Homogeneity of the reaction.

^a Clean Pyrex vessel.

^b Vessel seasoned with allyl bromide.

^c k-values up to 50-55% reaction.

^d Average *k*-value.

P _s , torr	P_i , torr	P_i/P_s	$10^4 k_1, { m s}^{-1}$
	3-Buten-1-methanes	ulphonate at 300.2°C	
88	_	-	9.68
91	51.5	0.6	9.69
62	104	1.7	9.65
68	179.5	2.6	9.73
37	201.5	5.5	9.66
	3-Methyl-3-buten-1-meth	anesulphonate at 310.1°C	
115	_	-	21.36
126 121		0.96	21.62
92 162.5		1.8	21.88
97.5	294.5	3.0	21.38
75	308	4.1	21.68
29.5	207	7.0	21.48

TABLE IV. The effect of the inhibitor on rates.

 P_s = pressure of the substrate. P_i = pressure of the inhibitor propene and/or toluene.

		3-Buten-1-met	thanesulphonate	e at 315.2°C		
P_o , torr	40	50	77	93.5	124	
$10^4 k_1, { m s}^{-1}$	21.62	22.74	22.84	22.80	22.62	
	3-N	1ethyl-3-buten-1	l-methanesulph	onate at 310.0°C	0	· · · · · · · · · · · · · · · · · · ·
P_o , torr	29.5	61	75	91	97.5	122
$10^4 k_1, s^{-1}$	21.48	21.74	21.68	21.21	21.38	21.72

TABLE V. Invariability of rate coefficients with initial pressure.

TABLE VI. Rate coefficients at different temperatures.

3-Buten-1-methanesulphonate						
Temp., °C $10^4 k_1$, s ⁻¹	290.3 4.94	300.2 9.68	310.2 17.68	315.2 22.84	320.9 34.14	328.8 55.55
		3-Methyl-3-bı	iten-1-methanes	ulphonate		
Temp., °C $10^4 k_1, s^{-1}$	290.0 6.03	$\begin{array}{c} 300.2\\11.21\end{array}$	310.2 21.39	$\begin{array}{c} 320.1\\ 39.05 \end{array}$	330.0 71.07	

TABLE VII. Comparative rates and Arrhenius parameters of ZCH₂CH₂OSO₂CH₃ at 320°C.

Z	$10^4 k_1, { m s}^{-1}$	Relative rate per H	E _a , kJ/mol	$Log A, s^{-1}$	Ref.
Н	11.48	1.0	171.7 ± 1.3	12.18 ± 0.12	[3]
$CH_2 = CH$	32.36	4.2	175.3 ± 5.9	12.95 ± 0.53	This work
$CH_2 = C(CH_3)$	38.90	5.1	174.7 ± 4.5	12.98 ± 0.40	This work

In association with the reported work on the influence of Π -bond participation in the gas phase of 2-phenylethyl methanesulphonate, the allylic β -hydrogen was not considered responsible in assisting the leaving CH₃SO₃ group. Rather, the Π -bond substituent in the 2-substituted ethyl methanesulphonate described in Table VII appears to be providing assistance in the rate of elimination of CH₃SO₃H by considering the three-membered conformation as a very favorable structure for participation.

According to these results, the mechanism of these reactions may be explained in terms of an intimate ion-pair intermediate as shown in eq. (2).

$$CH_{2} = CCH_{2}CH_{2} \xrightarrow{\delta^{+}} OSO_{2}CH_{3} \longrightarrow \begin{bmatrix} R \\ I \\ CH_{2} = CH_{2} \xrightarrow{(I)} CH_{2} \\ CH_{2} = CH_{2} \xrightarrow{(I)} CH_{2} \\ CH_{2} = CR \xrightarrow{(I)} CH_{2} + CH_{3}SO_{3}H$$

The present work may well be associated and find support with the rate of dehydrochlorination of several chloroalkenes with a structure— $C=C-CH_2CH_2Cl$. These types of compounds have shown to give a very pronounced increase in rate of HCl elimination when compared to the unsubstituted parent compound ethyl chloride [4,5]. These dehydrochlorination reactions were also believed to proceed through neighboring olefinic double bond participation, and in terms of an intimate ion-pair type of mechanism.

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