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ELECTRONIC FACTORS IN THE ELIMINATION KINETICS OF 2-HALOSUBSTITUTED METHANESULPHONATES IN THE GAS PHASE*

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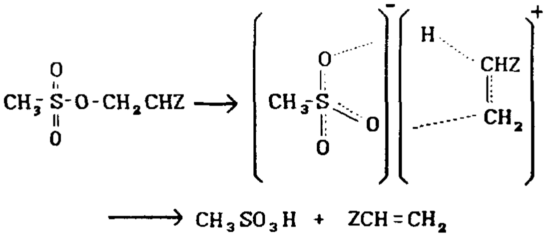
The kinetics of the gas-phase elimination of two 2-haloethyl methanesulphonates were determined in a static system over the temperature range 310–380 °C and pressure range 26–174 Torr. The reactions in seasoned vessels, with the free-radical inhibitor propene and/or toluene always present, are homogeneous and unimolecular, and follow a first-order rate law. The rate coefficients are given by the Arrhenius equations: for 2-bromoethyl methanesulphonate $\log k_1$ (s^{-1}) = $(11{\cdot}70 \pm 0{\cdot}43) - (172{\cdot}8 \pm 4{\cdot}8)$ kJ mol^{-1} $(2{\cdot}303RT)^{-1}$ and for 2-chloroethyl methanesulphonate $\log k_1$ (s^{-1}) = $(11{\cdot}67 \pm 0{\cdot}50) - (173{\cdot}9 \pm 6{\cdot}0)$ kJ mol^{-1} $(2{\cdot}303RT)^{-1}$. The bromo compound was found to be more reactive than the chloro compound. At 340 °C, for Br $k_1 = 9{\cdot}46 \times 10^{-4}$ s^{-1} and for Cl $k_1 = 7{\cdot}12 \times 10^{-4}$ s^{-1}. Apparently, electronic factors seem to be operating in these elimination reactions.

INTRODUCTION

The homogeneous, unimolecular gas-phase elimination kinetics of alkyl 2-substituted ethylmethanesulphonates showed good correlation lines when $\log k/k_0$ was plotted against several steric parameters.[1] In this respect, steric acceleration appeared to be operating in these elimination reactions. Moreover, the primary alkyl methanesulphonates were found to give faster rates of olefin formation in comparison with the pyrolyses of other primary organic esters. The mechanism of the reaction was rationalized in terms of a tight intimate ion-pair intermediate [equation (1)]



(1)

Z = alkyl

Similar effects of steric acceleration was attributed to the branching of alkyl groups in the elimination kinetics of 2-substituted ethyl acetates.[2] In contrast to this influence, polar 2-substituents in the primary acetates were found to affect the rates owing to electronic factors.[3] In view of these observations, it therefore seemed interesting to examine whether any other factor might influence the gas-phase elimination of polar 2-substituted ethylmethanesulphonates. This work was aimed at studying the effect of Br and Cl in 2-bromoethyl and 2-chloroethyl methanesulphonates.

RESULTS AND DISCUSSION

The products of the gas-phase elimination of 2-bromoethyl and 2-chloroethyl methanesulphonates in a static system seasoned with allyl bromide, and in the presence of the free-radical suppressor propene and/or toluene, are mainly the corresponding olefin and methanesulphonic acid [equation (2)].

$$CH_3SO_3CH_2CH_2X \rightarrow CH_3SO_3H + CH_2{=}CHX \quad (2)$$
$$X = Br, Cl$$

The stoichiometry based on equation (2) demanded that, for long reaction times, the final pressure P_f should be twice the initial pressure P_0. The average

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experimental P_f/P_0 values at five different temperatures and ten half-lives were 2·04 for 2-bromoethyl and 2·05 for 2-chloroethyl methanesulphonate.

Additional agreement of the above stoichiometry, up to 80% reaction, was satisfactorily verified by comparing the percentage decomposition of the substrate calculated from pressure measurement with that obtained from the chromatographic analyses of the olefin products.

The effect of the surface on the rate of elimination was examined by carrying out several runs in a vessel with a surface-to-volume ratio of 6·0 relative to that of the normal vessel (1·0). When the packed and unpacked vessels are seasoned with allyl bromide, the reaction is homogeneous. However, in packed and unpacked clean Pyrex vessels, a dramatic decrease in the rates suggests a heterogeneous effect and polymerization of the corresponding vinyl halide. The pyrolysis of these methanesulphonate substrates in seasoned vessels was not affected by the presence of different proportions of a free-radical inhibitor such as propene or toluene. No induction period was observed. The rate coefficients are reproducible with a relative standard deviation not greater than 5% at a given temperature. The methanesulphonates were always pyrolysed in seasoned vessels and in the presence of at least an equal amount of the free-radical chain inhibitor.

The first-order rate coefficients of these methanesulphonates calculated from $k_1 = (2\cdot303/t)\log P_0/(2P_0 - P_t)$ were independent of their initial pressures (Table 1). A plot of $\log(2P_0 - P_t)$ against time (t) gave a good straight line up to 55–75% reaction. The variation of the rate coefficients with temperature is shown in Table 2. The data in Table 2 were fitted to the following Arrhenius equations, where 90% confidence limits are quoted:

Table 1. Invariability of rate coefficient with initial pressure

	2-Bromoethyl methanesulphonate at 340·5 °C				
P_0 (Torr)	26	97	111	131	174
10^4k_1 (s^{-1})	9·36	9·54	9·31	9·10	9·17
	2-Chloroethyl methanesulphonate at 350 °C				
P_0 (Torr)	64	79	98	123	149
10^4k_1 (s^{-1})	11·36	10·90	11·14	10·93	10·87

2-bromoethyl methanesulphonates:

$$\log k_1(\mathrm{s}^{-1}) = (11\cdot70 \pm 0\cdot43) - (172\cdot8 \pm 4\cdot8)\mathrm{kJ\,mol}^{-1}(2\cdot303RT)^{-1}$$

2-chloroethyl methanesulphonate:

$$\log k_1(\mathrm{s}^{-1}) = (11\cdot67 \pm 0\cdot50) - (173\cdot9 \pm 6\cdot0)\mathrm{kJ\,mol}^{-1}(2\cdot303RT)^{-1}$$

The data in Table 3 indicate that the halogen substituents Z in $\mathrm{ZCH_2CH_2OSO_2CH_3}$ do not influence the rate of elimination by steric acceleration as described for alkyl 2-substituted ethyl methanesulphonates pyrolysis in the gas phase[1] [equation (1)]. This consideration derives from the fact that both rates are much lower than for the corresponding parent compound with Z = H, i.e. ethyl methanesulphonate (Table 3). Moreover, the positions of Br and Cl on plots of the reported correlations of log $k_{\mathrm{rel.}}$ against known steric parameters[4] (Taft's E_s, Hancock's E_s^c and Charton's γ values[5]) lie far below the slopes of the lines.[1] Consequently, steric effects are not an important factor in the rate of elimination of halo 2-substituted ethyl methanesulphonates.

As described in the Introduction, steric acceleration was found to be responsible for the rate of pyrolyses of alkyl and several polar substituents interposed by at least three methylene groups with respect to C_α—O of 2-substituted ethyl acetates.[2] An approximate linear relationship was obtained by plotting log k/k_0 against Hancock's E_s^c values.[2] However, electron-withdrawing polar substituents slowed the elimination rates according to their electronegativity differences. In this case,

Table 3. Kinetic parameters from pyrolysis of $\mathrm{ZCH_2CH_2OSO_2CH_3}$ at 340·0 °C

Z	10^4k_1 (s^{-1})	E_a (kJ mol^{-1})	Log A (s^{-1})	Ref.
H[a]	35·47	171·7 ± 1·3	12·18 ± 0·12	1
Br	9·46	172·8 ± 4·8	11·70 ± 0·43	This work
Cl	7·12	173·9 ± 6·0	11·67 ± 0·50	This work

[a] Confidence limits 80%.

Table 2. Temperature dependence of the rate coefficient

	2-Bromoethyl methanesulphonate						
Temperature (°C)	310·0	320·0	330·0	340·5	350·0	360·0	370·0
10^4k_1 (s^{-1})	1·61	3·15	5·48	9·29	15·84	26·70	48·37
	2-Chloroethyl methanesulphonate						
Temperature (°C)	319·3	330·0	340·4	350·0	360·2	369·8	380·1
10^4k_1 (s^{-1})	2·41	3·95	6·85	11·00	19·77	35·59	64·06

plotting log $k_{rel.}$ against σ^* and σ_I resulted in good linear relationships.[3] The small difference in reactivity between the halogen substituents (Table 3) is similar to those found in the gas-phase pyrolyses of esters[3,6] and alkyl halides.[7] However, it was found that the greater the electronegativity of the halogen, the slower is the pyrolysis. In association with these studies,[2,3,6,7] it is reasonable to assume that the Br and Cl atoms at the 2-position of ethyl methanesulphonate influence the rates via electronic effects. This means that the electron-withdrawing effect of the halogens tends to reduce the C_α—O bond polarization ($S—O^{\delta-}\cdots C^{\delta+}$) in the transition state, which is the determining factor, and thus slows the rate of elimination.

EXPERIMENTAL

The 2-halosubstituted methanesulphonates were prepared by treating 2-bromoethanol (Aldrich) and 2-chloroethanol (Aldrich) with methanesulphonyl chloride in diethylether as described.[8] The products 2-bromoethyl methanesulphonate (b.p. 125 °C at 6 Torr; lit.[8] b.p. 126–128 °C at 5 Torr) and 2-chloroethyl methanesulphonate (b.p. 130 °C at 11 Torr; lit.[8] b.p. 130 °C at 11 Torr) were distilled several times, and the fraction over 98·7% purity (gas–liquid chromatography) was used (OV-17, 50% methylsilicone–50% phenylsilicone, on Gas-Chrom Q, 80–100 mesh). Vinyl bromide (Merck) and vinyl chloride (Aldrich) were analysed quantitatively in a Porapak Q column. The identities of the reagents and products were further verified by mass spectrometry and by infrared and nuclear magnetic resonance spectroscopy.

The kinetic experiments were carried out in a static system with the reaction vessel seasoned with allyl bromide, and in the presence of the inhibitor propene and/or toluene. The rate coefficients were determined manometrically. The temperature was found to be within ±0·2 °C when measured with a calibrated platinum–platinum–13% rhodium thermocouple. The reaction vessel showed no temperature gradient at different points.

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