

CORRELATION OF ALKYL AND POLAR SUBSTITUENTS IN THE ELIMINATION KINETICS OF 2-SUBSTITUTED ETHYL METHANESULPHONATES IN THE GAS PHASE

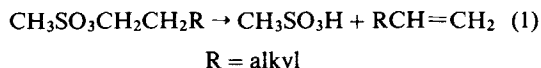
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The kinetics of the elimination of several polar 2-substituted ethyl methanesulphonates in the gas phase were determined in a static system, seasoned with allylbromide, and in the presence of at least equal amount of the free-radical suppressor propene and/toluene. The working temperature and pressure ranges were 290–360 °C and 31–199 Torr (1 Torr = 133.3 Pa), respectively. The reactions are homogeneous, unimolecular, show a first-order rate law and take place according to the following equations: for 3-chloropropyl methanesulphonate, $\log k_f$ (s^{-1}) = $(12.01 \pm 0.18) - (171.7 \pm 2.1) \text{ kJ mol}^{-1} (2.303RT)^{-1}$; for 4-chlorobutyl methanesulphonate, $\log k_f$ (s^{-1}) = $(11.78 \pm 0.31) - (166.1 \pm 3.5) \text{ kJ mol}^{-1} (2.303RT)^{-1}$; for 3-methoxypropyl methanesulphonate, $\log k_f$ (s^{-1}) = $(11.50 \pm 0.36) - (163.3 \pm 4.0) \text{ kJ Mol}^{-1} (2.303RT)^{-1}$; and for 2-ethoxyethyl methanesulphonate, $\log k_f$ (s^{-1}) = $(11.52 \pm 0.37) - (167.3 \pm 4.1) \text{ kJ mol}^{-1} (2.303RT)^{-1}$. The present data together with those reported in the literature show that alkyl 2-substituted ethyl methanesulphonates give an approximate straight line when $\log k/k_0$ vs σ^* values ($\rho^* = -0.82 \pm 0.088$, intercept = 0.0084 ± 0.0209 and correlation coefficient $r = 0.967$ at 320 °C) are plotted. However, polar substituents at the 2-position of ethyl methanesulphonates give rise to an inflection point at $\sigma^*(\text{CH}_3) = 0.00$ into another very good straight line ($\rho^* = -0.29 \pm 0.013$, intercept = -0.0065 ± 0.0213 and $r = 0.994$ at 320 °C). The mechanism of these reactions is considered to be heterolytic in nature, proceeding in terms of an intimate ion-pair intermediate.

INTRODUCTION

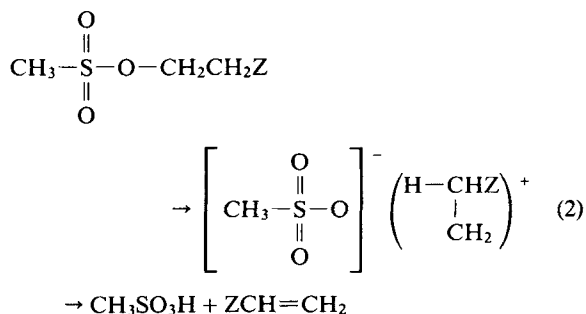
Under homogeneous conditions, the kinetics of the unimolecular gas-phase elimination of alkyl 2-substituted ethyl methanesulphonates¹ gave a good correlation on plotting $\log k_{\text{rel}}$ of alkyl substituents Z in $\text{ZCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$ against well known steric parameters.² According to this result, steric acceleration was thought to be responsible for the rate of elimination of $\text{CH}_3\text{SO}_3\text{H}$ [equation (1)]



In addition to this consideration, the fact that the methanesulphonate leaving group is easily eliminated was believed to be due to the greater stability of the negatively charged oxygen atom towards sulphur in the

transition state. This high stabilization of the methanesulphonate leads to a faster elimination rate when compared with the gas-phase elimination of other organic esters (Table 1).

In the light of the large difference in rates of the alkyl methanesulphonates, the mechanism of the reaction was rationalized in terms of an intimate ion-pair intermediate as shown in equation (2):



To provide additional support for the heterolytic nature of the transition state of the methanesulphonate

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‡ Taken from the thesis of Jaime Alvarez G., submitted to the Faculty of IVIC, 1989, in partial fulfilment of the requirements for the Degree of Magister Scientiarum.

Table 1. Leaving group (Z) in the well known elimination reaction at 350 °C^a

$ZCH_2CH_3 \rightarrow ZH + CH_2=CH_2$		
Z	$10^4 k_1$ (S ⁻¹)	Relative rate
CH ₃ COO	0.56	1.0
CH ₃ OCOO	2.00	3.6
ClCOO	17.78	31.8
CH ₃ SO ₃	60.26	107.6

^a See Ref. 1.

pyrolyses, the effect of the phenyl group along the carbon chain of ω -phenylalkyl methanesulphonates was examined.³ This study was able to show that a C₆H₅ substituent in the 2- and 4-positions with respect to the C—O bond of the methanesulphonate assisted anchimerically in the pyrolysis rates. The five-membered conformation in 4-phenyl-1-butyl methanesulphonate, which is a favourable structure for participation, yielded by virtue of a spiro intermediate and *trans*-elimination the corresponding unsaturated aromatic hydrocarbon and the rearranged product tetralin. Neighbouring group assistance of the C₆H₅ group at the 3-position in 3-phenyl-1-propyl methanesulphonate for a four-membered conformation was found to be absent.

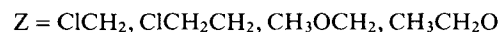
A recent study was able to show that Br and Cl substituents in the 2-position of ethyl methanesulphonate do not affect the rate of elimination by steric acceleration.⁴ This conclusion was deduced from the fact that their rates are much lower than those for the corresponding unsubstituted parent compound ethyl methanesulphonate. Further, the positions of the points for Br and Cl substituents on the plot of the reported correlation of $\log k_2/k_H$ versus known steric parameters¹ lie far below the slopes of the lines. Since the electron-withdrawing effect of the halogens slowed the rate of elimination of CH₃SO₃H, their influence was suggested to be electronic in nature.

In this study we examined the effect of several polar electron-withdrawing substituents Z at the 2-position in ZCH₂CH₂OSO₂CH₃. We also intended to establish any possible correlation for polar substituents in order to deduce a more adequate mechanism for these eliminations. In this respect, the gas-phase pyrolysis kinetics for Z = ClCH₂, ClCH₂CH₂, CH₃OCH₂ and CH₃CH₂O in ZCH₂CH₂OSO₂CH₃ were determined.

RESULTS AND DISCUSSION

The products of the pyrolysis of the polar 2-substituted ethyl methanesulphonates in a seasoned, static reaction vessel and in the presence of a free-radical chain inhibitor are mainly the corresponding olefin and

methanesulphonic acid (3):



The stoichiometry of equation (3) requires that the final pressure, P_f , be double the initial pressure, P_0 . The average experimental P_f/P_0 values measured after ten half-lives and at five different temperatures were 1.98 for 3-chloropropyl methanesulphonate, 1.98 for 4-chlorobutyl methanesulphonate, 1.93 for 3-methoxypropyl methanesulphonate and 2.07 for 2-ethoxyethyl methanesulphonate. The stoichiometry [equation (3)] was also verified by comparing the percentage decomposition of the methanesulphonate substrate from pressure measurements with those obtained from chromatographic analyses of the corresponding unsaturated products.

The stoichiometry of 3-ethoxyethyl methanesulphonate was difficult to determine, since the quantitative analysis of the product ethyl vinyl ether resulted in a low yield. Apparently, this olefinic product undergoes some kind of reaction or polymerization when attempts are made to collect it from the reaction vessel. However, the consideration that the pyrolysis of this substrate yields CH₃SO₃H and CH₃CH₂OCH=CH₂ may be valid, since these are the only products detected.

The products from these gas-phase elimination reactions, within the rate determination, were the following 3-chloropropyl methanesulphonate, up to 80% decomposition, gave 3-chloroprop-1-ene (allyl chloride) and methanesulphonic acid, 4-chlorobutyl methanesulphonate, up to 70% decomposition, yielded 4-chlorobut-1-ene and methanesulphonic acid; 3-methoxypropyl methanesulphonate, up to 60% reaction, produced methyl allyl ether and methanesulphonic acid; and 2-ethoxyethyl methanesulphonate, up to 55% reaction, gave only ethyl vinyl ether and methanesulphonic acid as products.

The presence of different proportions of an effective free-radical inhibitor, propene and/or toluene, had no effect on the rate coefficient. The substrate 3-chloropropyl methanesulphonate in the absence of the free-radical suppressor shows a decrease in the initial pressure, probably owing to the polymerization of the product allyl chloride. Consequently, the kinetic determination was always carried out in the presence of at least an equal amount of the inhibitor toluene. In addition to these observations, no induction period was observed.

The homogeneity of these pyrolytic eliminations was examined by using a vessel with a surface-to-volume ratio of 6.0 relative to the normal vessel with a value equal to 1. Packed and unpacked clean Pyrex vessels gave a significant increase in rates, suggesting some surface heterogeneous effect on pyrolysis. However, packed and unpacked vessels seasoned with allyl

bromide showed no effect on the rate coefficients (relative standard deviation not greater than 5% at each temperature). The substrates were always pyrolysed in seasoned vessels and in the presence of a nearly equal amount of the free-radical suppressor propene and/or toluene.

The rate coefficients of the methanesulphonates were found to be independent of their initial pressure, and the first-order plots gave good straight lines for up to 80% decomposition of 3-chloropropyl methanesulphonate, up to 70% decomposition of 4-chlorobutyl methanesulphonate, up to 60% decomposition of 3-methoxypropyl methanesulphonate, up to 55% decomposition of 2-ethoxyethyl methanesulphonate.

The variation of the rate coefficient with temperature, in a seasoned reaction vessel and in the presence of the

inhibitor propene and/or toluene is shown in Table 2. These data were fitted to the Arrhenius equations shown, where 0.90 confidence coefficients from a least-squares procedure are quoted.

Table 3 lists the kinetic parameters of the compounds studied, together with those obtained in previous investigations.^{1,3,4} A careful analysis of Table 3 indicates that polar substituents Z in ZCH₂CH₂OSO₂CH₃ do not affect the rate of elimination by steric acceleration as described in the gas-phase pyrolyses of alkyl 2-substituted ethyl methanesulphonate.¹ This conclusion derives from the fact that the rates are in some instances close to or lower than those for the corresponding parent compound, Z = H, ethyl methanesulphonate (Table 3). In addition to this observation, on plotting the point positions of the polar substituents (Table 3,

Table 2. Variation of rate coefficients with temperature

Compound	Parameter	Values						
3-Chloropropyl methanesulphonate	Temperature (°C)	300	310	320	330	340	350	
	10 ⁴ k ₁ (s ⁻¹)	2.26	4.21	7.48	13.75	23.40	41.02	
	Rate equation Log k ₁ (s ⁻¹) = (12.01 + 0.18) - (171.7 + 2.1) kJ mol ⁻¹ (2.303RT) ⁻¹							
4-Chlorobutyl methanesulphonate	Temperature (°C)	290	300	310	320	330	340	350
	10 ⁴ k ₁ (s ⁻¹)	2.31	4.14	8.34	14.16	24.55	41.56	73.21
	Rate equation Log k ₁ (s ⁻¹) = (11.78 + 0.31) - (166.1 + 3.5) kJ mol ⁻¹ (2.303RT) ⁻¹							
3-Methoxypropyl methanesulphonate	Temperature (°C)	290	300	310	320	330	340	350
	10 ⁴ k ₁ (s ⁻¹)	2.14	4.32	7.78	13.32	22.16	38.78	69.93
	Rate equation Log k ₁ (s ⁻¹) = (11.50 + 0.36) - (163.3 + 4.0) kJ mol ⁻¹ (2.303RT) ⁻¹							
2-Ethoxyethyl methanesulphonate	Temperature (°C)	300	310	320	330	340	350	360
	10 ⁴ k ₁ (s ⁻¹)	1.83	3.63	6.09	10.34	17.47	30.06	56.28
	Rate equation Log k ₁ (s ⁻¹) = (11.52 + 0.37) - (167.3 + 4.1) kJ mol ⁻¹ (2.303RT) ⁻¹							

Table 3. Kinetic parameters of ZCH₂CH₂OSO₂CH₃pyrolyses at 320 °C^a

No.	Z	10 ⁴ k ₁ (s ⁻¹)	10 ⁴ k _H (s ⁻¹) ^b	Log (k _Z /k _{CH₃})	E _a (kJ mol ⁻¹)	Log A (s ⁻¹)	Ref.
1	H	11.48	3.83	-0.366	171.7 ± 1.3	12.18 ± 0.12	1
2	CH ₃	17.78	8.89	0.000	171.6 ± 3.3	12.36 ± 0.28	1
3	CH ₃ CH ₃	19.95	9.98	0.050	168.7 ± 2.3	12.16 ± 0.20	1
4	CH ₃ CH ₂ CH ₂	21.38	10.69	0.080	169.4 ± 1.0	12.25 ± 0.09	1
5	CH ₃ CH ₂ CH ₂ CH ₂	21.38	10.69	0.080	168.9 ± 3.3	12.21 ± 0.19	1
6	(CH ₃) ₂ CH	22.39	11.20	0.100	174.7 ± 2.2	12.74 ± 0.19	1
7	CH ₃ CH ₂ (CH ₃)CH	30.90	15.45	0.240	167.9 ± 1.9	12.28 ± 0.17	1
8	(CH ₃) ₃ C	38.90	19.45	0.340	165.2 ± 1.3	12.14 ± 0.17	1
9	Br	3.02	1.51	-0.770	172.8 ± 4.8	11.70 ± 0.43	4
10	Cl	2.25	1.13	-0.912	173.9 ± 0.6	11.67 ± 0.50	4
11	CH ₃ CH ₂ O	6.03	3.02	-0.469	167.3 ± 5.4	11.52 ± 0.52	This work
12	ClCH ₂	7.70	3.85	-0.364	171.7 ± 2.6	12.01 ± 0.23	This work
13	C ₆ H ₅	28.84	14.42	0.210	167.1 ± 2.6	12.18 ± 0.24	3
14	C ₆ H ₅ CH ₂	14.17	7.09	-0.098	167.1 ± 4.4	11.87 ± 0.39	3
15	C ₆ H ₅ CH ₂ CH ₂	28.18	14.09	0.200	168.9 ± 2.8	12.33 ± 0.26	3
16	CH ₃ OCH ₂	13.21	6.61	-0.129	163.3 ± 4.0	11.50 ± 0.36	This work
17	ClCH ₂ CH ₂	14.03	7.02	-0.103	166.1 ± 3.5	11.78 ± 0.31	This work

^a Substituent constant values taken from Ref 2.

^b k_H = rate per β-hydrogen.

Nos, 9–17) against the steric parameters, they fall well below the slope of the line. This means that steric acceleration is not an important factor with regard to the rate of $\text{CH}_3\text{SO}_3\text{H}$ elimination. However, the polar groups correlate only when plotting $\log k_{\text{rel.}}$ versus σ^* values,² yielding a very good straight line with $\rho^* = -0.029 \pm 0.013$, intercept = -0.0065 ± 0.0213 and correlation coefficient $r = 0.994$ at 320°C (Figure 1). This result implies that the electron-withdrawing effect of the polar substituents retards the rate of elimination according to their electronegativity differences.

In the light of the above observation, it was necessary

to reconsider which substituent effect is common, if any, in the rate of elimination and the mechanism of these reactions. Since the polar substituents showed a good relationship with Taft σ^* values² (Figure 1), both alkyl and polar groups are plotted in Figure 2.

The $\log k_Z/k_{\text{CH}_3}$ values of alkyl substituents give an approximate straight line with $\rho^* = -0.823 \pm 0.088$, intercept = 0.0084 ± 0.0209 and $r = 0.967$ at 320°C (Figure 2). This apparently means that branching of the alkyl group enhances the pyrolysis rates owing to their electron-releasing effect. The negative value of ρ^* suggests that a positively charged carbon atom in the transition state is the limiting factor in these reactions. The

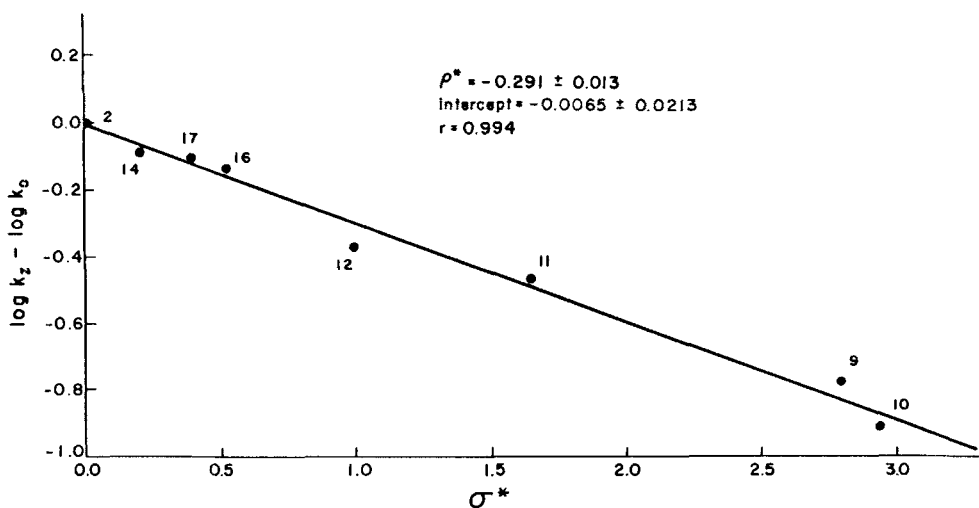


Figure 1. $\text{Log}(k_Z/k_o)$ vs σ^* values for electron-withdrawing substituents at 320°C

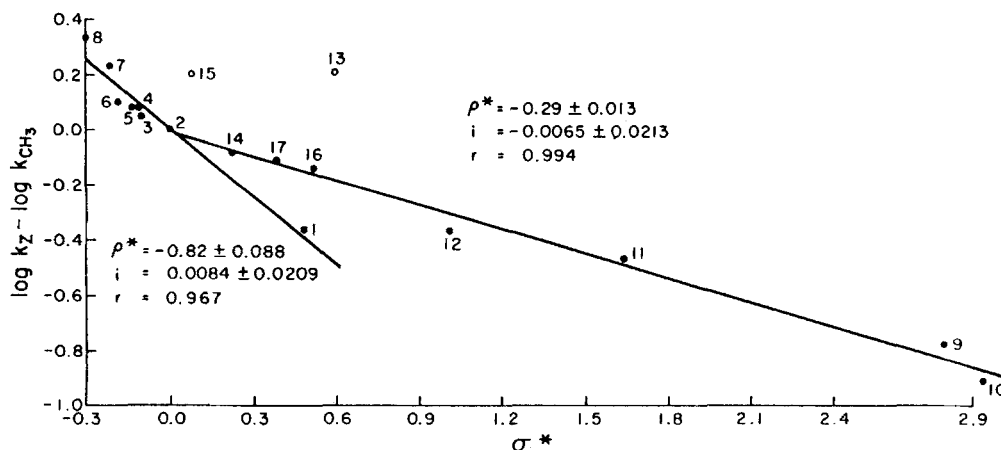
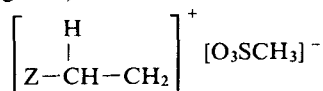


Figure 2. Plot of $\log(k_Z/K_{\text{CH}_3})$ versus σ^* values for alkyl and polar substituents in gas-phase pyrolysis of 2-substituted ethyl methanesulphonates at 320°C . The lines were drawn by the least-squares procedure

Taft plot of several polar substituents given in Table 3 gives an inflection point of the line at $\sigma^*(\text{CH}_3) = 0.00$ into another good straight line (Figure 2) with $\rho^* = -0.291 \pm 0.013$, intercept = 0.0065 ± 0.0213 and $r = -0.994$ at 320°C . The negative slope of -0.291 suggest a very small polarization of the $\text{C}^{\delta+} \cdots \text{O}^{\delta-}$ in the transition state. The occurrence of one slope with electron-releasing groups and another slope at $\sigma^*(\text{CH}_3) = 0.00$ with polar electron-withdrawing substituents may well be ascribed to a slight alteration in the polarity of the transition state due to changes in electron transmission at the carbon reaction centre. Therefore, a simultaneous effect appears to be operating at the transition state during the process of pyrolysis, especially with polar electron-withdrawing substituents. This means that polar groups decrease the reaction rates while the hydrogen adjacent to Z (Scheme 1) becomes more acidic and thus assists the leaving methanesulphonate group. Such a phenomenon may sometimes result in the pyrolysis rate being similar to or slightly higher with respect to the unsubstituted compound ethyl methanesulphonate (Z = H) (Table 3, Figure 2).



Scheme 1

The positions of the points for C_6H_5 (Table 3, No. 13) and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$ (Table 3, No. 15) as substituent Z in $\text{ZCH}_2\text{CH}_2\text{OSO}_2\text{CH}_3$ lie far from the slope of the line shown in Figure 2. This implies, as reported, anchimeric assistance of the C_6H_5 at the 2-position for three-membered conformation and at the 4-position for a four-membered conformation with rearrangement.³

The present and previous studies^{1,3,4} suggest a very polar transition state for the gas-phase pyrolyses of 2-substituted ethyl methanesulphonates where the C—O bond polarization, in the direction $\text{C}^{\delta+} \cdots \text{O}^{\delta-}$, is a determining factor. Consequently, the mechanism may be explained in terms of an intimate ion pair as described in equation (2).

EXPERIMENTAL

The methanesulphonate substrates were prepared by adding $\text{CH}_3\text{SO}_2\text{Cl}$ to the corresponding alcohol (Aldrich) in diethylether as described.⁵ 3-Chloropropyl methanesulphonate was distilled at $144\text{--}146^\circ\text{C}$ at 13 Torr (1 Torr = 133.3 Pa) (lit.⁵ b.p., $144\text{--}46^\circ\text{C}$ at 13 Torr), while 4-chlorobutyl, 3-methoxypropyl and 2-

ethoxyethyl methanesulphonates were purified by alumina column chromatography using hexane–diethyl ether (4:1) as solvent. The purity of the substrates was found to be greater than 99.3% as determined by gas–liquid chromatography [3% OV-17 on Gas Chromosorb QII (80–100 mesh)]. Allyl chloride (Aldrich), 4-chlorobut-1-ene (K & K Labs), methyl allyl ether, prepared as reported,⁶ and ethyl vinyl ether (Aldrich) were determined using Porapak Q (80–100 mesh), 5% diisodecyl phthalate on Chromosorb G AW DMCS (60–80 mesh) and 20% bis(methoxyethyl)adipate on Chromosorb P AW DMCS (80–100 mesh) columns. The identities of the substrates and products were further confirmed by mass spectrometry and infrared and nuclear magnetic resonance spectroscopy.

The kinetics were determined in a static system,⁷ seasoned with allyl bromide and in the presence of at least equal amount of the free-radical suppressor propene and/or toluene. 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 measurements. The temperature was measured to within $\pm 0.2^\circ\text{C}$ with a calibrated platinum–platinum–13% rhodium thermocouple. The reaction vessel showed no temperature gradient at different points.

An important precaution was that after a few runs with each methanesulphonate substrate, the reaction vessel was seasoned again with allyl bromide in order to obtain reproducible k values.

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REFERENCES

1. G. Chuchani, S. Pekerar, R. M. Domínguez, A. Rotinov and I. Martín, *J. Phys. Chem.* **93**, 201 (1989).
2. C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*. Wiley, New York (1979).
3. G. Chuchani, R. M. Domínguez, A. Rotinov, I. Martín and J. Alvarez G., *J. Phys. Chem.* **94**, 3341 (1990).
4. J. Alvarez G. and G. Chuchani, *J. Phys. Org. Chem.* **3**, 456 (1990).
5. W. C. Ross and W. Davis, *J. Chem. Soc.* 2420 (1957).
6. G. Chuchani and I. Martín, *J. Phys. Chem.* **90**, 431 (1986).
7. A. Maccoll, *Chem. Rev.* **69**, 33 (1969).