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MOLECULAR REARRANGEMENTS IN HOMOGENEOUS GAS-PHASE ELIMINATION REACTIONS. PYROLYSIS KINETICS OF ALKYL METHANESULPHONATES

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The rates of elimination of several alkyl methanesulphonates were determined in a seasoned, static reaction vessel over the temperature range 300–420 °C and the pressure range 28–163 Torr. The reactions are homogeneous, unimolecular and follow a first-order rate law. The overall rate coefficients are given by the following equations: for isobutyl methanesulphonate, $\log k_1\ (\mathrm{s}^{-1}) = (12{\cdot}51 \pm 0{\cdot}38) - (177{\cdot}0 \pm 2{\cdot}1)\ \mathrm{kJ\,mol^{-1}}\ (2{\cdot}303RT)^{-1}$; for 2-phenyl-1-propyl methanesulphonate, $\log k_1(\mathrm{s}^{-1}) = (12{\cdot}62 \pm 0{\cdot}04) - (176{\cdot}2 \pm 0{\cdot}5)\ \mathrm{kJ\,mol^{-1}}\ (2{\cdot}303RT)^{-1}$; for neopentyl methanesulphonate, $\log k_1(\mathrm{s}^{-1}) = (13{\cdot}35 \pm 0{\cdot}42) - (198{\cdot}2 \pm 5{\cdot}2)\ \mathrm{kJ\,mol^{-1}}\ (2{\cdot}303RT)^{-1}$; and for 3-chloro-2,2-dimethyl-1-propyl methanesulphonate, $\log k_1(\mathrm{s}^{-1}) = (13{\cdot}87 \pm 0{\cdot}42) - (218{\cdot}2 \pm 5{\cdot}4)\ \mathrm{kJ\,mol^{-1}}\ (2{\cdot}303RT)^{-1}$. Rearrangements in these methanesulphonate pyrolyses may proceed via an intimate ion-pair type of mechanism. Consequently, the results appear to confirm that intramolecular migration through autosolvation is possible in gas-phase elimination reactions of certain types of organic molecules.

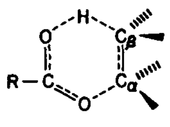
INTRODUCTION

The homogeneous, unimolecular gas-phase pyrolysis or elimination kinetics of carboxylic esters are found to produce the corresponding olefins and carboxylic acid: For molecular elimination, the presence of a β-hydrogen at the alkyl side of the ester **1** is necessary.

$$\underset{\mathbf{1}}{\mathrm{RCOOCH_2CH_2R'}} \longrightarrow \mathrm{RCOOH} + \mathrm{CH_2{=}CHR'} \qquad (1)$$

In 1938, Hurd and Blanck[1] suggested that the elimination of esters proceeds through a concerted six-membered cyclic transition state in which the oxygen of the carbonyl and the β-hydrogen are oriented in such a way that a *cis* elimination occurs **2**. Since then, the mechanism for the gas-phase pyrolysis of **1** has been frequently described in terms of a semi-polar six-membered cyclic transition state **3**,[2–7] rather than concerted **2**,[1] the intimate ion pair **4**,[8,9] semi-ion pair **5**[10] or concerted heterolysis **6**.[11]

Consideration of these mechanisms suggests that the transition states **2**, **3**, **5** and **6** would be limited to *cis* elimination, whereas the intimate ion-pair type of intermediate **4** would permit both *cis* and *trans* elimination.



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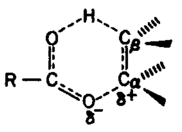

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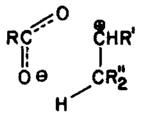

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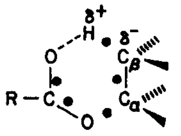

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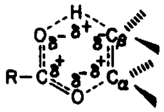

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With this in mind, when we started to study the gas-phase elimination of organic molecules, our aim was to establish whether the intimate ion-pair mechanism is possible in the pyrolysis of carboxylic esters **1** and of organic alkyl halides. This type of mechanism was believed to be possible if the said molecules could be stabilized through neighouring group participation involving an intramolecular solvation or autosolvation, *trans* elimination and probably intramolecular migration or rearrangement.

Benzenesulphonates, tosylates and brosylates, known to be excellent leaving groups in nucleophilic substitu-

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tion and elimination reactions in solution, are expected to be difficult to pyrolyse in the gas phase, owing to a lack of volatatility. They are generally heavy oils or solids. If the aryl part of the sulphonate is replaced with the small methyl group to give methanesulphonates, it is possible to expect volatile liquid substrates and, as already proposed,[12] interesting reaction mechanisms in the gas phase. Because of the greater stability of the negatively charged oxygen atom towards sulphur, the transition state must be very polar. Therefore, *trans* elimination, rearrangements and faster elimination rates are to be expected in comparison with the pyrolyses of carboxylic esters **1**.

The above considerations led to the successful use of a structure–reactivity relationship when plotting $\log k/k_0$ versus Taft σ^* values of alkyl and polar 2-substituted ethyl methanesulphonate pyrolyses in the gas phase.[13] According to the results, the mechanism was suggested to be heterolytic in nature, in the sense that the C—O bond polarization, $C^{\delta+}\cdots O^{\delta-}$, is rate determining, with the process occurring via an intimate ion-pair intermediate.

Further work on the gas-phase pyrolyses of ω-phenylalkyl methanesulphonates[14] showed that the C_6H_5 substituent at the 2- and 4-positions with respect to the C—O bond of the methanesulphonate assisted in the rate of elimination. The spiro five-membered conformation, a favourable structure for neighbouring group participation, yielded through rearrangement a small but significant amount of a cyclic product, tetralin. Anchimeric assistance of the C_6H_5 at the 3-position was found to be absent.

According to these observations, an intimate ion-pair mechanism for methanesulphonate pyrolyses in the gas phase must be considered if molecular rearrangements take place under such conditions. Consequently, this work was aimed at examining the gas-phase elimination kinetics of several alkyl methanesulphonates, with or without the presence of a β-hydrogen in the alkyl group of the sulphonate ester, thereby forcing migration in the latter case.

RESULTS

Isobutyl methanesulphonate

The gas-phase pyrolysis of isobutyl methanesulphonate in a vessel seasoned with allyl bromide and in the presence of propene inhibitor gives isobutene, very small amounts of but-1-ene and *cis,trans*-but-2-ene and CH_3SO_3H [equation (2)].

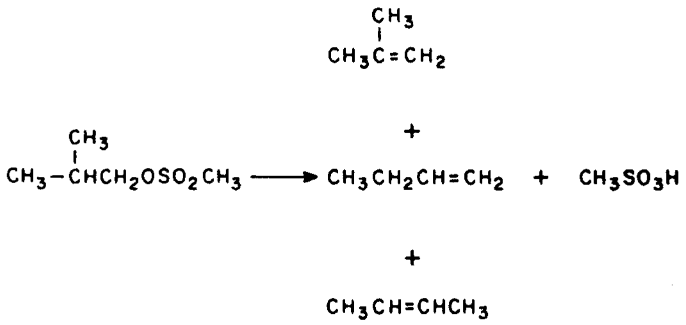
The stoichiometry based on equation (2) suggests that at long reaction time $P_f = 2P_0$, where P_f and P_0 are the final and initial pressures, respectively. The average experimental P_f/P_0 ratio at four different temperatures and ten half-lives was 1·90. The departure of P_f/P_0 from 2 is due to a small extent of polymerization of isobutene. However, the above stoichiometry was verified by comparing, up to 70% reaction, the percentage decomposition of the substrate from pressure measurements with those obtained by the sum of chromatographic analysis of the olefin products.

This methanesulphonate substrate yielded largely isobutene. However, the very small formation of but-1-ene and *cis,trans*-but-2-ene (*ca* 5%) suggested a rearrangement process from the isobutyl methanesulphonate. Tables 1 and 2 show almost no variation of products with increasing percentage decomposition at one temperature and at different temperatures.

Table 1. Yields (%) of isobutyl methanesulphonate products at 330·0 °C[a]

Reaction (%)	Isobutene	But-1-ene	*cis,trans*-But-2-ene
17·8	95·6	2·0	2·4
35·9	95·3	2·3	2·4
47·8	96·1,	2·1,	1·8,
59·7	95·2	2·6	2·7
66·7	95·2	2·7	2·2

[a] Vessel seasoned with allyl bromide and in the presence of the inhibitor propene.



$$CH_3\text{-}\overset{CH_3}{\overset{|}{C}}HCH_2OSO_2CH_3 \longrightarrow \overset{CH_3}{\overset{|}{CH_3C}}{=}CH_2 + CH_3CH_2CH{=}CH_2 + CH_3CH{=}CHCH_3 + CH_3SO_3H \qquad (2)$$

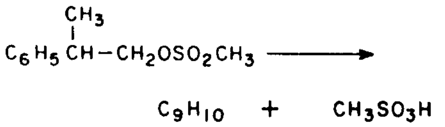
Table 2. Yields (%) of isobutyl methanesulphonate products at different temperatures[a]

Temperature (°C)	Isobutene	But-1-ene	*cis,trans*-But-2-ene
310	95·1	2·1	2·1
320	95·1	2·5	2·3
330	95·5,	2·5,	2·0,
340	94·8	2·3	2·1
350	95·1	2·2	2·1

[a] Reaction up to 70% decomposition. Vessel seasoned with allyl bromide and in the presence of the inhibitor propene.

2-Phenyl-1-propyl methanesulphonate

The pyrolysis products of 2-phenyl-1-propyl methanesulphonate, in a vessel seasoned with allyl bromide, were four isomers, α-methylstyrene, *cis*-β-methylstyrene, *trans*-β-methylstyrene and allylbenzene, and CH_3SO_3H. The stoichiometry as represented in equation (3) requires $P_f = 2P_0$. The average experimental P_f/P_0 values at five different temperatures and ten half-lives was 1·6. The departure from $P_f = 2P_0$ results from the polymerization of the corresponding styrene products. However, the stoichiometry of equation (3) was confirmed; up to 65% reaction, the percentage decomposition of the methanesulphonate from pressure measurements agreed with those obtained from chromatographic analysis of the unsaturated aromatic hydrocarbons.



$$C_6H_5\overset{CH_3}{\overset{|}{C}H}-CH_2OSO_2CH_3 \longrightarrow C_9H_{10} + CH_3SO_3H \qquad (3)$$

The analyses of the pyrolysis products of phenylpropyl methanesulphonate in a seasoned vessel and in the presence of cyclohexene inhibitor are given in Table 3.

The olefin formation does not seems to change, within the experimental error, as the reaction progresses at a given temperature. In addition, the invariability of the yields of the unsaturated aromatic hydrocarbons with temperature is shown in Table 4.

The pure authentic samples of the olefin products were examined for isomerization, under similar reaction conditions of pyrolysis, that is, in the presence of CH_3SO_3H and cyclohexene inhibitor and at 350.0 °C. Only traces of isomerization were detected.

Neopentyl methanesulphonate

The stoichiometry based on neopentyl methanesulphonate pyrolysis, [equation (4)], implies that for long reaction times $P_f = 2P_0$. The average experimental P_f/P_0 ratio at four different temperatures and ten half-lives was 1·95. Further confirmation of the stoichiometry was made by comparing, up to 50% decomposition, the percentage reaction of the substrate from pressure measurements with those obtained from the chromatographic analysis of the olefin products.

The analyses of the products of decomposition of neopentyl methanesulphonate as a function of reaction

Table 3. Yields (%) of 2-phenyl-1-propyl methanesulphonate products at 320·0 °C[a]

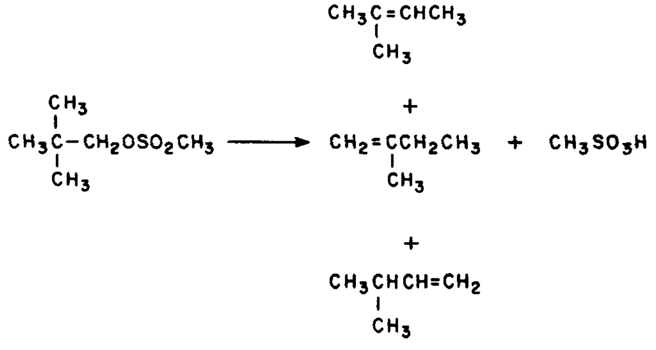
Reaction (%)	α-Methylstyrene	*cis*-β-Methylstyrene	*trans*-β-Methylstyrene	Allylbenzene
25.0	39·0	9·8	30·2	20·5
49·1	32·3	11·4	30·2	25·4
59·6	36·9	10·0	28·4	24·4
65·0	38·9	10·4	28·7	24·2

[a] Vessel seasoned with allyl bromide and in the presence of a fourfold excess of the inhibitor cyclohexene. Traces of isopropylbenzene were detected.

Table 4. Yields (%) of 2-phenyl-1-propyl methanesulphonate products at different temperatures[a]

Temperature (%)	α-Methylstyrene	*cis*-β-Methylstyrene	*trans*-β-Methylstyrene	Allylbenzene
310	32·7	12·5	26·1	28·3
320	38·9	10·4	26·0	24·2
330	40·7,	9·3,	26·3,	23·2,
340	37·6	9·2	25·2	26·5
350	40·6	9·6	24·5	22·8

[a] Vessel seasoned with allyl bromide and in the presence of a fourfold excess of the inhibitor cyclohexene. Traces of isopropylbenzene were detected.



$$\mathrm{CH_3\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2OSO_2CH_3 \longrightarrow CH_3\underset{CH_3}{\underset{|}{C}}=CHCH_3 + CH_2=\underset{CH_3}{\underset{|}{C}}CH_2CH_3 + CH_3\underset{CH_3}{\underset{|}{C}}HCH=CH_2 + CH_3SO_3H} \qquad (4)$$

percentages at one temperature and at different working temperatures are reported in Tables 5 and 6.

According to these results, the olefin formation does not seem to change, within the experimental error, with temperature. However, the gradual variation of the yields of the products as the reaction progresses suggests isomerization in the presence of CH_3SO_3H until an equilibrium mixture is reached. Further, the analysis of the pure olefins 2-methylbut-2-ene and 2-methylbut-1-ene (Table 7), when subjected to similar conditions of the experimental reaction and in the presence of CH_3SO_3H, yielded about the same product distribution

Table 5. Yields (%) of neopentyl methanesulphonate products at 350·5 °C[a]

Reaction (%)	2-Methylbut-2-ene	2-Methylbut-1-ene	3-Methylbut-1-ene
17	45·1	52·0	2·9
32	59·7	38·5	1·8
53	69·3	29·2	1·5
65	71·9	27·1	1·0

[a] Vessel seasoned with ally bromide and in the presence of the inhibitor propene.

Table 6. Yields (%) of neopentyl methanesulphonate products at different temperatures[a]

Temperature (°C)	2-Methylbut-2-ene	2-Methylbut-1-ene	3-Methylbut-1-ene
340·8	72·2	27·2	0·6
350·5	71·9	27·1	1·0
360·8	73·4	26·0	0·6
370·8	71·9	27·5	0·6
379·5	72·6	27·1	0·3

[a] Reaction up to 65% decomposition. Vessel seasoned with allyl bromide and in the presence of the inhibitor propene.

Table 7. Isomerization (%) of the pure olefin products[a]

Olefin	Temperature (°C)	2-Methylbut-2-ene	2-Methylbut-1-ene	3-Methylbut-1-ene
2-Methylbut-2-ene	350·5	70·4	27·6	2·0
	379·5	72·5	27·1	0·4
2-Methylbut-1-ene	350·5	70·9	26·9	2·2
	379·5	68·0	31·3	0·7
3-Methylbut-1-ene	350·5	21·9	7·9	70·2
	379·5	3·2	0·7	96·1

[a] Seasoned vessel, in the presence of CH_3SO_3H and propene inhibitor and at 50% reaction.

as in the pyrolysis of neopentyl methanesulphonate. In the case of the pure 3-methylbut-1-ene, it gives very little isomerization at higher temperatures.

The results in Tables 5–7 indicate that the presence of CH_3SO_3H product appears to be responsible for the isomerization process.

3-Chloro-2,2-dimethyl-1-propyl methanesulphonate

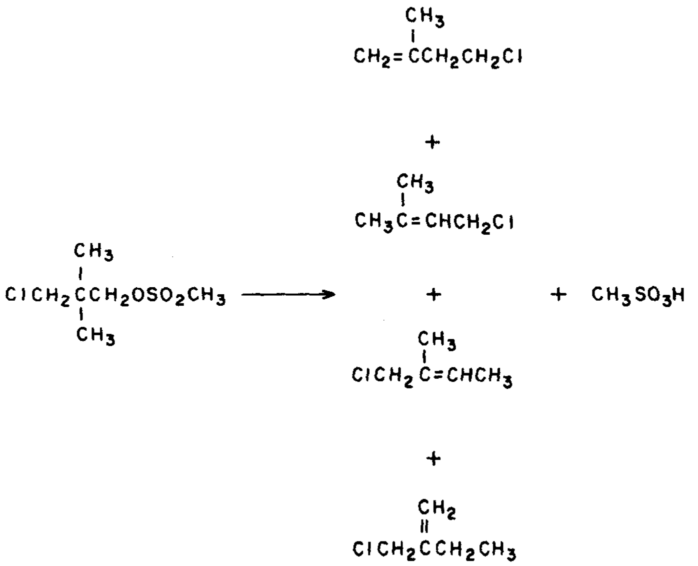
The stoichiometry of this elimination reaction [equation (5)] was difficult to assess, because the rearranged product 4-chloro-2-methylbut-1-ene decomposes partially to 2-methylbuta-1,3-diene [equation (6)]. The former compound was reported to dehydrochlorinate in the gas phase through olefinic double bond participation.[15]

In view of the previous results, the ratio of the final pressure, P_f, to the initial pressure, P_0, should be > 2 and < 3. The average experimental P_f/P_0 at four different temperatures and ten half-lives was 2·75. An additional verification of the above stoichiometry by comparing the chromatographic analyses of the amount of substrate reacted with those of olefin formation was also difficult, because the methanesulphonate reagent could not be trapped quantitatively from the static system. However, several runs at a given temperature gave reproducible k values to about 50% decomposition from the analyses of olefin products.

The quantitative chromatographic analyses of the pyrolysis products of this methanesulphonate in vessels seasoned with allyl bromide and in the presence of the free radical suppressor propene are reported in Tables 8 and 9.

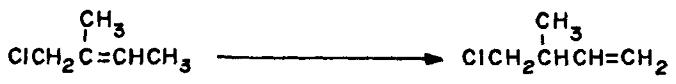
The results in Table 8 suggest that only the yield of 4-chloro-3-methylbut-2-ene decreases slightly, whereas that of 2-methylbuta-1,3-diene increases as the reaction progresses with time. To rationalize these observations, it appears that the former product chloromethylbutene may be isomerizing to an unstable intermediate 4-chloro-3-methylbut-1-ene [equation (7)], which rapidly decomposes to the butadiene and HCl [equation (8)].

However, the data in Table 9 show that 4-chloro-3-methylbut-2-ene tends to increase whereas 2-methylbuta-1,3-diene decreases slightly as the

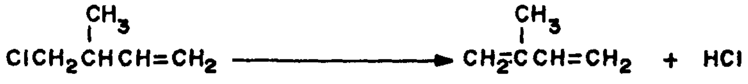


$$ClCH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2OSO_2CH_3 \longrightarrow CH_2{=}\overset{CH_3}{C}CH_2CH_2Cl + CH_3\overset{CH_3}{C}{=}CHCH_2Cl + ClCH_2\overset{CH_3}{C}{=}CHCH_3 + ClCH_2\overset{CH_2}{\overset{\|}{C}}CH_2CH_3 + CH_3SO_3H \tag{5}$$

$$CH_2{=}\overset{CH_3}{C}CH_2CH_2Cl \longrightarrow CH_2{=}\overset{CH_3}{C}CH{=}CH_2 + HCl \tag{6}$$



$$ClCH_2\overset{CH_3}{C}{=}CHCH_3 \longrightarrow ClCH_2\overset{CH_3}{C}HCH{=}CH_2 \tag{7}$$



$$ClCH_2\overset{CH_3}{C}HCH{=}CH_2 \longrightarrow CH_2{=}\overset{CH_3}{C}CH{=}CH_2 + HCl \tag{8}$$

Table 8. Yields (%) of 3-chloro-2,2-dimethyl-1-propyl methanesulphonate products at 390·0 °C[a]

Time (min)	Reaction[b] (%)	4-Chloro-2-methyl-but-1-ene	4-Chloro-2-methyl-but-2-ene	4-Chloro-3-methyl-but-2-ene	3-Chloro-2-ethyl-prop-1-ene	2-Methyl-buta-1,3-diene
10	24·6	11·5	2·5	36·8	5·3	32·9
15	35·6	9·6	9·5	28·2	3·0	49·1
20	41·8	11·2	9·9	29·2	3·3	45·7
30	51·5	12·8	8·2	24·4	3·9	49·9

[a] Vessel seasoned with allyl bromide and in the presence of the inhibitor propene.
[b] The percentages of reaction are an approximate estimation.

Table 9. Yields (%) of 3-chloro-2,2-dimethyl-1-propyl methanesulphonate products at different temperatures[a]

Temperature (°C)	4-Chloro-2-methyl-but-1-ene	4-Chloro-2-methyl-but-2-ene	4-Chloro-3-methyl-but-2-ene	3-Chloro-2-ethyl-prop-1-ene	2-Methyl-buta-1,3-diene
370·1	10·8	12·6	23·7	4·0	48·2
390·0	11·2	9·9	29·2	3·3	45·7
410·0	12·5	9·1	32·6	3·5	42·0

[a] Reaction up to 50% decomposition. Vessels seasoned with allyl bromide and in the presence of the inhibitor propene.

temperature increases. Apparently, the former compound isomerizes less to 4-chloro-2-methylbut-1-ene, which consequently lowers the yield of methylbutadiene according to equation (8).

The homogeneity of these eliminations was studied by using a vessel with a surface-to-volume ratio of 6·0 relative to the normal vessels (1·0). The rates of decomposition of the methanesulphonate substrates were similar in the packed and unpacked seasoned vessels, whereas some surface effect was observed in the clean packed and unpacked Pyrex vessels. The lack of a free radical reaction was demonstrated by performing several runs in the presence of different proportions of an inhibitor such as propene and/or cyclohexene. No induction period was observed.

The rate coefficients for the pyrolytic eliminations of the methanesulphonate substrates were found to be independent of their initial pressures. The first-order plots gave good straight lines up to 70% decomposition for isobutyl methanesulphonate, 65% decomposition for 2-phenyl-1-propyl methanesulphonate and 50% decomposition for both neopentyl and 3-chloro-2,2-dimethyl-1-propyl methanesulphonate. The variation of the rate coefficients with temperature in a seasoned vessel and in the presence of propene and/or cyclohexene is shown in Table 10. The data were fitted to the Arrhenius equations shown, where 90% confidence coefficients from a least-squares procedure are quoted.

DISCUSSION

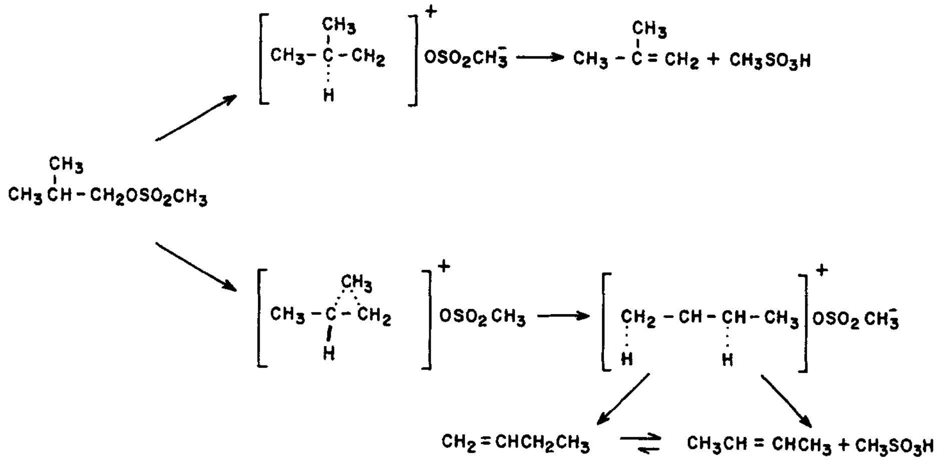
The elimination kinetics of isobutyl methanesulphonate yielded, in addition to the formation of isobutene, very small amounts of but-1-ene and *cis,trans*-but-2-ene (Tables 1 and 2). This observation suggested that some rearrangement by a 1,2-methyl migration had occurred owing to the highly polar nature of methanesulphonate pyrolyses in the gas phase.[13,14] In this respect, the mechanism for the process may be explained in terms of an intimate ion-pair intermediate as described in equation (9), where the C—O bond polarization, in the $C^{\delta+}\cdots O^{\delta-}$ direction, is the limiting factor.

In view of the previous results, the phenyl ring, which is a better migrating group than the methyl group, prompted the examination of 2-phenyl-1-propyl methanesulphonate. The elimination kinetics of this substrate showed, through neighbouring group participation of the aromatic nuclei, an appreciable amount of molecular migration of the phenyl substituent (Tables 3 and 4). Consequently, according to the product formation, the mechanism of the process appears to proceed through a common highly polar intermediate [equation (10)].

Table 11 lists the Arrhenius parameters and comparative overall rates for isobutyl methanesulphonate and 2-phenyl-1-propyl methanesulphonate. Because the phenyl group assists anchimerically through a spiro

Table 10. Variation of rate coefficients with temperature

Compound	Parameter	Values					
Isobutyl methanesulphonate	Temperature (°C)	300·0	310·1	320·0	330·0	340·1	350·1
	$10^4 k_1$ (s^{-1})	2·50	4·38	8·37	15·41	27·59	48·88
	Rate equation	Log k_1 (s^{-1}) = (12·51 ± 0·38) − (177·0 ± 2·1) kJ mol^{-1} (2·303RT)$^{-1}$					
2-Phenyl-1-propyl methanesulphonate	Temperature (°C)	310·0	320·0	330·2	340·2	350·1	
	$10^4 k_1$ (s^{-1})	6·88	12·68	23·54	41·55	72·35	
	Rate equation	Log k_1 (s^{-1}) = (12·62 ± 0·04) − (176·0 ± 0·5) kJ mol^{-1} (2·303RT)$^{-1}$					
Neopentyl methanesulphonate	Temperature (°C)	340·8	350·5	360·8	370·8	379·8	389·3
	$10^4 k_1$ (s^{-1})	3·10	5·48	10·03	18·37	29·79	53·90
	Rate equation	Log k_1 (s^{-1}) = (13·35 ± 0·42) − (198·2 ± 5·2) kJ mol^{-1} (2·303RT)$^{-1}$					
3-Chloro-2,2-dimethyl-1-propyl methanesulphonate	Temperature (°C)	370·1	380·5	390·0	400·0	410·9	420·2
	$10^4 k_1$ (s^{-1})	1·48	2·66	4·80	8·78	15·94	28·10
	Rate equation	Log k_1 (s^{-1}) = (13·87 ± 0·42) − (218·2 ± 5·4) kJ mol^{-1} (2·303RT)$^{-1}$					



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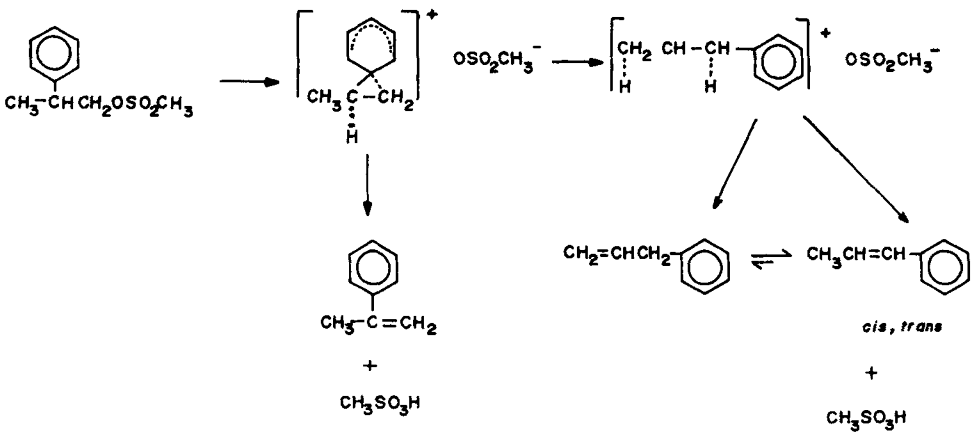


(10)

Table 11. Comparative kinetic parameters at 340·0 °C

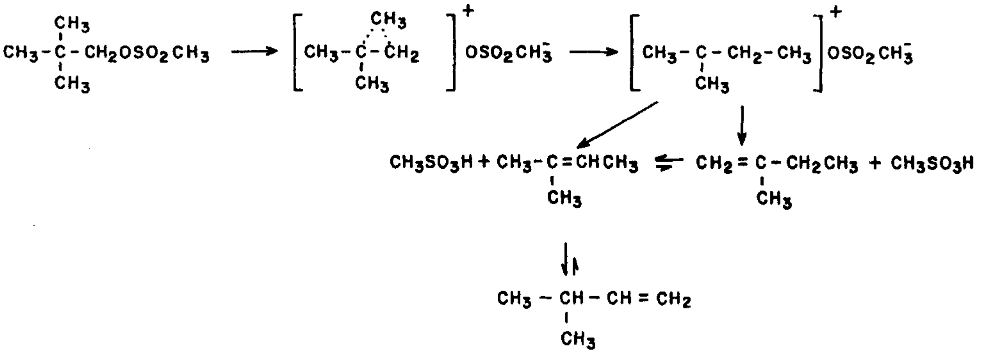
Compound	10^4k_1 (s^{-1})	10^4k_H (s^{-1})[a]	E_a (kJ mol^{-1})	log A (s^{-1})
$(CH_3)_2CHCH_2OSO_2CH_3$	26·92	13·46	177·0 ± 2·1	12·51 ± 0·38
$CH_3CHPhCH_2OSO_2CH_3$	40·74	20·37	176·2 ± 0·5	12·62 ± 0·04
$(CH_3)_3CCH_2OSO_2CH_3$	2·88	2·88	198·2 ± 5·2	13·35 ± 0·42
$(CH_3)_2C(CH_2Cl)CH_2OSO_2CH_3$	0·19	0·19	218·2 ± 5·4	13·87 ± 0·42

[a] k_H = rate per β-hydrogen.

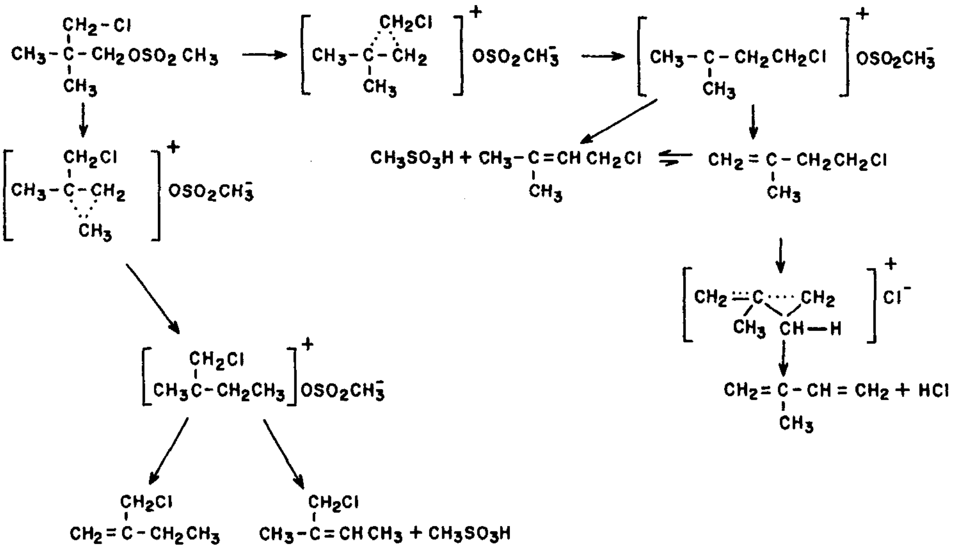
three-membered conformation to give greater stabilization of the positive carbon reaction centre, the rate coefficient of this substrate has to be, and is, faster than that of isobutyl methanesulphonate.

In spite of the presence of a β-hydrogen in the gas-phase elimination of the two previous methanesulphonate substrates, the 1,2-methyl and -phenyl shifts obliged us to examine neopentyl methanesulphonate. The gas-phase pyrolysis of this compound, without a β-hydrogen and up to 65% reaction, gave mainly rearranged olefin products (Tables 6 and 7). Consequently, the molecular migration of the methyl group must occur via an intimate ion-pair type of mechanism to yield the methylbutenes shown in equation (11).

Among the substrates without a β-hydrogen for molecular rearrangement, the elimination kinetics of 3-



(11)



(12)

chloro-2,2-dimethyl-1-propyl methanesulphonate were studied. The reaction in the gas phase was found to be homogeneous and unimolecular, yielding the olefin products described in Tables 8 and 9. As mentioned before, the yields of some of the olefin products varied in the temperature range 370–420 °C and at the same time they isomerized as the reaction progressed with temperature. CH_3SO_3H appears to be responsible for this isomerization until an equilibrium mixture is reached. The molecular rearrangement in this elimination reaction may also be explained in terms of an intimate ion-pair type of mechanism, as represented in equation (12).

CONCLUSION

The observations described in this paper suggest that intramolecular migration through autosolvation is possible in the gas-phase elimination of certain types of organic molecules, where the reaction centre has to be stabilized through participation within the molecule. In this respect, the rearrangement phenomenon found in these methanesulphonate pyrolyses must occur via a highly polar transition state, where the C—O bond polarization, in the sense of the $C^{\delta+}\cdots O^{\delta-}$ direction, is rate determining, and may be rationalized in terms of an intimate ion-pair intermediate.

EXPERIMENTAL

Isobutyl methanesulphonate. Isobutyl alcohol (Baker) in pyridine and dimethyl ether was treated with CH_3SO_2Cl as described[16] [b.p. 75 °C at 1·0 Torr (1 Torr = 133·3 Pa)]. The product was distilled to 98·8% as determined by GLC [3% OV-17 on Gas Chromosorb

QII (80–100 mesh)]. The pyrolysis products isobutene, but-1-ene and *cis,trans*-but-2-ene were acquired from Matheson and analysed on a 19% picric acid on a Carbopack C (80–100 mesh) column.

2-Phenyl-1-propyl methanesulphonate. Treatment of 2-phenylpropan-1-ol (Aldrich) with CH_3SO_2Cl in pyridine and diethyl ether yielded 2-phenyl-1-propyl methanesulphonate.[16] This compound decomposes on distillation and analysis with GLC. However, it was possible to purify it in a high-vacuum system. The purity was found to be better than 95% as determined by NMR. The unsaturated olefins allylbenzene, α-methylstyrene and *cis,trans*-β-methylstyrene (Aldrich) were analysed on a 10 ft column of 10% SP-2100 on Supelcoport (100–120 mesh).

Neopentyl methanesulphonate. CH_3SO_2Cl was added to neopentyl alcohol (Aldrich) as reported[16] (b.p. 76 °C at 1·0 Torr). Several distillations of the reaction product gave a purity of 99·8% [GLC with 5% diisodecyl phthalate on Chromosorb G AW DMCS (60–80 mesh)]. The olefins 2-methylbut-2-ene (K & K Laboratories), 2-methylbut-1-ene (K & K Laboratories) and 3-methylbut-1-ene (Janssen) were analysed using the same diisodecyl phthalate column.

3-Chloro-2,2-dimethyl-1-propyl methanesulphonate. The alcohol (Aldrich) was reacted with CH_3SO_2Cl as described[16] (b.p. 91·0 °C at 1 Torr). After several distillations of the products, the fraction of 98·9% purity was used [GLC on 10% Gas Chromosorb QII on OV-101 (80–100 mesh)]. The corresponding pyrolysis products were quantitatively analysed in the OV-101 column.

The identities of the substrates and products were additionally verified by mass, infrared and NMR spectrometry.

The pyrolysis reactions were carried out in a static system with the vessel seasoned by the decomposition products of allyl bromide, and in the presence of the free radical inhibitor propane and/or cyclohexene. The rate coefficients were determined by pressure increase or by quantitative analyses of the products. The temperature was controlled by a resistance thermometer controller type RT 5/R MK2 of AEI and Shinko DIC-PS maintained within ±0·2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient along the reaction vessel was observed.

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