JOURNAL
OF
THE CHEMICAL SOCIETY

PERKIN TRANSACTIONS II
Physical Organic Chemistry

Stability of α-Sulphur- and α-Oxygen-substituted Carbonium Ions

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The rates of hydrolysis of dimethoxymethane and methoxymethylthiomethane have been measured in aqueous sulphuric acid at 25 °C. The rate constant ratios for the oxygen and sulphur compounds (k_O/k_S) vary between 0.12 and 0.08 depending on the acid concentration. The solvolysis of chloromethyl methyl ether and sulphide gives, in dioxan–water, a k_O/k_S ratio of *ca.* 115. Comparison with other published data on reactions leading to α-sulphur- or α-oxygen-substituted carbonium ions shows that k_O/k_S ratios may range between *ca.* 0.1 and *ca.* 440. This is explained by implying different degrees of carbonium ion character in the transition states and the greater ability of sulphur to stabilize a fully developed carbonium ion as opposed to the greater overall π stabilization for the oxygen derivative in the ground state.

CONTRASTING reports are found in the literature on the relative ability of CH_3O or CH_3S groups to stabilize an adjacent positive charge. A frequently cited work [1] on the hydrolysis of chloromethyl methyl ether and sulphide indicates greater π donating ability for oxygen than for sulphur. Examination of the u.v. spectra has led,[2] however, to the conclusion that sulphur is a better donor than oxygen, at least in the photoexcited state. Stabilization energies of substituted methyl cations generated by electron impact in the gas phase show that the methylthiomethyl cation is more stable than the methoxymethyl cation [3] by *ca.* 5 kcal mol^{-1}. In agreement with this finding, Field and Weeks [4] have found that methylthiomethyl cation is formed by chemical ionization much more readily than methoxymethyl cation. Finally, in recent *ab initio* calculations [5] on CH_2OH^+ and CH_2SH^+ cations, more positive charge was found on sulphur than on oxygen, as well as a greater π overlap population in the CH_2SH^+ than in the CH_2OH^+ cation.

This difference in behaviour between the gas phase and solution is not unique and it is obvious to attribute it to solvation effects.[4] However, we have recently shown that the relative basicities (ability to share a lone pair with a proton) of oxygen and sulphur bases are strongly solvent dependent even in aqueous sulphuric acid.[6] This indicates that, perhaps, a further variable should be taken into consideration when discussing the relative electron donor abilities of sulphur and oxygen, *i.e.* the composition of the solvent in which the experiments are run.

To investigate this point we have studied the hydrolysis of dimethoxymethane and methoxymethylthiomethane in aqueous sulphuric acid and the solvolysis of chloromethyl methyl sulphide in dioxan–water. The results are discussed in this paper together with other pertinent data taken from the literature.

RESULTS

Hydrolysis of Dimethoxymethane and Methoxymethylthiomethane.—The rates of hydrolysis of dimethoxymethane and methoxymethylthiomethane were measured by an n.m.r. technique in aqueous 0.5—4.5M-sulphuric acid. Both reactions follow pseudo-first-order kinetics at each acid concentration and the rates increase steadily with acidity. This has been already observed by other authors when studying the hydrolysis of dimethoxymethane.[7] The pertinent data are collected in Table 1.

TABLE 1

Rates of dimethoxymethane and methoxymethylthiomethane hydrolysis [a]

Dimethoxymethane		Methoxymethylthiomethane	
c_{H^+}/M	10^4k_ψ/s^{-1}	c_{H^+}/M	10^4k_ψ/s^{-1}
0.85	0.336	0.50	0.534
1.20	0.649	0.85	1.38
1.61	1.32	1.20	2.64
2.49	4.09	1.69	6.88
2.87	6.95	2.49	21.4
4.45	34.2	2.87	44.2

[a] In aqueous sulphuric acid at 25 °C; monitored by n.m.r.

The acid dependence of the pseudo-first-order rate coefficient (k_ψ) was analysed in terms of the Bunnett–Olsen [8] equation (1). As we discussed recently,[9] equation (1) must be used when dealing with bases which are too weak to

$$\log k_{\psi} + H_0 = \phi_{\ddagger}(H_0 + \log c_{\mathrm{H}^+}) + \log(k_0/K_{\mathrm{SH}^+}) \quad (1)$$

be substantially protonated in the range of acidity studied. The rapid hydrolysis of dimethoxymethane and methoxymethylthiomethane prevents direct evaluation of their $\mathrm{p}K_{\mathrm{BH}^+}$ values. However, from published data on the protonation of sulphides [10] and ethers [6,11] it may be safely assumed that: (i) both substrates are protonated on oxygen (ethers are stronger bases than sulphides in aqueous sulphuric acid solutions below 60—65% H_2SO_4); [6,10,11] (ii) neither compound should be protonated to any significant extent even in the most concentrated acid solution studied, *i.e.* 4.45M-H_2SO_4. In this solution the protonation ratio ($c_{\mathrm{BH}^+}/c_{\mathrm{B}}$) for dimethyl ether, which should be more basic than either dimethoxymethane or methoxymethylthiomethane, may be estimated as 2.6×10^{-2}.

The slope parameter $\phi_{\ddagger}$ obtained from equation (1) is related [9] to the changes in solvation which the reacting system experiences in going from the initial to the transition state.

We have discussed this point elsewhere [9] by expressing the linear free energy relationship leading to equation (1), and the similar expressions for moderately and strongly basic substrates, in terms of activity coefficients [equation (2)].

$$\log f_{\mathrm{H}^+} - \log (f_{\ddagger}/f_{\mathrm{S}}) = (1 - \phi_{\ddagger})[\log f_{\mathrm{H}^+} - \log (f_{\mathrm{BH}^+}/f_{\mathrm{B}})] \quad (2)$$

It suffices to say here that a negative $\phi_{\ddagger}$ value indicates that the activity coefficient ratio $f_{\ddagger}/f_{\mathrm{S}}$ increases with acidity less than the ratio $f_{\mathrm{BH}^+}/f_{\mathrm{B}}$, and therefore [9] that the solvation requirements of the transition state are not very high, as happens in those reactions where the positive charge is fairly well delocalized in the transition state. This is expected for reactions leading to carbonium ions.[9,12] The $\phi_{\ddagger}$ values obtained for hydrolysis of dimethoxymethane and methoxymethylthiomethane are −0.13 and −0.59 respectively.

TABLE 3

Hydrolysis of several CH_3XR derivatives

R	Solvent	X = O k_{ψ}/s^{-1}	X = S k_{ψ}/s^{-1}	$k_{\mathrm{O}}/k_{\mathrm{S}}$	Reference
C≡CH	Acidic H_2O	77 ± 0.8 [a]	1.78×10^{-1} [a]	437	14, 15
CH=CH_2	Acidic H_2O	7.14×10^{-1} [a]	2.10×10^{-2} [a]	34	16
CH_2Cl	80% dioxan–20% water	3.0×10^{-1}	2.63×10^{-3}	114	13, this work
	95% dioxan–5% water	3.4×10^{-3}	3.0×10^{-4}	113	
	Aq. 0.28M-H_2SO_4	7.43×10^{-4}	4.50×10^{-4}	1.65	17, 18
$CH_2OC(O)CH_3$	Aq. 2.12M-H_2SO_4	2.04×10^{-2}	1.14×10^{-2}	1.79	
CH_2OCH_3	Aq. 0.85M-H_2SO_4	3.36×10^{-5}	1.38×10^{-4}	0.12 [b]	This work
	Aq. 2.87M-H_2SO_4	6.95×10^{-4}	4.42×10^{-3}	0.08 [b]	

[a] Catalytic rate constants for the hydronium ion, expressed in l $\mathrm{mol}^{-1}\ \mathrm{s}^{-1}$, obtained by dividing the experimental rate constant by the activity of the proton. [b] The rate constants for the dimethoxymethane solvolysis have been divided by a factor of 2, to allow for statistical correction of $\mathrm{p}K_{\mathrm{BH}^+}$ values (see text).

As mentioned before, the hydrolysis of dimethoxymethane has been studied by McIntyre and Long [7] who measured the rates in aqueous 1.2—1.9M-H_2SO_4 solutions. Our rate data in this range are in fair agreement (*ca.* 10% slower) with the published values.[7]

Solvolysis of Chloromethyl Methyl Ether and Sulphide.— The rates of solvolysis of chloromethyl methyl ether have been carefully determined by Jones and Thornton [13] for a series of solvents and solvent mixtures by using a conductimetric technique. To evaluate the slower rates for chloromethyl methyl sulphide we have used a potentiometric technique, checked by evaluating the rate of solvolysis for the chloro-ether in 95% dioxan–water. Our results are within the experimental error reported by Jones and Thornton.[13] The data for the solvolysis of the chloro-ether and sulphide in dioxan–water are collected in Table 2.

TABLE 2

Rates of solvolysis of chloromethyl methyl ether and sulphide in dioxan–water (v/v) [a]

Dioxan (%)	Y [b]	Ether [c] $10^3 k_{\psi}/\mathrm{s}^{-1}$	Sulphide $10^3 k_{\psi}/\mathrm{s}^{-1}$
80	−0.83	300.6	2.63
85	−1.43	149.0	1.31
90	−2.03	35.1	0.36
95	−3.05	3.4 ± 0.29 3.7 [d]	0.030

[a] At 25°. [b] From E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846. [c] From ref. 13 unless otherwise indicated. [d] This work.

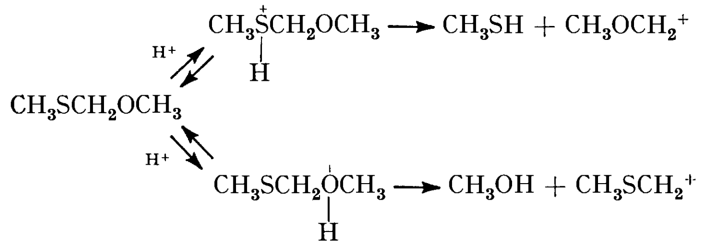
The most significant data from the literature relevant to the problems discussed in this paper are those for the hydrolysis of ethynyl methyl ethers [14] and sulphides,[15] of methyl vinyl ethers [16] and sulphides,[16] and of methoxymethyl acetate [17] and methylthiomethyl acetate.[18] They are summarized, together with our results, in Table 3 which also presents the reactivity ratios between the oxygen and the sulphur compounds ($k_{\mathrm{O}}/k_{\mathrm{S}}$).

The experimental pseudo-first-order constants (k_{ψ}) for the acid-catalysed solvolysis of methoxymethyl acetate, dimethoxymethane, and their sulphur analogues, and hence the reactivity ratios reported in Table 3, depend [see equation (1)] on the solvent composition ($\phi_{\ddagger}$ and H_0) and the $\mathrm{p}K_{\mathrm{BH}^+}$ of the substrates. As mentioned above, it is not possible to evaluate the protonation equilibria of these compounds directly because of their fast hydrolysis. We are, however, only interested in the relative $\mathrm{p}K_{\mathrm{BH}^+}$ values and therefore on the relative effect on the basicity of the groups CH_3OCH_2 and CH_3SCH_2. Both the steric (E_{S}) [19] and the polar (σ_{I}) [20] parameters for the two groups are very similar: E_{S} −1.43 and −1.58; σ_{I} +0.07 and +0.04 for the oxygen- and sulphur-containing group, respectively. This, and the fact that only modest effects on $\mathrm{p}K_{\mathrm{BH}^+}$ upon alkyl group substitution have been reported for alkyl acetates [21] and for alkyl methyl ethers,[6] leads us to believe that, as a first approximation, we may take as equal the overall substituent effect of the two groups on the protonation equilibrium constant. No correction has been made for the solvent effect and the ratios k_O/k_S are reported at two acid concentrations.

Dimethoxymethane, but not methoxymethylthiomethane, has two equivalent sites of protonation and, therefore, the experimental rate constants have been divided by a statistical factor of 2 in evaluating the k_O/k_S ratios.

DISCUSSION

Two reaction pathways (a) and (b) are available for the acid-catalysed hydrolysis of methoxymethylthiomethane. Although paths (a) and (b) give the same final products and it is very difficult to distinguish between them on a kinetic basis, we believe that the reaction occurs exclusively *via* the sulphur stabilized cation [path (b)] for the following reasons. First, taking as a model the protonation of dimethyl ether (DME) and dimethyl sulphide (DMS),[11] the fraction of *O*-protonated substrate at the highest acidity studied (2.87M-H_2SO_4), although small ($[BH^+]/[B_{st}]$ for DME *ca.* 1.4×10^{-2}), is *ca.* 34 000-fold higher than in the *S*-protonated case ($[BH^+]/[B_{st}]$ for DMS *ca.* 4×10^{-6}). Secondly, the leaving group ability from a cationic centre is much larger for CH_3OH than for CH_3SH. In fact, we have measured the rates of methyl t-butyl ether fragmentation in aqueous sulphuric acid to give methanol and t-butyl cation.[9] The reaction is too fast to be followed with conventional techniques at 8M-H_2SO_4, where the protonation fraction $[BH^+]/[B_{st}]$ is *ca.* 0.2.[9] By contrast, the protonation of methyl t-butyl sulphide may be studied even in solutions as concentrated as 17.9M-H_2SO_4, where it is completely in the acid form.[10] The greater stability to cleavage of protonated sulphides, compared with the corresponding protonated ethers, has been also observed by Olah *et al.* for FSO_3H–SbF_5–SO_2 solutions.[22] They reported that protonated methyl t-butyl sulphide is stable at −60° and very slowly cleaves to CH_3SH and t-butyl cation at −15°.[23] The corresponding protonated ether is rapidly cleaved at −70°.[24] Finally, the proposal by Fife *et al.* that 1,3-oxathiolans [25a] and benzaldehyde methyl *S*-substituted-phenyl thioacetals [25b] are cleaved in acid at the C–S bond has been convincingly challenged by Pihlaja [26] and by Lamaty *et al.*[27,28] Of particular relevance is the finding by Lamaty *et al.*[27] that 2,2-dimethyl-1,3-oxathiolan is cleaved in FSO_3H–SbF_5–SO_2 to give exclusively the $(CH_3)_2\overset{+}{C}SCH_2CH_2OH_2^+$ dication, *i.e.* that derived from C–O bond breaking.

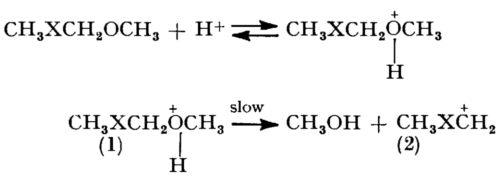


$$CH_3\overset{+}{S}(H)CH_2OCH_3 \longrightarrow CH_3SH + CH_3OCH_2^+ \qquad (a)$$

$$CH_3SCH_2\overset{+}{O}(H)CH_3 \longrightarrow CH_3OH + CH_3SCH_2^+ \qquad (b)$$

Having thus established the site of fragmentation, we may now turn to considering in more detail the reaction mechanism for hydrolysis of the methoxymethylthiomethane and dimethoxymethane. Clear evidence has been collected [29] to suggest the assignment of dimethoxymethane hydrolysis to the *A*-1 type of reaction. The analysis of our results on the acid dependence of the rates of hydrolysis of dimethoxymethane and methoxymethylthiomethane confirms that both reactions occur *via* rate-determining unimolecular cleavage of the conjugate acid of the substrate as shown in the Scheme.

In fact, the $\phi_\ddagger$ values obtained from equation (1) (−0.13 and −0.59, for the oxygen and sulphur derivative, respectively) is a clear indication [9] that the transition states of the two reactions have low solvation and hence that they must be closer to a carbonium ion [such as (2)] than to an oxonium ion [such as (1) or (1) plus a water molecule, if one consider an *A*-2 type reaction].



$$CH_3XCH_2OCH_3 + H^+ \rightleftharpoons CH_3XCH_2\overset{+}{O}(H)CH_3$$

$$\underset{(1)}{CH_3XCH_2\overset{+}{O}(H)CH_3} \xrightarrow{\text{slow}} CH_3OH + \underset{(2)}{CH_3X\overset{+}{C}H_2}$$

SCHEME

The $\phi_\ddagger$ values, more negative for methoxymethylthiomethane than for dimethoxymethane, suggest more developed carbonium ion character in the transition state for the sulphur than for the oxygen derivative. However, since a part of the positive charge should be carried by the heteroatom, the difference in $\phi_\ddagger$ values may also reflect intrinsically different solvation requirements for the two cations. Indeed, on the basis of activity coefficients,[30,31] one would expect that the larger sulphur cation would have a more dispersed charge than the oxygen analogue and, hence, a smaller solvation energy.

The rates of hydrolysis of methoxymethylthiomethane increase with acid concentration more rapidly than those of dimethoxymethane, making, obviously, the reactivity ratios different in the various acid solutions. However, as the ratio k_O/k_S is less than unity over the range of acid concentration, these reactions represent the first studied example in the condensed phase in which sulphur appears to behave as a better electron donor than oxygen. We will return to this point later.

Chloromethyl methyl ether has been shown [7] to solvolyse by an S_N1-like mechanism. In particular, the

m value obtained by the Winstein m–Y correlation[32] in a series of solvents and solvent mixtures was within experimental error of that defined for t-butyl chloride.[7] From the solvolysis rate constants of chloromethyl methyl sulphide in dioxan–water we have evaluated m as 0.90 ± 0.08, compared with the value of 0.90 ± 0.07 found for the ether[7] in the same solvent mixture. This is a good indication of the similarity between the two reaction mechanisms. It must be pointed out that in this case the ratio k_O/k_S is *ca.* 110 over the solvent range. The reactivity ratio is much smaller than that derived from Böhme's data.[1]

Before considering in some detail the data reported in Table 3, we must briefly discuss the mechanism of the other reactions leading to oxygen- or sulphur-stabilized carbonium ions. Drenth and his co-workers[14,15] have clearly proved that the hydrolyses of ethynyl methyl ether and sulphide are general acid catalysed processes, with protonation of the ethynyl group as the rate-determining step. McClelland[16] has shown that the hydrolysis of vinyl sulphides proceed *via* a mechanism analogous to that for vinyl ethers,[33] with slow proton transfer to the carbon–carbon double bond. The acid-catalysed hydrolyses of methoxymethyl acetate[17] and methylthiomethyl[18] acetate were shown to occur by A-1 type mechanisms. The $\phi_\ddagger$ values which may be evaluated from published data[17,18] are -0.20 and -0.15 for the oxygen and sulphur compound, respectively, in agreement with the hypothesis of a delocalized positive charge in the transition state.

Relative Stabilities of Methoxymethyl and Methylthiomethyl Cations.—The relative stabilities of carbocations R^+ have been frequently estimated from rate constants for solvolysis under identical conditions. To use the same approach in the case of $CH_3OCH_2^+$ and $CH_3SCH_2^+$ cations it is necessary (i) that all the reactions studied reach the transition state at the same point along the reaction co-ordinate and that the transition state is close in energy to the cation; (ii) that the solvation requirements in going from the reactants to the transition states are similar in all cases; and (iii) that the reactants have similar energies. Inspection of the data reported in Table 3 suggests that these three conditions are not very likely to be obeyed. As a matter of fact the reactivity ratio k_O/k_S ranges from *ca.* 400 to *ca.* 0.1. Clearly, caution must be used in interpreting these rate data in terms of sulphur or oxygen stabilizing ability for cations.

It was suggested[34] that, qualitatively, the stabilizing effect on adjacent cations by heteroatoms should depend on the ionization potential (which predicts sulphur as a better donor than oxygen) and on the strength of the π bond formed in 'resonance structures' (which favour oxygen over sulphur for carbocations). Recent calculations offer a more quantitative interpretation of these ideas.[5] The π stabilization energy (SE) due to the conjugate interaction of a heteroatom X with an acceptor is given by equation (3) where H_{AB} is the interaction matrix element between ψ_A (p_π lone pair of the heteroatom) and ψ_B (the vacant $2p_\pi$ orbital of the acceptor fragment), and ΔE is the energy separation between

$$SE = 2H_{AB}^2/\Delta E \qquad (3)$$

ψ_A and ψ_B. It has been found[5] that the matrix element (H_{AB}) tends to favour lower group elements ($O > S$; $F > Cl$) whereas the energy term (ΔE) always favours the higher group element ($S > O$; $Cl > F$) as the ionization potential of the heavier element is always lower than that of the corresponding lighter one.

It follows that when the LUMO of the acceptor is high in energy, as for example for the antibonding π orbital of the ethylene fragment in $CH_2{=}CHX$, the matrix element is dominant and the overall π stabilization is greater for oxygen than for sulphur. On the other hand when the LUMO is of low energy, as for the empty p orbital of the carbonium ion in $^+CH_2X$, the energy term is dominant and the *S*-stabilized cation is more stable than the *O*-stabilized one.

It is therefore possible to rationalize the data in Table 3 by considering the differences in carbonium ion character of the transition states. Let us first consider reactions involving a proton, *i.e.* the hydration of ethynes and ethylenes and the hydrolysis of acetals and acylals.

The hydration reactions occur through the rate-determining attack of the proton (see above). Hence, it is expected that the transition states resemble the reactant more than the intermediate carbonium ion or vinyl cation. In this case, as suggested by calculations[5] and by n.m.r.[35,36] and dipole moment[36] data, oxygen must be a better donor than sulphur and hence the oxygen derivative must be more reactive than the sulphur one, as found.

The acid catalysed hydrolysis of acylals ($CH_3XCH_2OCOCH_3$) and acetals ($CH_3XCH_2OCH_3$) has been proved to occur *via* an A-1 type mechanism (see above).[17,18] On the basis of basicity measurements on methanol (pK_{BH^+} -2.05 ϕ_e 0.87)[11] and acetic acid (pK_{BH^+} *ca.* -3.8, estimated from data on methyl acetate[37]), as well as from the acid catalysed fragmentation rates, faster for t-butyl acetate than for methyl t-butyl ether in aqueous sulphuric acid,[9] we expect methanol to be a worse leaving group than acetic acid. Hence, the transition state for the hydrolysis of acylals should be reached earlier along the reaction co-ordinate than for the hydrolysis of acetals, and it should have less carbonium ion character. This is also reflected by the $\phi_\ddagger$ values. As discussed elsewhere,[9] a reaction going from an oxonium to a carbonium ion should have negative ($\phi_\ddagger - \phi_e$) values,* because of the lower solvation requirements of the latter ion. The greater the carbonium ion character of the transition state, the more

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* The ($\phi_\ddagger - \phi_e$) value is the slope of $\log k_\psi - \log (c_{BH^+}/c_{st})$ *versus* $H_0 + \log c_{H^+}$ plots.[9] This plot correlates the reaction rates with acidity for moderately basic substrates, *i.e.* for compounds which are substantially protonated in the range of acidity studied. The slope ($\phi_\ddagger - \phi_e$) is related to the difference between the activity coefficients of the protonated substrate and the transition state. The slope ϕ_e is related to the solvent effect on the protonation equilibrium and may be evaluated as the slope of the plot of $\log (c_{BH^+}/c_B) + H_0$ against $H_0 + \log c_{H^+}$.[6,9,11,30]

negative are the $(\phi_{\ddagger} - \phi_{e})$ values found.[9] In the present case $(\phi_{\ddagger} - \phi_{e})$ values may be estimated as *ca.* -0.8 for the acylals and -0.95 to -1.4 for the acetals on the basis of the experimental $\phi_{\ddagger}$ values and assuming that the ϕ_{e} values are similar to those of unsubstituted methyl acetate and dimethyl ether ($+0.6$ and $+0.82$, respectively).[11,37] It follows from the larger carbonium ion character for acetal hydrolysis that the reactivity ratio k_O/k_S should be smaller than in the hydrolysis of acylals, as found (*ca.* 0.1 *versus ca.* 1.7).

We must finally consider the solvolysis of chloromethyl methyl ether and sulphide. These reactions are not strictly comparable with those discussed above since they have been studied in different solvents and do not require acid catalysis. Since the solvolysis of the chloro derivatives involves charge separation, we expect that the transition state is reached through a much steeper reaction path than in the solvolysis of the protonated acetals and acylals. Even if the chloro derivatives are more stable than the protonated oxy-compounds, they will reach the transition state earlier and this will be closer to the reactants than to the carbonium ion. This implies, according to the above discussion, that the oxygen derivative reacts faster than the sulphur and, in fact, the ratio k_O/k_S is 110.

It is evident from the above data and discussion that is is not possible simply to take reactivity ratios as representing the relative ability of heteroatoms in stabilizing an adjacent positive charge. In the particular case of sulphur- and oxygen-substituted carbonium ions it is concluded that sulphur has a greater ability to disperse the positive charge of the fully formed carbonium ion, although the oxygen derivative is often more reactive since the transition state is reactant-like, so that interactions are more important with the oxygen than with the sulphur heteroatom.

EXPERIMENTAL

N.m.r. spectra were recorded on a Bruker HX-90 spectrometer. B.p.s are uncorrected.

Materials.—Reagents grade dioxan was purified according to the procedure given by Fieser.[38] Sulphuric acid solutions were made by dilution of concentrated reagent grade acid with distilled water. The solutions were standardized by titration with 1M-NaOH. Commercial dimethoxymethane, chloromethyl methyl ether, and chloromethyl methyl sulphide were purified by distillation.

Methoxymethylthiomethane. Methanol (5 g) was added to a solution of chloromethyl methyl sulphide (5 g) in pyridine (12.5 ml) and the mixture was stirred at 0 °C for 3 h. The title compound was recovered pure by dilution of the mixture with a large excess of saturated NaCl aqueous solution, b.p. 98—99 °C; $\delta(CCl_4)$, 2.05 (SCH_3), 3.28 (OCH_3), and 4.51 (CH_2).[39]

Hydrolysis of Methoxymethylthiomethane.—The title reaction was followed by monitoring the changes in the n.m.r. spectra of a sulphuric acid solution of methoxymethylthiomethane. The initial spectrum in 2.45M-H_2SO_4 shows three signals at 466 (CH_2), 350 (CH_3O), and 239 Hz (CH_3S) from tetramethylsilane as external standard. Three different signals appear with time: at 350 (attributed to CH_3OH by comparison with an authentic sample) and at 470 and 243 Hz, attributed respectively to the methylene and methyl protons of the α-hydroxy-sulphide CH_3SCH_2OH, the first product of methoxymethylthiomethane hydrolysis. It is known that carbonyl compounds and thiols are in equilibrium with hydroxy sulphides in aqueous media.[40] When the conversion to the α-hydroxy-sulphide is almost complete three signals appear at 482 [$CH_2(OH)_2$], 380 [$CH_2(SCH_3)_2$], and 240 Hz [$CH_2(SCH_3)_2$], attributed by comparison with authentic samples. The overall reaction may be therefore written as (4).

$$2\,CH_3OCH_2SCH_3 + 2\,H_2O \longrightarrow CH_3SCH_2SCH_3 + 2\,CH_3OH + CH_2(OH)_2 \quad (4)$$

Reaction of formaldehyde with methanethiol in 2.46M-H_2SO_4 gives bismethylthiomethane (3), as expected.

Hydrolysis of Dimethoxymethane.—The n.m.r. spectrum of dimethoxymethane in 2.46M-H_2SO_4 shows two signals at 463 (CH_2) and 351 Hz (OCH_3) from tetramethylsilane as external standard. With time another signal appears at 482 Hz, attributed to hydrated formaldehyde (see above). The signal corresponding to the other product, methanol, should appear at 350 Hz but it is not distinguishable from the OCH_3 signal of dimethoxymethane.

Kinetic Procedure.—The hydrolysis reactions of dimethoxymethane and methoxymethylthiomethane were monitored by following the disappearance of the methylene n.m.r. signal, using a slightly different procedure according to the acidity of the solution. In more dilute solutions ($<$2.5M-H_2SO_4), the methylene proton signal appears near the water signal, and therefore an extraction technique was followed. Substrate (*ca.* 30 μl) was added to thermostatted (25 °C) aqueous H_2SO_4 (10 ml) of the appropriate concentration. Portions (1 ml) were withdrawn at intervals and extracted with 1 ml of a solution of CH_2Cl_2 (25 μl) in CCl_4 (30 ml). The n.m.r. spectra of the carbon tetrachloride solutions were then taken and the ratio between the methylene signal of dimethoxymethane or methoxymethylthiomethane and that of the CH_2Cl_2 used as standard (h_{CH_2}/h_{st}) was evaluated by comparing the peaks heights.

In more concentrated acid solutions ($>$2.5M-H_2SO_4), dimethoxymethane or methoxymethylthiomethane (*ca.* 3 μl) were added to aqueous H_2SO_4 (1 ml) of the appropriate concentration containing dimethyl sulphoxide (*ca.* 1 μl) or dioxan (*ca.* 0.3 μl). DMSO and dioxan do not react in these acid solutions and give a sharp singlet in the n.m.r. spectrum. The spectra of the acid solutions were taken at intervals. The ratios between the methylene signal of dimethoxymethane or methoxymethylthiomethane and that of the internal standard (h_{CH_2}/h_{st}) were evaluated by comparing the peaks heights. The pseudo-first-order rate constants (k_ψ) were evaluated from the slope of plots of log (h_{CH_2}/h_{st}) *versus* time.

The hydrolysis of chloromethyl methyl ether and sulphide were followed by a potentiometric technique. In a three-necked thermostatted flask equipped with glass and calomel electrodes, substrate (50 μl) was added to dioxan–water (25 ml), made by mixing the appropriate amount of thermostatted solvents. The increase in acidity of the solution was monitored by using a Radiometer 26 pH meter. Calibration curves, showing the linearity of the electrode response with the acid concentration, were made for each solvent mixture by using different amounts of HCl. The pseudo-first-order rate constants (k_ψ) were evaluated from the slopes of plots of $[(\mathrm{mV})_\infty - (\mathrm{mV})_t]$ *versus* time.

[7/1843 *Received, 20th October*, 1977]

REFERENCES

[1] H. Böhme, *Ber.*, 1941, **74**, 248; H. Böhme, H. Fischer, and R. Fank, *Annalen*, 1949, **563**, 54.

[2] A. Mangini, *Gazzetta*, 1958, **88**, 1063; R. C. Passerini, in 'Organic Sulphur Compounds,' ed. N. Kharasch, Pergamon, London 1961, vol. 1, p. 57.

[3] R. W. Taft, R. H. Martin, and F. W. Lampe, *J. Amer. Chem. Soc.*, 1965, **87**, 2490.

[4] F. H. Field and D. P. Weeks, *J. Amer. Chem. Soc.*, 1970, **92**, 6521; F. H. Field, in 'Ion–Molecule Reactions,' ed. J. L. Franklin, Butterworths, London, 1972.

[5] F. Bernardi, I. G. Csizmadia, H. B. Schlegel, and S. Wolfe, *Canad. J. Chem.*, 1975, **53**, 1144; F. Bernardi, A. Mangini, N. D. Epiotis, J. R. Larson, and S. Shaik, *J. Amer. Chem. Soc.*, 1977, **99**, 7465.

[6] P. Bonvicini, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, *J. Amer. Chem. Soc.*, 1973, **95**, 5960.

[7] D. McIntyre and F. A. Long, *J. Amer. Chem. Soc.*, 1954, **76**, 3240.

[8] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1899.

[9] V. Lucchini, G. Modena, G. Scorrano, and U. Tonellato, *J. Amer. Chem. Soc.*, 1977, **99**, 3387.

[10] P. Bonvicini, A. Levi, V. Lucchini, and G. Scorrano, *J.C.S. Perkin II*, 1972, 2267.

[11] G. Perdoncin and G. Scorrano, *J. Amer. Chem. Soc.*, 1977, **99**, 6983.

[12] G. Modena, F. Rivetti, G. Scorrano, and U. Tonellato, *J. Amer. Chem. Soc.*, 1977, **99**, 3392.

[13] T. C. Jones and E. R. Thornton, *J. Amer. Chem. Soc.*, 1967, **89**, 4863.

[14] E. J. Stamhuis and W. Drenth, *Rec. Trav. chim.*, 1961, **80**, 797.

[15] H. Hogeveen and W. Drenth, *Rec. Trav. chim.*, 1963, **82**, 375.

[16] R. A. McClelland, *Canad. J. Chem.*, 1977, **55**, 548.

[17] R. A. McClelland, *Canad. J. Chem.*, 1975, **53**, 2763.

[18] R. A. McClelland, *Canad. J. Chem.*, 1975, **53**, 2772.

[19] S. H. Unger and C. Hansch, *Progr. Phys. Org. Chem.*, 1976, **12**, 91.

[20] The σ_I values have been computed from data and equations reported in R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 709.

[21] D. G. Lee and M. H. Sadar, *J. Amer. Chem. Soc.*, 1974, **96**, 2862.

[22] G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, 1970, **70**, 561.

[23] G. A. Olah, D. H. O'Brien, and C. U. Pittman, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 2996.

[24] G. A. Olah and D. H. O'Brien, *J. Amer. Chem. Soc.*, 1967, **89**, 1725.

[25] (*a*) T. H. Fife and L. K. Jao, *J. Amer. Chem. Soc.*, 1969, **91**, 4217; (*b*) T. H. Fife and E. Anderson, *ibid.*, 1970, **92**, 5464.

[26] K. Pihlaja, *J. Amer. Chem. Soc.*, 1972, **94**, 3330.

[27] F. Guinot, G. Lamaty, and H. Münsch, *Bull. Soc. chim. France*, 1971, 541.

[28] F. Guinot and G. Lamaty, *Tetrahedron Letters*, 1972, 2569.

[29] E. H. Cordes and H. G. Bull, *Chem. Rev.*, 1974, **74**, 581.

[30] E. M. Arnett and G. Scorrano, *Adv. Phys. Org. Chem.*, 1976, **13**, 83.

[31] K. Yates and R. A. McClelland, *Progr. Phys. Org. Chem.*, 1974, **11**, 323.

[32] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963.

[33] A. J. Kresge, H. J. Chen, and Y. Chiang, *J. Amer. Chem. Soc.*, 1977, **99**, 802 and previous papers of this series.

[34] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, London, 1969.

[35] W. Drenth and A. Loewenstein, *Rec. Trav. chim.*, 1962, **81**, 635; H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, 1959, **31**, 1278; J. Feeney, A. Ledwith, and C. H. Sutcliffe, *J. Chem. Soc.*, 1962, 2021; R. T. Hobgood, jun., G. S. Reddy, and J. H. Goldstein, *J. Phys. Chem.*, 1963, **67**, 110.

[36] W. Drenth, G. L. Hekkert, and B. G. Zwanenburg, *Rec. Trav. chim.*, 1960, **79**, 1056.

[37] G. Scorrano, unpublished results.

[38] L. F. Fieser, 'Experiments in Organic Chemistry,' D. C. Heath, Boston, 1957, p. 284.

[39] K. Torssell, *Acta Chem. Scand.*, 1967, **21**, 1.

[40] I. B. Johns and R. M. Hixon, *J. Amer. Chem. Soc.*, 1934, **56**, 1333; G. E. Lienhard and W. P. Jencks, *ibid.*, 1966, **88**, 3982; R. G. Kallen and W. P. Jencks, *J. Biol. Chem.*, 1966, **241**, 5851; L. Field and B. J. Sweetman, *J. Org. Chem.*, 1969, **34**, 1799; L. Field, B. J. Sweetman, and M. Bellas, *J. Medicin. Chem.*, 1969, **12**, 624.