Sulphene–Tertiary Amine Zwitterions: Intermediates in the Multiexchange of Hydrogen in a Sulphene Reaction

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Summary With sterically unhindered tertiary amines and deuterium oxide or other deuteriated sulphene traps, alkanesulphonyl halides with more than one α-hydrogen may yield products having more than one of the α-hydrogens exchanged; evidence is presented for a mechanism involving reaction of the intermediate sulphene with the amine to form a zwitterion ($\overset{-}{C}HR^1SO_2\overset{+}{N}R^2_3$) which may then exchange hydrogens *via* its conjugate acid.

ONE of the key points in the proof of the formation of sulphenes by the action of bases on alkanesulphonyl chlorides is the observation of the uptake of one and only one deuterium atom when the reaction is carried out in the presence of deuteriated sulphene traps of the general formula DZ, where Z may be OR^1, NR^2R^3, *etc.*[1,2] In a series of experiments with different sulphonyl chlorides (and bromides) and amines, monoexchange had been found in all cases examined. We were therefore surprised to find that the reaction of methanesulphonyl chloride (**1**) in 1,2-dimethoxyethane (DME) containing D_2O (*ca.* 15%) with 1,4-diazabicyclo[2,2,2]octane (DABCO) at room temperature gave the $CD_3SO_3^-$ salt as the major product, with diminishing amounts of the $CHD_2SO_3^-$, $CH_2DSO_3^-$, and $CH_3SO_3^-$ materials.† This anomaly led to the experiments summarized

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† Control experiments showed the absence of exchange in both unchanged starting material and product under these conditions.

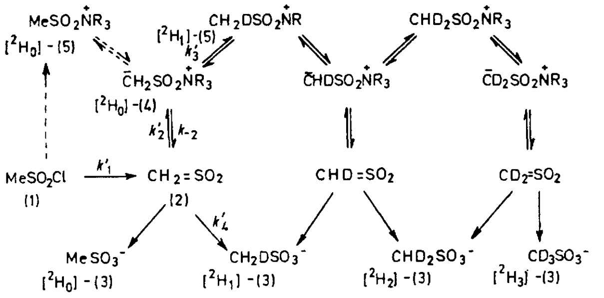
in the Table, from which it is evident that monoexchange occurs with the relatively bulky amines and that multiexchange increases as the non-bonding repulsions in the vicinity of the nitrogen decrease. To determine if sulphene (**2**) is present during the multiexchange reactions, we treated (**1**) with DABCO in DME–D_2O containing an enamine [1-(2-methylpropenyl)pyrrolidine] and obtained the cycloadduct (2,2-dimethyl-3-pyrrolidinothietan 1,1-dioxide[3]) in 50% yield; the methylene group of the new ring was found to be partly deuteriated† (average composition $CH_{1\cdot25}D_{0\cdot75}$), showing that partly deuteriated sulphene is formed and then trapped by the enamine.

The solid arrows in the Scheme describe a mechanism which in our view most satisfactorily explains our observations. The key intermediate is zwitterion (**4**) which may pick up a deuteron (or proton) to form the sulphonammonium ion (**5**) or lose NR_3 and revert to sulphene. Zwitterion (**4**) is the simplest member of a class of compounds of which a few stabilized members (*e.g.* $MeSO_2\overset{-}{C}HSO_2\overset{+}{N}Me_3$)[4] have been characterized;[4,5] the nitrogen and oxygen analogues, respectively $R^1_3\overset{+}{N}SO_2\overset{-}{N}R^2$ and $R_3\overset{+}{N}SO_3^-$ (sulphur trioxide–tertiary amine complexes), are known as well,[6] From the proportions of the isotopically substituted methanesulphonates given in the Table together with an expression derivable from the relationships summarised in the Scheme, one may calculate values for the ratios k'_2/k'_4 and k_{-2}/k'_3, and that as expected from the mechanism the former ratio decreases and the latter increases as the bulk of the base increases; *i.e.* the mechanism is compatible with the values in the Table.

Hydrogen deuterium exchange in the reaction of alkanesulphonyl chlorides with tertiary amines and water or alcohols

Sulphonyl chloride	Reaction medium[a]	Percentages of other products			
		$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$
$MeSO_2Cl$	Quinuclidine, 2·3; D_2O, 28 (6·3)	1·8	13·1	21·0	63·1
,,	DABCO, 2·0; D_2O, 28 (6·3)	1·3	16·1	22·8	50·8
,,	Me_3N, 2·6; D_2O, 28 (6·3)	1·8	25·8	24·7	49·0
,,	Me_2EtN, 2·2; D_2O, 21 (6·3)	4·8	71·4	17·6	6·2
,,	$MeEt_2N$, 2·5; D_2O, 28 (6·3)	4·8	92·0	2·5	0·8
,,	Et_3N, 2·5; D_2O, 28 (6·3)	9·6	89·8	0·5	0·0
,,	Bu_3N, 19; D_2O, 25 (2·0)	6	94		
,,	DABCO, 2·1; MeOD, 27 (14)	*ca.* 0	*ca.* 15	*ca.* 25	*ca.* 60
$EtSO_2Cl$	DABCO, 2·1; D_2O, 28 (6·3)	5·5	81·4	13·1	—
$PhCH_2SO_2Cl$	Et_3N, 6·7; D_2O, 250 (29)	2·5	95·6	1·9	—
,,	DABCO, 6·7; D_2O, 250 (29)	2·8	88·6	8·6	—
,,	DABCO, 6·7; D_2O, 50 (7·4)	4·5	93·0	2·5	—
,,	DABCO, 6·7; Bu^tOD, 50 (29)	6·3	58·1	35·6	—
p-NO_2-$C_6H_4CH_2SO_2Cl$	Et_3N, 6·7; D_2O, 250 (29)	5·7	88·4	5·9	—
,,	DABCO, 6·7; D_2O, 250 (29)	2·7	20·7	76·6	—

[a] The reaction was carried out at room temperature in 1,2-dimethoxyethane (DME) solution. The number in parentheses gives the volume percentage of the D_2O (or the ^2H-alcohol in the initial mixture, the other numbers give the molar ratio of the reagents relative to the sulphonyl chloride. [b] Estimated from the mass spectra of the derived sulphonyl chlorides, except for the experiments with tributylamine and with MeOD, which were estimated from n.m.r. spectra.



Scheme

Three other mechanisms for multiexchange may be excluded as follows. (i) Exchange *via* the conjugate base of sulphene ($CH{=}SO_2$) fails to account for the base "size" effects; *e.g.* triethylamine and trimethylamine have similar base strengths in this medium but give quite different exchange patterns. (ii) Formation of (**5**) in a one-step reaction from (**2**) can be shown to require a highly unlikely variation in kinetic isotope effects from one base to another in order to yield the values in the Table. (iii) The reactions indicated by the broken arrows are excluded by the finding[7] that there is a close linear free energy correlation with monobasic tertiary amines regardless of whether they give mono- or multi-exchange; this indicates that they all react by the same mechanism, which involves a direct *E*2 reaction[8] of (**1**) to form (**2**).

As is shown in the Table, other sulphonyl chlorides and sulphene traps also lead to multiexchange though the extent of exchange is less than with (**1**) and D_2O, except with *p*-nitrophenylmethanesulphonyl chloride which can lead to a comparatively favourable zwitterion. Multiexchange with phenylmethanesulphonyl chloride is increased by using Bu^tOD rather than D_2O as the sulphene trap, as would be expected from the lower value for k'_4 with the alcohol.

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