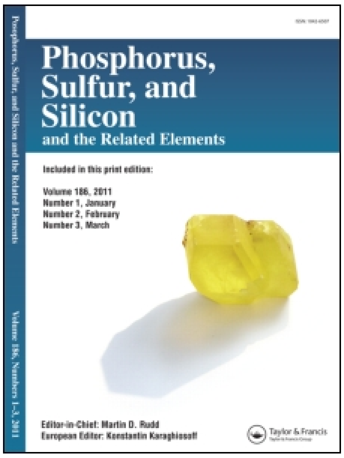

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MECHANISTIC VARIATION IN ALKANESULFONYL CHLORIDE HYDROLYSIS AND RELATED REACTIONS

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Abstract Kinetic and product ratio studies are consistent with the following mechanisms for the hydrolysis of methanesulfonyl chloride: (a) in acidic medium (pH 1-6) via a direct substitution on sulfur (S_N2-S), (b) in mildly basic medium (pH 8-10) by way of sulfene ($CH_2{=}SO_2$) formation followed by trapping with water, and (c) in strongly basic solution (pH >10) via sulfene with trapping by the hydroxide ion. The reactions of primary and secondary alkanesulfonyl chlorides are qualitatively similar.

The systematic study of the hydrolysis of alkanesulfonyl halides and related processes can be traced back to 1940[1], but the mechanisms of these reactions are still only incompletely understood. About thirty years ago it was suggested[2,3] that the hydrolysis of methanesulfonyl chloride and other simple alkanesulfonyl halides was an S_N2 reaction in which water attacked the sulfonyl sulfur atom and displaced the halide ion. In 1965, in a paper from this laboratory[4] dealing primarily with reactions in organic media, it was pointed out that the hydrolysis of $PhCD_2SO_2Cl$ in aqueous dioxane (1:1) proceeded without hydrogen-deuterium exchange to give $PhCD_2SO_3H$, whereas NaOD in D_2O-dioxane (1:5) with $PhCH_2SO_2Cl$ yielded the monodeuterated product $PhCHDSO_3^-$. This led to the proposal[4] that the hydroxide reaction proceeded *via* an elimination-addition (*EA*) process going by way of the intermediate sulfene, $PhCH{=}SO_2$. No attempt was made in that work to define either (a) the threshold hydroxide concentration above which the sulfene (*EA*) reaction becomes the major process with $PhCH_2SO_2Cl$ or any other sulfonyl chlorides, or (b) the nature of the reaction of the sulfene to form the sulfonate anion.

Subsequent reports have added further observations, including (a) α-deuterium exchange in the reaction of 2-propanesulfonyl chloride with

NaOD in D_2O[5], (b) lack of hydrogen exchange in the hydrolysis of methanesulfonyl or chloromethanesulfonyl chlorides in D_2O, but, surprisingly, exchange of the hydrogen by deuterium not only in the hydrolyzed product, dichloromethanesulfonic acid, but also in the unreacted dichloromethanesulfonyl chloride, on standing in D_2O[6], (c) rate constants for the reaction of hydroxide with certain alkanesulfonyl chlorides in mixed aqueous-organic media[7-9].

This paper describes recent work on the mechanisms of substitution in alkanesulfonyl chlorides, in aqueous and organic media. Figure 1 shows typical pH-rate profiles, in this case for CH_3SO_2Cl and CD_3SO_2Cl at 25°C in 0.1 M aqueous KCl, as determined by pH-stat rate measurements. The rate law, which also includes a component for general base catalysis by tertiary amines, may be written as follows.

$$k_{obs} = k_W + k_{OH}[OH^-] + k_B[R_3N]$$

Values of k_{obs}, k_W and k_{OH}, for a series of alkanesulfonyl chlorides and their α-perdeuterated isotopomers are listed in the Table. Among the key points are (i) the regular changes in k_W and k_{OH} with changes in structure ascribable to conventional steric and electronic factors, (ii) the absence of any kinetic isotope effects (KIE's) in k_W and (iii) the sizeable KIE's (4 to 7.7) for k_{OH}. In addition, the products from deuterium labelling experiments under kinetic conditions were carefully examined; the results, combined with the above observations, were consistent with the following conclusions.

(i) The simple hydrolysis component ("k_W reaction") proceeds exclusively (>99%) by a direct displacement (S_N2-S) mechanism.

(ii) The hydroxide promoted reaction ("k_{OH} reaction") (as well as that induced by triethylamine proceeds entirely (>99%) by an elimination-addition (sulfene) process; there appears to be no detectable sign of a hydroxide S_N2-S or a water *EA* process. This result accords with previous work though the uniqueness of reaction for each reagent had not previously been established.

A further point which emerges from this study is the variation of transition state structure with substrate, reagent, and solvent, as shown by change in the KIE values. For ethanesulfonyl chloride, for example, deuterium substitution experiments show that the hydroxide (in water), triethylamine in water, and triethylamine and 2-propanol in methylene chloride reactions all proceed via the sulfene; the KIE's are respectively 5.6, 2.9 and 1.0 (1).

The final point is the mechanism of trapping of sulfene in aqueous base. This was explored by carrying out the hydrolysis in the presence of a sulfene trap (e.g. ArO^-, $CH_3SO_2N^-Ph$) capable of competing with the trapping by water, and which yields a stable product. The variation of the product ratio with pH, see Figure 2, indicated trapping by both water and hydroxide, with the water reaction predominating below pH 11.8 and the hydroxide trapping reaction above 11.8.

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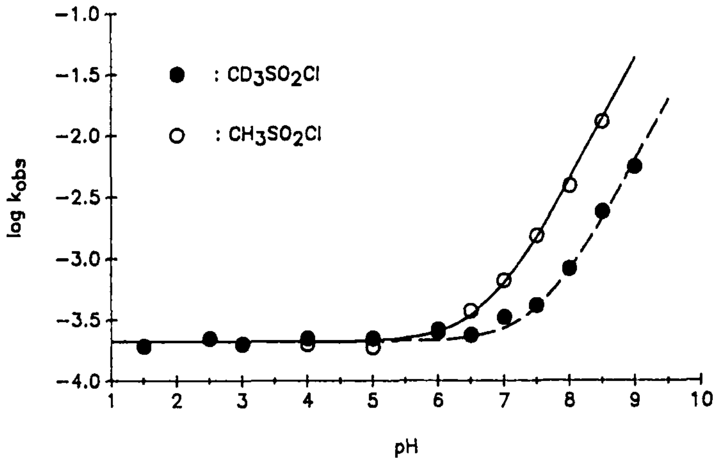

Fig.1 pH–rate profiles for the hydrolyses of CH_3SO_2Cl and CD_3SO_2Cl.

Rate Constants for the Hydrolysis of Alkanesulfonyl Chlorides (25.0°C, 0.1M KCl).

Alkanesulfonyl Chloride	$k_W(s^{-1})$	$k_{OH}(M^{-1}s^{-1})$	k_H/k_D[a]
CH_3SO_2Cl	2.1×10^{-4}	4200	7.0
CD_3SO_2Cl	2.1×10^{-4}	600	
$CH_3CH_2SO_2Cl$	3.2×10^{-4}	500	5.6
$CH_3CD_2SO_2Cl$	3.2×10^{-4}	90	
$CH_3CH_2CH_2SO_2Cl$	3.8×10^{-4}	520	
$CH_3CH_2CH_2CH_2SO_2Cl$	3.6×10^{-4}	480	
$C_6H_{11}CH_2SO_2Cl$	3.9×10^{-4}	340	
$(CH_3)_2CHSO_2Cl$	3.8×10^{-5}	120	4.0
$(CH_3)_2CDSO_2Cl$	3.8×10^{-5}	30	
$CH_3CH_2CH(CH_3)SO_2Cl$	3.4×10^{-5}	100	
$CH_2{=}CHCH_2SO_2Cl$	4.5×10^{-4}	270,000	
$PhCH_2SO_2Cl$	2.0×10^{-4}	85,000	7.7
$PhCD_2SO_2Cl$	2.0×10^{-4}	11,000	

a : for k_{OH}

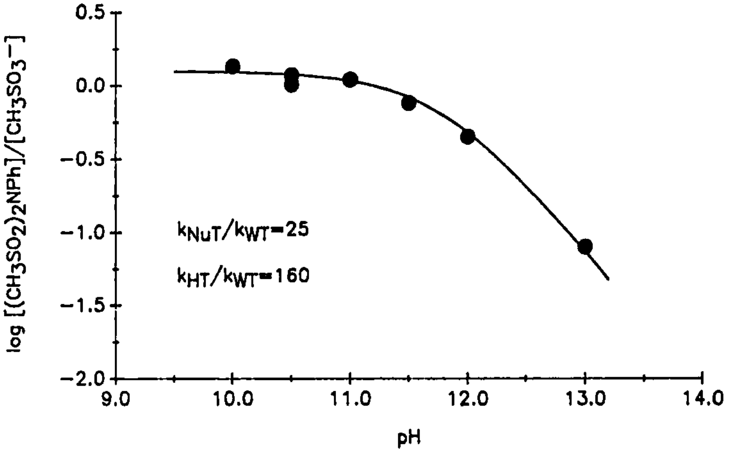

Fig.2 Variation of product ratios with pH in the hydrolysis of CH_3SO_2Cl in the presence of $[CH_3SO_2NPh^-]$=0.05M at 25°C.