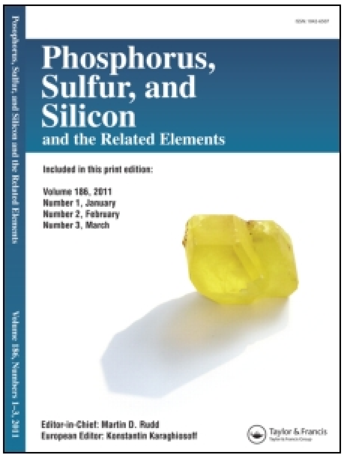

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TERTIARY AMINES-CATALYZED REACTION OF ALKANE SULPHONIC ESTER FORMATION

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TERTIARY AMINES-CATALYZED REACTION OF ALKANE SULPHONIC ESTER FORMATION

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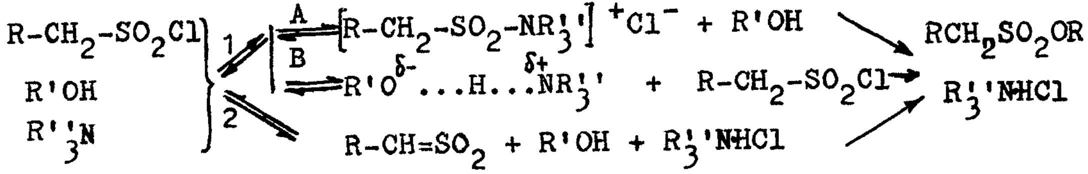
The tertiary amines-catalyzed alkanesulphonylation of phenols and alcohols is a complex process representing, at least, three parallel pathways.



This reaction proceeds as nucleophilic substitution at the sulphur atom (1), the catalysis by tertiary amine being effected by nucleophilic (A) or general base (B) mechanisms. In addition, the sulphene mechanism of elimination-addition (2) characteristic of alkane sulphonic chloride can be realized.

The studies of the competing interaction of phenol and methanol with lower alkane sulphonic chlorides in the presence of various tertiary amines [triethyl amine (TEA), tributil amine (TBA), pyridine (Py) etc.] show that in the case of Py as a weak base (pK_a=5.23), the conversion of methanol predominates, i.d. nucleophilic catalysis. In the case of more basic tertiary amines (TEA pK_a= 10.87; TBA pK_a= 11.23) the conversion of phenol increases significantly telling of the predominance of the general base catalysis.

$$\begin{array}{l} C_6H_5OH \\ CH_3OH \end{array} + RCH_2SO_2Cl \xrightarrow[-R''_3\,NHCl]{+\,R''_3N} \begin{array}{l} RCH_2SO_2OC_6H_5 \\ RCH_2SO_2OCH_3 \end{array}$$

Mor favourable conditions for the reaction to proceed by the general base catalysis scheme are created in aprotic solvents (hexane, benzene). The conversion of phenol decreases consi -

derably in solvents able to form hydrogen bonds (diethyl ether, dioxane) at the expense of lowering the complex stability $R'\overset{\delta+}{O}...H...\overset{\delta-}{N}R''_3$.

The results of the investigation of the tertiary amines - catalyzed alkane-sulphonylation of deutero - phenol (PhOD), - me - thanol (MeOD), - β -chloro-ethanol (ClC_2H_4OD) indicate that the degree of proceding the reaction in point by the E1cB (sulphene) mechanism significantly depends on the compositions of the reagents, the solvent and the catalyst.

$$RCH_2SO_2Cl \xrightleftharpoons[-R''_3N{\cdot}HCl]{+\,R''_3N} R\text{-}CH{=}SO_2 \xrightarrow{R'OD} R\text{-}CHD\text{-}SO_2\text{-}OR'$$

On passing from PhOD to MeOD in the reaction of alkanesulphonylation in the presence of TEA in benzene the moiety of the E1cB mechanism falls from 95% to 84% in the case of methane sulpho - nic chloride, and from 83% to 63% in the case of bensyl sulphonic chloride.

The variation of solvent (benzene, diethyl ether, acetonitrile) shows, that the moiety of sulphene mechanism is dependent essentially on the solvent specific solvation ability.

The use of the tertiary amines of different basicity shows, that the more basic is the catalyst the higher is the moiety of the D-esters, i.d. the better is the formation of sulphene and hence the E1cB mechanism is realized. So, the moiety of the D-ester of phenylmethanesulphonate, obtained in benzene in presence of TEA is equal to 95%, of dimethylbensylamine - 57%, of Py - 44%.

The variation of alkane sulphonic chloride compositions shows that the moiety of the sulphene mechanism is dependent on the α-proton basicity and on the ability of the sulphene intermediate for stabilization similarly to the known reaction of alkane sulphonic chlorides.