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CHLORINE ISOTOPIC EXCHANGE AT SULPHUR IN SULPHONYL CHLORIDES. ACCELERATING EFFECT OF THE ORTHO-ALKYL GROUPS

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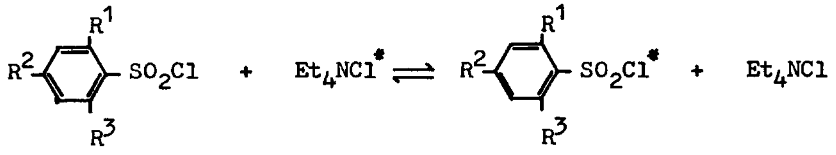
Recently there has been considerable interest shown in the mechanism of nucleophilic substitution at the sulphonyl sulphur atom[1]. Apart from the limited stereochemical[2], halogen-halogen exchange (Finkelstein reaction)[3] and ^{18}O tracer experiments[4], the vast majority of these studies have dealt with hydrolysis of sulphonyl halogenides[5].

We report here preliminary results on the chloride-radiochloride ion exchange between radioactive tetraethylammonium chloride and sulphonyl chlorides I - IV as well as a rather unexpected observation that the ortho-alkyl groups provide no steric hindrance during substitution at sulphonyl sulphur.



I, $R^1 = R^2 = R^3 = H$
II, $R^1 = R^3 = H$, $R^2 = Me$
III, $R^1 = R^2 = R^3 = Me$
IV, $R^1 = R^2 = R^3 = Pr^i$

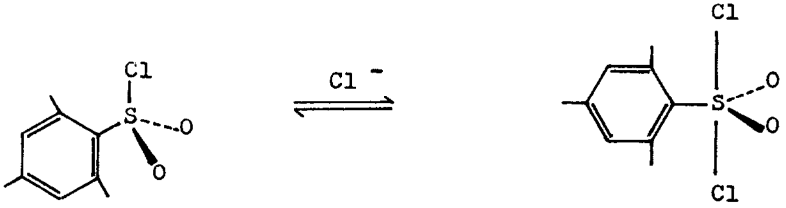
The isotopic exchange experiments were carried out in acetonitrile solution with reacting mixtures of 0.01M ammonium salt and 0.02M sulphonyl chloride. The reaction was initiated by very fast mixing of the solutions and stopped by refrigeration of the reaction mixture in liquid nitrogen. Separation of the two reactants was achieved by extraction using the water: carbon tetrachloride: methanol (1:5:0.2) system. The ^{36}Cl-activity of the water solution was counted with a liquid scintilation technique. With each sulphonyl chloride the exchange was studied at least at five temperatures in the range between -28°C ÷ 0°C. In a separate set of experiments with sulphonyl chlorides I and IV it was found that the exchange is the second-order reaction. The rate constants, energy and enthropy of activation are summarized in Table.

TABLE. Rate constants and activation paramethers for isotopic exchange between sulphonyl chlorides and $Et_4N^{36}Cl$

Sulphonyl Chloride	k·10 $l\cdot mol^{-1}\cdot sec^{-1}$	E $kcal\cdot mol^{-1}$	lg A	S $cal\cdot mol^{-1}\cdot deg^{-1}$
I	1.33 ± 0.04	14.4 ± 0.8	10.62 ± 0.32	- 11.8
II	0.67 ± 0.05	14.5 ± 1.1	10.44 ± 0.37	- 12.6
III	6.10 ± 0.26	12.4 ± 1.6	9.66 ± 0.53	- 16.1
IV	3.72 ± 0.06	12.8 ± 0.7	9.78 ± 0.18	- 15.6

$k = k_{ex}/a+b$; a and b - concentrations of the reactants.

Some years ago Bunnett and Bassett[6] have advanced the view that the steric hindrance by ortho methyl groups has no importance in nucleophilic displacement at sulphonyl sulphur. Our results clearly show that the presence of the ortho alkyl substituents in the benzene ring may accelerate nucleophilic substitution at the sulphonyl centre. This effect may be attributed to relief of steric interactions between alkyl groups and the sulphonyl oxygen atoms upon transformation of a tetrahedral sulphonyl structure into a trigonal bipyramidal intermediate.



For the exchange under discussion the most likely geometry of the latter is that with the two apical sulphur-chlorine bonds and the two sulphur-oxygen and sulphur-carbon bonds lying in a basal plane.

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