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RADIOSULPHUR STUDIES ON THE REARRANGEMENT OF PHENYLSULPHAMIC ACID TO SULPHANILIC ACID

W.J. Spillane and F.L. Scott
Department of Chemistry, University College, Cork,
Ireland.

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The migration from nitrogen to the aryl ring of the sulphonic acid group of phenylsulphamic acid on heating its salts in the solid state has been known for many years (1,2). Under strictly anhydrous conditions however, barium phenylsulphamate did not rearrange, while its dihydrate did (3).

More recently (4) the above rearrangement has been reported to take place to the extent of about 20% on heating potassium phenylsulphamate in the presence of an equimolar quantity of sulphuric acid in dry dioxane at 100°C for 55 hours. The only product isolated was sulphanilic acid. Migration to the ortho position has not been reported for either the solid or the liquid phase rearrangements of phenylsulphamates. The absence of orthanilic acid as a product of the rearrangement suggests an intermolecular mechanism for the conversion. We now present evidence to show that the rearrangement involves such a mechanism embodying a fast desulphonation of the sulphamate followed by a slow resulphonation in the para position of the ring.

When the rearrangement was carried out under the conditions described by Illuminati (4) (except that we used sealed glass ampoules as reaction vessels) but, employing S^{35}-labelled sulphuric acid, the sulphanilic acid isolated had an activity corresponding to approximately 50% exchange. When sulphanilic acid itself was subjected to similar conditions it was recovered in high yield (87%) and was found to be inactive, thus eliminating the possibility of exchange between the product of the rearrangement and the medium. Further, orthanilic acid could not be an intermediate in the rearrangement since it was recovered in good yield (and inactive) on being subjected to Illuminati's rearrangement conditions for 55 hours in equimolar radiolabelled acid.

The percentage (50%) incorporation of radiosulphur in the sulphanilic acid obtained from phenylsulphamic acid under Illuminati's conditions is then consistent with first desulphonation of the substituted sulphamate to form aniline and an additional equimolar quantity of sulphuric acid. This desulphonation dilutes by half the radiolabelled sulphuric acid with non-labelled acid. These two species are then involved (randomly and with a 50% incorporation of radiosulphur) in the sulphonation of the aniline present to yield sulphanilic acid.

The potassium phenylsulphamate and the anilinesulphonic acids were characterised by formation of their S-benzyl-thiouronium derivatives (5) and from a comparison of their infra-red spectra with the spectra of authentic samples of these compounds.

Table I records the specific activities (cpm/mmole) of the sulphanilic acid (isolated from the rearrangement), of the S-benzyl derivative of the same sulphanilic acid, of the orthanilic and sulphanilic acids isolated after subjection of these materials separately to rearrangement conditions and the aniline sulphate used to determine the activity of the sulphuric acid standard solution. The experimental percentage exchange is compared with that expected for complete intermolecular character.

TABLE I

Specific activities[a] of Products and Standards and the Comparison of the Experimental and the Theoretical Exchange

Compound[b]	Specific Activity (cpm/mmole)	% Exchange	
		Experimental	Theoretical
Sulphanilic Acid (from rearrangement)	2.91 x 10^5	50.5	50
S-Benzyl of Sulphanilic Acid (from rearrangement)	2.62 x 10^5	49.4	50
Sulphanilic Acid (under rearrangement conditions)	0		
Orthanilic Acid (under rearrangement conditions)	0		
Aniline Sulphate[c]	5.75 x 10^5		

[a] Radioactive assays were carried out in a Nuclear-Chicago model D47Q gas-flow counter with a ''Micromil'' window, on samples of finite thickness with appropriate corrections for efficiency and self-absorption; [b] all substances were recrystallised from water (or 50% ethanol in the case of the S-benzyl derivative) to constant activity; [c] the activity of the sulphuric acid stock solution was determined by the formation (in ethanol), from two moles of aniline and one mole of the acid, of aniline sulphate in quantitative yield.

A further series of experiments were performed to throw light on the rearrangement. In these we again used the conditions described by Illuminati, namely, dry dioxane as solvent, a reaction temperature of 100°C and equimolar quantities of the two reagents, potassium phenylsulphamate and this time non-labelled concentrated sulphuric acid. In these runs pairs of ampoules were subjected to the rearrangement conditions for different periods of time. After the allotted time, one member of each pair was worked up and the total sulphate content present analysed as barium sulphate; the other member was analysed for the quantity of sulphanilic acid present using the procedure of Illuminati.

The results of these experiment were as follows : (i) potassium phenylsulphamate under the reaction conditions was completely hydrolysed in 15 minutes to aniline sulphate; (ii) after 14 hours, the reaction afforded 4.0% sulphanilic acid and 96.0% of aniline sulphate, and (iii) after 55 hours, 20% sulphanilic acid was obtained and 78% aniline sulphate. Evidently, under the conditions used by Illuminati, the rearrangement takes place in two distinct stages: first rapid hydrolysis of the potassium phenylsulphamate followed by a slow sulphonation reaction.

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REFERENCES

(1) E. Bamberger and E. Hindermann, Ber. 30, 654, (1897)

(2) A. Seyewets and Bloch, Bull. soc. chim. (4), 1, 320, (1907)

(3) E.R. Alexander, J.Am.Chem.Soc. 70, 1274, (1948)

(4) G. Illuminati, J.Am.Chem.Soc. 78, 2603, (1956)

(5) Organic Reagents for Organic Analysis, Hopkin and Williams Ltd., Chadwell Heath, Essex, England. (1956).