

466. *Carbon-Sulphur Fission in Thioethers. Part VII.* Kinetics and Mechanism of the Carbanion-Sulphenium Fission in Thioethers.*

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The rates of alkaline hydrolysis of (α -benzoylbenzylthio)acetic acid (I) and β -(4-nitrobenzylthio)propionic acid have been measured. The rate of disappearance of the latter was of the first order, and the reactions are considered to occur by a bimolecular mechanism. A competitive experiment between the above acetic acid and the corresponding 4-nitrobenzylthio-derivative showed that the former reacted much the faster.

It has been concluded from the qualitative studies in Parts I—VI of this series that alkaline hydrolysis of the thioethers (sulphides) studied proceeds by the nucleophilic attack of the hydroxyl ion on the sulphur atom where the C-S bond is conjugated with a carbonyl or a nitro-group. Support for this conclusion was sought by a quantitative investigation. The rates of the hydrolyses were followed at different concentrations of alkali.

Compounds were employed in which the C-S fission occurs without complications such as "benzoyl" elimination, enolisation, or α -proton-extraction. Examples of the straightforward reactions of this series are those leading to the formation of methane derivatives ($RSZ + H_2O \longrightarrow RH + Z \cdot S \cdot OH$) or to 4,4'-diformylazoxybenzene formed by rearrangement of the 4-nitrobenzyl anion more rapidly than it extracts a proton from the solvent to give the methane derivative. One compound from each of these two classes was chosen. The first was (α -benzoylbenzylthio)acetic acid (I) which gives deoxybenzoin, in almost a quantitative yield, and carboxymethanesulphenic acid which is transformed in the alkaline medium into glyoxylic acid and sodium sulphide.¹ The rate of this reaction was followed by the determination of the sulphide ion liberated. The second compound chosen was β -(4-nitrobenzylthio)propionic acid (II) which gives a quantitative yield of 4,4'-diformylazoxybenzene (III) and the sulphenic acid which does not decompose to give a sulphide ion in solution but changes to the stable disulphide;² no products consuming alkali are formed in the reaction. The corresponding α -(*p*-nitrobenzylthio)acetic acid (IV) was not chosen because it gives a sulphide ion [in the same way as (I)] which reduces the azoxyaldehyde (III) to 4,4'-diformylazobenzene and the product will therefore contain a mixture of the two aldehydes. A competitive experiment, however, was carried with equivalent amounts of acids (I) and (IV), and one equivalent only of the alkali, to examine the difference in the electron-attractive influences of their radicals

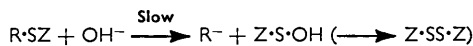
From the present and earlier results it is likely that the reactions proceed by a

* Part VI, preceding paper.

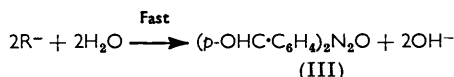
¹ Schöberl, *Annalen*, 1933, 507, 111.

² Iskander and Riad, *J.*, 1951, 2054.

bimolecular mechanism. The reactions are specific to alkali and do not occur in aqueous-alcoholic ³ acid. Increase in the concentration of the alkali increases the rate of the reaction. The reaction between the acid (II) and alkali is of the first order (cf. Table), since the alkali concentration remains constant throughout the reaction. Since one molecule only of the acid is involved in the rate-determining stage, this is probably the first one:

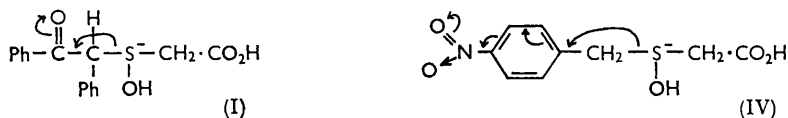


followed by



Experiment (a) (cf. the Experimental part) was designed to trap the anion, before rearrangement, with acetaldehyde or acetone but this failed.

The competitive experiment (b) shows that, although the nitro-group is more strongly electron-attracting than the carbonyl group, acid (I) undergoes C-S fission faster than acid (IV):



This is probably because conjugation through the benzene ring necessitates a higher energy.

Experiment (c) may be explained in the same way: while the acid (I) easily undergoes C-S fission by NaSH or Na₂S, the acid (IV) is not hydrolysed by these reagents.

EXPERIMENTAL

(α -Benzoylbenzylthio)acetic acid (I) (0.01M) was allowed to react with alkali (2, 3, or 4 equiv.) at 30°. The sulphide ion liberated was estimated by a new, simple, accurate procedure: 5 ml. of the reaction mixture were added to 10 ml. 0.01N-silver nitrate acidified with 10 ml. of 0.02N-sulphuric acid, the end of the pipette being dipped under the surface of the solution; the solution was left overnight, then filtered from the silver sulphide with rinsing, and 10 ml. of 0.01N-potassium chloride solution were added; chloride ion was determined by a sensitive electrometric method.⁴ The infinity reading never required 10 ml. of 0.01N-silver nitrate. With 4 equiv. of alkali it was only 7.6 ml., with 3 equiv. of alkali it decreased to 6.85 ml.; and with 2 equiv. of alkali it was noticed that as the reaction proceeded the maximum value was 5.55 ml. which began to decrease until the infinity value became 3.65 ml. (these results could not therefore be used in the determination of the order of the reaction). This indicates that the sulphide ions began to act as the nucleophilic reagent. To test this, the reaction was carried out by using disodium sulphide or sodium hydrogen sulphide instead of the alkali:

(i) The acid (I) (1 g.) was treated with aqueous sodium sulphide (prepared from 0.32 g. of sodium in absolute alcohol as usual, by saturating one-half of the sodium ethoxide solution with hydrogen sulphide, adding this to the other half of the ethoxide solution, evaporation of the alcohol, and dissolving the residue in 50 ml. of water). The mixture was boiled on the water-bath for 30 min. The turbid solution, on cooling, precipitated deoxybenzoin (about 0.5 g.). The filtrate, on acidification gave hydrogen sulphide and free sulphur.

(ii) The acid (1 g.) was boiled with aqueous sodium hydrogen sulphide (prepared from 0.16 g. of sodium metal, as above); the same result was obtained.

The second compound β -(*p*-nitrobenzylthio)propionic acid (II) was subjected to the action of two different concentrations of alkali at 30° and at 40°. Every reading was taken from a separate experiment because the *p*-azoxy-aldehyde cannot be suspended homogeneously in a stock reaction mixture. Satisfactory results (see Table) were obtained gravimetrically by using relatively high concentrations to minimise the errors in weighing.

³ Iskander, *J.*, 1948, 1549.

⁴ Best, *J. Agric. Sci.*, 1929, **19**, 533.

Temp.	Acid (II)	OH-	Reaction (%) at (min.)				10 ³ k ₁ (min. ⁻¹)	
	(M)	(M)	10	30	60	120		
30°	0.2	0.2	6.8	20.1	40.2	64.2	81.5	8
30	0.2	0.4		43.4	62.8	100		
40	0.2	0.2	19.5	49.5	72.9			22

The activation energy was calculated to be 19 kcal. mole⁻¹.

In all the above experiments duplicate runs were carried out; the values so obtained were almost the same as the recorded ones.

Further Qualitative Experiments.—(a) Alkaline hydrolysis of (*p*-nitrobenzylthio)acetic acid (IV) in the presence of a few ml. of acetaldehyde did not proceed as usual,⁵ but in the presence of acetone reaction occurred with the precipitation of the *p*-azo-aldehyde.⁵

(b) Heating equimolecular amounts of compounds (I) and (IV) with one equivalent only of sodium hydroxide resulted in the precipitation of deoxybenzoin in nearly a quantitative yield, but contaminated with a trace of a brown substance. The filtrate, on acidification, liberated hydrogen sulphide and a brown acid mixture which on extraction with carbon tetrachloride gave some unchanged acid (IV); the brown acid residue which was insoluble in the carbon tetrachloride contained nitrogen and sulphur.

(c) Unlike acid (I), the acid (IV) was not hydrolysed with disodium sulphide or sodium hydrogen sulphide but the product was a brown acid containing nitrogen and sulphur.

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⁵ Schönberg and Iskander, *J.*, 1942, 90.