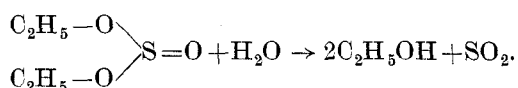


# POSITION OF BOND FISSION DURING HYDROLYSIS OF DIETHYL SULPHITE IN WATER UNDER ACIDIC AND ALKALINE CONDITIONS\*

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The position of bond fission during the acidic hydrolysis of diethyl sulphite in water has been studied, using oxygen-18 as a tracer, by Bunton, de la Mare, and Tillett (1959). Under the experimental conditions used, complete hydrolysis occurred, according to the equation,



The ethanol isolated showed an apparent oxygen-18 atom percentage in excess which could be taken to indicate up to 15% alkyl-oxygen fission for *one* alkyl group. These authors, however, attribute the excess oxygen-18 in the sample analysed, to the incomplete removal of oxygen-18 water before analysis and assume that only sulphur-oxygen fission occurs. However, no evidence is produced to support this assumption.

If alkyl-oxygen fission occurs to a small extent during the first-stage acid catalysed hydrolysis of diethyl sulphite, it seems unlikely that it would occur during the second-stage hydrolysis because the mechanism of the second-stage hydrolysis would probably involve sulphur-oxygen fission judging from the behaviour of the nearest related compounds, the alkyl sulphates. First-stage hydrolysis of dialkyl sulphates involves 100% alkyl-oxygen fission (Lauder, Wilson, and Zerner 1961) but the second-stage acid-catalysed hydrolysis reaction occurs via sulphur-oxygen fission alone (unpublished work with Mr. B. D. Batts). Hence the observation of excess oxygen-18 in the product alcohol from acidic hydrolysis of diethyl sulphite should be considered as possibly arising from alkyl-oxygen fission during first-stage hydrolysis only.

The hydrolysis of dimethyl sulphite under alkaline conditions has been studied by Tillett (1960). Complete hydrolysis occurred under the reaction conditions. The methanol isolated showed an apparent oxygen-18 atom percentage in excess which could indicate up to 20% alkyl-oxygen fission for *one* alkyl group. However, Tillett assumes that oxygen-18 water was incompletely removed from the alcohol before analysis and that reaction occurs by sulphur-oxygen fission only.

Anbar *et al.* (1954) have studied the position of bond fission during alkaline hydrolysis of a number of esters of inorganic oxy-acids. The position of bond fission is related to the acid strength of the inorganic acid and to the electro-

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positive character of the alkyl group. In general esters of strong oxy-acids hydrolyse by alkyl-oxygen fission (mechanism 1) while esters of the weaker acids hydrolyse by fission of the O—X bond (mechanism 2), where X is the central atom of the inorganic group, e.g. the alkaline hydrolysis of t-butyl nitrate occurs by mechanism 1, that of n-butyl nitrate by a mixed mechanism, 1 and 2, while n-butyl nitrite hydrolyses by mechanism 2. These results suggested that the uncertainty in the oxygen-18 tracer studies with the dialkyl sulphites mentioned above was too large to be left unchecked and for this reason we have investigated the position of bond fission during acidic and alkaline hydrolysis of diethyl sulphite using oxygen-18 as a tracer.

Diethyl sulphite was dried (anhydrous sodium sulphate) and distilled twice at atmospheric pressure. A middle fraction was collected, b.p. 157–158 °C/759 mmHg,  $n_D^{25.2}$  1.4129 (lit. data b.p. 157 °C/763 mmHg,  $n_D^{20}$  1.4144 (Vogel and Cowan 1943)).

#### *Acidic Hydrolysis*

Diethyl sulphite (5 m-moles) was added to water (10 ml), atom % oxygen-18, 0.700, and made 3N in perchloric acid. After 17 hr at 35 °C the solution was neutralized with a slight excess of anhydrous sodium carbonate. The solution was degassed to remove carbon dioxide and sulphur dioxide. The alcohol was then isolated and analysed mass spectrometrically using techniques developed in this laboratory. References are given in the paper by Adam, Lauder, and Stimson (1962). Duplicate results indicated 99.84 and 100.00% sulphur-oxygen fission.

#### *Alkaline Hydrolysis*

Sufficient sodium metal was added to water (10 ml), atom % oxygen-18, 0.700, to make the solution 2N in sodium hydroxide and then diethyl sulphite (5 mm) was added. After 20 hr at 35 °C, during which time complete hydrolysis occurred, the solution was degassed. The alcohol was isolated and analysed mass spectrometrically. Duplicate results showed 99.98 and 100.00% sulphur-oxygen fission.

It is probable that dimethyl sulphite shows the same type of behaviour as diethyl sulphite and thus the present work removes any possible doubt about the interpretation of the kinetic data by Bunton, de la Mare, and Tillett (1959) and by Tillett (1960), who assumed the result we have demonstrated.

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