237. 2 : 2′ : 4 : 4′-*Tetranitrodiphenyl Sulphoxide and* 2 : 2′ : 4 : 4′-*Tetranitrodiphenyl Sulphone.*

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The substance, m. p. 241°, obtained by oxidation of 2 : 2′ : 4 : 4′-tetranitrodiphenyl sulphide is stated in the literature to be the corresponding sulphone. It is now shown to be the sulphoxide. The corresponding sulphone, m. p. 175°, has been prepared, both by direct oxidation of the sulphide and by further oxidation of the sulphoxide.

It is well known that diaryl sulphides may be oxidised successively to the corresponding sulphoxides and sulphones, by, *e.g.*, hydrogen peroxide or chromium trioxide in acetic acid or by fuming nitric acid. The ease of oxidation depends on the number and nature of the substituent groups in the aromatic nuclei, and Blanksma (*Rec. Trav. chim.*, 1901, **20**, 425) reports that dipicryl sulphide resists nitric acid (*d* 1·52) at 200°.

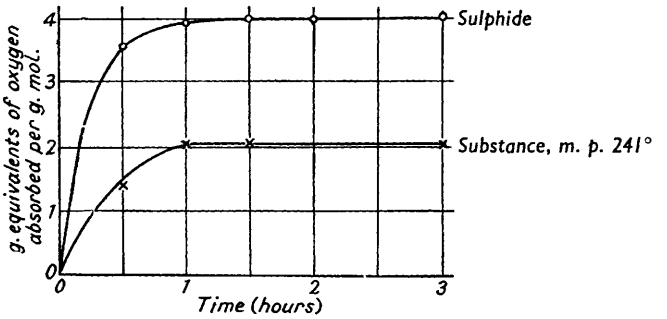
Beilstein and Kurbatow (*Annalen*, 1879, **197**, 75) heated 2 : 2′ : 4 : 4′-tetranitrodiphenyl sulphide for 6 hours with nitric acid (*d* 1·52) in a sealed tube at low pressure and isolated a pale yellow product, m. p. 241°. This they concluded was the sulphone, undeterred by a discrepancy of 10% in the sulphur analysis. Blanksma (*loc. cit.*) obtained the " sulphone," m. p. 240°, from the sulphide by using chromium trioxide in acetic acid; the analysis does not support his conclusion that this substance is the sulphone, for by arithmetical error the calculated percentage of sulphur is given as 8·25% instead of 8·04%; he found 8·28%, which agrees much more closely with the value for the sulphoxide.

From the behaviour of dipicryl sulphide cited above, it appeared to us that the product of m. p. 241° could be the sulphoxide. When the sulphide was refluxed with a very large excess of chromium trioxide in glacial acetic acid for at least 6 hours, an almost white neutral substance of m. p. 175° was obtained in good yield. This resists further oxidation even by potassium dichromate in concentrated sulphuric acid, and may be conveniently

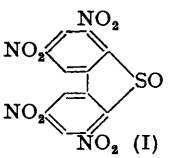
and rapidly prepared directly from the sulphide by means of this reagent. Oxidation of the product, m. p. 241°, by either of these methods also yields that of m. p. 175°.

Sulphur analyses indicate that the products of m. p. 241° and 175° are respectively the sulphoxide and sulphone, and this is supported by the following quantitative oxidations.

A 1% solution of potassium dichromate in 80 : 100 (v/v) sulphuric acid–water can be boiled for a long period with negligible loss of oxidising power and the rate of attack by the boiling reagent on the sulphone is extremely slow. This afforded a basis for quantitative oxidation of the sulphide and the product, m. p. 241°; control blanks contained the same volume of oxidising solution, together with an amount of product, m. p. 175°, equal to that which would finally be formed by oxidation. The results are shown in the Figure, those for the product of m. p. 241° being based on its being the sulphoxide. For all points lying on the horizontal parts of the curves, the final product had m. p. 175°. Our contention is thus proved, except for a slight possibility that the final product might be a cyclised sulphoxide (I).



Attempts to synthesise the sulphone by an unequivocal method proved unsuccessful, but the material of m. p. 175° underwent " sulphone exchange " (Louden, *J.*, 1935, 537) with sodium toluene-*p*-sulphinate, yielding 2 : 4-dinitrophenyl *p*-tolyl sulphone. This alone does not prove that the substance is a sulphone, since an identical product is obtained, though with greater difficulty, from sodium toluene-*p*-sulphinate and the product of m. p. 241°, which suggests nucleophilic attack by the sulphinate ion on the $C_{(1)}$ in both cases, the sulphonyl group in the resultant unsymmetrical sulphone originating from the attacking sulphinate ion. It does, however, exclude the cyclised sulphoxide structure (I).



(I)

Our identification of the product, m. p. 241°, is at variance with the results of Hodgson and Dodgson (*J.*, 1948, 1002) who claim to have prepared the sulphoxide, m. p. 190°, by the action of nitric acid (*d* 1·52) on the sulphide at room temperature for an hour. We find that this method invariably yields mainly the product, m. p. 241°, with a very small amount of alcohol-soluble material, m. p. 180—190°, possibly a mixture of sulphide and sulphoxide.

Experimental

2 : 2′ : 4 : 4′-Tetranitrodiphenyl sulphide was prepared by Twiss's method (*J.*, 1914, **105**, 1678) and was freed from disulphide by recrystallisation from glacial acetic acid. The pure sulphide had m. p. 196° (Found : S, 8·7; 8·8. Calc. for $C_{12}H_6O_8N_4S$: S, 8·7%).

2 : 2′ : 4 : 4′-*Tetranitrodiphenyl Sulphoxide.*—(*a*) *Hydrogen peroxide oxidation.* 2 : 2′ : 4 : 4′-Tetranitrodiphenyl sulphide (2·0 g.) was boiled in glacial acetic acid (50 ml.) under reflux, while hydrogen peroxide (25 ml.; 100-vol.) was added during 1 hour. On cooling, very pale yellow prisms separated and, recrystallized from acetone, had m. p. 241° (yield, almost 100%).

(*b*) *Nitric acid oxidation.* The sulphide (10 g.) was slowly added to cold nitric acid (*d* 1·52; 25 ml.). On warming, the sulphide dissolved. The solution was refluxed for 2 hours, cooled, and poured into a large bulk of ice-water; the precipitate, washed free from acid and recrystallized from acetone, had m. p. 241° (Found : S, 8·3, 8·4. Calc. for $C_{12}H_6O_9N_4S$: 8·4%).

2 : 2′ : 4 : 4′-*Tetranitrodiphenyl Sulphone.*—(*a*) *Chromium trioxide oxidation of the sulphide.* To a boiling solution of the sulphide (5·0 g.) in glacial acetic acid (150 ml.) chromium trioxide

(20 g.) was added in small portions. Refluxing was continued for 6 hours, and the solution poured into a large bulk of water; the precipitate, washed free from chromium compounds and recrystallized from aqueous acetone, had m. p. 174—175°.

(*b*) *Dichromate–sulphuric acid oxidation of the sulphide.* The sulphide (2 g.) was added to sulphuric acid (*d* 1·84; 10 ml.), potassium dichromate (2 g.), and water (2 ml.). The whole was warmed to *ca.* 120° and kept thereat for 20 min. with frequent shaking. On cooling and pouring of the mixture into ice-water the *sulphone* separated in fine crystalline form, was washed free from chromium salts, and recrystallized from aqueous acetone; it had m. p. 174—175° (yield, almost 100%) (Found : S, 8·05, 8·1. $C_{12}H_6O_{10}N_4S$ requires S, 8·0%). It is insoluble in water, sparingly soluble in acetic acid, readily soluble in acetone, and easily decomposed by alkali.

Quantitative Oxidation of Sulphide and Sulphoxide.—Very finely powdered sulphide (0·183 g., 0·0005 mole) or sulphoxide (0·191 g., 0·0005 mole) was refluxed in all an-glass apparatus with 25 ml. of a solution of potassium dichromate in aqueous sulphuric acid [10 g. of potassium dichromate, 555 ml. of water and 444 ml. of sulphuric acid (*d* 1·84)] with frequent shaking, for 0·5—3 hours. Control solutions of sulphone (0·199 g., 0·0005 mole) in 25 ml. of the dichromate–sulphuric acid were refluxed for the corresponding periods, at the end of which both test and control solutions were diluted with water to about 150 ml. and the residual dichromate was determined with potassium iodide and thiosulphate.

The solid precipitated from the test portions was recovered and crystallized from aqueous acetone. Except in the case of the half-hour period where oxidation was visibly incomplete, the product had m. p. 174—175°.

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