

914. *Oxidation of Organic Sulphides. Part IX.* The Reaction of Ozone with Organic Sulphur Compounds.†*

By D. BARNARD.

Organic monosulphides are oxidised by somewhat less than the theoretical amount of ozone, to give high yields of the respective sulphone *via* the sulphoxide. Disulphides undergo a more complex reaction, giving the sulphonic anhydride as the major product and smaller amounts of thiol-sulphonate and disulphone. Tetrasulphides also give sulphonic anhydride in high yield, together with sulphur dioxide. Reaction mechanisms are suggested based upon ozone-absorption measurements, the effect of ozone on related sulphur compounds, and rate data derived from competitive ozonolyses.

OZONOLYTIC degradation of natural rubber and related polymers is generally attributed to the interaction of ozone with the double bonds of the polyisoprenic chains. Where rubber has been vulcanised with sulphur, other potential sites of attack are available to the ozone, namely, the cross-links formed in the vulcanisation process and composed of chains of from one to five sulphur atoms. This work describes the reactions of ozone with such groups in model mono-, di-, and poly-sulphides and some related compounds.

The experimental procedure was to pass an accurately controlled stream of ozonised

FIG. 1. Ozonolysis of (a) carbon tetrachloride (50 ml.) and (b) di-*n*-butyl sulphide (2 g.) in carbon tetrachloride.

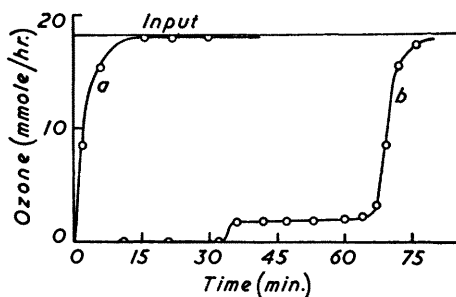
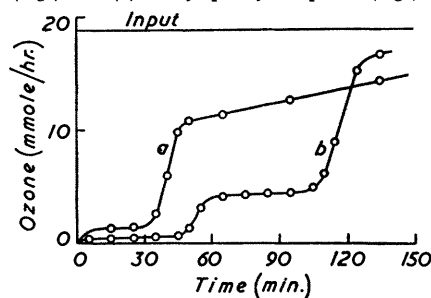


FIG. 2. Ozonolysis of (a) diphenyl sulphide (2 g.) and (b) methyl phenyl sulphide (2 g.).



oxygen (*ca.* 0.3 mmole of ozone/min.) through a 1–3% solution of the compound at -25° in a reaction vessel similar to that described by Boer and Kooyman.¹ Carbon tetrachloride or, where a more polar solvent was necessary, carbon tetrachloride–nitromethane (1:3 v/v) were satisfactory solvents, allowing 98–99% of the ozone to pass through unchanged with no solute present. By periodic analysis of the exit gas stream an uptake curve was plotted from which the absorption of ozone could be derived with an accuracy of *ca.* $\pm 3\%$, as determined by calibration with pure olefins. Large differences in rates of ozonolysis were visible from these curves but the determination of relative rates, where possible, had to be made by a competitive method. Product analyses were performed either at the end or at intermediate stages of the ozonolysis.

Monosulphides.—Monosulphides are oxidised to sulphones by an excess of ozone.² Uptake curves for some representative examples are given in Figs. 1 and 2. The yield of sulphones was 90–100%, traces of the appropriate aldehyde and acid indicating some concomitant C–S bond fission. The uptake curves show that oxidation occurs in two

* Part VIII, Bateman, Cunneen, and Ford, *J.*, 1957, 1539.

† Presented, in part, at the 14th Internat. Congr., Union Pure Appl. Chem., Zürich, 1955.

¹ Boer and Kooyman, *Analyt. Chim. Acta*, 1951, **5**, 550.

² Böhme and Fischer, *Ber.*, 1942, **75**, 1310.

well-defined stages to give, first, the sulphoxide and then the sulphone. By using a flowing cell device³ to follow the ozonolysis of *cyclohexyl methyl sulphide* by infrared spectroscopy, at least 98–99% of the sulphide was found to be converted into sulphoxide before any sulphone was detected, indicating a minimum factor of 50–100 between the rates of the two stages. The reactivity of the sulphides decreases with the introduction of aryl groups: diphenyl sulphoxide is so resistant to further oxidation that it is difficult to obtain diphenyl sulphone free from sulphoxide (Böhme and Fischer² record similar behaviour with chloromethyl ethyl sulphide). These observations are in accord with considerations of electron-availability at the sulphur atom. Competitive ozonolyses indicated that oct-1-ene reacts with ozone at least 50 times more rapidly than does di-*n*-butyl sulphide which was the most easily oxidised of the sulphides investigated.

The reaction



was found not to be quantitatively followed, less than the theoretical amount of ozone being required for a virtually quantitative yield of sulphone. Table 1, in which the

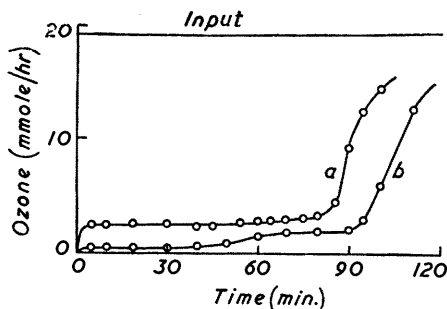


FIG. 3. Ozonolysis of (a) diphenyl disulphide (2 g.) and (b) di-*n*-butyl disulphide (2 g.).

sulphides are arranged in descending order of their rates of ozonolysis, shows that the most easily oxidised sulphides require the least ozone. As the sulphides are normally inert to molecular oxygen, ozone must either catalyse their oxidation by oxygen or give rise, after the loss of an oxygen atom, to activated oxygen molecules some of which, depending on the oxidisability of the sulphide, themselves participate in the oxidation of sulphide or sulphoxide.

TABLE 1. *Ozone required for sulphone formation.*

Sulphide	Ozone (mol.)	Sulphide	Ozone (mol.)
Di- <i>n</i> -butyl	1.40	Dibenzyl	1.75
<i>cycloHexyl methyl</i>	1.53	Methyl phenyl	1.85
2-Ethyl-2-methyl-5-isopropylthiophan	1.70	Diphenyl	1.03 *

* To sulphoxide.

Disulphides.—By analogy with the oxidation of monosulphides, disulphides would be expected to yield successively thiol sulphinate, $R\cdot SO_2\cdot S\cdot R$, thiol sulphonate, $R\cdot SO_2\cdot S\cdot R$, or disulphoxide, $R\cdot SO\cdot SO\cdot R$, and disulphone, $R\cdot SO_2\cdot SO_2\cdot R$. Ozone-uptake curves (cf. Fig. 3) did not reveal such stepwise reaction and indicated, for "normal" disulphides, the absorption of a 2.5–3 mols. of ozone (cf. Table 2). The crude products contained *ca.* 5 oxygen atoms for each original disulphide molecule and dissolved almost completely in water to give the corresponding sulphonic acid. Their infrared spectra showed the initial absence of hydroxyl groups, but strong absorption at *ca.* 1400 and 1190 $cm.^{-1}$ suggested the presence of the $R\cdot SO_2\cdot O$ group, and the identity of the major products as a sulphonic anhydride, $R\cdot SO_2\cdot O\cdot SO_2\cdot R$, was confirmed by their isolation. Yields of the anhydrides were conveniently measured by the titration of the acids produced on

³ Higgins, unpublished work.

hydrolysis or by the comparison of the intensity of either of the above infrared absorption bands with calibration curves. For the small-scale preparation of sulphonic anhydrides ozonolysis of the appropriate disulphide appears to compare favourably with other methods available.⁴

Neutral products (after removal of the sulphonic anhydride) were purified chromatographically and shown to consist of the corresponding thiolsulphonate with traces of disulphone and unidentified material.

Dibenzyl disulphide gave no sulphonic anhydride: sulphur dioxide, sulphuric acid, benzaldehyde, and benzoic acid were identified as products. Dimethyl disulphide was also atypical in that methyl methanethiolsulphonate, and not methanesulphonic anhydride, was the major product.

TABLE 2. *Products of ozonolysis of disulphides, R₂S₂.*

R	O ₃ absorbed (mols.)	Sulphonic anhydride (%)	Thiol-sulphonate (%)	R	O ₃ absorbed (mols.)	Sulphonic anhydride (%)	Thiol-sulphonate (%)
Ph	2.6	90	6	Me	2.0	39	ca. 50
<i>p</i> -Cl·C ₆ H ₄ ...	2.9	84	10	CH ₂ Ph	5	—	—
Bu ⁿ	2.6	80	ca. 10				

The ozonolysis of diphenyl disulphide was examined in greater detail. It was significant that *ca.* 3 molecules of ozone supply 5 atoms of oxygen; thus the reaction probably involves at least three steps, an ozone molecule being incorporated in one step with normal donation of oxygen to sulphur in the others. In agreement with this phenyl benzenethiolsulphinic acid, in which one sulphur atom has already acquired an oxygen atom, gave a high yield (87%) of benzenesulphonic anhydride when ozonised, each molecule receiving a further 4 oxygen atoms from *ca.* 2 molecules of ozone. Other thiolsulphinates behaved similarly. Nevertheless, thiolsulphinic acid is not an intermediate in the formation of sulphonic anhydride.

When diphenyl disulphide was treated with, for example two-fifths of the ozone required for complete conversion into sulphonic anhydride an intermediate containing two oxygen atoms per molecule was not found and only the normal products of complete ozonolysis of almost exactly two-fifths of the disulphide were identified. This suggests that the initial attack of ozone on the disulphide must be the slowest step of the overall reaction. It was shown that thiolsulphinic acid reacts with ozone at only two-thirds of the rate of the disulphide and since it could never be detected amongst the products of partial ozonolysis, although control experiments indicated that it was stable enough to survive the isolation procedure, it follows that it is not formed in significant amount by the oxidation of disulphide. Table 3 illustrates the results of differing degrees of ozonolysis of diphenyl

TABLE 3. *Partial ozonolysis of diphenyl disulphide.*

Ozonolysis (%)	Disulphide recovered (%)	Yield of sulphonic anhydride (%)	Yield of thiol-sulphonate (%)	Ozonolysis (%)	Disulphide recovered (%)	Yield of sulphonic anhydride (%)	Yield of thiol-sulphonate (%)
29	63	48	32	49	49	73	15
36	55	55	20	86	16	80	—
41	58	61	21	100	—	90	6
44	54	67	20				

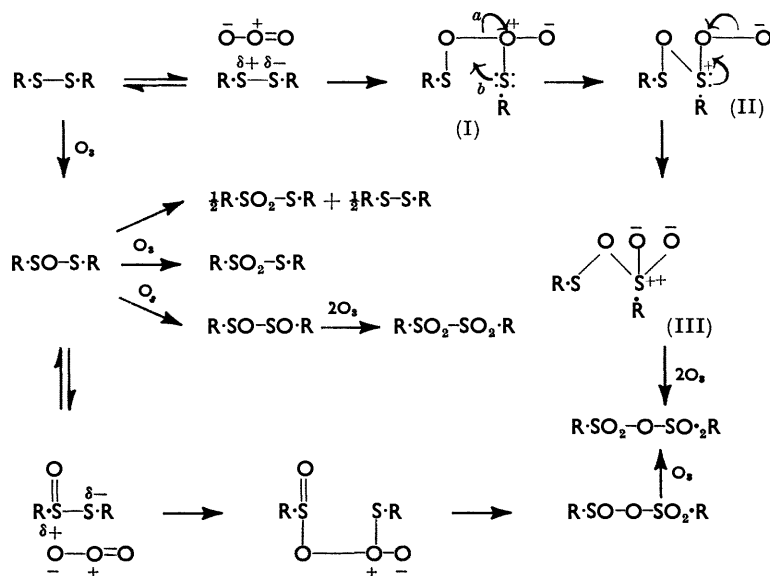
disulphide. At the lower extents of reaction the yield of thiolsulphonate is increased at the expense of sulphonic anhydride. This implies that virtually all the thiolsulphonate is formed at the onset of ozonolysis, the reason for which is not apparent. Wibaut and his co-workers⁵ have found that Lewis acids catalyse the reaction of ozone with benzene

⁴ Billeter, *Ber.*, 1905, **38**, 2015; Shepherd, *J. Org. Chem.*, 1947, **12**, 275; Field, *J. Amer. Chem. Soc.*, 1952, **74**, 394; Field and Settlege, *ibid.*, 1954, **76**, 1222; Owen and Whitelaw, *J.*, 1953, 3723; Standard Oil Co., B.P. 672,640.

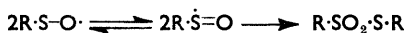
⁵ Wibaut, Sixma, Kampschmidt, and Boer, *Rec. Trav. chim.*, 1950, **69**, 1355.

and other aromatic hydrocarbons and it is possible that sulphonic anhydride formation becomes increasingly favoured as the reaction proceeds by the catalytic influence of the small amounts of sulphonic or sulphuric acids invariably present. Thiolsulphonate was shown to be inert to ozone under the reaction conditions, presumably owing to the electron-attracting effect of the sulphone group on the unoxidised sulphur atom. A formally similar deactivation was observed in thiol-esters. Thiolsulphonate added initially to disulphide was recovered completely after ozonolysis, together with the normal yield of thiolsulphonate and sulphonic anhydride from the disulphide, indicating that it did not participate in any stage of the reaction.

The reaction sequence in the annexed scheme appears to explain the known facts and bears a formal resemblance to the mechanism of ozonisation of olefins formulated by Criegee.⁶ The disulphide, polarised by the approaching reagent, adds to an ozone molecule to give (I) which by rapid rearrangement yields (II) and (III), the last product being oxidised by a further 2 mols. of ozone (in view of the results with monosulphides only



1.6—1.8 mols. would probably be required) to the final product. The electron switches *a* and *b* in (I) are envisaged as sequential, the driving force for *b* being the great electron-affinity of the momentarily positively charged oxygen atom left by *a*. If the O—O bond cleavage were in part homolytic the R·S·O· radicals so formed could be the source of the thiolsulphonate since it has been shown⁷ that this type of radical left after the abstraction of chlorine by zinc from sulphanyl chlorides readily undergoes the reaction



The accompanying R·SO₂· radical could conceivably give rise to the small amounts of disulphone formed. Alternative sources of thiolsulphonate and disulphone are the disproportionation and asymmetrical or symmetrical oxidation of thiolsulphinate. However, the similarity of the yields of thiolsulphonate from ozonolysis of disulphide and thiolsulphinate would demand that almost the whole of the disulphide would have to react *via* the thiolsulphinate, and this, as has been shown, is not acceptable. The formation of sulphonic anhydride from (III) demands ready oxidation of the grouping R·S·O·. That

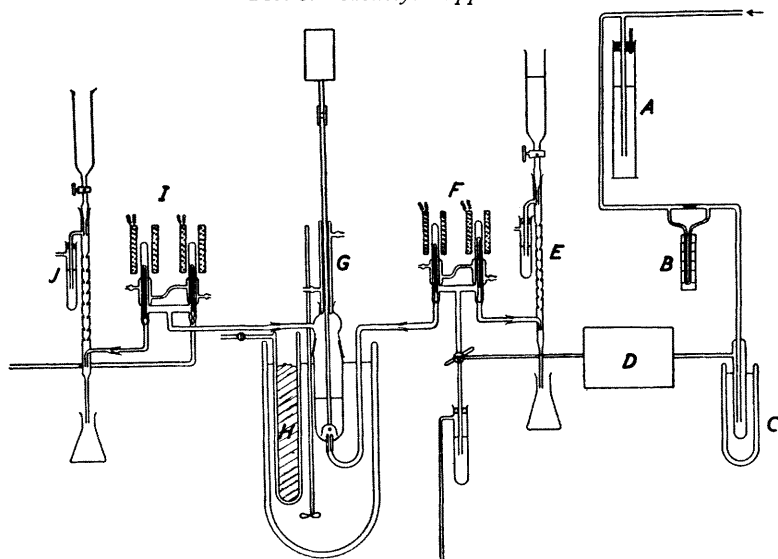
⁶ Criegee, 120th Meeting Amer. Chem. Soc., Sept., 1951.

⁷ Barnard, unpublished work.

cross-links in vulcanised rubber can be regarded as unimportant compared with the degradation of the rubber trunk chains.

EXPERIMENTAL

Fig. 5 illustrates the apparatus used. Oxygen from a cylinder passed through a chromic acid bubbler (not shown) to the pressure regulator *A* (filled with sulphuric acid), flowmeter *B*, and liquid-oxygen cooled trap *C* before reaching the silent-discharge ozoniser *D* which produced *ca.* 0.3 mmole of ozone per min. with a gas flow of 8 l./hr. The ozone stream could be led to the atmosphere, the analyser ¹ *E*, or the reaction vessel *via* a three-way tap and the solenoid-operated, all-glass valve system *F*, the hydrostatic pressure head being adjusted in each case to maintain a constant flow. The valves were switched either manually or by a timer unit which accurately switched the gas stream between the reaction vessel and analyser (in cycles of 3 min. : 10 sec.) and were water-cooled. From the ozone estimated in the analyser the input of ozone to the reaction vessel during a given time could be calculated with the minimum of error

FIG. 5. *Ozonolysis apparatus.*FIG. 6. *Vacuum-crystallisation apparatus.*

due to variations in the rate of ozone production. However, with the ozoniser in thermal equilibrium and with careful control of flow rates such variations were negligible ($\pm 1.5\%$) during a run of average duration ($\frac{1}{2}$ —2 hr.). The precision-bore stirrer *G*, lubricated with Silicone oil, proved to be gas-tight under the small pressure differentials used, and the unsilvered Dewar flask *H*, filled with crushed, solid carbon dioxide, could be partially evacuated to maintain the ethanol (4 l.) in the large Dewar vessel at $-25^\circ \pm 0.5^\circ$ for several hours. The exit gas stream was led to ozone analysers *J* and *K* (not shown) *via* a second valve system *I* also controlled by the timing unit and switching in phase with the reaction vessel valve *F*. Taps and ground-glass joints were lightly lubricated with Silicone stopcock grease.

Solvents.—“AnalaR” carbon tetrachloride was further purified and dried by fractional distillation. Nitromethane was subjected to a preliminary ozonolysis for 6 hr. in the presence of water, dried (CaCl_2), and after fractional distillation had b. p. 100.6 — $101.0^\circ/740$ mm.

Sulphur Compounds.—These were purified commercial samples except for the following: The preparation and physical properties of cyclohexyl methyl and methyl phenyl sulphide have been previously described.⁸ Di-*p*-chlorophenyl disulphide and tetrasulphide were respectively prepared from *p*-chlorobenzenethiol by oxidation with alkaline hydrogen peroxide and condensation with sulphur monochloride. The disulphide had m. p. 70.8 — 71.2° (Found: C, 50.1; H, 2.8; Cl, 24.6; S, 22.2. Calc. for $\text{C}_{12}\text{H}_8\text{Cl}_2\text{S}_2$: C, 50.2; H, 2.8; Cl, 24.8; S, 22.3%) and

⁸ Barnard, Fabian, and Koch, *J.*, 1949, 2442.

the tetrasulphide had m. p. 21—25° (Found: C, 41.2; H, 2.3; S, 36.5. Calc. for $C_{12}H_8Cl_2S_4$: C, 41.0; H, 2.3; S, 36.5%). Phenyl benzenethiolsulphinic acid⁹ had m. p. 69—70° (Found: C, 61.4; H, 4.2; S, 27.3. Calc. for $C_{12}H_{10}OS_2$: C, 61.5; H, 4.27; S, 27.4%). Phenyl benzenethiolsulphonate, obtained by the thermal decomposition of benzenesulphinic acid, had m. p. 37—38° (Found: C, 57.6; H, 4.1; S, 25.6. Calc. for $C_{12}H_{10}O_2S_2$: C, 57.6; H, 4.0; S, 25.6%). 2 : 4-Dinitrobenzenesulphinic anhydride¹⁰ had m. p. 117—118° (decomp.) (Found: C, 34.6; H, 1.7. Calc. for $C_{12}H_6O_6N_4S_2$: C, 34.8; H, 1.5%). Methyl benzenesulphenate, synthesised by the reaction of methanol with benzenesulphenyl chloride,¹¹ had b. p. 54—55°/0.7 mm., n_D^{20} 1.5633 (Found: C, 60.2; H, 5.7; S, 22.8. Calc. for C_7H_8OS : C, 60.0; H, 5.7; S, 22.9%). Diphenyl disulphone, m. p. 191—192° (Found: C, 50.9; H, 3.5; S, 22.6. Calc. for $C_{12}H_{10}O_4S_2$: C, 51.0; H, 3.6; S, 22.7%), was obtained by the oxidation of benzenesulphinic acid with potassium permanganate.¹² Analytically pure samples of diisopropyl tetrasulphide and *n*-butyl thiolacetate were kindly presented by Dr. C. G. Moore and Mr. J. Ford respectively.

Ozonolysis of Monosulphides.—Samples (2 g.), ozonised just to completion, gave:

Di-*n*-butyl sulphone (2.47 g.), m. p. 41.5—43.5°, smelling of butyraldehyde and butyric acid and reacting acid to litmus (Found: C, 53.6; H, 9.75; S, 17.8. Calc. for $C_8H_{18}O_2S$: C, 53.95; H, 10.1; S, 18.0%). After one crystallisation from light petroleum (b. p. 60—80°) the m. p. and mixed m. p. of the product (2.0 g.) was 44—44.5°.

*cyclo*Hexyl methyl sulphone (2.50 g.), n_D^{20} 1.4912, b. p. 93.4°/0.04 mm. (Found: C, 51.7; H, 8.45; S, 19.7. Calc. for $C_7H_{14}O_2S$: C, 51.8; H, 8.7; S, 19.7%).

Dibenzyl sulphone (2.41 g.), m. p. 143—147°, acid to litmus and with an odour of benzaldehyde. The filtrate after washing of the crystals with ethanol (3 ml.) gave a small precipitate of benzaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 236—236.5°, on treatment with Brady's reagent. The residue had m. p. and mixed m. p. 150.5—151.5° after one crystallisation from light petroleum (b. p. 60—80°)—chloroform.

Methyl phenyl sulphone (2.45 g.), m. p. 84—86°, which, after one crystallisation from light petroleum (b. p. 60—80°)—chloroform, had m. p. and mixed m. p. 86—86.5°.

2-Ethyl-2-methyl-5-*isopropyl*thiophan 1 : 1-dioxide, a pale-red oil (2.60 g.) which after molecular distillation had n_D^{20} 1.4765 (Found: C, 58.3; H, 9.8; S, 15.3. Calc. for $C_{10}H_{20}O_2S$: C, 58.8; H, 9.8; S, 15.7%).

Diphenyl sulphone: no sample free from diphenyl sulfoxide was obtained. An increased time of ozonolysis lessened the amount of sulfoxide but produced more resinous by-products derived from attack on the benzene ring.

Ozonolysis of Disulphides.—Examination of diphenyl disulphide may be considered typical. The disulphide (2 g.) in nitromethane (50 ml.)—carbon tetrachloride (18 ml.) was ozonised to completion (*ca.* 90 min.) to give, after the removal of solvent *in vacuo*, a white crystalline residue which became red and oily. This decomposition could be prevented by the addition of anhydrous potassium carbonate (1 g.) before ozonolysis. The residue was transferred, *via* a dry box, to limb *A* of the vacuum-crystallisation apparatus (Fig. 6), and 1 : 1 anhydrous light petroleum (b. p. 30—40°)—ether (90 ml.) distilled *in vacuo* into the apparatus which was then sealed at *C*. The anhydride dissolved on warming to 40° and the solution was filtered into *B* where crystallisation occurred at –60°. The mother-liquor was filtered back into *A* and clean solvent distilled into *B*. After 4 crystallisations the anhydride was dried by cooling *A* in liquid air. The benzenesulphonic anhydride obtained (1.05 g.) had m. p. and mixed m. p. 91—92° (*cf.* Field⁴) (Found: C, 48.2; H, 3.4; S, 21.5%; equiv., 148.8. Calc. for $C_{12}H_{10}O_5S_2$: C, 48.35; H, 3.35; S, 21.5%; equiv., 149). The infrared spectrum with characteristic absorption at 1191 (ϵ 1185) and 1402 cm^{-1} (ϵ 797) was identical with that of the authentic specimen.

The residue from a similar ozonolysis in the absence of potassium carbonate was immediately dissolved in water (50 ml.), and the resulting sulphonic acid titrated with 0.1969N-alkali (84.2 ml., 90%) to screened methyl-red. After extraction with ether (2 × 50 ml.) and concentration to small volume (10 ml.) the solution was treated with *S*-benzylthiuronium chloride (4 g.) in water (14 ml.), to give the benzenesulphonate (3.76 g.), m. p. 139—141°, m. p. and mixed m. p. 146—147° after one crystallisation from light petroleum (b. p. 60—80°)—acetone. The ethereal extracts left a pale brown oil (0.3 g.) on evaporation. This was dissolved in

⁹ Backer and Kloosterziel, *Rec. Trav. chim.*, 1954, **73**, 129.

¹⁰ Kharasch, King, and Bruce, *J. Amer. Chem. Soc.*, 1955, **77**, 931.

¹¹ Lecher, *Ber.*, 1925, **58**, 409.

¹² Hilditch, *J.*, 1908, 1524.

carbon tetrachloride (25 ml.) and fractionally eluted from a column of silica gel (15 g., 100—200 mesh) with carbon tetrachloride (100 ml.) and then chloroform (100 + 50 ml.) to give diphenyl disulphide (10 mg.), phenyl benzenethiolsulphonate (0.17 g.), m. p. 34—35° [m. p. and mixed m. p. 37—38° after one crystallisation from light petroleum (b. p. 60—80°)—ethanol], and a brown oil (0.04 g.) which was identified by its infrared spectrum as impure diphenyl disulphone.

The products from the partial ozonolyses of diphenyl disulphide were estimated and identified as above.

Other ozonolyses gave the following products:

Di-p-chlorobenzenesulphonic anhydride, m. p. 148—149°, obtained in 84% yield (by titration), had strong absorption at 1196 (ϵ 1150) and 1415 cm^{-1} (ϵ 1090) (Found: C, 39.3; H, 2.2; Cl, 19.3; S, 16.9%; equiv., 184.9. $\text{C}_{12}\text{H}_8\text{O}_5\text{Cl}_2\text{S}_2$ requires C, 39.3; H, 2.2; Cl, 19.3; S, 17.4%; equiv., 183.5). Amongst the neutral products (0.21 g.) also obtained from disulphide (1 g.) were *p*-chlorophenyl *p*-chlorobenzenethiolsulphonate (0.11 g.), m. p. 177—178° (Found: C, 45.0; H, 2.5. Calc. for $\text{C}_{12}\text{H}_8\text{O}_2\text{Cl}_2\text{S}_2$: C, 45.1; H, 2.5%), and di-*p*-chlorophenyl disulphone (30 mg.), m. p. >230°, identified by its infrared spectrum (Found: C, 40.9; H, 2.5. Calc. for $\text{C}_{12}\text{H}_8\text{O}_4\text{Cl}_2\text{S}_2$: C, 41.0; H, 2.3%).

The oil (5.61 g.), obtained from the ozonolysis of dimethyl disulphide (4 g.), was separated by distillation into methyl methanethiolsulphonate (2.57 g.) and the anhydride (2.93 g.). The latter, after 3 crystallisations *in vacuo* from light petroleum (b. p. 30—40°)—ether, had m. p. 69—70° (Found: C, 13.7; H, 3.4; S, 37.0%; equiv., 86.2. Calc. for $\text{C}_2\text{H}_6\text{O}_5\text{S}_2$: C, 13.8; H, 3.45; S, 36.8%; equiv., 87.0) and strong absorption at 1187 (ϵ 1124) and 1391 cm^{-1} (ϵ 1100). The thiolsulphonate after refractionation had b. p. 104—105°/10 mm., n_D^{20} 1.5128 (Found: C, 19.2; H, 4.8; S, 50.5. Calc. for $\text{C}_2\text{H}_6\text{O}_2\text{S}_2$: C, 19.1; H, 4.8; S, 50.8%), with absorption at 1141 (ϵ 724) and 1343 cm^{-1} (ϵ 554).

n-Butanesulphonic anhydride (1.35 g.), obtained from di-*n*-butyl disulphide (1 g.), had a purity of 85% (by titration) as anhydride and rapidly darkened. The purity was not raised by molecular distillation at 85°/10⁻³ mm. (Found: C, 37.0; H, 7.25; S, 24.5. Calc. for $\text{C}_8\text{H}_{18}\text{O}_5\text{S}_2$: C, 37.2; H, 6.98; S, 24.8%). The product contained *ca.* 10% of thiolsulphonate (infrared spectroscopy with methyl methanethiolsulphonate as standard).

Ozonolysis of Tetrasulphides.—This was carried out as for the disulphides except that the whole, or a part, of the exit gas stream was led through standard sodium hydroxide solution. Sulphur dioxide was converted into sodium sulphite and then by the ozone present into sodium sulphate and was estimated by back-titration of the alkali or gravimetrically as benzidine sulphate. Only traces of sulphur trioxide were detected (as sulphate) in the reaction vessel.

Di-*p*-chlorophenyl tetrasulphide (1 g.) in carbon tetrachloride (50 ml.) gave sulphur dioxide equiv. to 46.7 ml. of 0.2045*N*-alkali and *p*-chlorobenzenesulphonic anhydride equiv. to 22.3 ml. of 0.1952*N*-alkali (75%). In other experiments the anhydride was isolated as previously described.

Diisopropyl tetrasulphide (0.5 g.) gave sulphur dioxide and 1-methylethanesulphonic anhydride, respectively equiv. to 49.0 and 19.5 ml. (82%) of 0.1965*N*-alkali. The anhydride was not isolated.

Ozonolysis of Miscellaneous Sulphur Compounds.—2 : 4-Dinitrobenzenesulphonic anhydride. The product derived from the ozonolysis of the anhydride (0.272 g.), after evaporation of solvent, dissolved completely in water and required 6.5 ml. (100%) of 0.1965*N*-alkali for neutrality to screened methyl-red. Addition of *p*-toluidine hydrochloride (0.25 g.) in water (2 ml.) to the neutral solution reduced to small volume (2 ml.) gave *p*-toluidine 2 : 4-dinitrobenzenesulphonate, m. p. and mixed m. p. 244—245°.

Methyl benzenesulphenate. Ozonolysis of the sulphenate (2.0 g.) in carbon tetrachloride (50 ml.) ceased after an uptake of 0.7 mol. of ozone and gave an oil (2.3 g.), b. p. 55°/0.2 mm., n_D^{20} 1.5440 (Found: C, 53.8; H, 5.1; S, 20.0%; equiv., 155. Calc. for $\text{C}_7\text{H}_8\text{O}_2\text{S}$: C, 53.8; H, 5.1; S, 20.5%; equiv., 156). Alkaline hydrolysis gave sodium benzenesulphinatate, as shown by the isolation of *S*-benzylthiuronium benzenesulphinatate, m. p. and mixed m. p. 155.5—156°.

Thiophenol. The thiol (1 g.) was converted by ozone (1.6 mol.) into benzenesulphonic acid equiv. to 45.2 ml. (Calc., 44.5 ml.) of 0.2047*N*-alkali and characterised as the *S*-benzylthiuronium salt, m. p. and mixed m. p. 146—147°. In a further experiment the product left after the removal of solvent was treated in dry ether with an excess of aniline. No benzenesulphonanilide was detected, showing sulphonic anhydride to be absent: anilinium benzenesulphonate, m. p. and mixed m. p. 217—218°, was obtained in almost theoretical yield.

Phenyl benzenethiolsulphinates. Benzenesulphonic anhydride (85% yield by titration) and phenyl benzenethiolsulphonate (10%) were isolated from the products of ozonolysis as already described. *p*-Tolyl and *p*-chlorophenyl benzenethiolsulphinates also gave sulphonic anhydrides in 78 and 63% yield respectively, estimated by titration and by infrared spectroscopy, which also indicated thiolsulphonates (*ca.* 10%) to be formed in both cases.

Competitive Ozonolyses.—An equimolar mixture of oct-1-ene and di-*n*-butyl sulphide in carbon tetrachloride was treated with ozone equivalent to half of the octene. The olefin remaining and the solvent were distilled *in vacuo* from the products and by the comparison of the absorption (at 910 cm.⁻¹) of the distillate with a calibration curve from oct-1-ene it was found that the octene consumed was equivalent ($\pm 2\%$) to the ozone introduced, indicating a minimum rate factor between olefin and sulphide of 50 : 1.

Equimolar mixture of disulphides and thiolsulphinates with di-*n*-butyl sulphide were similarly ozonised to convert not more than half the sulphide into sulphoxide. On the assumption that, in the case of the disulphides and thiolsulphinates, the absorption of the first molecule of ozone constitutes the rate-determining step the rate of ozonolysis relative to that of monosulphide was calculated, approximately, from the ratio of the yields of acid (anhydride) produced in the presence and absence of monosulphide. Correction was made for the small amount of acidic products derived from the monosulphide.

Acknowledgment is made to Mr. G. M. C. Higgins and Mr. M. B. Evans for the spectroscopic data, and to Mr. P. W. Jones for experimental assistance. This work forms part of a programme of research undertaken by the Board of the British Rubber Producers' Research Association.

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
48-56, TEWIN ROAD, WELWYN GARDEN CITY, HERTS.

[Received, June 28th, 1957.]
