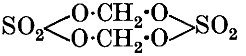
11. *Cyclic Esters of Sulphuric Acid. Part II. The Constitution of Methylene and Glyoxal Sulphates, and the Reaction of Methylene Sulphate with Tertiary Bases.*

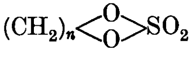
By WILSON BAKER and (in part) FREDERICK BLANCHARD FIELD.

THE formula $\mathrm{CH_2}<\substack{\mathrm{O}\\\mathrm{O}}>\mathrm{SO_2}$ (I) ascribed to methylene sulphate by its discoverer Delépine (*Compt. rend.*, 1899, **129**, 831 ; *Bull. Soc. chim.*, 1899, **21**, 1055) appears to have been accepted without challenge by subsequent workers (Delaby, *Bull. Soc. chim.*, 1926, **39**, 1612 ; Fuchs and Katscher, *Ber.*, 1927, **60**, 2288). In Part I (Baker, J., 1931, 1765) it was suggested that methylene sulphate does not possess this structure, and the evidence now available points to the conclusion that the substance is of double the molecular weight required by the formula $\mathrm{CH_2SO_4}$ and has the 8-membered ring structure * (II).



$$\mathrm{SO_2}<\substack{\mathrm{O\cdot CH_2\cdot O}\\\mathrm{O\cdot CH_2\cdot O}}>\mathrm{SO_2}$$

(II.)



$$\mathrm{(CH_2)_{\mathit{n}}}<\substack{\mathrm{O}\\\mathrm{O}}>\mathrm{SO_2}$$

(III.)

$$\mathrm{SO_2}<\substack{\mathrm{O}\\\mathrm{O}}>\mathrm{CH\cdot CH}<\substack{\mathrm{O}\\\mathrm{O}}>\mathrm{SO_2}$$

(IV.)

The formula (I) is improbable, since a compound which is so readily formed could scarcely be expected to be a 4-membered ring.

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* An 8-membered ring compound, $\mathrm{CCl_3\cdot CH<(O\cdot CH_2\cdot O)_2>CH\cdot CCl_3}$, m. p. 189°, has been obtained by Pinner (*Ber.*, 1898, **31**, 1931) by the condensation of chloral and formaldehyde.

Further, from the physical properties of methylene sulphate and methyl sulphate it is clear that the two substances are not similarly constituted, and the former has a considerably higher molecular weight than the latter. The melting point of methylene sulphate is some 182° higher than that of methyl sulphate, whereas generally no great difference in physical properties exists between a methylene ether of a compound and the corresponding dimethyl ether. The methylene ethers of simple compounds have, in fact, almost invariably slightly lower melting points and boiling points than the dimethyl ethers, as is evident from the following examples. An exception is afforded by the melting points of the ethers of trimethylene glycol.

	M. p.	B. p.
Methylene sulphate	155°	decomp.
Methyl sulphate	−26·8 *	188°
Ethylene glycol methylene ether	−95 †	77
Ethylene glycol dimethyl ether	−58 †	83
Trimethylene glycol methylene ether	−45 †	105
Trimethylene glycol dimethyl ether	−82 †	106 †
Catechol methylene ether	−18 †	173
Catechol dimethyl ether	+22	206

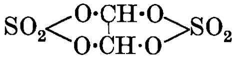
* Dubroca, *J. Chim. physique*, 1907, **5**, 463.

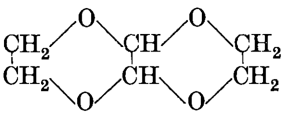
† Not previously recorded.

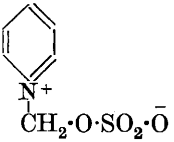
Further evidence against the formula (I) has been obtained by a study of the properties of *ethylene sulphate* (III; $n = 2$) and *trimethylene sulphate* (III; $n = 3$). These substances have been obtained by the interaction of the corresponding dibromides with silver sulphate; they possess the normal molecular weights, melt at 99° and 63° respectively, and are easily soluble in organic solvents, thus indicating that methylene sulphate, which is very sparingly soluble, has a higher molecular weight than either of the compounds (III).

Determination of the molecular weight of methylene sulphate is difficult owing to its very slight solubility in inert solvents and its instability in hot solutions (compare Baker, *loc. cit.*, p. 1767). A saturated solution of methylene sulphate (crystallised rapidly from acetone, washed with benzene, and dried in a vacuum) in pure benzene, prepared at room temperature during 48 hours, was slightly diluted, and the freezing point determined. The freezing point of the benzene, similarly treated, was determined, the same degree of supercooling being allowed in each case. The methylene sulphate in the solution was estimated, after evaporation of the benzene, by titrating the sulphuric acid produced by hydrolysis (Part I, *loc. cit.*, p. 1767). As the depressions were only 0·04—0·05°, no great accuracy can be claimed for the results, but the average of three fairly concordant determinations was 211. Since formula (I) requires $M = 110$ and (II) requires $M = 220$, the 8-membered ring structure can definitely be assigned to methylene sulphate.

The abandonment of the formula (I) for methylene sulphate bears on the constitution of glyoxal sulphate. This substance, $C_2H_2(SO_4)_2$, m. p. 176—177°, which is prepared by the action of fuming sulphuric acid on acetylene tetrachloride in presence of mercury or copper salts (Ott, D.R.-P. 362,743; Ruggli and Henzi, *Helv. Chim. Acta*, 1929, **12**, 364), has been represented by the double 4-membered ring structure (IV), which is very improbable, and the alternative (V) containing two fused 5-membered rings has not been previously considered, although it accounts equally as well as (IV) for the chemical properties of the substance.


(V.)


(VI.)


(VIII.)

Formula (V) differs only from the formula of methylene sulphate (II) in the union of the two carbon atoms, and this is in agreement with the remarkably similar physical properties of the two substances (m. p., solubility in organic solvents). Further evidence in support of the formula (V) is not available, but it is to be accepted as the formula of glyoxal sulphate as being the more probable of the two alternatives.

Glyoxal sulphate reacts with ethyl alcohol to give glyoxal tetraethyl acetal, and with ethylene glycol to give a glyoxal diethylene acetal, probably 2 : 3-ethylenedioxydioxan (VI), which is identical with the product of interaction of glyoxal, glycol, and hydrogen chloride (Donciu, *Monatsh.*, 1895, **16**, 8) to which formula (VI) was given.* By analogy with the formation of cyclic ethylene acetals from monoaldehydes and glycol, Donciu's product might be represented by the alternative double 5-membered ring structure $C_2H_4{:}O_2{:}CH{\cdot}CH{:}O_2{:}C_2H_4$ (VII), and it is formulated as such in the 12th edition of Richter–Anschütz's "Chemie der Kohlenstoff-

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* (*Note added in the proof.*) Böeseken, Tellegen, and Henriquez (*Rec. trav. chim.*, 1931, **50**, 909) have recently prepared two stereoisomeric "naphtho-1 : 4 : 5 : 8-dioxans," m. p. 109—112° and 133—136°, from "2 : 3-dichlorodioxan" and ethylene glycol; no mention is made of the work of Donciu. We find that the higher-melting isomeride has m. p. 137° and is identical (mixed m. p.) wtih the 2 : 3-ethylenedioxydioxan described in this paper, and hence the constitution of this compound is established. A reversal of the argument here presented is therefore possible, and the formation of (VI) from glyoxal sulphate and glycol provides additional evidence in favour of the formula (V) for glyoxal sulphate.

verbindungen" (1928, **1**, 437). A consideration of the methods of formation of the acetal from glyoxal and formaldehyde, however, shows that the reaction might equally well lead to (VI) or (VII). Again, the reaction between glyoxal sulphate (V) and glycol might occur in a number of ways, but it is more likely to lead to (VI) than (VII); hence, since the compound is identical with Donciu's product, the original formulation (VI) of the latter compound is to be preferred to the alternative (VII).

Reaction of Methylene Sulphate with Tertiary Bases.—Methylene sulphate readily reacts with an aqueous solution of pyridine to give a compound $C_6H_7O_4NS$, which has the properties of an internal neutral salt, being readily crystallised from hot water and insoluble in benzene. In aqueous solution it has the molecular weight required by the above formula, *i.e.*, is not split into ions, and gives no precipitate with barium chloride. Prolonged heating with water causes hydrolysis to pyridine, formaldehyde, and sulphuric acid. Similar compounds are given by quinoline and dimethylaniline, the latter being sufficiently stable to separate unchanged from hot dilute sodium hydroxide solution. The only possible structure for these compounds is that of an internal quaternary ammonium salt of the betaine type (VIII), which by analogy with the methosulphates, may be called *methylenosulphates.*

EXPERIMENTAL.

Ethylene Sulphate (III; $n = 2$).—A mixture of ethylene dibromide (10 g.), silver sulphate (20 g.), and xylene (10 c.c.) was shaken at the boiling point for $\frac{1}{4}$ hour and then distilled under diminished pressure, the crystalline material in the distillate being collected after the addition of light petroleum and washed with the same solvent (yield 1·5 g.). It separated from benzene–light petroleum in long (sometimes more than 4 cm.), tough, fibrous needles, m. p. 99° (Found: C, 19·3; H, 3·6; *M*, cryoscopic in benzene, 129. $C_2H_4O_4S$ requires C, 19·4; H, 3·3%; *M*, 124). *Ethylene sulphate* is dimorphous and also separates from benzene–light petroleum in small flat prisms, m. p. 99°. When warmed with water, it rapidly dissolves owing to partial hydrolysis to β-hydroxyethylsulphuric acid, and on exposure to the air is slowly hydrolysed by moisture and becomes liquid. The equivalent of the compound as a potential monobasic acid was estimated by hydrolysing the substance with water for 5 minutes on the water-bath and titrating the acid produced with standard alkali (Found: equiv., 125·4. $C_2H_4O_4S$ requires equiv., 124).

By treating catechol in aqueous-alkaline solution with ethylene sulphate, catechol ethylene ether is produced.

Trimethylene Sulphate (III; $n = 3$).—This compound was prepared in the same way as ethylene sulphate (yield, 2 g.). It separates from benzene–light petroleum in lustrous flat prisms, m. p. 63° [Found: C, 26·1; H, 4·6; S (hydrolysis with water at 200° and precipitation as $BaSO_4$), 23·5; *M*, cryoscopic in benzene, 140·8; equiv. (as potential monobasic acid; see ethylene sulphate), 140·5. $C_3H_6O_4S$ requires C, 26·1; H, 4·4; S, 23·1%; *M* and equiv., 138]. When heated with water, it dissolves and slowly undergoes hydrolysis, but the compound is much more stable than is ethylene sulphate and can be crystallised from methyl alcohol; it is not hydrolysed on exposure to the air.

Trimethylene Glycol Dimethyl Ether.—To a solution of sodium (20 g.) in methyl alcohol (250 c.c.) was added trimethylene glycol (33 g.), the whole evaporated to dryness under diminished pressure, methyl sulphate (100 g.) and ether (50 c.c.) added, and the mixture heated on the water-bath. The distillate was twice rectified over solid potassium hydroxide, the fraction boiling above 90° was distilled over sodium until no further reaction occurred, and finally fractionated, yielding *trimethylene glycol dimethyl ether* (6 g.), b. p. 106°/753 mm. [compare Dionneau, *Ann. Chim. Phys.*, 1915, **3**, 260, for the b. p.'s of the compounds $MeO\cdot(CH_2)_n\cdot OMe$], m. p. – 82° (Found: C, 57·4; H, 11·4. $C_5H_{12}O_2$ requires C, 57·7; H, 11·6%). It has a faint ethereal odour and is somewhat soluble in water. It was obtained in smaller yield from trimethylene dibromide and sodium methoxide in methyl alcohol.

Glyoxal Tetraethyl Acetal.—Glyoxal sulphate (10 g.) and absolute alcohol (40 c.c.) were heated and agitated under reflux until a vigorous reaction set in. The solution was then heated on the water-bath for 1 hour, poured into water, and extracted with ether, and the extracts were dried and distilled over solid potassium hydroxide. The high-boiling portion was repeatedly distilled over sodium till no further reaction occurred. Glyoxal tetraethyl acetal (1·3 g.) was obtained, b. p. 195—196°/753 mm. (compare Pinner, *Ber.*, 1872, **5**, 151; Harries and Temme, *Ber.*, 1907, **40**, 171).

2 : 3-*Ethylenedioxydioxan* (VI).—Glyoxal sulphate (5 g.), ethylene glycol (10 c.c.), and water (5 c.c.) were heated on the water-bath for 1 hour. After addition of water (10 c.c.), chloroform extracted colourless 2 : 3-ethylenedioxydioxan (0·85 g.), which separated from alcohol in striated diamond-shaped plates, m. p. 137° (Found: C, 49·0; H, 6·6. Calc. for $C_6H_{10}O_4$: C, 49·3; H, 6·9%).

Pyridine Methylenosulphate (VIII).—Methylene sulphate (22 g.) was slowly added to pyridine (32 c.c.) and water (32 c.c.) initially at 40—50°, so that the liquid did not quite boil. Crystals separated on cooling and were collected and washed with cold water (yield, 15 g.). The *substance* crystallises readily from hot water in colourless prismatic needles, m. p. about 228° with evolution of gas (rapid heating) [Found : C, 38·4; H, 3·9; N, 7·6; S (Carius), 17·3; SO_4 (hydrolysis with excess of dilute standard NaOH and back-titration), 51·3; *M*, cryoscopic in water, 185. $C_6H_7O_4NS$ requires C, 38·1; H, 3·7; N, 7·4; S, 16·9; SO_4, 50·8%; *M*, 189].

Quinoline Methylenosulphate.—A mixture of quinoline (10 g.), acetone (50 c.c.), and methylene sulphate (5 g.) was boiled for a few minutes, a white solid separating. Water was added to the cold mixture, and the crystalline product was collected, washed with much dilute sulphuric acid and then with water, and dried in a vacuum over calcium chloride [Found : C, 50·7; H, 4·1; N, 5·7; S, 13·9; SO_4 (by hydrolysis), 40·5. $C_{10}H_9O_4NS$ requires C, 50·2; H, 3·8; N, 5·9; S, 13·4; SO_4, 40·2%]. *Quinoline methylenosulphate* decomposes readily on boiling with water into formaldehyde, quinoline and sulphuric acid, being much less stable under these conditions than the pyridine derivative, and it can only be crystallised from water in small quantities. It darkens at about 230° and melts with evolution of gas at 260—265°.

Dimethylaniline Methylenosulphate.—A mixture of dimethylaniline (10 g.) in acetone (50 c.c.) and methylene sulphate (10 g.) was agitated and rapidly heated until the solution suddenly became cloudy and boiled. When cold, the acetone layer was decanted and the residual oil was shaken with water (20 c.c.). The product at once crystallised; it was washed with cold water, in which it was almost insoluble, and recrystallised from hot water, from which it separated in thin colourless prisms (7 g.), m. p. about 168—169° (rapid heating; evolution of gas) (Found : C, 46·9; H, 5·5; N, 6·3. $C_9H_{13}O_4NS$ requires C, 46·8; H, 5·6; N, 6·1%). The aqueous solution has a very bitter taste, and is slowly hydrolysed on boiling.

THE DYSON PERRINS LABORATORY,
OXFORD.

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