

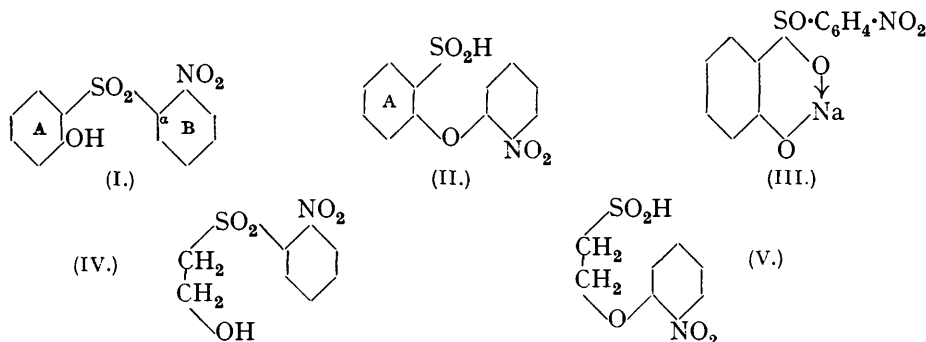
95. *The Reversibility of the Rearrangement of *o*-Hydroxy-sulphones.*

By ROBERT R. COATS and DAVID T. GIBSON.

o-Hydroxy-sulphones were shown by Smiles to rearrange to sulphino-ethers. We find the rearrangement is reversible, and have investigated the conditions of reversibility.

SULPHONES of type (I) were shown by Smiles and his collaborators (J., 1931, 3264; 1934, 422; 1937, 1017) to undergo rearrangement in alkaline media to sulphinic acids (II). We have found that this is a reversible transformation, for 2-nitrophenyl 1-sulphino-2-naphthyl ether (II; A = naphthyl) was almost quantitatively converted into the sulphone (I) when its solution was kept at 50° for a few hours. We therefore extended the investig-

ation to a number of other sulphonic acids of type (II), with the view of determining the extent to which the reverse reaction (II \rightarrow I) is general, and how far it is influenced by



conditions of molecular structure and the p_H of the medium. Factors which favour the original transformation (I \rightarrow II) were shown by Kent and Smiles (J., 1934, 422) to be (a) the positive character of the α -carbon atom, (b) the capacity of oxygen to act as a donor of electrons, and (c) the tendency of the medium to remove protons from the hydroxyl group.

Qualitative experiments showed that the optimum p_H for the reverse change is not the same for all the sulphonic acids (for some revert best in sodium acetate solution, others in sodium formate, and others merely on recrystallisation from aqueous acetone), and as the p_H of acetate solutions is very sensitive to small amounts of a stronger acid (cf., *e.g.*, Walpole, J., 1914, 105, 2514), we undertook a roughly quantitative investigation of the behaviour of Smiles' sulphonic acids in sufficient acetate buffer to maintain the p_H within 0.2 unit. Within this limit, even in the most concentrated standard buffers, it is not possible to make up solutions stronger than $N/150$. This entails a certain loss of material due to solubility, but we satisfied ourselves that, except in one case, this was not significant. The reaction was carried out at $50^\circ \pm 2^\circ$, the actual sulphone formed being filtered off and weighed. Excluding amino-derivatives, Smiles records (Kent and Smiles, *loc. cit.*; McClement and Smiles, J., 1937, 1017) rearrangements of some seventeen sulphones, and we examined the sulphonic acids obtained from nine of these. In the following table the rates of the forward and the reverse reactions are compared. Under A and B are given the substituents present in the aromatic nuclei of the parent 2-hydroxy-sulphone (I).

The times in the third column (in minutes) are for the completion of the reaction in $N/15$ -solution at 50° ; those in the fourth column are the times (in hours) for the attainment of equilibrium at the most favourable p_H in *ca.* $N/150$ -solution at 50° .

No.	A.	B.	I \rightarrow II.	II \rightarrow I.
1	5-Methyl	2-Nitro	315	400
2	3 : 5-Dimethyl	2-Nitro	93	250
3	5 : 6-Benzo	2-Nitro	5	5
4	5-Hydroxy	2-Nitro	125	Too soluble for comparison
5	5-Methoxy	2-Nitro	360	No reversal observed
6	5-Methyl	2 : 4-Dinitro	Rapid with hydrolysis	2
7	5-Chloro-4 : 6-dimethyl	2-Nitro	5	5
8	3-Chloro-5-methyl	2-Nitro	150	450
9	β - <i>o</i> -Nitrophenoxyethane sulphonic acid		Practically instantaneous	No reversal observed

With one significant exception (9), the corresponding reversals (II \rightarrow I), though distinctly slower, follow roughly the same order, and, in particular, 6-methyl or 5 : 6-benzo substitution, which was present in all the very rapid rearrangements studied by McClement and Smiles (*loc. cit.*), also favours rapid reversal (Nos. 3 and 7, Fig. 2), whereas those not so substituted reverse very much more slowly (Fig. 1). In general, it is to be expected that (I \rightarrow II) will be more rapid than the reverse change, for the α -carbon atom in the former is influenced by both the nitro- and the sulphonyl group, but only by the nitro-group in the latter.

Interconversion of (I) and (II) is evidently facilitated in both directions by the positive

character of the α -carbon atom, for we find that the formation of the sulphone from 2 : 4-dinitrophenyl 3-sulphino-*p*-tolyl ether is very much more rapid than in the case of the corresponding mononitro-derivative.

Kent and Smiles (*loc. cit.*) found that with a sulphone with an aliphatic hydroxyl group (IV), the change (IV \rightarrow V) is very much more rapid than in any of the aromatic types (I \rightarrow II).

FIG. 1.

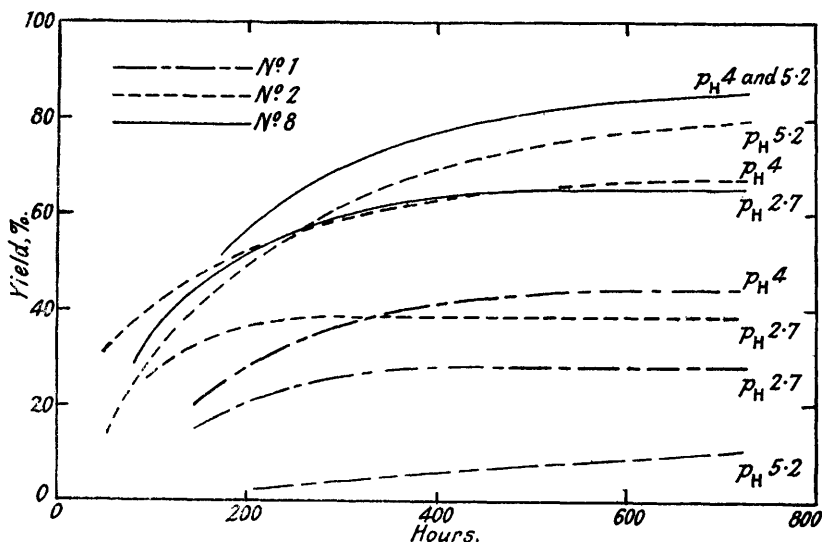
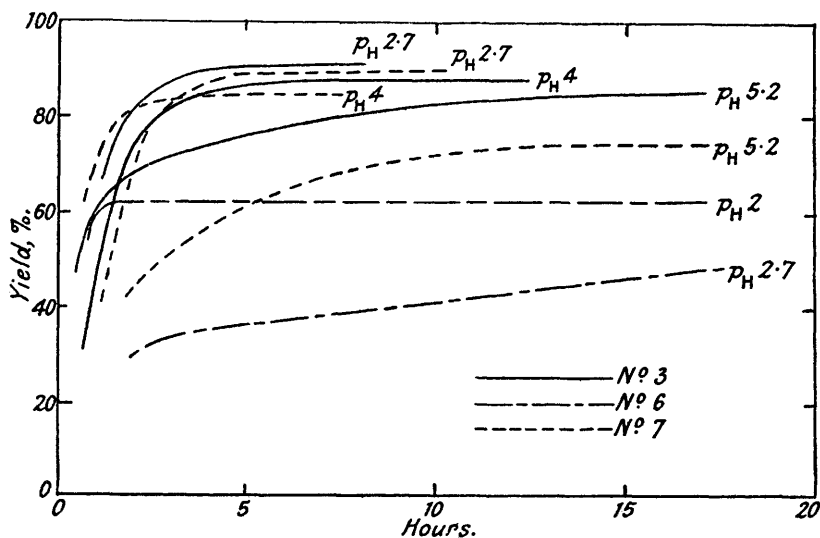


FIG. 2.



This may be attributed to the fact that with the former, the oxygen is "insulated" by an aliphatic chain and so its donor capacity is not diminished by the kationoid action of the sulphonyl group. We found no detectable reversal (V \rightarrow IV) with β -*o*-nitrophenoxyethanesulphonic acid (V). This suggests (1) that the superior velocity (IV \rightarrow V) is to some extent due to the absence of reversibility, and (2) that, if the kationoid tendency of the sulphonyl group is a handicap to (I \rightarrow II) by withdrawing electrons from the hydroxyl group, it is a predominant influence in (II \rightarrow I), for, where oxygen is insulated, no reversal

occurs (case 9). Consequently, 6-methyl substitution, by causing electron accession at the sulphonated carbon atom, at least partly overcomes the adverse influence of the sulphonyl group, and so the reversal is more rapid with compounds so substituted.

The reversal was observed in buffer solutions of p_H 2—6, and from the curves it will be seen that increasing acidity increases the initial rate of formation, although the total amount of sulphone finally formed is not always greatest in the most acid media because the resulting increased solubility of the sulphone tends to drive the equilibrium (I \rightarrow II) to the right. The most striking case of this is 2'-nitro-4-hydroxy-2-sulphinodiphenyl ether, where the sulphone is so much more soluble than the others that, although a 25% yield of sulphone from the sulphinic acid was obtained in a small volume of sodium acetate solution (2/3 mol.; 0.17N), the p_H of the solution changed so very considerably during the reaction that no comparative figures are possible. In fact the equilibrium value did not exceed the solubility in the much larger volume of buffer solution required to maintain the p_H within 0.2 unit, and so no sulphone was precipitated at all. The corresponding 2'-nitro-4-methoxy-2-sulphinodiphenyl ether did not undergo reversal.

Note on the Strength of Sulphinic Acids.

It was suggested by Lovén (*Z. physikal. Chem.*, 1896, **19**, 462) that the strengths of sulphinic acids would run parallel to those of the corresponding carboxylic acids, and the same was assumed by Gibson and Loudon (*J.*, 1937, 487). Actually, the only recorded measurements are on benzenesulphinic acid and toluenesulphinic acids by Lovén, who found that they were too strong to give satisfactory dissociation constants. We find, however, that if Lovén's data are recalculated by Dippy and Williams' method (*J.*, 1934, 162), the thermodynamical "*k*" is much more nearly constant; but for *o*-toluenesulphinic acid the values are much less regular.

Benzenesulphinic acid :

100 <i>k</i> (class.).....	3.84	3.58	3.36	3.04	(2.72)	(2.5)	3.42	3.11	3.05
100 <i>k</i> (therm.)	2.93	2.96	3.14	2.94	2.81	2.95	3.14	3.09	3.33

p-Toluenesulphinic acid :

100 <i>k</i> (class.).....	2.49	2.48	2.32	2.18	1.98	2.67	2.78	2.56	2.34	2.13
100 <i>k</i> (therm.)	2.05	2.2	2.18	2.04	2.11	2.13	2.41	2.37	2.30	2.22

o-Toluenesulphinic acid :

100 <i>k</i> (class.).....	5.20	4.22	3.77	3.20	2.22
100 <i>k</i> (therm.)	3.2	3.34	4.01	3.85	2.60

EXPERIMENTAL.

The sulphones were prepared as described by Smiles, by the oxidation of the corresponding sulphides with perhydrol. In some cases Smiles characterised the sulphinic acids by derivatives without isolating them, and in those cases in which he isolated the pure sulphinic acid, he did so by precipitating it from the aqueous solution of its sodium salt with acid, and recrystallising it from alcohol or acetone. This, it was found, yielded a product contaminated in some cases by a considerable amount of sulphone, and is doubtless one reason why the melting points recorded by Smiles are often considerably lower than those obtained by ourselves. It was necessary in some cases to extract the acidified solution with ether and isolate the sulphinic acid by precipitating it from the dried solution with ligroin. It was then recrystallised from ether or ether-ligroin.

The sulphones gave strong orange-red colours with alkali and no colour with concentrated sulphuric acid; the sulphinic acids gave an intense blue with concentrated sulphuric acid and practically no colour with alkali. Hence the purity of individual crystals could be checked, and the progress of the conversion in a single crystal seen under the microscope.

The sulphinic acids (0.1 g.) were dissolved in 50 c.c. of the buffer solutions (prepared according to Walpole, *J.*, 1914, **105**, 2514), and the solution maintained at 50° in stoppered flasks, the sulphone being filtered off at intervals and weighed in sintered glass funnels prepared as described by Briscoe and Lowe (*J.*, 1934, 1379).

2'-Nitrophenyl-2-hydroxy-1-naphthylsulphone (Levi, Rains, and Smiles, *J.*, 1931, 3268).—The direct oxidation of the sulphide (3 g.) in glacial acetic acid (75 c.c.) gave a yellow product,

m. p. 180—181°. Microscopically, it was a mixture of white and yellow crystals. The two forms, mechanically separated, melted at the same temperature, alone or mixed. The yellow form was obtained by prolonged extraction with light petroleum, and the white form became yellow before melting (Found, yellow : C, 58.5; H, 3.4; N, 4.4. $C_{16}H_{11}O_5NS$ requires C, 58.35; H, 3.4; N, 4.3%).

In attempting to confirm Heppenstall and Smiles' suggestion (J., 1938, 900) that (III) is an intermediate of the rearrangement (I \rightarrow II) by comparing the rates of reaction in aqueous lithium, sodium, and potassium hydroxide solution, we failed to observe any significant difference, and abandoned the experiments when we observed that in aqueous ammonia (where co-ordination is impossible) the sulphinic acid was also formed (identified by m. p. and colour with concentrated sulphuric acid).

2-Nitrophenyl 1-Sulphino-2-naphthyl Ether.—Purified from ether-ligroin, this had m. p. 116°. It gave the sulphone when recrystallised from aqueous acetone, and even when recrystallised from dry ether-ligroin it was always contaminated with microscopic particles of yellow sulphone. In an attempt to purify it by dissolution in aqueous sodium acetate, the filtered solution deposited, in the course of a few hours, a practically quantitative yield of sulphone.

*2-Nitrophenyl 3-sulphino-*p*-tolyl ether* (Levi, Rains, and Smiles, *loc. cit.*) had m. p. 134° after crystallisation from aqueous acetone.

*2 : 4-Dinitrophenyl 3-sulphino-*p*-tolyl ether* (Kent and Smiles, *loc. cit.*), purified from dry ether-ligroin, had m. p. 140° (decomp.) (Smiles, 117—118°) (Found : C, 46.4; H, 3.3; N, 8.2. Calc. for $C_{13}H_{10}O_7N_2S$: C, 46.15; H, 3.0; N, 8.3%).

4-Chloro-2'-nitro-6-sulphino-3 : 5-dimethyldiphenyl ether (McClement and Smiles, *loc. cit.*) had m. p. 131° (from ether) (Found : N, 4.2. Calc. for $C_{14}H_{12}O_5NCIS$: N, 4.1%).

2'-Nitro-2-sulphino-4 : 6-dimethyldiphenyl ether (Kent and Smiles, *loc. cit.*) had m. p. 153° (from aqueous acetone) (Smiles, 129°) (Found : C, 54.7; H, 4.4. Calc. for $C_{14}H_{13}O_5NS$: C, 54.75; H, 4.3%).

2-Chloro-2'-nitro-6-sulphino-4-methyldiphenyl ether (McClement and Smiles, *loc. cit.*) had m. p. 170° (Found : C, 47.9; H, 3.3. Calc. for $C_{13}H_{10}O_5NCIS$: C, 47.6; H, 3.05%).

2'-Nitro-4-hydroxy-2-sulphinodiphenyl Ether (Kent and Smiles, *loc. cit.*).—Recrystallised from water, this formed hexagonal plates soluble in dry ether. The solution soon deposited felted needles, which were reconverted into plates by recrystallisation from water. Both forms melt at 98° and are evidently the monohydrate of the ether [Found (plates) : C, 46.2; H, 3.7; N, 4.6; equiv., 315. Found (needles) : C, 46.0; H, 3.8; N, 4.35. $C_{12}H_9O_6NS.H_2O$ requires C, 46.0; H, 3.7; N, 4.4%; equiv., 313]. Kent and Smiles (*loc. cit.*) record the ether as anhydrous, m. p. 64°, but our attempts to dehydrate the monohydrate over phosphoric oxide at the ordinary temperature and $\frac{1}{2}$ mm. pressure were unsuccessful, and at 45° led to decomposition.

2'-Nitro-4-methoxy-2-sulphinodiphenyl ether (Kent and Smiles, *loc. cit.*) had m. p. 128° (from ether) (Smiles, 122—123°).

β -2-Nitrophenoxyethanesulphinic acid (Kent and Smiles, *loc. cit.*) had m. p. 124° (Smiles 121°).

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