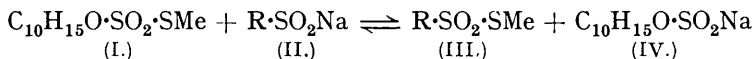


108. *The Exchange of Sulphonyl Groups.*

By D. T. GIBSON and J. D. LOUDON.

WE have independently recorded exchange of sulphonyl groups by the action of sulphinate ions on (a) methylthioacetyl sulphones (Gibson, J., 1932, 1819; Cowie and Gibson, J., 1933, 306; 1934, 46), (b) 2 : 4-dinitrodiphenyl sulphones (Loudon, J., 1935, 537), and (c) thiolsulphonic esters (Loudon and Livingston, J., 1935, 896). The results show qualitatively that there is produced in each case an equilibrium which, it was suggested in cases (b) and (c), is chiefly determined by the relative anionic stabilities (as inferred from the strengths of the corresponding carboxylic acids) of the competing sulphonyl groups. A similar interpretation is not inconsistent with most of the data for case (a), except that the replacement of arylsulphonyl by alkylsulphonyl groups could not be effected. In all cases, however, in which the exchange was demonstrated, a considerable excess of the attacking ion was employed and the equilibrium point was not determined. We have now collaborated in obtaining data of a more quantitative character by measuring the change of rotation incurred by interaction with an optically active component.

Thiolsulphonic esters provided the most suitable material for investigation. Methyl camphor-10-thiolsulphonate (I) and sodium camphor-10-sulphinat (IV), having respectively $\alpha_{5461}^{19} = -0.53^\circ$ and $+0.62^\circ$ for *N*/20-solutions in aqueous alcohol, were selected as reference compounds and the equilibrium value for each sulphinate (II) was calculated as the percentage of the possible rotational change ($0.53^\circ + 0.62^\circ = 1.15^\circ$) effected by mixing *N*/10-solutions of (I) and (II) or of (III) and (IV).



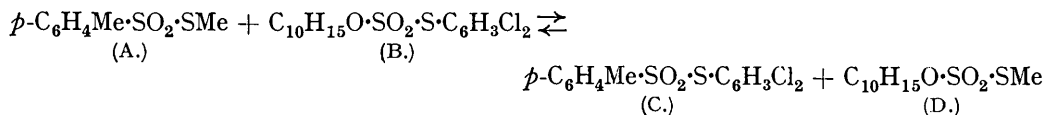
Although a strictly quantitative procedure was not adhered to, our results are justified by the fact that, wherever all the reactants were readily available, we were able to observe approximately the same equilibrium point by measuring both the forward and the reverse reaction and, in a test case, by actual isolation of the purified thiolsulphonic ester product in upwards of 90% of the quantity indicated. In examining a series of fourteen sulphinates, two significant points were observed : (1) The reaction proceeded so rapidly in cold aqueous alcohol that equilibrium was attained before a polarimetric reading could be taken. A similarly rapid reaction also occurred when mercaptides were employed instead of sulphinates. (2) The percentage decomposition of methyl camphor-10-thiolsulphonate increased with the various sulphinates ($\text{R}\cdot\text{SO}_2\text{Na}$) approximately as the dissociation constant for the corresponding carboxylic acid diminished. (The dissociation constants for sulphinic acids have been determined in only a few cases.) To detect any effect contributed by the SR radical, we examined 2 : 5-dichlorophenyl camphor-10-thiolsulphonate, and for solubility reasons were forced to make the comparison with the methyl ester in aqueous alcoholic dioxan solution. It will be seen (table, cols. 3 and 4) that, with the single exception of *p*-toluenesulphinat, the concordance of the values (within experimental error) suggests that the

change effected in the group SR has little influence on the equilibrium, but comparison of the values (cols. 2 and 3) resulting from modification of the solvent shows that it may be influenced by other factors.

R in R·SO ₂ Na.	Methyl camphor-10-thiolsulphonate in :		2 : 5-Dichlorophenyl camphor-10-thiol- sulphonate in	Dissociation constants for R·CO ₂ H (× 10 ⁻⁵) (Beilstein).
	aq. alcohol.	aq. alc. dioxan.	aq. alc. dioxan.	
<i>n</i> -Pentyl	99	100	98	1·45
Ethyl	80	—	—	1·34
<i>p</i> -Tolyl	78	69	77·5	4·3
	$\left\{ \begin{array}{l} \rightleftharpoons \\ \rightleftharpoons \\ \rightleftharpoons \end{array} \right.$	$\left\{ \begin{array}{l} \rightleftharpoons \\ \rightleftharpoons \\ \rightleftharpoons \end{array} \right.$	$\left\{ \begin{array}{l} \rightleftharpoons \\ \rightleftharpoons \\ \rightleftharpoons \end{array} \right.$	
<i>p</i> -Acetamido	27	35	25	
Phenyl	70	64	61	5·17
4-Methoxy- <i>m</i> -tolyl	68	56	55	6·6
	$\left\{ \begin{array}{l} \rightleftharpoons \\ \rightleftharpoons \\ \rightleftharpoons \end{array} \right.$	$\left\{ \begin{array}{l} \rightleftharpoons \\ \rightleftharpoons \\ \rightleftharpoons \end{array} \right.$	$\left\{ \begin{array}{l} \rightleftharpoons \\ \rightleftharpoons \\ \rightleftharpoons \end{array} \right.$?
<i>p</i> -Fluorophenyl ...	63	51·5	51	
	$\left\{ \begin{array}{l} \rightleftharpoons \\ \rightleftharpoons \\ \rightleftharpoons \end{array} \right.$	$\left\{ \begin{array}{l} \rightleftharpoons \\ \rightleftharpoons \\ \rightleftharpoons \end{array} \right.$	$\left\{ \begin{array}{l} \rightleftharpoons \\ \rightleftharpoons \\ \rightleftharpoons \end{array} \right.$	
<i>p</i> -Naphthyl	39	50	44	
<i>α</i> -Naphthyl	54	39	41	7·39 *
<i>β</i> -Naphthyl	53	39	39	20·4
<i>p</i> -Bromophenyl ...	43	42·5	39	6·8
<i>p</i> -Chlorophenyl ...	41·5	33	31	10·8 *
<i>m</i> -Nitrophenyl	41	32	34	9·3
<i>o</i> -Nitrophenyl	11	—	8	34
<i>o</i> -Tolyl	2	—	0	630
2 : 5-Dichlorophenyl	1	0	0	12·5
			$\left\{ \begin{array}{l} \rightleftharpoons \\ \rightleftharpoons \\ \rightleftharpoons \end{array} \right.$?
			96	

* J., 1935, 343.

The analogy which emerges between these reactions and those of the ester dismutation type is confirmed by the observation that the equilibrium



can be displaced either way in cold alcohol in presence of sodium acetate, C and B being isolated by using an excess of A and D respectively.

With the aid of this more sensitive optical method we confirmed that in the series (*a*) the structure R·SO₂·CH(Salk)·CO·CH₃ (V) is necessary and sufficient for exchange. Thus a solution of *α-p*-toluenesulphonyl-*α*-methylthioacetone heated in alcohol with sodium camphorsulphonate for seventy hours at 60° showed a fall in rotation from $\alpha_{5461} - 0\cdot5^\circ$ to $\alpha_{5461} - 0\cdot27^\circ$, whereas a number of other compounds, in which not all the conditions were satisfied (experimental), showed no change. It was hoped to submit a typical compound (V) to a detailed optical investigation to clear up the discrepancy regarding exchange by aliphatic sulphinates, but in these cases exchange is so much slower that other reactions, *e.g.*, hydrolysis of acetyl, confuse the issue. It is now evident that the failure (Gibson, J., 1933, 306) to exchange arylsulphonyl for alkylsulphonyl is to be attributed not to differences in the reactivity of the sulphinates but to the incidence of hydrolysis—especially noticeable when the reagents are salts derived from relatively weaker sulphinic acids, resulting in removal of a factor (CH₃·CO) necessary for exchange. In former experiments the substituted acetone was specially sought as being the more significant index of the course of the reaction. We have now repeated some experiments of this type and, searching for displaced sulphinate, have shown that 2 : 5-dichlorophenylsulphonyl and 4-chlorophenylsulphonyl can be displaced by camphor-10-sulphonyl, benzylsulphonyl, and ethylsulphonyl.

The application of the method to the reaction between 10-camphor-2 : 4-dinitrophenylsulphone and sulphinates was found to be impracticable because attendant reduction processes coloured the solutions and rendered the end-point indefinite.

EXPERIMENTAL.

Polarimetric Procedure.—The sodium sulphinates were dried, recrystallised from alcohol, and dried. For experiments in col. 2 of the table, equal volumes of *N*/10-sulphinate in 50% alcohol

and *N*/10-methyl camphorthiolsulphonate in absolute alcohol were mixed and examined in a 1 dm. tube with mercury light (λ 5461). Reference solutions were made by diluting (a) *N*/10-sodium camphorsulphinate in 50% alcohol with an equal volume of absolute alcohol, and (b) *N*/10-methyl camphorthiolsulphonate in absolute alcohol with 50% alcohol. The solutions for cols. 3 and 4 were prepared in a similar way from the requisite volumes of *N*/10-sulphinate in 50% alcohol and *N*/20-thiolsulphonate in dioxan.

Tests for Mobility of the Sulphonyl Group (compare V above).—Phenacylphenylsulphone, α -methylsulphonyl- α -*p*-tolylthioacetone, α -tolylsulphonyl- α -2 : 5-dichlorophenylthioacetone, 4-chlorophenylsulphonylmethylthiomethane, and *p*-tolylsulphonylacetonitrile were heated severally with an alcoholic solution of sodium camphorsulphinate in sealed tubes for periods up to 40 hours. No change in rotation was observed. Solutions of sulphinate in open vessels readily undergo oxidation to sulphonate with resulting change of rotation. α -Phenylsulphonyl- α -methylthioacetone (0.2 g.) and sodium *p*-toluenesulphinate (3 g., carefully freed from carbonate), on warming with alcohol, gave α -*p*-tolylsulphonyl- α -methylthioacetone and *p*-tolylsulphonylmethylthiomethane, both identified by comparison with authentic specimens.

2 : 5-Dichlorophenyl 2 : 5-dichlorobenzenethiolsulphonate, heated in alcohol with (i) sodium camphorsulphinate, gave 2 : 5-dichlorophenyl camphorthiolsulphonate, m. p. 121—122° (Found : Cl, 18.2. $C_{16}H_{18}O_3Cl_2S_2$ requires Cl, 18.0%); with (ii) sodium 4-chlorobenzenesulphinate, it gave 2 : 5-dichlorophenyl 4-chlorobenzenethiolsulphonate, m. p. 121—122° (Found : Cl, 30.5. $C_{12}H_7O_2Cl_3S_2$ requires Cl, 30.2%); and with (iii) sodium 4-methoxy-*m*-toluenesulphinate, it gave 2 : 5-dichlorophenyl 4-methoxy-*m*-toluenethiolsulphonate, m. p. 96° (Found : Cl, 19.6. $C_{14}H_{12}O_3Cl_2S_2$ requires Cl, 19.55%).

2 : 4-Dinitrophenyl-10-camphorylsulphone, prepared from 2 : 4-dinitrochlorobenzene and sodium camphorsulphinate by heating in aqueous alcohol for 1 hour, and crystallised from alcoholic dioxan, melted at 168° and had $[\alpha]_{5461}^{18} - 165^\circ$ ($c = 0.97$ in dioxan) (Found : N, 7.5. $C_{16}H_{18}O_7N_2S$ requires N, 7.3%).

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