

8. A Spectroscopic Method for the Determination of the *ortho* : *para*-Ratio in Phenolsulphonates.

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A method has been developed for determining the *ortho* : *para*-ratio of phenolsulphonates by means of the ferric chloride colour, by the use of which the effect of temperature on the isomer distribution in the sulphonation of phenol has been studied.

IN connexion with another problem we required a rapid and convenient way of determining *o*- and *p*-phenolsulphonate in mixtures of the two. The only methods recorded appeared to be those based on the fractionation of barium salts¹ or on the melting point of *S*-benzylisothiuronium salts,² neither of which was convenient for our purpose. The statement^{1,3} that ferric chloride gives a much more intense colour with the *ortho*- than the *para*-isomer suggested another approach. Pure *S*-benzylisothiuronium *o*- and *p*-phenolsulphonate were prepared and the absorption spectra of their ferric complexes determined. Both showed a broad band (cf. ref. 4) with a peak at 535 m μ and under standard conditions the apparent extinction coefficient of the *ortho*- was more than ten times that of the *para*-isomer. Rigorously purified samples of the corresponding sodium salts gave the same values. Synthetic mixtures showed intensities in excellent agreement with those calculated from the isomer composition, indicating that each compound obeyed Beer's law.

It remained to find a convenient method for the determination of the total phenolsulphonate present in mixtures of the two. Attempted bromometric estimation⁵ failed owing to partial displacement of the *o*-sulphonate group. Potentiometric titration of the phenolic groups with aqueous alkali gave unsatisfactory end-points, but non-aqueous titration in ethylenediamine with tetrabutylammonium hydroxide worked well.

Other phenolic materials interfere and must if possible be removed before the estimation, for example by sublimation or solvent-extraction. Phenol itself gives a very weak colour under our conditions and the presence of small amounts does not introduce serious error. The intensity of the ferric chloride colour is somewhat dependent on pH, so all readings should be taken at the same pH. As would be expected from an anionic ligand the intensity increases with increasing pH, but since precipitation of ferric hydroxide occurs at about pH 4 it is desirable to work at pH <3; the use of an excess of ferric chloride (~60 mol.) to give pH 2.2 and considerable buffering effect has proved convenient.

TABLE 1.

Sulphonation of phenol.

Temp.	Ether-soluble (%) Reagent: 20% oleum.	<i>ortho</i> -Isomer (%)	Temp.	Ether-soluble (%) Reagent: 98% H ₂ SO ₄	<i>ortho</i> -Isomer (%)
20°	0.18	42	20°	16.3	49
40	0.05	37.5	30	12.8	41
50	—	35.5	40	6.6	35
60	0.20	34	60	3.6	33
70	—	27	70	3.3	25
80	0.01	18	80	2.7	14.5
100	0.64	12	100	2.7	9.5
120	1.80	9	120	3.5	11
			140	6.6	10.5

The use of the ferric chloride method has enabled us to study the effect of temperature on the *ortho* : *para*-ratio in the sulphonation of phenol (see Table 1). It has long been

¹ Obermiller, *Ber.*, 1907, **40**, 3623.

² Muramoto, *Science and Industry (Japan)*, 1955, **29**, 315.

³ Olsen and Goldstein, *Ind. Eng. Chem.*, 1924, **16**, 66.

⁴ Wesp and Brode, *J. Amer. Chem. Soc.*, 1954, **56**, 1037.

⁵ Sager, Schooley, and Acree, *J. Res. Nat. Bur. Stand.*, 1943, **31**, 197.

known⁶ that lower temperatures favoured the *ortho*-isomer but no quantitative studies were reported until Obermiller¹ showed that with sulphuric acid, even at low temperatures, no more than about 40% of *o*-phenolsulphonic acid was formed, the remainder of the product being the *para*-isomer and phenyl hydrogen sulphate. More recently Muramoto² has shown that with sulphuric acid the *ortho*-content falls from 39% at 20° to 4% at 100° (see also Olsen and Goldstein³). Our results are in broad agreement with his although we find a slightly higher *ortho*-content at all temperatures. Sulphonation with oleum has now been shown to give a similar trend of isomer composition but, as would be expected, sulphonation is more nearly complete at all temperatures than with sulphuric acid.

EXPERIMENTAL

p-Phenolsulphonates.—Equimolar quantities of phenol and 98% sulphuric acid were mixed, kept at 120° for 4 hr., and poured on ice. After neutralisation to pH 5 and filtration (from the sulphone) the solution was concentrated and cooled, and the mixed sodium phenolsulphonates were collected. Several recrystallisations from water gave the pure *para*-isomer as dihydrate. Recrystallisation of B.D.H. sodium *p*-phenolsulphonate (~95% of *para*-isomer) was equally satisfactory. The *S*-benzylisothiuronium salt had m. p. 169—170° (Muramoto² m. p. 171·3°).

o-Phenolsulphonates.—(a) (Cf. Obermiller¹) Equimolar quantities of phenol and 98% sulphuric acid were mixed, with cooling, and kept at room temperature for 48 hr. The product was dissolved in water, neutralised (pH 7) with barium hydroxide, filtered from barium sulphate, and concentrated until crystallisation occurred on cooling. The barium salt was recrystallised once, converted into the sodium salt by use of one equivalent of sodium sulphate, and recrystallised successively until the intensity of the ferric chloride colour remained constant.

(b) More conveniently the crude phenolsulphonic acid was neutralised with sodium hydroxide, treated with carbon dioxide, extracted with ether, and evaporated to dryness. Extraction with boiling methanol followed by concentration of the extract gave sodium phenolsulphonate containing 80% of the *ortho*-isomer. Three further crystallisations from methanol gave pure sodium *o*-phenolsulphonate. The yield by either method was 5—10 g. on a molar scale.

Attempts to achieve separation by fractional crystallisation of the aniline or *p*-toluidine salts gave some enrichment but no pure *ortho*-isomer could be isolated. The *S*-benzylthiuronium salt had m. p. 117—118° (Muramoto² m. p. 118·9°).

Estimation of Total Phenolsulphonate.—(a) *Bromometric estimation*. Under the conditions described⁵ for the estimation of potassium *p*-phenolsulphonate the sodium salt also consumed 4·0 equiv. of bromine, but sodium *o*-phenolsulphonate consumed ~4·5 equiv. and 2,4,6-tribromophenol (m. p. 90—92°) was isolated.

(b) *Non-aqueous titration*. Sodium *o*- and *p*-phenolsulphonate gave poor end-points in dimethylformamide but could be satisfactorily titrated in ethylenediamine with tetrabutylammonium hydroxide in benzene-methanol as base and *o*-nitroaniline as indicator.⁷

Measurement of Ferric Chloride Complexes.—(a) *Determination of absorption spectra*. To a freshly prepared 1% solution (0·061M) of anhydrous ferric chloride in water was added an equal volume of aqueous *S*-benzylisothiuronium *o*- or *p*-phenolsulphonate (0·001M). Absorption spectra were determined within 5—30 min. on a Unicam S.P. 500 spectrophotometer. The "blank" cell contained 0·0305M-ferric chloride. Under these conditions, at 535 m μ , the *ortho*-isomer showed maximum optical density of 0·404 and the *para*-isomer 0·038. Identical spectra were given by the corresponding sodium salts. Wesp and Brode,⁴ using barium salts, record 535 m μ as the peak wavelength for both isomers but state that the *para*-isomer has slightly greater absorption than the *ortho*. In contrast, Olsen and Goldstein,³ apparently quoting Obermiller,¹ report that the *ortho*- gives a colour approximately eight times as intense as that of the *para*-isomer.

(b) *Mixtures of o- and p-isomers*. Solutions containing known proportions of pure sodium *o*- and *p*-phenolsulphonate at a total concentration of 0·001M were prepared and the optical

⁶ Kekulé, *Z. Chem.*, 1867, 197; *Ber.*, 1869, 2, 330; Schultz and Ichenhaeuser, *J. prakt. Chem.*, 1908, 77, 114.

⁷ Beckett and Tinley, "Titration in Non-aqueous Solvents," The British Drug Houses Ltd., Poole, 3rd edn.

densities of their ferric chloride complexes determined as in (a). In Table 2 the "calculated" optical density assumes a linear relation between percentage composition and intensity and uses the values obtained for the pure isomers. Similar results were obtained with *S*-benzylisothiuronium salts.

TABLE 2.

<i>ortho</i> -Isomer (%) ...	10	20	30	40	50	60	70	80	90
Optical density, obs.	0.074	0.115	0.147	0.184	0.220	0.258	0.290	0.330	0.365
„ calc.	0.075	0.111	0.148	0.184	0.221	0.258	0.294	0.331	0.367

In the determination of the isomer composition of other samples of mixtures the total phenolsulphonate was determined by non-aqueous titration and a suitable quantity taken to give a 0.001M-solution. The composition was then calculated (or determined graphically) from the ferric chloride colour.

Isomer Composition of Phenolsulphonates formed by Sulphonation of Phenol at Different Temperatures.—(a) *With oleum.* Oleum (20% SO₃; 24.7 ml.) was added dropwise with stirring to phenol (47 g.), the mixture being maintained at 115–120° during addition and subsequently at 120° ± 1°. After 4 hr. the product was poured on ice (200 g.) and rapidly neutralised with 4*N*-sodium hydroxide. The solution was saturated with carbon dioxide, extracted with ether (250 ml.), evaporated to dryness under reduced pressure, and dried for 2 hr., at 120°. The isomer composition was determined as outlined above. Similar runs were carried out at other temperatures (see Table 1). Some difficulty was experienced in achieving adequate mixing and temperature control during addition of oleum at 20° and 40°. Both "ether-soluble (%)" (representing unchanged phenol and sulphone) and "*ortho*-isomer (%)" figures are % by weight of the total phenolsulphonate.

(b) *With sulphuric acid.* Sulphuric acid (98%; 52.5 g., 5% excess) was used in place of oleum in (a).

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