

XXXI.—*The Melting Points of Mixtures of o- and p-Toluenesulphonyl Chlorides.*

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IN connexion with an investigation of the toluenesulphonyl chlorides, it became desirable to obtain accurate data concerning the melting points of mixtures of the ortho- and para-isomerides. This question has been investigated by Holleman (*Ber.*, 1911, **44**, 2504), but his method of preparing *o*-toluenesulphonyl chloride did not appear very satisfactory, and he did not directly determine the eutectic point. His data indicate that the eutectic temperature is in the neighbourhood of  $1^{\circ}$ , and the eutectic mixture contains between 15 and 25 per cent. of the *p*-sulphonyl chloride.

*Preparation of o- and p-Toluenesulphonyl Chlorides.*

Holleman prepared the *o*-sulphonyl chloride after fractional crystallisation of the mixed barium salts obtained from the sulphonation product of toluene. The following method seems preferable as ensuring the purity of the *o*-sulphonyl chloride. Pure *o*-toluenesulphonamide (m. p.  $156^{\circ}$ ) is readily obtained by repeated fractional precipitation from a hot, approximately normal solution of the sodio-derivative. A portion of the solution is titrated, and

the amount of acid required to precipitate the whole of the amide determined. After heating the main portion of the solution to  $90^{\circ}$ , a proportion of this amount of acid is slowly added, the proportion depending on the purity of the amide taken and the temperature at which the precipitate is filtered. Using an amide, m. p.  $152-154^{\circ}$ , and filtering at  $65^{\circ}$ , the amount of acid taken is 90 per cent. of that required for total precipitation. The pure amide is but very slowly hydrolysed by prolonged boiling with mineral acids or sodium hydroxide solution; the hydrolysis is completely effected by dissolving the amide (250 grams) in concentrated sulphuric acid (1100 grams), adding powdered sodium nitrite (110 grams) at  $0^{\circ}$ , and allowing the mixture to remain in the refrigerator overnight and at the ordinary temperature during the following day. The product is then poured into water, the solution neutralised with sodium hydroxide, evaporated to dryness, and the sodium *o*-toluenesulphonate extracted with boiling alcohol.

The *o*-toluenesulphonyl chloride, prepared by treating this salt with phosphorus pentachloride in the ordinary way, is purified by distillation under reduced pressure, and is thus obtained as a colourless liquid, b. p.  $126^{\circ}/21$  mm.,  $D_4^{20}$  1.3383; after freezing, the substance melts at  $10.17^{\circ}$ . The refractive indices were determined at  $17.2^{\circ}$  by the hollow prism method,  $n_a$  1.5528,  $n_D$  1.5575,  $n_B$  1.5713, and  $n_v$  1.5937; determinations made with the Pulfrich refractometer gave  $n_D^{20}$  1.55653.

*p*-Toluenesulphonyl chloride was purified by repeated fractional crystallisation from light petroleum, followed by fractional distillation under reduced pressure; it melted at  $67.2^{\circ}$ .

### *The Melting-point Curve.*

Mixtures of the two chlorides were weighed into a large test-tube fitted with a thermometer reading to  $0.1^{\circ}$ , and a suitable stirrer, precautions being taken to prevent access of water vapour; the test-tube was supported by a rubber fitting in a larger one suspended in a water-bath. After the mixture had been partly frozen by slow cooling, the bath was gradually heated, and the temperature at which the last fragments of crystal disappeared recorded as the melting point. The melting points of the different mixtures were determined several times, fresh mixtures being either made up anew or prepared by adding one or the other chloride to the mixture already contained in the tube.

When the results recorded in the following table were plotted on a curve, the eutectic temperature was found to be  $1.6^{\circ}$ . This was confirmed by measurements made on the eutectic mixture itself

and by the fact that, when completely frozen mixtures were gradually melted, a marked arrest on the temperature-time curve occurred at  $1.6^{\circ}$ . The eutectic mixture contained 17.5 per cent. of the para-isomeride.

<i>p</i> -Sulphonyl chloride, per cent.	M. p.	<i>p</i> -Sulphonyl chloride, per cent.	M. p.
0.0	10.17°	18.0	3.9°
2.0	9.9	19.0	6.6
5.8	8.0	20.0	7.9
8.0	7.0	25.0	14.7
10.0	5.8	29.1	20.2
12.0	4.9	35.3	26.9
14.0	3.8	42.2	33.6
15.0	3.0	50.2	39.8
16.0	2.6	56.2	44.1
17.0	2.1	62.8	48.4
17.25	1.9	68.8	51.9
17.5 eutectic	1.6	78.2	57.3
17.75	3.3	89.7	62.6
		100.0	67.2

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