For the solutions with sodium chloride and cobaltous sulfate as added salts, titration gave directly the concentration of cobaltous iodate. Subtracting the weight of this salt present in each liter of solution from the weight of that volume of solution gave the weight of the solution of the added salt which entered into it. It was then a simple matter to calculate the weight of added salt and of water per liter. Calculation of the molalities of the salts present gave the data of Table I.

TABLE I

SOLUBILITIES OF $Co(IO_3)_2 \cdot 2H_2O$ AT 30°

In NaCl Solutions

Molalities		
NaCl	$Co(IO_3)_2$	Densities
0.0	0.01165	1.0006
.0029	.0119	1.0007
.0052	.0120	1.0008
.0069	.0121	1.0009
.0111	.0124	1.0010
.0140	.0125	1.0011
.0267	.0131	1.0016
.0355	.0134	1.0020
.0532	.0139	1.0029
.0941	.0149	1.0054
.1449	.0158	1.0085

In $NaIO_3$ Solutions

$NaIO_3$		
0.0	0.01165	1.0006
.0044	.0102	1.0006
.0076	.0093	1.0007
.0087	.0090	1.0008
.0127	.0080	1.0011
.0174	.0069	1.0014
.0202	.0063	1.0017
.0280	.0050	1.0026
.0360	.0040	1.0037
.0483	.0030	1.0056
.0999	.0010	1.0135

In $CoSO_4$ Solutions

$CoSO_4$		
0.0	0.01165	1.0006
.0026	.0113	1.0008
.0052	.0111	1.0011
.0061	.0111	1.0012
.0123	.0107	1.0019
.0129	.0106	1.0020
.0235	.0102	1.0034
.0258	.0101	1.0037
.0516	.0095	1.0076
.0774	.0094	1.0117
.1032	.0093	1.0155

Summary

The solubility of cobaltous iodate dihydrate in solutions of sodium chloride, sodium iodate and cobaltous sulfate has been studied in the region of concentration 0 to approximately 0.1 molal for the added salt.

STILLWATER, OKLAHOMA RECEIVED FEBRUARY 28, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Allotropic Forms of Diphenylsulfone and the Determination of their Transition Point

BY VLADIMIR J. MIKESKA, NICHOLAS T. FARINACCI AND MARSTON TAYLOR BOGERT

In the course of an examination of certain still residues remaining from the preparation of phenol by the fusion of sodium benzene sulfonate with sodium hydroxide, we separated a crystalline solid, in a yield of over 30%, whose chemical properties and analysis coincided with those of diphenylsulfone. The formation of this compound as a by-product in the manufacture of phenol by the process stated has been known for years. The only puzzling thing about our product was its melting point. The literature on this subject is confusing, some investigators giving the figure as 124°, others as 128°.

It seemed of interest, therefore, to ascertain if possible the reason for this discrepancy, and our study of the problem disclosed the following facts. (1) Diphenylsulfone exists in two reciprocally convertible allotropic forms, one melting at 124° and the other at 128°. (2) The transition temperature for the two is in the neighborhood of 75°. When crystallization is induced (no matter how) above this temperature, the product always melts (if pure) at 128°; if induced below this, it melts at 124°.

Otto[1] obtained both forms, but concluded that the 124° form, because of its lower m. p., was probably impure.

Remsen and Saunders[2] gave 124° as the correct m. p. for the sulfone. Because they were unable by recrystallization to raise this m. p. to the

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[1] Otto, *Ann.*, **136**, 160 (1865).

[2] Remsen and Saunders, *Am. Chem. J.*, **17**, 364 (1895).

128° reported by Otto, they at first doubted the identity of the two products, but analysis and comparison of other properties convinced them that their product was also the diphenylsulfone.

In the light of the results of our own experiments, it seems most likely that Otto carried out his final crystallization above 75°, and Remsen and Saunders carried out theirs below that temperature.

The sulfone can be supercooled to 72°. Hence crystallization can be induced at any temperature between 72 and 124°. If the sulfone is fused and then cooled rapidly, as is the usual case, it yields the 128° form, because under these conditions it solidifies above 75°. But when the fused sulfone is cooled slowly, it supercools below the transition point before it congeals, and the 124° form is produced. It is therefore possible to change the m. p. of the sulfone at will, by fusing and then inducing crystallization above or below the transition point.

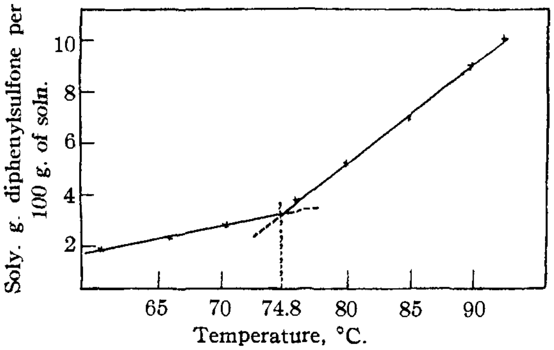

Fig. 1.—Allotropic forms of diphenylsulfone. The intersection of the three lines shows the transition point: α-form, m. p. 124°, stable below 74.8°, β-form, m. p. 128°, stable above 74.8°.

The method of inducing crystallization does not appear to make any difference. Cooling of the molten material was only one of several methods used. Seeding was another one. If the molten sulfone were seeded above 75° with either the 124 or the 128° form, it congealed immediately to the 128° form.

When the sulfone was crystallized from hot solvents under ordinary conditions, the 124° form generally resulted, because the crystals did not begin to separate until the solution had cooled below 75°. In these experiments, the solvents used were water, methyl and ethyl alcohols, ether, acetone, acetic acid, ligroin and chloroform. In every case, the 124° form was obtained, irrespective of whether the solute had been the 124 or the 128° form.

When the temperature of the solution was maintained above 75°, so that crystallization had to take place above this transition point, the 128° form resulted. Alcohol and acetic acid were the solvents employed. From the former, at 75 and at 78° the 128° type separated, at 66 and at 70° the 124° type. From acetic acid at 100°, the 128° type separated. When 50 g. of the 128° form, suspended in 600 cc. of 95% ethanol, was stirred for eight hours at 30°, it was transformed into the 124° form, a rearrangement which indicates that the lower-melting is the stabler form at the lower temperatures.

Another method used to induce crystallization at a desired temperature was to employ a mixture of two solvents, such as water and alcohol, in one of which (alcohol) it dissolved freely and in the other but slightly. An alcoholic solution of the sulfone saturated at the requisite temperature was treated with water heated to the same temperature. Crystallization ensued immediately at this temperature. When this mixing occurred above 75°, the 128° form was obtained, when below this the 124° form.

That the 124° form is not an impure 128° form was proved by the fact that no amount of purification enabled us to change the lower to the higher melting form.

The assumption that the 124° is a hydrated form of the 128° type is also untenable, for no water was evolved when the 124° form was heated, and the analysis of the two evidenced the identity of their composition, and both types could be obtained from water–alcohol mixtures. Further, as already noted, the 128° form could be changed to the 124° under strictly anhydrous conditions, *i. e.*, by fusing it and allowing it to crystallize slowly below 75°.

The transformation of the solid forms into each other seems to be slow. When the 128° form was kept at 66° for twenty-four hours, there was no evidence of its having changed; but when the 124° form was maintained at 100° for the same length of time it was partly converted into the 128° form. The higher velocity of transformation at the latter temperature may account for this partial transformation. The fact that the 124° type is obtained by metathesis in solution at low temperatures indicates that it is the stable form below the transition point.

A more precise determination of the transition point seemed to us desirable. The thermometric method was unsatisfactory, because of the slowness of the change of one solid form into the other, and also because there occurs appreciable sublimation of the sulfone above about 80°. We fell back, therefore, upon the solubility method, which was applied as follows.

A three-necked 500-cc. flask, containing a saturated solution of the sulfone in 45% aqueous acetic acid in contact with a large excess of the solid, was heated in a four-liter water-bath provided with a coil of perforated copper pipe. The water in the bath was kept in motion by air bubbles forced through pin-holes in this pipe, while the contents of the flask were agitated by a motor-driven glass stirrer. With the flask contents and bath liquid in vigorous agitation, the temperature of the solution in the flask was raised to 90°, and was then allowed to fall slowly, samples being removed at 76, 70.5, 66, and 60.5°. After this, the temperature was gradually raised again and samples taken at 80, 85, 90, and 92.5°. This procedure was adopted in order to ensure saturation and to facilitate the attainment of equilibrium. The samples were blown out of the flask by air pressure, through a preheated tube containing a plug of cotton wool to filter out any crystals, into tared bottles. The weights of liquid and solid were determined by evaporation to dryness, and the solubilities calculated on the basis of grams of solid per 100 g. of solvent. Eight determinations were made, with temperatures so chosen as to bring the transition point about halfway between the extremes. The graph shows these experimental results, with the transition point at 74.8°.

Summary

1. Diphenylsulfone exists in two reciprocally convertible allotropic forms, one melting at 128°, and the other at 124°.
2. The conditions are explained under which one form can be changed into the other, the transition temperature being about 74.8°.
3. Some of the confusion in the literature on this subject is thus explained.

NEW YORK, N. Y. RECEIVED JULY 17, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

The Condensation of 2-Butanone with Aldehydes of the Type RR'CHCHO[1,2]

BY S. G. POWELL AND MAYNARD M. BALDWIN

It has been shown that certain straight-chain aldehydes react with 2-butanone under the influence of alkaline condensing agents to form ketols of the type $RCHOHCH(CH_3)COCH_3$.[3] On the other hand, Thoms and Kahre found that with isobutyraldehyde the ketol $(CH_3)_2CHCHOHCH_2$-COC_2H_5 was obtained.[4] It seemed therefore desirable to investigate the behavior of other aldehydes of the type RR'CHCHO.

2-Butanone was treated with methylethylacetaldehyde, diethylacetaldehyde, and ethyl-*n*-butylacetaldehyde in the presence of dilute potassium hydroxide. In each case the resulting ketol was dehydrated to the unsaturated ketone; this was reduced to the saturated secondary alcohol and this in turn oxidized to a mixture of acids as described in previous papers.[3c,3d,5] The water-insoluble acids obtained were then investigated and in each case the acid of the type RCH_2COOH (where the aldehyde in each instance is designated as RCHO) was found and in no case could the acid of the type RCOOH be identified, showing that the secondary alcohols were of the type $RCH_2CH_2CHOHC_2H_5$ and not $RCH_2CH(CH_3)$-$COCH_3$, and that these aldehydes, like isobutyraldehyde, had reacted with the methyl group of the 2-butanone. The identity of the acids was established by a comparison of their piperazonium salts with those prepared from known samples of the acids which might be formed. Of the acids required for purposes of comparison β-ethylenanthic and γ-ethylcaprylic acids could not be found described in the literature and their preparation is given in detail. The other acids were

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[1] Presented before the Division of Organic Chemistry at the San Francisco meeting of the American Chemical Society, August, 1935.

[2] Based upon a thesis submitted by Maynard M. Baldwin in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Washington.

[3] (a) U. S. Patent 981,668; (b) Salkind, *J. Russ. Phys.-Chem. Soc.*, **37**, 484 (1905); (c) Powell, THIS JOURNAL, **46**, 2514 (1924); (d) Powell, Murray and Baldwin, *ibid.*, **55**, 1153 (1933).

[4] Thoms and Kahre, *Arch. Pharm.*, **263**, 241–252 (1925).

[5] Powell and Secoy, THIS JOURNAL, **53**, 765 (1931).