

LXI.—*The Stability of Tautomeric Formaldehyde-phenylhydrazones.*

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BAMBERGER AND SCHMIDT (*Ber.*, 1901, **34**, 574, 2001) have shown that a series of substitution products of the phenylhydrazone of formaldehyde, of the type $\text{CHR:N}\cdot\text{NHPh}$, occur in two modifications, which are certainly different in solution as well as in the solid state (see Sidgwick, T., 1915, **107**, 678), and are very probably *cis*- and *trans*-isomerides. They find that with such substances one form may be obtained by crystallisation from alcohol, and the

other from light petroleum. From this they infer that the stability of the form is determined by the solvent with which it is in contact. Dimroth (*Annalen*, 1910, **377**, 136) accepts this conclusion, and explains its apparent contradiction to the van't Hoff-Dimroth law (which makes the stability independent of the solvent) by assuming that the substances are polymerised in one solvent. It is easy to show that this explanation will not hold: if we take polymerisation into account, the van't Hoff-Dimroth equation assumes a somewhat different form, but still gives the stability as independent of the solvent. The only condition under which the solvent can determine the stability is when the heat of transformation is so small as to be comparable with that developed when the crystals are wetted with one or other solvent. Only one such case is known for certain, but this curiously is a substance of the same type as Bamberger and Schmidt's products, namely, the phenylhydrazone of acetaldehyde (Lockemann and Liesche, *Annalen*, 1905, **342**, 14; Laws and Sidgwick, *T.*, 1911, **99**, 2085). It seemed therefore not impossible that the formaldehydephenylhydrazones offered another example of this peculiarity, and it was interesting to examine their behaviour from this point of view.

Two of these compounds were prepared and investigated, benzoyl-formaldehydephenylhydrazone (phenylglyoxalphenylhydrazone), $C_6H_5 \cdot CO \cdot CH : N \cdot NH \cdot C_6H_5$, and nitroformaldehydephenylhydrazone, $NO_2 \cdot CH : N \cdot NH \cdot C_6H_5$.

I. Phenylglyoxalphenylhydrazone.

This was prepared by Bamberger and Schmidt's method (*loc. cit.*). According to these authors, the α -form, obtained from benzene or light petroleum, melts at 114—117°, and the β -form, from alcohol, at about 138°.

The crude product from benzoylacetic ester and the diazonium salt (which is mainly the β -form) was boiled for several hours with light petroleum (b. p. 60—80°) until it was all dissolved. On cooling, short orange prisms of the α -form separated out, which melted at 111—112°.

Mere recrystallisation of this from alcohol was usually insufficient to cause any serious conversion into the β -form. A better method is to digest the crystals for several hours at 40—55°, or for a few days in the cold, with insufficient alcohol to dissolve them. The remaining crystals on drying were found to melt at 132—133°.

An attempt was made to distil the α -form under diminished pressure. At 23 mm. it came over with considerable decomposition at 215—230°, and condensed to an orange mass melting at 120°.

On distillation of the α -form with steam the compound came over slowly, separating from the distillate as a pale yellow, flocculent precipitate which melted at $134\text{--}135^\circ$, and appeared to be the pure or nearly pure β -form. But when this was digested with a little alcohol for several hours at 32° , its melting point rose to $145\text{--}146^\circ$. This seemed the most satisfactory method of obtaining the β -compound, and was that subsequently adopted. The exact melting point varied slightly with different preparations, but $145\text{--}146^\circ$ was the highest observed, and is presumably the melting point of the pure β -modification.

In order to determine whether the stability of the forms is really dependent on the solvent, several samples of the α -form, melting at $111\text{--}112^\circ$, were left in contact with small quantities of light petroleum and alcohol respectively at the ordinary temperature, and from time to time portions of the solid were removed, dried, and their melting points measured. In all cases the melting point rose gradually, the final values reached, and the time required, being :—

In alcohol, 1 month	141°.
„ 1 month (another experiment)	138°.
In light petroleum, 15 hours	127°.
„ „ 1 month	133°.

It is therefore evident that the β -form is stable in contact with either solvent. The peculiar behaviour of the substance must be due to the fact that the change of each modification into the other in solution is slow, and that the proportion of the α -form is much larger in non-associated solvents than in alcohol. Hence when the β -form is boiled with light petroleum a solution is ultimately obtained which contains a large excess of the α -modification, and if this is rapidly cooled, the α -form crystallises out before it has time to change back into the β -form. But if sufficient time is given for the change, by leaving the crystals in contact with the solvent, the β -form is the ultimate product, whatever solvent is used. On distillation of the α -form with steam, the conversion into the β -form is nearly complete, so that the α -form must be almost absent from the vapour, or the conversion in water unusually rapid.

The exact melting point of any given sample varies with the rate of heating, and it is evident that the transformation is fairly rapid in the fused state. We were able to determine the natural freezing point by heating some of the substance in a test-tube containing a thermometer, in a bath of which the temperature was very slowly raised. Whether the α -form (m. p. 112°) or the β -form (m. p. 135°) was used, the last crystals were found to disappear at 128.5° .

The solubilities were measured by the synthetic method in alcohol, benzene, and *n*-heptane. In alcohol, the only form the solubility of which can be measured is the β , since the α is transformed into this before saturation is reached. But with benzene and heptane it is possible to measure the solubility of both forms in the same tube. If the tube is heated until all is dissolved, and then cooled rapidly, the orange crystals of the α -form separate, and the temperature can then be observed at which these are all dissolved; whilst if the tube is left for some time, a yellow powder of the β -form appears, and the solubility of this form can now be measured.

It is obvious that with a substance of this kind we might measure for each form two solubilities; (*A*) when the solution contains only that form, and (*B*) when it contains a mixture of the two in chemical (allelotropic) equilibrium. With these substances the isomeric change is too rapid at temperatures above the ordinary for it to be possible to measure (*A*), and it was only (*B*) that we could hope to determine.

The results are given in the following table, the first column indicating the number of grams of substance in 100 grams of solution. They cannot be made very accurate, because the chemical equilibrium is not completely established for a long time, but they give an approximation to the true values.

Solubility of Phenylglyoxalphenylhydrazone.

In Ethyl Alcohol.		In Benzene.			In Heptane.		
Per cent.	Temp.	Per cent.	Temperature.		Per cent.	Temperature.	
(β -form)			α -form	β -form		α -form	β -form.
(100·0	128·5°)	(100·0	—	128·5°)	(100·0	—	128·5°)
90·2	113·5	89·8	—	115·0	55·9	96·0°	113·0
74·9	103·4	70·8	75·3°	98·0	35·4	94·0	111·0
55·2	98·0	45·0	56·0	79·5	17·0	84·7	103·2
39·5	93·5	38·6	50·0	74·3	10·1	75·8	93·5
19·6	83·4	30·2	40·8	67·2	4·63	58·2	80—81
8·8	70·0	19·9	29·0	59·8	1·82	—	71—72
		10·4	8·0	44·2			
		4·8	—	26·0			

In benzene, the solubility of the α -form could not be determined at the highest temperatures, as it was converted into the β before saturation was reached; whilst at the lowest concentrations in heptane the exact temperatures were difficult to measure, owing to the small quantity of crystals which separated.

It can easily be shown that the ratio of the solubilities (if they are small) of the two forms of a substance in contact with the allelo-tropic solution must be the same at a given temperature in any solvent (for an example of this, see Chattaway and Lambert, *T.*, 1915, 107, 1781). To test this point, the solubilities were measured

in a thermostat at 32°, the hydrazone (either form) being stirred with the solvent until equilibrium appeared to be reached. The solutions were analysed by evaporating off the solvent at 100°. It was found that the time required for the β -form to reach equilibrium was usually one hundred to one hundred and fifty hours, whilst the α -form could not be left more than eight or nine hours in the other solvents, and not more than two hours in *cyclohexane*, before the solid began to change into the β -form. Hence the values for the α -form are all somewhat low, and that for *cyclohexane* is no doubt much too low.

Solubilities at 32°.

Solvent.	Per cent. α -form	Per cent. β -form	Ratio.
Benzene	25.1	8.0	3.1
Heptane	1.7	0.55	3.1
Carbon tetrachloride.....	8.8	2.27	3.9
<i>cycloHexane</i>	(2.56)	1.56	(1.7)

It will be seen that there is fair agreement, except in the last solvent, where the α -value is certainly too low, and hence the ratio likewise.

If the benzene values are plotted on the same diagram as the solubility determinations in this solvent given in the first table, they will be seen to be several units per cent. higher. There is no doubt that the determinations in the thermostat are more trustworthy, because a longer time was given for the attainment of equilibrium. By interpolation from the solubility curves we can get values of the ratio at every 10°. These, although only approximate, for the reasons given, are worth recording.

Temp.	Solubility in Benzene.			Solubility in Heptane.		
	α -form	β -form	Ratio.	α -form	β -form	Ratio.
90°	—	—	—	24.5	8.1	3.0
80	77.2	45.7	1.7	12.6	4.2	3.0
70	63.0	33.2	1.9	8.20	1.80	4.6
60	49.8	23.0	2.2			
50	37.5	15.0	2.5			
40	28.4	9.3	3.1			
30	20.7	5.5	3.8			
20	15.0	4.0	3.8			

The values of the ratio are much higher in heptane, probably owing to the difficulty of allowing enough time for saturation.

In benzene a fairly regular curve for the ratio is obtained, which extrapolates to a value between 4 and 5 at 0°. It is to be remembered that the generalisation is only strictly true in dilute solution, which may explain the fall in the ratio as the solution becomes

more concentrated; though it is also possible that the substance is approaching its transition point as the temperature rises.

The solubilities of the two forms in benzene at about $+3^\circ$ have been measured by the freezing-point method (Sidgwick, T., 1915, 107, 678), and were found to be: α , 5.84, β , 0.322 per cent. (assuming that they are not polymerised in solution). Under these conditions isomeric change is practically excluded, and these may be taken to be solubilities in sense (A), with only one form in solution. This enables us to arrive at an approximate value of the proportions of the two forms at allelotropic equilibrium in benzene.

As we have seen, the ratio of the solubilities of the two forms at allelotropic equilibrium (sense B) at $+3^\circ$ is between 4 and 5. Let us assume it to be 4; and let the ratio of the concentrations $\alpha : \beta$ in benzene solution at $+3^\circ$ be k . Then as we know that the percentage of α -form in solution in equilibrium with the solid α -form is 5.84, it follows that at allelotropic equilibrium there is also present in solution $5.84/k$ per cent. of the β -form. In the same way in a solution saturated with the solid β -form we have 0.322 per cent. of the β -, and $0.322 \times k$ per cent. of the α -form. Thus the total concentrations at equilibrium (sense B) are:—

$$\begin{array}{rcl} \text{Solution saturated with } \alpha\text{-} & 5.84 & + 5.84/k = x \\ \text{,, ,, ,, } \beta\text{-} & 0.322 & + 0.322 \times k = y \end{array}$$

The ratio $x/y = 4$, so that we have a quadratic for k , the value of which is found to be 4.5. If we assume the ratio to be 5 instead of 4, k will be 3.6. Taking the mean value $k = 4$, it follows that in benzene solution at $+3^\circ$ there is at equilibrium approximately 4 times as much α - as β -form.

This also enables us to calculate the value of the van't Hoff-Dimroth constant G for this substance at $+3^\circ$:—

$$\begin{aligned} G &= \frac{\text{Concentration of the } \beta\text{-form at equilibrium}}{\text{Concentration of the } \alpha\text{-form at equilibrium}} \times \frac{\text{Solubility of the } \alpha\text{-form}}{\text{Solubility of the } \beta\text{-form}} \\ &= \frac{1}{4} \times \frac{5.84}{0.322} = 4.5. \end{aligned}$$

II. Nitroformaldehydephenylhydrazone.

The crude product obtained by Bamberger's method from nitromethane was freed from the nitroformazyl mixed with it by dissolving it in the cold in sodium hydroxide solution, and adding concentrated hydrochloric acid until a definite red precipitate was formed. This was filtered off, and excess of hydrochloric acid added to the filtrate. Five grams of crude product gave 3.6 grams of the β -hydrazone melting at 83.5° (Bamberger and

Schmidt, 84.5—85.5°). 2.8 Grams of this were warmed with 5 c.c. of benzene for half an hour, by which time solution was complete, and on cooling 2 grams of the α -form, m. p. 74° (Bamberger and Schmidt, 74.5—75.5°) were obtained.

Samples of the α -form were put in test-tubes with small quantities of alcohol, benzene, and carbon tetrachloride respectively. After three days at 32°, they all showed signs of considerable decomposition, except the sample in contact with alcohol, which had been seeded with a trace of the β -form. In this the liquid had solidified to a mass of the β -form, m. p. 82—84°. The same results occurred in another set, after a week at the ordinary temperature. In carbon tetrachloride, after two months at the ordinary temperature, a distinct yellow coating of the β -form was visible on the sides of the tube, although it could not be separated from the partly decomposed mass well enough for its melting point to be determined.

The instability of the compound made further investigation impossible; but these results are enough to show that with this hydrazone, as with the preceding one, the β -form is stable in contact with non-associated as well as with associated solvents. We may fairly assume that the same is the case with the other hydrazones examined by Bamberger and Schmidt.

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