

THE MELTING-POINT OF FORMYL PHENYL ACETIC ESTER

BY C. G. L. WOLF

As Wislicenus has shown,¹ formyl phenyl acetic ester exists in two modifications, one of which, the true formyl compound, is solid at ordinary temperatures and partly changes on heating above its melting-point into the second modification, which so far has not been obtained in the solid condition. The melt re-solidifies on standing after different lengths of time, depending on the amount of tautomeric change which has taken place. As the change from the liquid to the solid modification takes place at room temperature, the stable triple point, where the solid is in stable equilibrium with solution and vapor, must be between room temperature and the melting-point.

Formyl phenyl acetic ester can be made to melt at temperatures varying from 60° to 70° if the operation be carried out in melting-point tubes in the ordinary way. If the heating be rapid, the thermometer will indicate 80° before the substance is completely melted, and Brühl has even given the melting-point as 90° without giving any explanation. The point at which no change takes place is a definite one. If sealed capillary tubes containing the substance be heated in a bath regulated with a thermoregulator and well stirred, fusion occurs at any point above 50° providing the heating be sufficiently prolonged. Below this temperature, the solid modification persists and this is therefore the stable triple point.

¹ Ber. chem. Ges. Berlin, 20, 2933 (1887); 28, 767 (1895); Liebig's Ann. 291, 147 (1896).

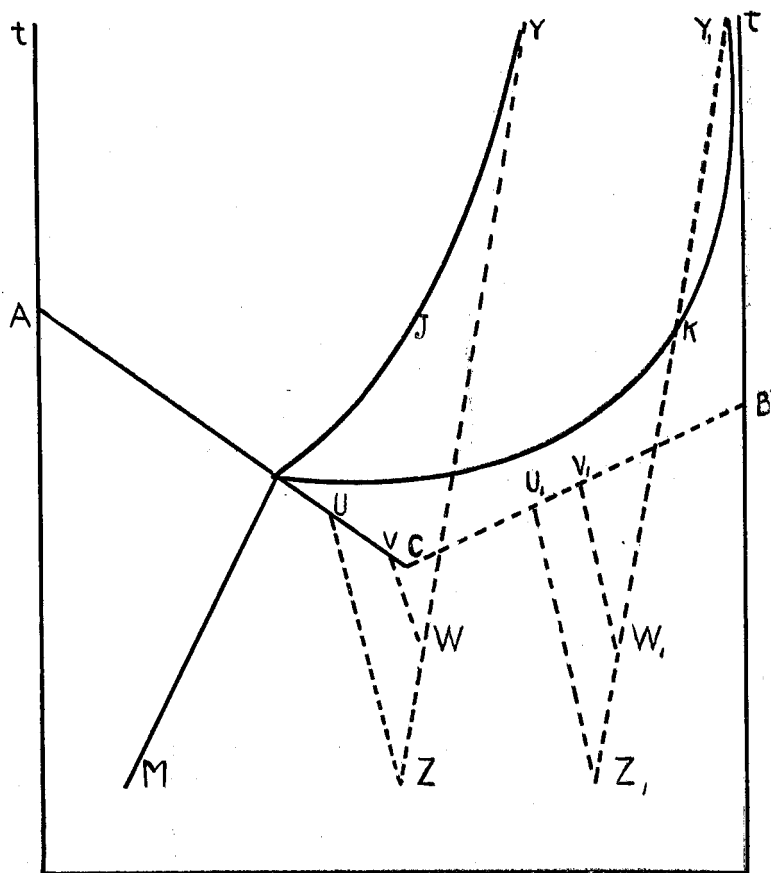
The pure formyl phenyl acetic acid was heated to 100° for some hours in order to obtain a concentration equilibrium at this temperature and cooled rapidly in a slush of solid carbon dioxide and ether. The temperature of the freezing mixture was -80° on the toluene thermometer. The substance set to a glass which did not crystallize on continued rubbing. On removing the tube from the freezing mixture, the liquid melted and was apparently unchanged. At the end of twenty-four hours crystals appeared which were tested in order to ascertain whether the substance was the solid formyl compound or was the enol modification. After washing carefully with benzol and drying on a porous plate, the substance gave no color with ferric chloride and was therefore the formyl compound.

The cooling of the ester to a low temperature had thus a marked effect in hastening the crystallization of the solid modification. Under ordinary circumstances, the formyl phenyl acetic ester heated to 100° for some time, requires weeks for crystallization to take place, although Wislicenus points out that the ester contained in a flask which is opened at various times may deposit crystals in the course of a few hours;¹ but this is certainly an exception to the general rule. According to Brühl (note, *ibid*) the solubility of the formyl compound in the liquid is small, so that the amount of change which takes place must be great at 70° , for, when the solid is melted at that temperature, and inoculated with a crystal of the formyl compound, but little of the latter separates out and the complete solidification of the liquid takes weeks owing to the slow velocity of the reverse change.

In order to understand the change which takes place in the melt it will be necessary to refer to a diagram. Let A represent the melting-point of the solid formyl phenyl acetic ester which lies above 80° , B the unknown melting-point of the enol modification, C the eutectic point of the two isomers, and X² the

¹ Liebig's Ann. 291, 166 (1896).

² In the diagram the letter X should come at the intersection of MY and AC.



stable triple point for A. Y is the point above the melting-point of A which in the case cited was 100° . M represents the equilibrium concentration at -80° . On heating A to the temperature Y, one would obtain a corresponding equilibrium. On allowing the temperature of the mixture to fall one obtains an instable point on the eutectic side of X because, when the mixture is sown with the crystals, the mass does not solidify. The equilibrium is not reached at a low temperature for the same reason, and, further, the velocity of reverse change must be slow. Hence the composition of the supercooled melt cannot be that of the equilibrium point but must be at some in-

stable point such as Z. If then the temperature be lowered to Z, the equilibrium must be displaced towards A, or in the case of oxymethylene phenyl acetic ester the melt, although not saturated with respect to A, is considerably more, than when simply allowed to fall to room temperature, as the rate of crystallization shows. On allowing the melt to rise to room temperature, one also gets a displacement of the concentration towards A, and hence at this point the relative amounts of the two isomers will be represented by U. Similarly if the temperature fell to W and were allowed to rise again one would obtain a corresponding amount of change represented by the concentration at V.

In other words, from the experimental data which formyl phenyl acetic ester has given one has obtained the saturation of the melt with respect to the formyl phenyl acetic ester more rapidly by cooling to a low temperature and allowing the temperature to rise slowly than if the melt were simply allowed to fall to the temperature of the room and to stay there. Since the velocity of reaction usually decreases with falling temperature, other things being equal, equilibrium should be reached more slowly by lowering and raising the temperature than by keeping it constant at the higher level.

In the case of tautomeric substances, however, another factor may enter into the reaction. The tendency to change in the melt from one substance to the other is more rapid the greater the difference between the actual point of instable equilibrium and the true equilibrium. Hence, other conditions being the same, the change would take place with greater speed at the temperature Z than at the higher point W. Against this one has to set the velocity of reaction which is ordinarily slowed by a lower temperature.

If on the other hand the potential difference were sufficient to overcome the slowing due to the temperature alone, then by alternately lowering the temperature and allowing it to rise, one would be able to hasten the saturation of the melt with the solid form to a greater or less extent depending on the amount of the change due to the action of the difference in the two factors.

The case is of interest because it shows that, in cases where tautomeric change takes place, repeated cooling may hasten the saturation point, and consequent crystallization.

That cooling to a low temperature does increase the apparent reaction velocity in some cases is shown by the results of Reicher and of Pope.

Reicher found with monoclinic sulfur that the change from this modification to the rhombic form took place with increasing velocity as the temperature fell from 95° to 35° , but below this point the rapidity of the conversion was decreased with falling temperature. So enormously did the lowering of the temperature affect the rate of change that at -35° , transformation was only accomplished in 500 times the length required at room temperature.¹ It is possible with formyl phenyl acetic ester that these low temperatures correspond to the interval between 95° and 35° in Reicher's case.

Pope² also shows that the rate of change in the crystallization of chloral hydrate from the form which separates out on sudden cooling to that which results on long standing is 12 times more rapid at -18° than at ordinary temperature.

This is not exactly analogous to the case of formyl phenyl acetic ester because in Pope's work the change is taking place in the solid state, whereas here we are dealing with the field for supercooled solution, but the analogy is sufficiently good to warrant mention.

In connection with the change which takes place above the triple point, two curves may represent the line of equilibrium. Brühl has assumed, in treating the change of formyl phenyl acetic ester into oxymethylene phenyl acetic ester, that at a comparatively low temperature the tautomeric change is great, and indeed in his later work has asserted that a complete transformation occurs.³ That this is not true is evident from a consideration of the law of mass action, for equilibrium is always reached

¹ Recueil Trav. Pays-Bas. 2, 251 (1883); 3, 1 (1884).

² Jour. Chem. Soc. 75, 455 (1899).

³ Zeit. phys. Chem. 30, 62 (1899); Ber. chem. Ges. Berlin, 32, 2326 (1899).

with both components in the melt. Should however the greater part of the change take place at low temperatures the equilibrium curve for the two forms in the solution would follow the general line of the curve $XK Y_r$. If the change took place more gradually with an equal increment of temperature the curve would rise more vertically from the origin and take the form $XJ Y$. From any experiments which have been made with formyl phenyl acetic ester no conclusions can be drawn as to the form of this curve. Attempts have however been made in this direction by observations of the length of time taken to obtain a saturated solution after heating for various periods and at various temperatures above the melting-point of the substance, and Wislicenus has shown¹ that crystals heated but a short time above 70° recrystallize more rapidly than those which have been heated for an hour at 80° .

This of course points more to the change not being instantaneous than to the completeness at the two points.

It would appear from theoretical considerations that an estimate of the temperature at which the greatest amount of change takes place could be deduced from the apparent specific heat.

As the transformation of the formyl compound into the oxy-methylene derivative takes place with absorption of heat, this absorption must be a measure of the amount of change taking place. Should one therefore determine the specific heat for the solution between 50° and 55° and follow calorimetrically the amount of heat necessary to raise the temperature of the melt through a definite range, one should find that if the curve had the general form $XJ Y$ the heat of change would be distributed approximately equally along the length of the curve. If on the other hand the greater amount of change took place at a low temperature, and should one attempt to raise a given weight of the liquid through a definite temperature interval starting at 50° , then the amount of heat would be equal to the specific heat plus the heat of reaction. In the case of the curve

¹ l. c. page 170.

X J Y, the amount of heat necessary to raise the liquid through the temperature range above K would be less than below that point, provided that the specific heat did not vary with the temperature, which is, of course, strictly speaking, not the case.

Cornell University.