LXXVIII.—*The Dynamic Isomerism of Phloroglucinol.*

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ON account of the difficulty of deciding from chemical reactions whether phloroglucinol is ketonic or enolic in constitution, Hartley, Dobbie, and Lauder (*Brit. Assoc. Report*, 1902), examined it by means of the spectrograph, and they concluded that it is purely enolic from the close analogy of its absorption curve to that of its trimethyl ether. As further confirmation of this view, they point to the great similarity which exists between the absorption curves of phloroglucinol and pyrogallol. The latter is well known to be enolic in constitution (Baeyer, *Ber.*, 1886, **19**, 163). It would appear that Baly and Ewbank (*Trans.*, 1905, **87**, 1347) join issue with Hartley, Dobbie, and Lauder, on the ground that as tautomerism exists in the mono- and di-phenols themselves, and not in their ethers, the conclusion arrived at regarding the constitution of phloroglucinol was not justified.

Baly and Desch (*Trans.*, 1904, **85**, 1029, and 1905, **87**, 766) have shown that the position of the absorption band of certain aliphatic tautomeric substances undergoes a displacement towards the less refrangible end of the spectrum when sodium hydroxide is added to their solutions, whilst, on the other hand, the addition of acid causes the absorption band to become less persistent. This method, which Baly and Ewbank (*loc. cit.*) applied to the study of the phenols, is also adopted in this investigation.

If the tautomeric process existing in phloroglucinol is of the same type as that existing in the mono- and di-phenols, then on the addition of sodium hydroxide the absorption band ought to be shifted towards the red. Two photographs of phloroglucinol (one milligram-molecule dissolved in 100 c.c. of water) in the presence of the alkali were taken, one with one equivalent and the other with two equivalents of sodium hydroxide. Curve I, Fig. 1, represents the absorption spectrum of the former, the latter being represented by Curve II, Fig. 1. In both

cases the band is greatly displaced towards the red. This displacement is considerably greater than that recorded by Baly and Ewbank (*loc. cit.*) in the cases of phenol, quinol, catechol, and resorcinol under the action of five equivalents of sodium hydroxide. It was thought advisable to examine whether the change taking place on the addition of sodium hydroxide to a solution of phloroglucinol was permanent in character. To decide this point, five equivalents of sodium hydroxide were added to an aqueous solution of phloroglucinol (one milligram-molecule in 100 c.c.). The solution, which was deep red, was left for sixty minutes. At the end of this time, five equivalents of hydrochloric acid were added, when the original colourless solution was immediately reproduced. If the change produced by the alkali was a permanent structural change, then, on photographing the solution to which the acid had been added, a series of spectra differing from those of phloroglucinol in neutral solution should result. On the other hand, if the colour and other changes produced by the alkali were of a temporary character, then, on neutralising the alkali, the absorption spectrum of phloroglucinol should be reproduced. These suppositions were tested experimentally and the latter view was definitely confirmed. It would therefore appear that the action of sodium hydroxide is simply to increase the number of ketonic molecules in the solution, and not to produce any other change.

Lowry (*Brit. Assoc. Report*, 1904), in his paper on dynamic isomerism, has pointed that in some cases it has been observed that an ionising solvent influences the equilibrium between two tautomerides in solution. It was therefore thought advisable to examine the absorption spectrum of phloroglucinol in a non-ionising solvent. One milligram-molecule of phloroglucinol was dissolved in 100 c.c. of ether and examined under exactly the same conditions as had existed when phloroglucinol was examined in aqueous solution. The series of spectra obtained were identical with that given by the aqueous solution, and this result shows that, in the present instance, the solvent does not affect the equilibrium between the two forms present in solution.

Finally, the absorption spectrum of phloroglucinol in the presence of hydrochloric acid was examined, with the object of ascertaining whether the persistency of the absorption band would be decreased, as was indicated by Baly and Desch (*loc. cit.*). Such a test applied to phloroglucinol should, if the compound exists in two modified forms, decrease the persistency of the absorption band. Ten equivalents of hydrochloric acid were added to a solution of phloroglucinol (one milligram-molecule of phloroglucinol dissolved in 100 c.c. of water, and examined through the same thicknesses of the cases discussed above. Here again Baly and Desch

supported, as the band was reduced in persistency and became more like phloroglucinol trimethyl ether. Curve I, Fig. 1, represents the band given by one milligram-molecule of phloroglucinol in 100 c.c. of water, and Curve IV that of the same concentration of phloroglucinol in the presence of ten equivalents of hydrochloric acid. The absorption of the trimethyl ether is given in the above-mentioned paper by Hartley, Dobbie, and Lauder.

The spectrum of pyrogallol in alkaline and acid solution has also been examined. Absolutely no difference can be perceived between the absorption of one milligram-molecule of pyrogallol in 100 c.c. of water and that of the same concentration in the presence of ten equivalents of hydrochloric acid, see Curve I, Fig. 2. In the presence of four equivalents of sodium hydroxide, a change is evident. The solution becomes deep brown, due to the absorption of oxygen from the air, and, in consequence, the general absorption is greatly increased, Curve II, Fig. 2. There is, however, no trace of a shift of the absorption band towards the red end of the spectrum, a result which was anticipated for chemical reasons. Great difficulty was experienced in making up the alkaline solution of the pyrogallol to prevent the colour becoming too intense. This was partially obviated by preparing a solution of sodium sulphite in boiling water, thus practically eliminating the dissolved oxygen. On adding four equivalents of sodium hydroxide, the solution assumed a deep amber colour instead of an intense brown. The only effect that this had on the spectrum was to decrease the extent of the general absorption by a very small amount. On adding four equivalents of sodium hydroxide to a solution of pyrogallol (one milligram-molecule dissolved in 100 c.c. of water), excluding the air, allowing to stand for sixty minutes, and then adding four equivalents of hydrochloric acid, the colour of the solution remained unchanged. A photograph of this solution compared with one of the alkaline pyrogallol solution exhibited no difference, thus indicating that the change produced by the alkali is permanent in character.

EXPERIMENTAL.

The method used in photographing the spectra was that described by Hartley (*Phil. Trans.*, 1885, **175**, 325), the lines of cadmium being used as reference. The method of plotting the curves is that employed

Baly and Desch (*Trans.*, 1904, **85**, 1029). In all cases the solutions were prepared by dissolving one milligram-molecule of the substance in 100 c.c. of the solvent, and when necessary these solutions were diluted to one-tenth of this concentration.

The phloroglucinol used was a portion of the specimen recrystallised by Hartley and described in the British Association Report,

1902. The pyrogallol, which was purified by recrystallisation, melted at $132-134^{\circ}$.

The dot and dash curve, Fig. 1, represents phloroglucinol in aqueous solution in the presence of two equivalents of sodium hydroxide. It will be noticed that the band is broad and persistent, its position being very much nearer the red end of the spectrum than that of phloroglucinol, Curve I, Fig. 1, representing the absorption band of the latter substance in aqueous solution.

The dotted curve, Fig. 1, represents phloroglucinol in aqueous solution in the presence of one equivalent of sodium hydroxide. The absorption band in this case is less persistent than in the former case, a fact to be expected.

FIG. 1.

Curve IV, Fig. 1, shows the absorption exerted by phloroglucinol in aqueous solution in the presence of ten equivalents of hydrochloric acid.

Curve I, Fig. 2, shows the absorption band characteristic of pyrogallol in aqueous solution. The persistency of the band is not so great as in the case of phloroglucinol; in other respects they are identical. Pyrogallol in aqueous solution and in the presence of ten equivalents of hydrochloric acid produces an absolutely identical absorption spectrum.

The dot and dash curve, Fig. 2, represents pyrogallol in aqueous solution in the presence of two equivalents of sodium hydroxide.

Conclusions.

1. Phloroglucinol exists in neutral solutions in both the ketonic and enolic modifications. That this is the case is shown from the fact that the absorption curve of its trimethyl ether is less persistent than that of phloroglucinol itself, and also because the equilibrium between the two forms is disturbed by the introduction into the solution of alkali and acid.

2. In neutral solution, the enolic form of phloroglucinol is greatly in excess of the ketonic form. This can be seen by comparing the curves of pyrogallol and phloroglucinol, the former being *entirely* enolic.

FIG. 2.

3. The change taking place on the introduction of a "third substance" is not tautomeric but is more correctly described, after Lowry's definition, as a case of dynamic isomerism.

4. The equilibrium between the two forms of phloroglucinol in neutral solution is not affected by the class of solvent used.

In conclusion, I should like to express my warmest thanks to Professor Hartley for affording me facilities for carrying out the experimental work, and for the suggestions and advice with which he has favoured me from time to time.

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