ON THE DISTINCTIVE TESTS FOR CARBOLIC ACID, CRESYLIC ACID AND CREASOTE.

By ALFRED H. ALLEN.

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SEVERAL observers have devised methods for distinguishing carbolic acid from wood-tar creasote, and have described tests which, when applied to the pure substances, leave little to be desired.

It appears, however, not to have been observed that cresylic acid, so largely present in the commoner kinds of carbolic acid, resembles creasote more closely than pure carbolic acid does, and fails altogether to respond to some of the tests which have been proposed for distinguishing carbolic acid from creasote. As any substitution of the coal-tar acid for wood-tar creasote is pretty certain to be made by the employment of a crude variety of carbolic acid, the presence in the latter of cresylic acid cannot rightly be ignored.

With a view of clearing up the discrepancies between the results recorded by other observers, and of ascertaining the most desirable tests for distinguishing carbolic and cresylic acids from wood-tar creasote, I have instituted a series of special experiments.

As the origin of some of the statements made by other observers cannot be traced,

owing to imperfect descriptions of the substances on which they worked, I think it well to define carefully the exact substances on which my own experiments were made.

The *Carbolic Acid* was a sample of Calvert's No. 1, for internal use; boiling point, 182° C.

The *Cresylic Acid* I prepared by fractional distillation of Calvert's No. 5 carbolic acid. The portion coming over between 195° and 205° C was collected separately, and again distilled, the first and last portions being rejected. The cresylic acid thus obtained, boiled chiefly at about 197° C, but another smaller fraction boiled at 203° C. I believe this difference is due to the presence of two isomeric creasols in coal-tar, having slightly different boiling points. Many of the experiments were made separately on both fractions, but without the least further distinction in their properties becoming apparent. The distillations were conducted in an atmosphere of coal-gas.

The *Creasote* was a sample of Morson's wood-tar creasote. It boiled at 217° C, and so probably consisted chiefly of creasol ($C_8H_{10}O_2$), as guaiacol boils at 200° C.*

It was pointed out by Calvert many years ago, that carbolic acid forms a crystalline hydrate of the composition C_6H_6O, H_2O , which fuses at 17° C. This fact is usually ignored by the book-makers, though well known to carbolic acid manufacturers. This hydrate would contain 16·07 per cent. of water. When water is gradually added to carbolic acid with repeated shaking, the crystals become liquified and at length a portion of the water remains at the surface.

In order to ascertain how much water carbolic acid would take up, a quantity of about 10 grammes of the crystallized acid was melted and boiled for a minute or two in a small weighed test tube to drive off traces of water. After cooling, it was weighed. Cold water was then added gradually, with repeated shaking, until about ·2 c.c. remained as a layer on the surface of the liquified acid. This was then removed by cautious use of wet blotting-paper, and the residual carbolic acid was weighed. 9·190 grammes were found to have increased to 12·527, which gives 26·6 per cent. as the proportion of water in the liquid acid. On repeating the experiment, a liquid acid containing 27·0 per cent. of water was obtained. This fact is of importance, as showing that carbolic acid will take up far more water than is commonly supposed. The proportion is also of interest, as it corresponds pretty closely with the formula $C_6H_6O, 2H_2O$.† Hence the liquid acid may be regarded a definite hydrate of phenol, but the fact that warm carbolic acid will take up a larger proportion of water than the above, and that the water is entirely separated by agitation with benzol, is against this supposition.

On trying a similar experiment with cresylic acid, I found that the water absorbed amounted to 13 per cent. of the hydrated acid. On repetition, the product contained 14 per cent.

C_7H_8O, H_2O requires 12·7 per cent. of water.

In the subsequent experiments, when mention is made of hydrous carbolic or cresylic acid, the products obtained as above are to be understood.

1. *Action of Cold*.—Absolute carbolic acid is solid at ordinary temperatures, and the hydrous substance solidifies in a freezing mixture of hydrochloric acid and crystallized sulphate of sodium. Neither absolute nor hydrous cresylic acid, nor creasote, shews any signs of freezing on exposure to the same degree of cold.

* According to some observers at 210° C.

† The theoretical proportion of water in this compound would be 27·69 per cent.

2. *Solubility in Water*.—20 c.c. of water at about 17° C dissolves 1·8 c.c. of hydrous carbolic acid. This corresponds to a solubility of 1 volume in 11·1 of water. Hence the saturated aqueous solution contains 8·56 per cent. by weight of the absolute acid, corresponding to a solubility of 1 part by weight of absolute acid in 10·7 parts of water. This is a far greater solubility than is generally attributed to carbolic acid, the discrepancy being probably due to an impure acid being generally used. In hot water carbolic acid is still more soluble.

Hydrous cresylic acid dissolves in about 29 measures of water at about 20° C, which represents a solubility of 1 part by weight of absolute cresylic acid in about 31 parts of water.

3. *Solubility at 15·5° C (=60° F) in Solution of Caustic Soda containing 6 per cent. of NaHO**.—Absolute carbolic acid is completely soluble in an equal volume of soda solution containing 6 per cent. of pure NaHO (free from alumina); addition of more of the alkaline solution up to 6 volumes causes no change, the liquid remaining perfectly clear.

Absolute cresylic acid is insoluble in small proportions of 6 per cent. soda solution. When a large excess (9 volumes) is added, it disappears and forms distinct crystals.

Creasote is practically insoluble in 6 per cent. soda.

4. *Solubility at 15·5° C in Solution of Caustic Soda containing 9 per cent. of NaHO**. Absolute carbolic acid is soluble in an equal measure of 9 per cent. soda. On addition of any proportion of water up to 7 volumes the liquid remains clear, but is precipitated by 8 volumes of water. Carbolic acid is also soluble in two measures of 9 per cent. soda, and is not precipitated by less excess of the reagent than 5 or 6 measures.

Absolute cresylic acid is soluble in an equal measure of 9 per cent. soda, but is precipitated when the proportion of the reagent is increased to 3½ volumes. If to a clear mixture of equal volumes of cresylic acid and 9 per cent. soda, a few drops of water be added, precipitation occurs, and when the proportion of water is increased to one volume the original bulk of cresylic acid separates out. Hence, cresylic acid is insoluble in two measures of 4½ per cent. soda solution.

Creasote is insoluble in any smaller quantity than two volumes of 9 per cent. soda. It is partially reprecipitated when the proportion of the solvent is increased to more than 3½ measures.

5. *Solubility at 15·5° C in Solution of Ammonia* (sp. gr. ·880.) Absolute carbolic acid is completely and readily soluble in an equal volume of strong ammonia. The solution is not precipitated by addition of less than 1½ volumes of water. A mixture of 1 part of carbolic and 3 of cresylic acid is soluble in an equal measure of ammonia, but the solution is precipitated on adding even a few drops of water.

Cresylic acid is almost insoluble in ammonia, requiring upwards of 16 volumes for solution, and then forming crystalline scales similar to those obtained by the use of soda.

Creasote is practically insoluble in ammonia, requiring 60 to 80 volumes for solution.

6. *Behaviour with Benzol*.—Absolute carbolic and cresylic acids and creasote are miscible with benzol in all proportions. The hydrous substances dissolve in 5 volumes of benzol with complete separation of the water. Hence benzol may be used for the determination of the proportion of water present in samples of carbolic and cresylic acid.

* These solutions contained respectively 94 and 91 grammes of water to each 6 and 9 grammes of pure caustic soda.

7. *With Chloroform, Carbon Disulphide, or Ether.*—Carbolic acid, cresylic acid, and creasote, react in much the same manner as with benzol. Agitation with 9 per cent. soda removes them from their solutions in the above solvents.

8. *Behaviour with Petroleum Spirit of sp. gr. .699* (commercial "benzoline.") Absolute carbolic acid dissolves half its volume of petroleum spirit, forming a clear liquid. On addition of a larger proportion of petroleum spirit precipitation occurs. With one volume of carbolic acid and three of petroleum spirit, the layers have about the same measures as the original liquid. Each layer however contains both liquids, as may be proved by cooling the tube with a freezing mixture (or by wrapping filter paper round it, and dropping CS₂ on the outside) when carbolic acid crystallizes out. Absolute carbolic acid is permanently soluble in about ten measures of petroleum spirit at 15.5°C (=60°F). The solubility is enormously increased by rise of temperature. Hence carbolic acid and *hot* petroleum spirit are miscible in all proportions; on the other hand, by cooling with a freezing mixture, the carbolic acid is almost wholly deposited. If the cooling occurs slowly, it forms a heavy liquid layer with a portion of the petroleum spirit, but by rapid cooling, the carbolic acid is deposited in long crystalline needles, which render the liquid semi-solid.*

Hydrous carbolic acid is almost insoluble in moderate quantities of cold petroleum spirit, which does not separate the contained water from it. (Another difference between benzol and petroleum spirit.)

Absolute cresylic acid appears to be miscible with petroleum spirit in all proportions. No separation, either of crystals or liquid, occurs by exposing a solution of one measure of the acid in three of petroleum spirit to a freezing mixture.

When hydrous cresylic acid is treated with cold petroleum spirit, the volume of the former increases somewhat by dissolving a little of the spirit, but on addition of a greater volume of petroleum spirit it undergoes slight solution. It is only very sparingly soluble in petroleum spirit, requiring upwards of twenty volumes for complete solution, when the water separates. Creasote is miscible with petroleum spirit in all proportions.

9. *Behaviour with Glycerine of 1.258 sp. gravity.*—Absolute carbolic acid is miscible with Price's glycerine in all proportions. A mixture of one volume of carbolic acid with one of glycerine is not precipitated by an addition of three volumes of water. In presence of 25 per cent. of cresylic acid, precipitation occurs on adding more than two volumes of water.

Absolute cresylic acid is miscible with Price's glycerine in all proportions. A mixture of one volume of glycerine and one of cresylic acid is completely precipitated by one volume of water. Creasote is insoluble in Price's glycerine, whether the latter be added in the proportion of one, two, or three volumes for one of creasote.

The sample of Price's glycerine used for the above experiments was found to have a density of 1.258.

10. *Behaviour with Collodion.*—Absolute carbolic or cresylic acid when shaken with half its measure of *Collodium B. P.* precipitates the nitro-cellulose in a transparent gelatinous form very difficult to see. It is best observed by inclining the tube and causing the

* Crystallized carbolic acid may be used for distinguishing between coal-tar, benzol and petroleum spirit. In the latter it is sparingly soluble, and is re-deposited in a crystalline state by rapid cooling. With benzol it is miscible in all proportions (the crystals of carbolic acid rapidly melting), and a solution of one measure in three deposits no crystals by rapid cooling.

liquid to flow gently from one end to the other. Creasote does not precipitate the nitro-cellulose from collodion, but mixes perfectly with its ethereal solution. Addition of much creasote to a mixture of collodion and carbolic or cresylic acid, causes the re-solution of the precipitated nitro-cellulose.

11. *Reaction with Ferric Chloride.*—The addition of one drop of a ten per cent. aqueous solution of ferric chloride to 15c.c. of an aqueous solution of cresylic or carbolic acid, causes a permanent violet-blue coloration. When creasote is similarly tested, a blue colour results, which almost instantly changes to green and brownish-yellow.

Other distinctive tests for creasote and carbolic acid are to be found in the books, but are almost worthless in practice. Thus the reactions with bromine, sulphuric acid, and nitric acid, are far too much alike to be of service for distinguishing between these bodies. It has been stated that creasote differs from carbolic in its power of rotating a ray of polarized light. I redistilled a sample of Morson's creasote to obtain it colourless, and carefully tried this test, expecting to find in it a possible means of determining the creasote in a mixture, but the rotatory power of creasote proved so exceedingly weak as to be quite worthless for the intended purpose, or even as a qualitative test. It is, however, quite possible that different samples of creasote may exhibit considerable differences in this respect, but if so, the test is valueless for quantitative purposes, and the problem is not so much to detect wood-tar creasote as to recognise an admixture of the coal-tar acids. I am also unable to confirm the statement that creasote gives a solid deposit when kept for some hours at the temperature of boiling water. I have not obtained satisfactory results by the reaction of an alkaline solution of the substances with hydrochloric acid and pine-wood, or with a solution of iodine in iodide of potassium.

From the foregoing details it will be seen that in various manners carbolic acid, cresylic acid and wood-tar creasote can be readily distinguished from each other. The case, however, is very different when we have to deal with a mixture of the three substances, such as occurs in the case of a sample of creasote adulterated with crude carbolic acid. In such a case many of the tests are greatly reduced in value or rendered absolutely worthless. As the problem is to detect the coal-tar acids in presence of wood-tar creasote rather than the reverse, only affirmative tests for the former bodies are of service, and in many cases these are seriously modified by the simultaneous presence of creasote. Thus, as has been pointed out by Mr. J. Williams, the ferric chloride test entirely fails to detect the presence of carbolic acid in a mixture of equal parts of that substance and creasote. The only marked differences I have been able to observe between Morson's creasote and a mixture of equal measures of that liquid and Calvert's No. 5 carbolic acid, are the following:—

4. When shaken with twice its bulk of 9 per cent. soda solution pure creasote was dissolved, and remained in solution when the solvent was increased to three volumes. The *mixture* was insoluble either in two, three or four times its volume of 9 per cent. soda. This anomalous result proved to be due to the presence of water, which reduced the strength of the soda solution. When the water was previously expelled by boiling the mixture of crude carbolic acid and creasote, solution took place with two volumes of soda.

9. When shaken with Price's glycerine (sp. gr. 1.258) pure creasote remained undissolved, though the proportion of glycerine was varied from one to three volumes. The mixed creasote dissolved completely and readily in an equal measure of glycerine.

The liquid was not affected by a drop or two of water, but a further addition caused precipitation. A mixture containing 25 per cent. of creasote, when shaken with an equal measure of glycerine, was not precipitated by less than one and a quarter volumes of water.

10. Shaken with half its volume of collodium (B.P.) pure creasote dissolved to a clear liquid. The mixed creasote showed decided signs of precipitation when the liquid was allowed to run gently from one end of the tube to the other. With a mixture of two volumes of Calvert's No. 5 acid to one of creasote, the precipitation of the nitro-cellulose was very marked.

As carbolic acid, cresylic acid, and creasote boil at temperatures tolerably widely apart, I thought it might be possible to effect a sufficient separation by fractional distillation, to enable the test for the coal-tar acid to be more readily applied. For this purpose I introduced a mixture of No. 5 carbolic acid and Morson's creasote into a small retort and distilled the liquid. The water, which came over first, was collected separately. The next portion of the distillate (amounting to about one-fifth of the whole bulk of the liquid) was boiled to free it from a little water, and was then tested with glycerine and with collodium. It dissolved readily in the glycerine, and precipitated half its volume of collodium. Hence the carbolic acid of the mixed creasote was fairly detected, and there seems no reason why fractional distillation should not serve for the detection of smaller proportions of carbolic acid, as it will certainly be most abundant in the first portion of the distillate. The ferric chloride test was not found of service for testing the distillate, sufficient creasote being present to produce a decided brown coloration.

As the tests with glycerine and collodium are the only reactions of service with mixtures of carbolic acid and creasote, I did not think it necessary to apply the other tests to the distillate.

It will be seen from my experiments that the high value usually attached to the glycerine test is amply justified. It has been stated that pure creasote was soluble in anhydrous glycerine. This is certainly not my experience, but if it be true that some varieties of creasote dissolve in absolute glycerine, they will doubtless be precipitated by the least dilution, and can thus be distinguished from mixtures containing considerable proportions of the coal tar acids.

Mr. J. Williams examined a sample of German creasote which was supposed to be pure and which dissolved in glycerine, but the fact that 40 per cent. of the sample distilled at 200° to 203°C., together with other characters, render it very probable that it contained an unacknowledged mixture of the coal-tar acids. It must not be forgotten that cresylic acid is much cheaper than carbolic acid, and is far more difficult to distinguish from creasote even when unmixed with the last substance.

I have thought it best to place my results on record in the fullest possible detail, as it is just the omission to do this that has caused so many confusing and incorrect statements to appear in our test books. The tests described are remarkably liable to failure when the conditions are slightly varied. This is notably the case with the reactions with solutions of soda, a change of a temperature or strength of the solvent causing extraordinary variations in the results.

Many of the experiments described in this paper were made under my direction by Mr. L. ARCHBUTT, to whose perseverance and accurate observation I am much indebted.