

been received. Fifty-nine members of the larger committee are therein recognized. Thirty-one voted for a table based upon $O = 16$ exclusively; two for $H = 1$ exclusively; and five for the simultaneous use of both standards. To the last vote should be added that of the four members of the smaller committee, making nine in all for the double table. Seventeen members refrained from voting. The vote, then, gives one more than a majority of the entire committee in favor of the oxygen standard alone, although the committee appointed by the Chemical Society of Paris in 1900 seems not to have been consulted.

Copies of the report as drawn and agreed to were sent to England, France, Germany, Italy and Japan for simultaneous publication. It is therefore, in the opinion of Professors Thorpe, Seubert, and myself, too late to attempt any change for the current year. To withdraw, rewrite, and re-sign the report would involve too great a delay. We therefore ask for patience on the part of the larger committee, whose wishes will receive due consideration next year.

F. W. CLARKE.

TRIBROMPHENOLBROMIDE: ITS DETECTION, ESTIMATION, RATE OF FORMATION, AND REACTION WITH HYDRIODIC ACID.

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THE following experiments form part of an investigation of the reaction between bromine and phenol, which was undertaken with the object of improving Koppeschaar's method of determining the latter substance.

The tribromphenolbromide used was prepared by Werner's¹ recipe, recrystallized three times from chloroform, and dried for three days over sulphuric acid in a vacuum; it formed golden-yellow crystals, melting-point 119° .

DETECTION.

When searching for a distinctive qualitative test for tribromphenolbromide, I found that ammonia, and chloroform solutions of many of the organic bases react with it to form colored products, as follows:

¹ *Bull. Soc. Chim.*, **43**, 372 (1885).

Ammonia	Brown.
Aniline	Deep red, turning muddy.
Dimethylaniline	Slight darkening.
Paratoluidine	Clear red
Diphenylamine	Light red.
α -Naphthylamine	Dark blue, turning purple.
β -Naphthylamine	Light rose-pink, appears very slowly.
Aminoazobenzene	Brown-red, appears very slowly and gradually deepens.
Pyridine	Light yellow.
Benzidine	Intense green, purple if concentrated.
Azoxybenzene, Metanitraniline, Acetanilide,	no change.

Of these, aniline and benzidine proved most suitable as reagents; with tribromphenol, tetrabromphenol and hexabromphenoquinone they give no color, while with bromine water an aniline solution is bleached, and benzidine gives a seal-brown, quite distinct from the green with tribromphenolbromide.

The benzidine solution may be prepared by warming 5 grams of benzidine sulphate with 50 cc. of a 10 per cent. potash solution, cooling, extracting the benzidine with chloroform, and filtering off the chloroform solution. Three drops of this reagent give a distinct green with 10 cc. of a solution containing 1 gram of tribromphenolbromide in a liter of chloroform. Shaking the tribromphenolbromide solution with decinormal sodium thiosulphate before adding the benzidine reagent does not interfere with the color reaction.

ESTIMATION.

As the reaction with potassium iodide is obviously unsuitable (see page 20), a basis for the method was sought in the action of reducing agents; Benedict¹ states that zinc and hydrochloric acid reduce tribromphenolbromide to tribromphenol, but does not seem to have made any quantitative measurements. After experimenting with sodium amalgam and with magnesium, I finally decided in favor of powdered zinc and sulphuric acid, which are without action upon tribromphenol, but remove one atom of bromine from tribromphenolbromide. By determining the bromine in the solution after reduction, it is thus possible to calculate the amount of tribromphenolbromide in the substance analyzed. The details of the method are as follows:

The tribromphenolbromide was placed in a 150 cc. flask, 20 cc.

¹ *Ann. Chem. (Liebig)*, 199, 127 (1879).

of alcohol (96 per cent.), 5 cc. N/4 sulphuric acid and about 0.25 gram powdered zinc¹ were added, and the flask heated on a water-bath until the whole of the tribromphenolbromide had dissolved and the solution had lost its characteristic yellow color. Excess of calcium carbonate was then added to neutralize the free sulphuric acid, and the alcohol together with most of the tribromphenol were distilled off on a water-bath; the residue was extracted with three successive portions of boiling water, 25 cc., 25 cc., and 10 cc., respectively; and in the filtrate, after cooling, the bromine was determined by N/10 silver nitrate with potassium chromate as indicator. Blank experiments with tribromphenol showed that no bromine was removed by this treatment.

TEST ANALYSES.

Tribromphenol- bromide. Gram.	AgNO ₃ found. cc.	AgNO ₃ calc. cc.	Per cent.
0.5023	12.45	12.46	99.92
0.5327	13.19	13.11	100.61
0.5249	12.80	12.92	99.07

NOT THE PRIMARY PRODUCT.

The precipitate formed by the action of bromine water upon phenol is at first pure white in color, but on standing with the solution containing excess of bromine it gradually assumes a yellowish tint; the change is due to the formation of tribromphenolbromide, the presence of which was detected by the qualitative tests described above. The change of color shows that tribromphenolbromide is not the primary product of the action of bromine water upon phenol, as imagined by Weinreb and Bondi,² but is formed by a gradual reaction between the precipitated tribromphenol and the excess of bromine.

RATE OF FORMATION.

By means of the method of analysis described above, the amount of tribromphenolbromide formed when the phenol was treated with bromine under varying conditions was determined.

The following solutions were employed: *Phenol*, 20 grams per liter; *silver nitrate*, 16.83 grams per liter; the tribromphenolbromide from 5 cc. of the phenol solution is thus equivalent to 10.74 cc. of the silver nitrate. *Hypobromite*, bromine was dissolved in a solu-

¹ This is more than enough, excess does no harm.

² *Monatshft. f. Chemie*, 6, 506 (1885).

tion of caustic potash of known alkalinity (about quarter normal) and a solution of *hydrochloric acid* equivalent to the potash was prepared, so that on mixing the alkaline solution of bromine with an equal volume of the equivalent acid a neutral bromine solution resulted. By titration with volumetric sodium thiosulphate after adding acid and potassium iodide, 50 cc. of the hypobromite solution were found to contain 0.6810 gram bromine; hence to convert 5 cc. of the phenol solution into tribromphenol requires 37.45 cc. of the hypobromite solution; to convert it into tribromphenolbromide requires 49.94 cc. Allen¹ states that hypobromite solutions prepared like that above, and containing a large excess of alkali do not appreciably alter their content of available bromine upon standing or heating.

The experiments were carried out as follows: 50 cc. of the hypobromite solution were pipetted into a glass-stoppered quarter-liter measuring flask, then 50 cc. of the equivalent acid added and finally 5 cc. of the phenol solution. The mixture was shaken for thirty seconds and allowed to stand for a measured interval, after which the mother-liquor was rapidly removed by means of a filter-pump and a large perforated porcelain funnel. The precipitate was washed with cold water until the addition of silver nitrate produced no cloudiness in the filtrate, and was then brought, filter-paper and all, into a 150 cc. flask, where the tribromphenolbromide was determined as described above.

In some of the experiments the concentration of the bromine was altered by adding bromine from a burette; in others, previous to the addition of phenol, the solution was acidified with hydrochloric acid (sp. gr. 1.2), while in others weighed quantities of potassium bromide were added. The results are contained in Tables I to VI.

The effect of varying the time during which the bromine water acted upon the tribromphenol, *i. e.*, the interval between adding the phenol and filtering, was first studied. The results of these experiments are contained in Table I; they afford ample proof that the tribromphenolbromide is a secondary product and show what a large amount of it may be formed in a few minutes under the ordinary conditions of a phenol determination.

¹ *J. Soc. Chem. Ind.*, **3**, 65 (1884).

TABLE I.—EFFECT OF TIME.

KOB_r, 50 cc. ; equiv. HCl, 50 cc. ; HCl (sp. gr. 1.2), 1 cc. ; phenol, 5 cc.

Time. Minutes.	AgNO ₃ . cc.	Tribromphenolbromide. Per cent.
5	2.36	22
10	4.11	38
15	5.13	48
30	7.49	70
Hours. 18	7.75	72

Under AgNO₃ is given the volume of the silver nitrate solution required in the analysis; the numbers under "Tribromphenolbromide" (obtained by dividing the figures in the second column by 10.74) represent the fraction of the phenol which has been converted into tribromphenolbromide.

The experiments of Tables II, III, IV, V and VI show that the amount of tribromphenolbromide formed from 5 cc. of the phenol solution in a constant interval (five minutes) increases with the excess of bromine and with the volume of the reacting mixture, and is diminished by adding acid or potassium bromide, or by lowering the temperature. They afford a striking parallel to the results obtained by Mr. Roebuck in his study of the rate of oxidation of arsenious acid by iodine,¹ where the rate is proportional to the concentration of the iodine and to the volume of the solution, and inversely proportional to the concentration of the acid and of the potassium iodide; Roebuck interpreted his results by assuming that hypiodous acid is the oxidizing agent in iodine solutions; a similar explanation of my own experiments, *vide*, that the formation of tribromphenolbromide from tribromphenol is due to the oxidizing action of hypobromous acid, naturally suggests itself.

TABLE II.—EFFECT OF VOLUME.

KOB_r, 50 cc. ; equiv. HCl, none ;* HCl (sp. gr. 1.2), 1 cc. ; phenol, 5 cc.

Volume. cc.	AgNO ₃ . cc.	Tribromphenolbromide. Per cent.
57	1.19	11
106	2.36	22
157	3.84	36
207	4.6	43

* To keep down the volume. The 1 cc. of strong hydrochloric acid was very slightly more than enough to neutralize the alkali of the hypobromite solution.

¹ *J. Phys. Chem.*, 6, 365 (1902).

TABLE III.—EFFECT OF BROMINE.

KOH, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Total excess bromine. Grams.	AgNO ₃ . cc.	Tribromphenolbromide. Per cent.
0.17	2.36	22
0.55	5.59	52
0.92	7.02	66
1.67	8.74	81

TABLE IV.—EFFECT OF ACID.

KOH, 50 cc.; equiv. HCl, 50 cc.; phenol, 5 cc.

Total acid. Mol.	AgNO ₃ . cc.	Tribromphenolbromide. Per cent.
0.016	2.36	22
0.029	2.78	17
0.068	1.37	13
0.068	1.35	13
0.133	0.35	3
0.198	0.1	1

TABLE V.—EFFECT OF POTASSIUM BROMIDE.

KOH, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Total KBr. Mol.	AgNO ₃ . cc.	Tribromphenolbromide. Per cent.
0.003	2.36	22
0.0073	1.69	15.7
0.0116	0.51	4.7
0.0288	0.25	2.3
0.0546	0.23	2.2

TABLE VI.—EFFECT OF TEMPERATURE.

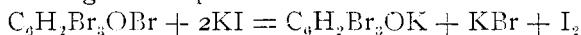
KOH, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Temperature. °C.	AgNO ₃ . cc.	Tribromphenolbromide. Per cent.
0	1.9	18
18	2.36	22

These experiments show clearly that in order to avoid the formation of tribromphenolbromide when titrating phenol with bromine, the liquid must be strongly acid or must contain an excess of potassium bromide; the excess of bromine must not be too great, and the time during which the precipitate of tribromphenol is in contact with the excess of bromine must not be too long. Under these conditions only a mere trace of tribromphenolbromide is formed, and it is precisely when the quantity of that substance is smallest that it is most easily acted upon by hydriodic acid (see Table VII).

REACTION WITH HYDRIODIC ACID.

The statement that tribromphenolbromide reacts with potassium iodide according to the equation



is founded on experiments of Weinreb and Bondi,¹ and of Werner.² The former obtained 95 per cent. of the theoretical iodine by digesting for twelve hours with an aqueous solution of potassium iodide at 18°, or 99 per cent. at 50°; the latter, using a chloroform solution, obtained 99.96 per cent. The more recent experiments of Kastle,³ however, show that in chloroform solution, in absence of water, hexabromphenoquinone is the sole product, in which case only half of the iodine called for by the above equation is liberated; while if a carbon bisulphide solution of tribromphenolbromide be treated with an aqueous solution of potassium iodide, the iodine liberated varies from 90 to 100 per cent. of the theoretical amount, depending upon the relative quantities of potassium iodide, water, and carbon bisulphide present. In none of my own experiments, the results of which are detailed in Tables VII and VIII, did I obtain a quantitative yield of iodine; although potassium iodide was present in excess, the acidity of the solution was varied, different solvents were tried, and the digestion was much more prolonged than would be convenient in an analytical method.

It is apparent, however, that as the amount of tribromphenolbromide is reduced, the amount of iodine liberated approaches nearer and nearer to the theoretical value.

TABLE VII.

Expt.	Tribromphenolbromide. Gram.	Solvent.	Time.	n HCl. cc.	Iodine. Per cent.	Chloroform or benzene residues.
<i>i</i>	0.2038	none	7 days	--	77	
<i>ii</i>	0.2031	"	7 days	--	78	
<i>iii</i>	0.1747	CHCl ₃	24 hrs.	--	87	Brown, not green with benzidine.
<i>iv</i>	0.1560	CHCl ₃	20 hrs.	2.5	91	Deep red with aniline
<i>v</i>	0.1775	CHCl ₃	8 hrs.	2.5	88	Yellowish red; not green with benzidine.
<i>vi</i>	0.2520	C ₆ H ₆	48 hrs.	--	76	Deep red with aniline.
<i>vii</i>	0.2685	C ₆ H ₆	36 hrs.	5	81	" " " "
<i>viii</i>	0.3045	C ₆ H ₆	24 hrs.	5	84	" " " "
<i>ix</i>	0.2073	C ₆ H ₆	10 min.	5	78	Green with benzidine.

¹ *Monatshefte f. Chem.*, 6, 506 (1885).

² *Bull. Soc. Chim.*, 43, 373 (1885).

³ *Am. Chem. J.*, 27, 31 (1902).

Expt.	Tribrom-phenol-bromide. Gram.	Solvent.	Time.	N HCl. cc.	Iodine. Per cent.	Chloroform or benzene residues.
<i>x</i>	0.2594	C ₆ H ₆	1 hr.	5	80	Green with benzidine.
<i>xvi</i>	0.0017	CHCl ₃	5 min.	5	98	Too dilute.
<i>xii</i>	0.0034	CHCl ₃	5 min.	5	94	" "
<i>xiii</i>	0.0068	CHCl ₃	5 min.	5	91	" "
<i>xiv</i>	0.0102	CHCl ₃	5 min.	5	87	" "
<i>xv</i>	0.0170	CHCl ₃	5 min.	5	83	" "

In Experiments *i* to *x* the amount taken for analysis was weighed out and placed in a 100 cc. glass-stoppered bottle, the benzene or chloroform (10 cc.) added, then the acid and finally the potassium iodide dissolved in water. In Experiment *v* four times the theoretical amount of potassium iodide was used, in the others twice. The mixture was well shaken and allowed to stand for a measured time, at the end of which the iodine set free was titrated against N/50 thiosulphate. The results of the analyses are entered in the table under "Iodine" as percentages of the amounts of iodine that would have been liberated from the tribromphenolbromide taken had the reaction proceeded according to Werner's equation.

In Experiments *xvi* to *xv* a weighed quantity of tribromphenolbromide was dissolved in chloroform, and a measured volume of this solution made up to 10 cc. for each experiment, 5 cc. of normal potassium iodide and 5 cc. of normal acid were added, and the mixture was well shaken and allowed to stand for five minutes, after which the iodine was determined as before.

After completing the analysis, the color of the chloroform or benzene solution was noted, and then a few drops of the aniline or benzidine reagent added. In Experiments *ix*, and *xvi* to *x*, the presence of unaltered tribromphenolbromide was established, but in Experiments *iii* and *v*, although the chloroform solutions were colored, no tribromphenolbromide could be detected. This shows that in the experiments in question the deficit of 15 per cent. or so in the iodine is due to the formation of a by-product, and not to the incompleteness of the reaction formulated above. The delicacy of the benzidine test is not sufficient to enable it to be of value in Experiments *xvi* to *xv*.

The experiments of Table VIII were carried out in the same way as the first ten of the preceding table, except that the hydrochloric acid was replaced by acetic, and an excess of sodium thiosulphate (5 cc. of a normal solution) was added to the reacting

mixture at the same time as the potassium iodide. The results are very similar to those of Table VII, and show that the deficit is not altogether due to the presence of iodine.

TABLE VIII.

No.	Tribrom-phenol-bromide. Gram.	Solvent.	Time. Hours.	n HAc. cc.	Iodine. Per cent.	Chloroform or benzene residues.	
1	0.3195	C ₆ H ₆	24	--	87	No reaction with benzidine.	
2	0.1470	C ₆ H ₆	20	5	95.8	"	"
3	0.1795	C ₆ H ₆	18	5	95.6	"	"
4	0.2145	C ₆ H ₆	24	5	92.1	"	"
5	0.2748	CHCl ₃	24	5	93.3	"	"

From these experiments it is apparent that if in a phenol determination part of the tribromphenol precipitate is converted into tribromphenolbromide, the latter will not be quantitatively transformed into tribromphenol by the action of potassium iodide, and an error will thus be introduced into the analysis.

SUMMARY.

(1) Aniline and benzidine may be used as qualitative reagents for tribromphenolbromide.

(2) Tribromphenolbromide is quantitatively reduced to tribromphenol by zinc and sulphuric acid; a convenient method for its determination, based on this reaction, is described.

(3) Tribromphenolbromide is not a primary product of the action of bromine on phenol, but is formed by the gradual action of bromine water on tribromphenol. As the rate of this reaction is decreased by adding acid or potassium bromide, and increased by adding water or bromine (or by raising the temperature), it is probably due to the presence of hypobromous acid in the bromine water.

(4) Tribromphenolbromide is not quantitatively reduced to tribromphenol by hydriodic acid under conditions convenient for analysis; this is due in part to the formation of other products.

My thanks are due to Prof. W. Lash Miller, at whose suggestion this research was undertaken and under whose supervision it has been carried out.