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Quantitative Bromination of Phenols

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The quantitative bromination of 47 phenols was carried out using 0.1 N potassium bromide—bromate solution and glacial acetic acid as the solvent. The required conditions were established for the analysis of various types of phenols whose reactivity toward bromine is also discussed.

For a long time bromination has been an important part of methods for the quantitative determination of phenol. It has also been used in the analysis of a limited number of other types of phenols such as alkylphenols, halophenols and nitrophenols. It was the basis of the first method [1] used for this purpose and, in spite of the introduction of conductometric titration [1-4] and more recently titration in nonaqueous solvents [5] as tools for the analysis of phenols, it is in some respects still superior. Thus the bromination method is the only one by which it is possible to analyze mixtures of isomers, such as the *meta*-substituted phenols in the presence of the corresponding *ortho* or *para* isomers.[6] * Furthermore, unlike the two other methods, bromination reveals the number of free *ortho* and *para* positions in the ring, a fact of great value for the identification of phenols.

Hitherto the quantitative bromination method has been applied only to a limited number of phenols. It was felt that the potential value of the method had not been utilized fully, partly because of the somewhat tedious procedure generally used, and partly because of unsuitable conditions which hinder its application to the quantitative analysis of a larger number of phenols. Furthermore no systematic study has been made of the relationship between the structure of a phenol and the conditions necessary for its quantitative bromination. It was proposed therefore to investigate the possibility of altering the procedure in such a way that the bromination method may be of more general use. Some relationships between structure and reactivity would also be studied. To give the background for the present work it is necessary to discuss, in some detail, the development of the quantitative bromination method.

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* Added in proof. After the completion of this work Karrman and Johansson[6a] have reported that a mixture of *o*-, *m*- and *p*-cresol can be analyzed using high frequency titration.

In 1876 Koppeschaar [1] introduced his method for the quantitative determination of phenol which with few alterations has been in use up to now (see, *e.g.* Ref. [7]). The principle of the method was to dissolve the phenol in water and add an excess of a solution containing sodium bromide and sodium bromate. On acidification with hydrochloric acid bromine was liberated, part of which reacted with the phenol to form tribromophenol. After 15 min potassium iodide was added and the iodine liberated titrated with thiosulfate. From the volume of bromide-bromate solution taken and the volume of thiosulfate used in the back-titration the amount of bromine consumed by the phenol could be calculated.

It was not until 1928 that this Koppeschaar "excess" method was tested on several other types of phenols. Thus Day and Taggart [8] were able to analyze about 10 phenols using essentially the same procedure as Koppeschaar. They also tried a so-called "direct" method developed by Callan and Henderson.[9] To the alkaline solution of the phenol a potassium bromide solution was added and then, after acidification, the necessary volume of standard potassium bromate. The end point was determined using spot tests on starch-iodide paper. This "direct" method is reported to be tedious and there is some possibility that bromine might be lost. Most analyses were made therefore using the "excess" method.

The work of Day and Taggart seems still to be the most comprehensive in its field although several papers on the same subject have appeared since. Riemschneider,[10] for example, used sodium sulphite for the reduction of the excess of bromine and determined the sum of the hydrogen bromide formed here and in the bromination reaction by a titration according to Volhard. Singh [11] recently used the Day and Taggart method for the analysis of some phenols with the modification that chloramine-B was substituted for the potassium bromate. Bielenberg *et al.*[12] stated that the Koppeschaar method gave inaccurate results, when applied to phenols other than cresolic acid. They proposed a modified procedure which, however, still utilized water as solvent (concerning water as solvent see below). Bielenberg [13] unsuccessfully tried to indicate the end point of the bromination reaction by methyl orange and other bromine-sensitive dyes.

Of special interest are two investigations by Sprung [14] and Ruderman [15], respectively, concerning the application of the Koppeschaar method to the quantitative analysis of alkylphenols. Sprung found that the method failed for most types of alkylphenols except for some with alkyl groups in the *meta* position or tertiary alkyl groups in the *ortho* or *para* position. Ruderman, varying the excess of bromine, concluded that phenols with primary and secondary alkyl groups *ortho* or *para* to the hydroxyl group tend to overbrominate in the presence of excess bromine while phenols with *ortho*, *meta*, or *para* tertiary alkyl groups brominate quantitatively regardless of the bromine excess. Furthermore hydroxymethyl groups were found to be displaced by bromine in certain instances.

Some attempts have also been made to use a potentiometric method for the indication of the end point in the quantitative bromination of phenols [16,17]. This method should be valuable in the analysis of dark coloured substances, but the number of phenols to which it has been applied is still too small to permit an estimation of its usefulness.

Day and Taggart reached a high precision in their analyses but at the cost of frequent changes of such variables as dilution, bromination time and the time elapsed between the addition of the potassium iodide and the back titration of the iodine. In spite of this such a simple phenol as *p*-cresol could not be analyzed either by the "excess" method or by the "direct" method. Reliable values for thymol and β-naphthol could be obtained only if chloroform was used as solvent instead of alkali. A decarboxylation reaction was also observed for salicylic acid which consumed 6 equiv. of bromine per molecule instead of the expected 4 equiv. * Another irregularity is the need of allowing the reaction mixture to stand in some cases between the addition of the potassium iodide and the back titration of the iodine. Thus in the case of resorcinol the mixture was kept for 5 min, in the case of *m*-cresol for 60 min. Some of these difficulties might be caused by the choice of solvent. Most of the phenols are not soluble enough in water, but have to be dissolved in alkali. On acidification prior to the addition of bromide-bromate there is a risk that the phenol is partly precipitated and that the reaction thus takes place in an inhomogeneous medium. The long reaction time (30 min) necessary in several cases might be due partly to this circumstance. As mentioned above thymol, which has a low solubility in water, could not be analyzed by the general "excess" method.

From the discussion above it follows that a solvent suitable for general use in the bromination method should have a good dissolving power for phenols. Of course it must be reasonably inert to bromine under the conditions used. It is also desirable that it is mixable with the titrant and has some dissolving capacity for the products of bromination. The last condition arises from the fact that the products of bromination when precipitated might enclose incompletely brominated compounds (*cf.* Ref. [8]). Day and Taggart used chloroform in some of their experiments. It is fairly stable toward bromine but is reported to retain the last of the iodine tenaciously. Furthermore it is not mixable with the titrant. Ethyl alcohol was employed as solvent by Francis and Hill.[6] Its stability toward bromine is, however, reported to be poor.[18] Acetic acid has been used in isolated cases with good results [18]. As it fulfills all the conditions above it was decided to investigate its general usefulness.

It was found that a large number of phenols could be directly titrated in acetic acid solution using 0.1 N bromide-bromate (see Table 1). Instead of the tedious spot test method used by Day and Taggart a small excess of bromide-bromate was added and then immediately back-titrated with standard thiosulfate. The average accuracy of this "direct" method was 0.3 %.

Phenols which could not be quantitatively determined by the "direct" method were analyzed using an "excess" method (see Table 2). In most of the cases the reaction was complete in 3 min with 100 % excess of bromide-bromate. The average accuracy of the "excess" method was 0.4 %.

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* Francis and Hill [6], using water, dilute sulphuric acid or ethyl alcohol as the solvent, also reported a decarboxylation to take place in the bromination of the hydroxybenzoic acids. Furthermore carbon monoxide was shown to be formed in the bromination of the hydroxybenzaldehydes, originating from the formyl group which was split off.

It was the objective of the present investigation to develop general procedures which were applicable to the largest possible number of phenols. This was attained so far in that 22 (84 %) of the 26 phenols determined by the "direct" method could be analyzed under identical conditions as could 15 (75 %) of the 20 compounds analyzed by the "excess" method. This unification of the bromination method was partly enabled by the fact that the same number of active centres (*ortho* and *para* positions) were present in each case which also permitted a comparison to be made between the reactivities of the various phenols (see below).

EXPERIMENTAL

Materials. Most of the phenols in Tables 1 and 2 were commercial products. Their purity was tested by melting point or boiling point determinations and they were, if necessary, recrystallized or redistilled.

Procedure for the direct method: 1.5 mequiv. * of the phenol were weighed and dissolved in the prescribed volume of glacial acetic acid (see Table 1). Five ml of conc. hydrochloric acid were added and then dropwise 16 ml of 0.1 N potassium bromide-bromate solution. A larger excess of bromide-bromate solution was never allowed to occur. After addition of 5 ml of a 10 % potassium iodide solution the iodine was immediately titrated with 0.1 N thiosulfate using starch solution as indicator.

Procedure for the excess method. The same amount of the phenol as in the previous method was weighed and dissolved in the prescribed volume of glacial acetic acid in a flask fitted with a ground joint (see Table 2). Thirty ml of 0.1 N potassium bromide-bromate solution were added and then 5 ml of conc. hydrochloric acid. The flask was immediately stoppered, shaken and left for generally 3 min (see Table 2). After that period 10 ml of a 10 % potassium iodide solution were added and the iodine at once titrated as above.

DISCUSSION

In the following the conditions necessary for the quantitative bromination of various types of phenols will be discussed in some detail.

The dominating influence in the bromination of phenols is exerted by the hydroxyl group whose well known activation of the aromatic ring towards electrophilic reagents causes bromine to replace hydrogen at the free *ortho* and *para* positions. Other substituents in the phenol molecule as a rule have only a minor influence on its reactivity.

Phenol and alkylphenols. All of the 5 monoalkylphenols tested (Nos. 2—6) could be analyzed under standard conditions (1.5 mequiv. of the phenol in 10 ml of glacial acetic acid) using the "direct" method. They were found to be more reactive than phenol (No. 1) as the bromine consumption of the latter was too low under standard conditions. This difference in reactivity is natural considering the electron releasing effect of alkyl groups toward the ring. In view of this the dialkyl- and polyalkylphenols might be expected to be even more reactive than the monoalkylphenols. However, for many of the compounds investigated the opposite was the case. Thus, while 2,4- and 2,6-xylenol (Nos. 7 and 8) could be analyzed by the "direct" method the "excess" method had to be used in most cases involving *meta*-substituted dialkyl- and polyalkylphenols (Nos. 27—33). The cause of the decrease in reactivity in those

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* It is assumed that each vacant *ortho* or *para* position consumes 2 equiv. of bromine.

Table 1. Bromide-bromate titration of phenols using the "direct" method.

No.	Compound	Ml of glacial acetic acid	Equiv. weight			% Error	Number of bromine atoms entering the molecule
			Found	Mean value	Calc.		
1	Phenol *	5	15.62 15.78	15.70	15.68	0.1	3
2	*o*-Cresol	10	26.96 26.93	26.95	27.03	0.3	2
3	*m*-Cresol	10	18.00 18.02	18.01	18.02	0.1	3
4	*p*-Cresol	10	27.02 26.94	26.98	27.03	0.2	2
5	*p*-*tert.*-Butylphenol	10	37.84 37.74	37.79	37.55	0.6	2
6	*p*-*tert.*-Amylphenol	10	41.30 41.28	41.29	41.06	0.6	2
7	2,6-Xylenol	10	61.52 60.92	61.22	61.08	0.2	1
8	2,4-Xylenol	40	61.13 60.84	60.99	61.08	0.1	1
9	2,4-Di-*tert.*-butyl-*m*-cresol	40	109.5 109.2	109.35	110.17	0.7	1
10	2,2-Bis-[*p*-hydroxyphenyl]-propane	10	28.75 28.72	28.74	28.53	0.7	4
11	*o*-Hydroxymethylphenol	10	30.91 31.08	30.99	31.03	0.1	2
12	*p*-Hydroxymethylphenol	10	30.93 30.71	30.82	31.03	0.7	2
13	*o*-Hydroxydiphenyl	10	42.50 42.68	42.59	42.55	0.1	2
14	*p*-Hydroxydiphenyl	10	42.34 42.52	42.43	42.55	0.3	2
15	*β*-Naphthol	10	71.69 71.76	71.73	72.08	0.5	1
16	Resorcinol	10	18.27 18.38	18.32	18.35	0.2	3
17	Phloroglucinol, 2 H_2O	10	27.08 27.05	27.07	27.02	0.2	3
18	2,4-Dihydroxyacetophenone	10	37.62 37.78	37.70	38.04	0.9	2
19	2,4-Dichlorophenol	10	81.39 81.52	81.45	81.50	0.1	1
20	2-Chloro-5-methylphenol	10	35.58 35.46	35.52	35.65	0.4	2
21	*p*-Chloro-*m*-cresol	10	35.60 35.65	35.63	35.65	0.1	2
22	Salicylic acid	10	34.48 34.58	34.53	34.53	0	2
23	*p*-Hydroxybenzaldehyde	10	30.52 30.53	30.53	30.53	0	2
24	*p*-Hydroxyacetophenone	10	34.02 34.10	34.06	34.04	0.1	2
25	*p*-Hydroxypropiophenone	10	37.55 37.52	37.54	37.54	0	2
26	*o*-Hydroxydiphenylether	30	46.24 46.30	46.27	46.55	0.6	2

* Alternatively the "excess" method may be used under standard conditions.

Table 2. Bromide-bromate titration of phenols using the "excess" method.

No.	Compound	Ml of glacial acetic acid	Time (min)	Equiv. weight			% Error	Number of bromine atoms entering the molecule
				Found	Mean value	Calc.		
27	2,3-Xylenol	10	3	30.55 30.39	30.47	30.54	0.2	2
28	2,5-Xylenol	10	3	30.56 30.29	30.43	30.54	0.4	2
29	3,5-Xylenol	10	3	20.26 20.13	20.20	20.36	0.8	3
30	3,4-Xylenol	20	3	30.66 30.41	30.54	30.54	0	2
31	2-*iso*-Propyl-5-methylphenol (Thymol)	10	3	37.37 37.49	37.43	37.55	0.3	2
32	2-Methyl-5-*iso*-propylphenol (Carvacrol)	10	4	37.88 37.80	37.84	37.55	0.8	2
33	2,3,5-Trimethylphenol	30	3	34.19 33.93	34.06	34.05	0	2
34	*m*-Hydroxymethylphenol	10	3	20.58 20.57	20.58	20.69	0.5	3
35	*o,o'*-Dihydroxydiphenyl	10	3	23.09 23.09	23.09	23.28	0.8	4
36	*o*-Chlorophenol	10	3	32.15 32.05	32.10	32.14	0.1	2
37	*m*-Chlorophenol	10	3	21.42 21.38	21.40	21.43	0.1	3
38	*p*-Chlorophenol	10	3	31.93 32.02	31.98	32.14	0.5	2
39	2,4,5-Trichlorophenol	10	3	98.65 98.61	98.63	98.73	0.1	1
40	*m*-Hydroxybenzoic acid	10	3	22.79 22.90	22.85	23.02	0.8	3
41	*o*-Hydroxybenzaldehyde	30	3	30.55 30.58	30.57	30.53	0.1	2
42	*m*-Hydroxybenzaldehyde	10	3	20.17 20.25	20.21	20.35	0.7	3
43	*o*-Hydroxyacetophenone	10	3	33.88 34.04	33.96	34.04	0.2	2
44	*o*-Nitrophenol	10	3	35.06 34.71	34.89	34.78	0.3	2
45	*m*-Nitrophenol	10	3.5	23.01 23.07	23.04	23.19	0.6	3
46	*p*-Nitrophenol	10	3	34.89 34.52	34.70	34.78	0.2	2
47	2,4-Dinitrophenol	10	3	91.80 91.80	91.80	92.05	0.3	1

cases where a free *ortho* position is flanked by an alkyl group might be, at least in part, that this position is less readily substituted by bromine.*

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* In fact it is often observed that substitution in an aromatic nucleus is retarded at a position flanked on both sides by substituent groups.

As seen from Tables 1 and 2 a higher dilution than 10 ml had to be used in some cases as the bromine consumption was too high under standard conditions. The reason for this might be an added substitution at vacant *meta* positions or in side chains. Another possible cause is the formation of compounds of the tribromophenol bromide type [19,20].

The phenols containing hydroxymethyl groups (Nos. 11, 12 and 34) may be discussed in connection with the alkylphenols. The difference in reactivity between the three monosubstituted isomers is here enhanced in comparison with the cresols as the *meta* isomer had to be analyzed by the "excess" method.

Chlorophenols. Four of the five chlorophenols which in addition to the hydroxyl group contained only chlorine (Nos. 36—39) had to be analyzed by the "excess" method. This result is to be expected from the standpoint of the deactivating influence of halogen on the aromatic ring. By introducing a methyl group the reactivity is increased as shown by the results of the titration of the two chlorocresols (Nos. 20 and 21).

Phenols with meta directing substituents. These compounds are conveniently discussed together. Phenols with the following *meta* directing groups have been tested: nitro, carboxyl, formyl and alkylketone (Nos. 22—25 and 40—47). Considering the electronwithdrawing influence of these groups a decreased reactivity in comparison with phenol might be expected *. However, with the exception of the nitrophenols, the *para* isomers (Nos. 23—25) and in one case also the *ortho* isomer (No. 22) are more reactive. The *meta* isomers are less readily substituted than the rest as the "excess" method invariably had to be employed. No splitting off of carboxyl or formyl groups has been observed.

Dihydroxy- and polyhydroxyphenols. Only *meta* isomers could be analyzed by the present bromination method (Nos. 16—18). The "direct" method was applicable.

Diphenylols and naphthols. Of the three diphenylols tested (Nos. 13, 14 and 35) *o*-hydroxy- and *β*-hydroxydiphenyl could be titrated directly, while *o,o'*-dihydroxydiphenyl was less reactive. This fact is obviously a result of decreased resonance due to steric hindrance and hydrogen bonding. *β*-Naphthol (No. 15) consumed only two bromine atoms per molecule although four might be expected **. *α*-Naphthol, on the other hand, consumed four equivalents of bromine. The values are not communicated, however, as the results were less accurate because of discolouration of the solution.

Phenol ethers. The bromination method was tried on several alkoxyphenols. However, it was found to be not suitable for the quantitative analysis of this type of phenols. The result of the direct titration of one aryloxyphenol showed, that only the ring containing the hydroxyl group was attacked (No. 26).

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* In the discussion above it has been assumed that alkyl groups increase the nucleophility of a phenol and *meta* directing groups and chlorine decrease it. Such an assumption is not necessarily correct. It must be taken into account that when one of these groups or atoms is substituted for a hydrogen atom in a phenol, the resonance between the oxygen atom of the hydroxyl and the ring also changes. The combined nucleophilic effect may well be contrary to that expected when only the influence of the substituent on the ring is considered. This fact in connection with other effects originating from steric hindrance and hydrogen bonding might explain the apparently contradictory results obtained in some cases.

** To obtain accurate results it is necessary to use a volume of bromide-bromate solution corresponding to the substitution of one hydrogen atom.

With the establishment of the suitable conditions for the quantitative analysis of the phenols collected in Tables 1 and 2 the application of the bromination method to other phenols should be considerably facilitated.

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