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Determination of the Number of Free *ortho* and *para* Positions in Phenols

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A method has been worked out for the determination of the number of free *ortho* and *para* positions in phenols, using bromide-bromate titration in glacial acetic acid and conductometric titration in ethyl alcohol-water. The majority of the phenols on which the method was tried gave the correct value for the number of free *ortho* and *para* positions. The significance of conductometric titration curves for the identification of various types of phenols has also been discussed.

On investigation of the structure of a phenol, a knowledge of the number of free *ortho* and *para* positions in the aromatic nucleus is of considerable value. The facile substitution by bromine of the hydrogen in the positions *ortho* and *para* to a phenolic hydroxyl should provide a suitable method for the determination of this number. However, there is no universal bromination procedure *, which can be used with confidence for the quantitative bromination of all types of phenols. This makes it more difficult to develop a successful application of the bromination method for the present structural problem. It is in general not possible to adapt the procedure to the type of phenol, since this is often unknown, and the same procedure must therefore be used in all cases. However, it must be remembered, that in this case a quantitative determination of the bromine consumption is not necessary since only an estimate of the number of bromine atoms entering the aromatic nucleus is required. Thus it is possible that a suitable compromise between the existing quantitative methods could be found which can give values accurate enough for this purpose. Recently [1] it was shown by the author that a large number of phenols could be quantitatively brominated in glacial acetic acid either by direct titration with bromide-bromate solution or by the use of an excess of this reagent. A hybrid between the two methods, applicable to the solution

* For a discussion of quantitative bromination methods for phenols, *cf.* Ref.[1].

of phenolic structural problems, has now been worked out and the results obtained are presented in this paper *.

The bromide-bromate titration gives only the number of equivalents of bromine consumed per gram of the phenol. To calculate the number of free *ortho* and *para* positions it is necessary to know the molecular weight of the phenol. Several methods are available for this purpose. Conductometric titration [8], titration in nonaqueous solvents [9,10] and, recently, high frequency titration [11] have been employed. Although the conductometric method might not be the most accurate one it has been chosen here because of its general applicability and its simplicity, which are important factors in identification work.

EXPERIMENTAL

Bromide-bromate titration. The phenol (50 mg) was weighed and dissolved in 20 ml of glacial acetic acid. Conc. hydrochloric acid (5 ml) was added and then 0.1 N potassium bromide-bromate dropwise until the solution of the sample had acquired a distinct yellow colour. Care should be taken not to add more than about 10 % excess of bromide-bromate solution. Five ml of a 10 % potassium iodide solution were then added and the iodine was titrated at once with 0.1 N thiosulphate using starch solution as indicator.

Conductometric titration. A Radiometer Conductometer model CDM2 was used. The phenol (300–500 mg) was weighed and dissolved in 25 ml of 96 % ethyl alcohol. The solution was then diluted with distilled water (usually 25 ml). For some phenols it was necessary to use a higher proportion of ethyl alcohol in order not to precipitate the phenol (see Table 1) but in all cases the total volume was 50 ml. From a microburette 0.5 N sodium hydroxide was added and the conductance read for each ml of the titrant. It is recommended that the addition should be carried on considerably beyond the first equivalence point in order to ascertain whether the molecule contains more than one acidic function. The observed conductance values were corrected for the dilution caused by the titrant by multiplying them by $(V+v) / V$ where V is the initial volume and v the volume of titrant added. The equivalence points were evaluated graphically by plotting the conductances against the volumes of titrant. The intersections of the straight lines drawn through these points define the equivalence points. The titration vessel was not thermostated but was shielded against rapid temperature changes.

RESULTS

Conductometric titrations. The accuracy of conductometric titrations of phenols is dependent on the concentration of the phenol in the solvent. Concentrations which are too low or too high should both be avoided. Here solutions which are 0.04 to 0.05 N have been titrated with good accuracy in most cases. It is of course difficult to weigh the correct amount of an unknown phenol. If, however, the first titration shows that the concentration of the solution has been considerably different from the values given above another titration should be made.

* Methods for the estimation of the number of free *ortho* and *para* positions in phenols by means of bromine have been described elsewhere. Veibel [2], for example, utilizes a modification of the well-known Koppeschaar procedure. In view of the reported inaccuracy of this method [3-7], which is partly connected with the replacement of various groups by bromine (Veibel mentions the risk of replacement of carboxyl groups) there is some doubt concerning the general usefulness of the Veibel procedure. There does not appear to be any published account of tests on different types of phenols of the procedure recommended.

Table 1. Bromide-bromate titration and conductometric titration of phenols.

No.	Compound	Equiv. wt bromide-bromate titration		Equiv. wt conductometric titration		Number of bromine atoms entering the molecule	
		Found	Calc.	Found	Calc.	Found	Calc.
1	Phenol	15.9	15.7	94.4	94.1	3.0	3
2	*o*-Cresol	27.0	27.0	108.6	108.1	2.0	2
3	*m*-Cresol	18.3	18.0	108.1	108.1	3.0	3
4	*p*-Cresol	26.9	27.0	108.0	108.1	2.0	2
5	*p-tert.*-Butylphenol	37.7	37.6	150.1	150.2	2.0	2
6	*p-tert.*-Amylphenol	41.3	41.1	164.5	164.2	2.0	2
7	*p*-Octylphenol	52.4	51.6	214.0*	206.3	2.0	2
8	2,3-Xylenol	30.7	30.5	123.0	122.2	2.0	2
9	2,4-Xylenol	62.1	61.1	122.5	122.2	1.0	1
10	2,5-Xylenol	31.0	30.5	123.0	122.2	2.0	2
11	2,6-Xylenol	51.0	61.1	123.6	122.2	1.2	1
12	3,4-Xylenol	30.1	30.5	121.6	122.2	2.0	2
13	3,5-Xylenol	20.8	20.4	122.7	122.2	2.9	3
14	Thymol	37.9	37.6	154.3	150.2	2.0	2
15	Carvacrol	45.0	37.6	156.8	150.2	1.7	2
16	2,3,5-Trimethylphenol	35.3	34.1	137.4	136.2	1.9	2
17	2,4,6-Trimethylphenol	53.8	—	142.8	136.2	1.3	0
18	2,6-Di*tert.*-butyl-*p*-cresol	96.6	—	244.0**	220.3	1.3	0
19	2,4-Di*tert.*-butyl-*m*(5)-cresol	101.3	110.2	235.6***	220.3	1.2	1
20	2,2-Bis-[*p*-hydroxyphenyl] propane	28.8	28.5	113.3	114.1	3.9	4
21	*o*-Hydroxymethylphenol	30.8	31.0	123.8	124.1	2.0	2
22	*m*-Hydroxymethylphenol	21.0	20.7	122.5	124.1	2.9	3
23	*p*-Hydroxymethylphenol	31.9	31.0	119.0	124.1	1.9	2
24	*o*-Hydroxybenzaldehyde	32.5	30.5	119.8	122.1	1.8	2
25	*m*-Hydroxybenzaldehyde	22.9	20.4	120.8	122.1	2.6	3
26	*p*-Hydroxybenzaldehyde	30.0	30.5	120.4	122.1	2.0	2
27	*o*-Hydroxyacetophenone	33.8	34.0	135.7	136.1	2.0	2
28	*p*-Hydroxyacetophenone	33.9	34.0	134.4	136.1	2.0	2
29	*p*-Hydroxypropiophenone	37.1	37.5	149.0	150.2	2.0	2
30	Salicylic acid	33.5	34.5	136.7	138.1	2.0	2
31	*m*-Hydroxybenzoic acid	23.8	23.0	69.4	69.1	2.9	3
32	*p*-Hydroxybenzoic acid	30.6	34.5	69.1	69.1	2.3	2
33	*o*-Chlorophenol	31.7	32.1	127.1	128.6	2.0	2
34	*m*-Chlorophenol	21.9	21.4	128.6	128.6	2.9	3
35	*p*-Chlorophenol	35.7	32.1	126.3	128.6	1.8	2
36	2,4-Dichlorophenol	82.4	81.5	160.9	163.0	1.0	1
37	2,4,5-Trichlorophenol	101.7	98.7	197.1	197.5	1.0	1
38	*p*-Chloro-*m*-cresol	36.2	35.7	142.7	142.6	2.0	2
39	2-Chloro-5-methylphenol	35.8	35.7	141.4	142.6	2.0	2
40	*o*-Nitrophenol	39.2	34.8	139.5	139.1	1.8	2
41	*m*-Nitrophenol	29.2	23.2	137.5	139.1	2.4	3
42	*p*-Nitrophenol	34.9	34.8	136.8	139.1	2.0	2
43	2,4-Dinitrophenol	122.5	92.1	182.1	184.1	0.7	1
44	Picric acid	no consumption of bromine	—	227.1	229.1	0	0

Table 1, continued.

45	*o*-Hydroxydiphenyl	42.7	42.6	170.7	170.2	2.0	2
46	*p*-Hydroxydiphenyl	41.6	42.6	169.6	170.2	2.0	2
47	2,2′-Dihydroxydiphenyl	24.6	23.3	183.6	186.2	3.7	4
48	α-Naphthol	33.6	36.1	143.4	144.2	2.1	2
49	β-Naphthol	68.1	72.1	143.2	144.2	1.1	1
50	*o*-Hydroxydiphenyl ether	42.2	46.6	184.8	186.2	2.2	2
51	Resorcinol	19.8	18.4	100.4 56.1	110.1 55.1	2.8	3
52	Phloroglucinol + $2H_2O$	27.2	27.0	78.3 52.5	81.1 54.0	2.9	3
53	2,4-Dihydroxybenzaldehyde	29.4	32.1	69.1	69.1	2.3	2
54	2,4-Dihydroxyacetophenone	38.1	38.0	150.5	152.1	2.0	2
55	*o*-Methoxyphenol	32.5	31.0	122.3	124.1	1.9	2
56	*m*-Methoxyphenol	22.7	20.7	126.0	124.1	2.8	3
57	*p*-Methoxyphenol	83.5	31.0	123.7	124.1	0.7	2

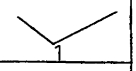
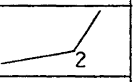
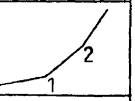
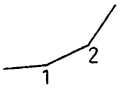
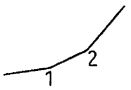
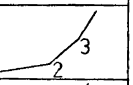
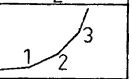
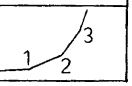
* Titrated in 75 % ethyl alcohol.
** Titrated in 96 % ethyl alcohol.
*** Titrated in 60 % ethyl alcohol.

The accuracy is sufficient for the purpose (*cf.* Table 1) except in a few cases such as some alkylphenols with several alkyl groups or large alkyl groups (*cf.* Nos. 7, 17, 18 and 19). One of the reasons for the decreased accuracy is that some of the compounds mentioned were not sufficiently soluble in 50 % ethyl alcohol and a solvent with less water had to be used which lowers the accuracy by increasing the angle at the equivalence point. In the case of phenols with several acidic functions one or more of the equivalence points were often of inferior accuracy. It was generally observed that the equiv. weight calculated from the last inflexion point was the most accurate one, provided that the inflexion was not too small (*cf.* No. 51 and below).

The shape of the titration curves will be discussed in some detail because of its significance in the identification of various types of phenols.

The phenols in Table 2 have been divided into nine groups according to the shape of their titration curves. The first group contains only picric acid, the titration curve being that of a strong acid titrated by a strong base. Group 2 contains the bulk of the phenols. Nearly all monobasic phenols yield the curve shown in the last column when titrated with sodium hydroxide under the present conditions. Pyrocatechol, salicylic acid and 2,2′-dihydroxydiphenyl also behave as monobasic compounds and give no indication of a second acidic function. 2,4-Dihydroxybenzaldehyde represents the third group. Both of the hydroxyls are titrated but only one break in the curve, at the second equivalence point, is obtained. *o*-Vanillic acid and 2,4-dihydroxyacetophenone (group 4) give two inflexion points on titration, the angle at the second one, however, is nearly 180°. Group 5 is composed of *m*-hydroxybenzoic acid, two *p*-hydroxybenzoic acids, ferulic acid (p-$HOC_6H_4CH_2$=$CHCOOH$), and *p,p′*-dihydroxydiphenyl-2,2-propan. As in group 4, one inflexion point is obtained for each equivalence point but this time the main inflexion is at point 2, the

Table 2. Conductometric titration curves for phenols.

Group No.	Compound	Number of acidic functions		Basicity	Shape of the titration curve
		Present	Found *		
1	Picric acid	1	1	1	
2	Monohydric phenols (except picric acid and phenols containing other acidic groups than hydroxyl groups)	1	1	1	
	Pyrocatechol	2	1	1	
	Salicylic acid	2	1	1	
	2,2′-Dihydroxydiphenyl	2	1	1	
3	2,4-Dihydroxy-benzaldehyde	2	1**	2	
4	*o*-Vanillic acid	2	2	2	
	2,4-Dihydroxy-acetophenone	2	2	2	
5	*m*-Hydroxybenzoic acid	2	2	2	
	p-Hydroxybenzoic acid	2	2	2	
	p-Vanillic acid	2	2	2	
	Ferulic acid	2	2	2	
	p,p′-Dihydroxydi-phenyl-2,2-propane	2	2	2	
6	Resorcinol	2	2	2	
	Hydroquinone	2	2	2	
7	Phloroglucinol + $2H_2O$	3	2**	3	
8	Pyrogallol	3	3	3	
9	Gentisic acid	3	3	3	

* Breaks in the titration curve.

** The values of the equiv. weights show, that these compounds cannot be monobasic and dibasic, respectively. It is also evident from the shape of the titration curve that the latter compound is tribasic.

angle at point 1 being nearly 180°. Resorcinol and hydroquinone which belong to group 6 are intermediate between the phenols in the two preceding groups, the angles at the two inflexion points being nearly alike.

Three phenols each with three acidic functions in the molecule were also titrated. The curves obtained for these compounds were all dissimilar and the

phenols accordingly placed into separate groups (Nos. 7, 8 and 9). According to Kolthoff * phloroglucinol behaves on conductometric titration as a dibasic acid and the curve has only one inflexion point. Under the present conditions phloroglucinol was found to behave as a tribasic acid. In addition to the inflexion point at the second equivalence point a slight change of the direction of the curve was obtained at the third equivalence point too. Pyrogallol also behaved as a tribasic acid, this time with an inflexion point at each equivalence point. Kolthoff [8] reported that pyrogallol behaved as a dibasic acid, giving two breaks in the curve. Gentisic acid (hydroquinonecarboxylic acid) also shows the three acidic functions, the main difference between this curve and that for pyrogallol being the large angle (small inflexion) at the third equivalence point.

It is evident from the foregoing that by using conductometric titration it is possible in most instances to determine the number of acidic functions present in a phenol molecule. For three phenols in group 2 the method failed, but in the case of 2,2′-dihydroxydiphenyl the bromide-bromate titration revealed the presence of two hydroxyl groups in the molecule (*cf.* below). Furthermore the shape of the titration curve often gives additional information about the structure.

Bromide-bromate titration. The results of the bromide-bromate titration of 57 phenols using the method previously described have been collected in Table 1, which gives the equiv. weights obtained and the number of bromine atoms entering each phenol molecule. The latter values were calculated from the molar weights determined by conductometric titration and the equiv. weights resulting from the bromide-bromate titration. As seen from the last column but one in Table 1 the results with few exceptions are satisfactory. For the 57 phenols collected in Table 1 the method gave the correct answer for the number of free *ortho* and *para* positions in 53 cases. It is, however, obvious that the method may give erroneous results in some cases.

The reaction, for example, between 2,4,6-trialkylsubstituted phenols (*cf.* Nos. 17 and 18) and bromine in acetic acid which proceeds easily with the formation of bromo*cyclo*hexadienones and other compounds [12–14] makes it difficult, using the present method, to ascertain the absence of free *ortho* and *para* positions in these compounds. The method also failed with *m*-nitrophenol, which has previously [1] been shown to be more resistant to attack by bromine than most other phenols. It has been pointed out that the quantitative bromination methods were less suited to the analysis of alkoxyphenols [1] and the same may be said about the method described in this paper. Although good values were obtained in many instances, rather divergent results were sometimes observed for phenols of similar structure (*cf.* Nos. 55 and 57). A contributory reason for this was that many of these compounds adopt a yellow colour as soon as the bromide-bromate solution is added, which makes it difficult to add the appropriate amount of this reagent.

Of the dihydric phenols tested, pyrocatechol consumed about 2 equivalents of bromine per mole and hydroquinone about 1. As seen from Table 1 the bromine consumption of phenols with the hydroxyl groups in *meta* position

* Kolthoff [8] used 1 N sodium hydroxide as titrant and water as solvent.

corresponds to the number of free *ortho* and *para* positions (*cf.* Nos. 51—54).

It is apparent from Table 1 that not more than 3 bromine atoms enter the molecule of a mononuclear phenol under the present conditions, provided that unsaturated or other bromine consuming side chains are absent. If the bromine consumption is found to exceed 6 equivalents per mole it is therefore an indication that a di- or polynuclear phenol may be present. Table 1 gives two examples of dinuclear phenols (Nos. 20 and 47). In the first case the presence of two hydroxyls was revealed by the conductometric titration, in the second, however, one break only was obtained in the titration curve. In both cases 4 bromine atoms entered, indicating that in the first the two hydroxyls were situated in separate rings and in the second not one but two hydroxyls were present, this time also in separate rings.

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