ACTA CHEMICA SCANDINAVICA 14 (1960) 1349—1352

Nonaqueous Titration of Phenolic Esters

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Potentiometric titration of phenolic esters using tetra-*n*-butylammonium hydroxide in acetone has been found suitable for differentiating between various types of phenolic esters. Esters of aliphatic carboxylic acids can be titrated as a rule, provided that strongly electron-repelling groups are absent in the phenolic ring. Unsubstituted esters of aromatic carboxylic acids do not react but replacement of hydrogen atoms in the aromatic nucleus by electron-attracting groups can also render the aromatic esters titratable.

It has been shown by Glenn and Peake [1] that phenolic esters of aliphatic as well as aromatic carboxylic acids can be titrated in ethylenediamine using potassium methoxide in benzene-methanol as titrant. It was assumed that the esters underwent aminolysis with the formation of phenols and amides of ethylenediamine. Attempts in this laboratory to titrate phenolic esters using acetone as solvent and tetra-*n*-butylammonium hydroxide in benzene-methanol as titrant revealed a remarkable difference in reactivity between various types of esters. While certain phenolic esters reacted, consuming about one equivalent of base per ester group, no reaction took place with other esters. In the case of phenyl acetate, which reacted with the tetra-*n*-butylammonium base, the formation of methyl acetate could be proved by gas chromatography. Thus the reaction seems to involve a transesterification of the phenolic ester by methanol under the catalytic influence of base.

$$RCOOAr + CH_3OH \rightleftharpoons RCOOCH_3 + ArOH$$

Methanol is present in the titrant and it has been shown recently [2] that the tetra-*n*-butylammonium base titrant prepared by the Cundiff and Markunas [3] method by reaction of tetra-*n*-butylammonium iodide with silver oxide in anhydrous methanol is an approximately 1 to 1 mixture of methoxide and hydroxide.

The base consumption was generally 10—20 % too high. The reason for this is not clear but it should be pointed out that, if the ester group reacts with a hydroxyl ion, two equivalents of base will be consumed per ester group. Because of the too high base consumption, this method is generally not suited

for the quantitative analysis of phenolic esters. For this purpose, the Glenn and Peake method is superior. However, the structure dependence of the present method makes it useful for differentiating between various types of phenolic esters.

Aryloxysilanes, which have previously been titrated by the Glenn and Peake method [4], were found also to respond to the present method.

The results of the titration of a number of phenolic esters are summarized in Table 1.

EXPERIMENTAL

Materials. Most of the phenolic esters were prepared in this laboratory. Their purity was ascertained by determination of appropriate physical constants.

Titration procedure. The titration was made according to the directions of Fritz and Hammond [5] using 0.1 N tetra-*n*-butylammonium hydroxide in benzene-methanol as titrant and acetone as solvent. Both reagent grade and superdry acetone were used with about the same results. Glass calomel electrodes were used and the titration was followed by means of a Radiometer Titrator model TTT 1.

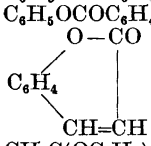
RESULTS and DISCUSSION

The phenolic esters in Table 1 are arranged in the following order: Unsubstituted phenolic esters of aliphatic acids (Nos. 1—5), phenolic esters of aliphatic acids with various substituents in the phenolic ring (Nos. 6—18), unsubstituted phenolic esters of aromatic acids (No. 19) and phenolic esters of aromatic acids with various substituents in the acid part of the molecule (Nos. 20—25). Compounds Nos. 26 and 27 have been included as examples of lactones and orthoesters. From the material in Table 1, certain conclusions may be drawn concerning the reactivities of various types of phenolic esters.

Phenolic esters of aliphatic carboxylic acids without substituents in the phenolic ring are split (*cf.* Nos. 1—5). Replacement of hydrogen atoms in the phenolic ring by strongly electron-donating groups, *e.g.* hydroxyl and amino groups, however, makes the ester group non-reactive (*cf.* Nos. 6—8). The presence of electron-donating groups of intermediate strength in the phenolic ring like the acetoxy group does not inhibit the splitting of the ester group (*cf.* Nos. 9—11). In diacetates of dihydric phenols, for example, one ester group was split with the formation of a phenoxide ion which then inhibited the splitting of the second ester group. Esters of phenols with weakly activating or deactivating groups can be titrated, as might be expected. An exception to this rule was provided by acetylsalicylic acid which was not split in contrast to its *meta* and *para* isomers (*cf.* Nos. 16—18). The reason for this will be discussed below.

Phenolic esters of aromatic carboxylic acids. For a phenolic ester of this type to be titratable under the conditions used in this work, the presence of electron-attracting groups in the molecule seems to be necessary (*cf.* Nos. 19—25). We have investigated the influence of substituents in the acid part of the molecule only but substituents in the phenolic ring can be expected to exert a similar influence as was found previously for esters of aliphatic carboxylic acids.

Table 1. Titration of phenolic esters in acetone using tetra-*n*-butylammonium hydroxide.

Compound			Base consumption equiv. per mole	Number of phenolic ester groups present	Number of phenolic ester groups split
No.	Name	Formula			
1	Phenyl acetate	$CH_3COOC_6H_5$	1.12	1	1
2	Phenyl *iso*butyrate	$(CH_3)_2CHCOOC_6H_5$	1.30	1	1
3	Diphenyl succinate	$C_6H_5OCOCH_2CH_2COOC_6H_5$	2.30	2	2
4	Phenyl succinate	$C_6H_5OCOCH_2CH_2COOH$	1.87*	1	1
5	β-Naphthyl acetate	$CH_3COOC_{10}H_7$	1.20	1	1
6	*o*-Hydroxyphenyl acetate	$CH_3COOC_6H_4OH$-*o*	1.09	1	0
7	*m*-Hydroxyphenyl acetate	$CH_3COOC_6H_4OH$-*m*	1.09	1	0
8	*p*-Aminophenyl acetate	$CH_3COOC_6H_4NH_2$-*p*	0	1	0
9	Pyrocatechol diacetate	$CH_3COOC_6H_4OCOCH_3$-*o*	1.08	2	1
10	Resorcinol diacetate	$CH_3COOC_6H_4OCOCH_3$-*m*	1.08	2	1
11	Hydroquinone diacetate	$CH_3COOC_6H_4OCOCH_3$-*p*	0.88	2	1
12	*o*-Cresyl acetate	$CH_3COOC_6H_4CH_3$-*o*	1.12	1	1
13	*o*-Chlorophenyl acetate	$CH_3COOC_6H_4Cl$-*o*	1.08	1	1
14	*o*-Nitrophenyl acetate	$CH_3COOC_6H_4NO_2$-*o*	1.11	1	1
15	*p*-Nitrophenyl acetate	$CH_3COOC_6H_4NO_2$-*p*	1.03	1	1
16	Acetylsalicylic acid	$CH_3COOC_6H_4COOH$-*o*	1.00	1	0
17	Acetyl-*m*-hydroxybenzoic acid	$CH_3COOC_6H_4COOH$-*m*	2.02*	1	1
18	Acetyl-*p*-hydroxybenzoic acid	$CH_3COOC_6H_4COOH$-*p*	2.02*	1	1
19	Phenyl benzoate	$C_6H_5COOC_6H_5$	0	1	0
20	Phenyl salicylate	*o*-$HOC_6H_4COOC_6H_5$	2.14	1	1
21	Phenyl *p*-hydroxybenzoate	*p*-$HOC_6H_4COOC_6H_5$	1.08	1	0
22	Phenyl *p*-aminobenzoate	*p*-$NH_2C_6H_4COOC_6H_5$	0	1	0
23	Phenyl *p*-nitrobenzoate	*p*-$NO_2C_6H_4COOC_6H_5$	1.03	1	1
24	Diphenyl phthalate	$C_6H_5OCOC_6H_4COOC_6H_5$-*o*	2.11	2	2
25	Phenyl phthalate	$C_6H_5OCOC_6H_4COOH$-*o*	1.75	1	1
26	Coumarin		0	1	0
27	Phenyl orthoacetate	$CH_3C(OC_6H_5)_3$	0	3	0

* Two inflexion points were obtained.

Mechanism of the phenolic ester splitting. As previously shown in eqn. 1, the reaction is a re-esterification reaction. The results presented in the previous sections are also compatible with a reaction mechanism involving a nucleophilic attack on the carbonyl carbon atom of the ester group. In accordance with this mechanism, the splitting of esters of aliphatic carboxylic acids is inhibited by the presence of strongly electron-donating groups in the phenolic ring because of the increased electron density at the carbonyl carbon atom. The decreased reactivity of esters of aromatic carboxylic acids in comparison with esters of aliphatic carboxylic acids can be ascribed to the conjugation

of the carbonyl carbon atom with the aromatic nucleus in the former case. Electron-attracting groups once again call the splitting mechanism into play.

In Table 1, there are some exceptions from the general rules. Thus, acetylsalicylic acid (No. 16) was not split unlike its *meta* and *para* isomers. The reason for this might be a steric factor, the bulky carboxyl ion or the corresponding tetra-*n*-butylammonium salt hindering the approach of the nucleophilic reagent. The negative charge on the carboxyl ion is also likely to render the attack more difficult. A similar but less pronounced effect of a "neighbouring" carboxyl group is discernable for phenyl succinate (No. 4) and phenyl phthalate (No. 25) for which the splitting of the ester group is only partial.

The other exception is provided by phenyl salicylate (No. 20) in which the ester group is split in spite of the presence of a hydroxyl group. We believe this to be due to hydrogen bonding which increases the electrophility of the carbonyl carbon atom. It must be assumed that the ester group is split prior to the neutralization of the phenolic hydroxyl group.

Coumarin (No. 26) is the only example of a lactone investigated in this work. No splitting occurred. Although coumarin is to be looked upon as a phenolic ester of an aliphatic carboxylic acid, a reaction is hardly to be expected because of the conjugation of the carbonyl group with the aromatic ring. The fixation of the carbonyl group might also be of some significance for the lack of reactivity. The last compound in Table 1 is phenyl orthoacetate. It did not react with the titrant because of the absence of a carbonyl groop.

Use in identification work. The material collected in Table 1 exemplifies the application of the present titration method for the identification of phenolic esters of various types. While, in the analytical investigation of phenolic esters, hydrolysis of the esters to form the free phenols is often performed, the reverse procedure might sometimes be of value, *i.e.* acetylation of a phenol in order to elucidate its structure by means of the ester splitting method described here.

Acknowledgement. This work was supported by a grant from the *Town Council of Gothenburg.*

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Received March 24, 1960.