Quantitative Analysis of Aryloxysilanes

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Two new methods for the quantitative analysis of aryloxysilanes have been developed. The first one involved bromide-bromate titration in glacial acetic acid, the second titration with potassium methoxide in anhydrous ethylenediamine using o-nitroaniline as an indicator. The scope and limitations of the methods have been discussed. The first method was also applicable to phenyl orthoesters of carboxylic acids.

The investigation of silanes, especially of those containing aryloxy, alkoxy, alkyl and aryl groups in different combinations bonded to a silicon atom has for a long time been hampered by the lack of convenient rapid methods for their quantitative analysis. To ascertain their purity it has been necessary generally to determine the silicon, carbon and hydrogen content which is, as a rule, a time consuming procedure. The present investigation was undertaken in an attempt to improve this situation.

BROMIDE-BROMATE TITRATION

Recently it was shown by the present author [1] that many phenols can be titrated directly in glacial acetic acid using bromide-bromate solution. In view of the ease with which aryloxy groups bonded to silicon are split off by hydrolysis it seemed justified also to investigate whether the method was applicable to aryloxysilanes. This proved to be the case for such aryloxysilanes in which the corresponding free phenol was directly titratable (see Ref.[1]). Thus phenoxy-, o-cresoxy-, m-cresoxy-, p-cresoxy- and 2,6-xylenoxysilanes could be accurately analyzed. Judging from the amount of bromine consumed, the bromine atoms entered the vacant *ortho* and *para* positions *. The bromide-, bromate method was applicable to all aryloxysilanes investigated, with the above-mentioned aryloxy groups, except those where tertiary butoxy groups

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* No investigation has been made of the mechanism of the reaction or of the products formed. Thus it is unknown whether hydrolysis takes place prior to the reaction with bromine or if the aryloxysilane is brominated as such.

also were linked to the silicon atom. A decreased reactivity of tertiary alkoxy-silanes in various reactions has been observed previously [2,3]. In the present case the inactivation is most likely due to shielding of the silicon atom and the *ortho* positions of the aryloxy group (see also p. 560). Although the "direct" titration method failed, the *tert.*-alkoxyaryloxysilanes could be analyzed by hydrolyzing the silanes in a mixture of glacial acetic acid and conc. hydrochloric acid and then titrating the mixture with bromide-bromate solution. The accuracy is, however, somewhat less than that of the "direct" titration method.

As might be expected the "direct" titration method failed for those aryl-oxysilanes where the corresponding phenol had to be analyzed by the excess method (see Ref.[1]). Thus, the bromine consumption of thymoxytriethoxy-silane and the corresponding carvacryloxysilane was too low. Application of the "excess" bromination method under the conditions used for the determina-tion of the free phenols (*cf.* Ref.[1]) resulted in a too high bromine consumption. Under the prevailing conditions bromine obviously reacts with the ethoxy groups or the ethyl alcohol formed by hydrolysis.

The direct titration method was also suitable for the quantitative determi-nation of phenyl orthoesters of carboxylic acids as demonstrated by the analy-sis of phenyl diethyl orthoformate and the corresponding orthoacetate.

PROCEDURE

About 1.5 mequiv.* of the aryloxysilane were dissolved in the prescribed amount of glacial acetic acid (see Table 1 and below) and 5 ml of conc. hydrochloric acid added. Sixteen ml of a 0.1 N potassium bromide-bromate solution were then dropped into the solution as fast as the bromine was consumed. After addition of 5 ml of a 10 % solution of potassium iodide the liberated iodine was titrated with 0.1 N thiosulfate using starch as an indicator.

In the case of aryloxysilanes with tertiary butoxy groups the solution was heated on a boiling water bath for half an hour after the addition of the conc. hydrochloric acid and then treated as above.

All of the phenoxysilanes as well as the phenyl orthoesters were titrated in 5 ml of glacial acetic acid, the rest of the aryloxysilanes in 20 ml of the same solvent. For accurate results it is recommended not to deviate too much from these volumes.

TITRATION WITH POTASSIUM METHOXIDE IN ETHYLENEDIAMINE

Day *et al.*[4,5] have investigated the reaction between esters of carboxylic acids and ammonia or amines. Among the most reactive participants in this reaction were phenolic esters and ethylenediamine. This circumstance was utilized by Glenn and Peake [6] for the quantitative determination of phenolic esters of carboxylic acids. These compounds undergo aminolysis in excess ethylenediamine at room temperature to form phenols and amides of ethylene-diamine. The resulting phenols were titrated using potassium methoxide in benzene-methanol.

The postulated mechanism of the reaction involves a nucleophilic attack by the amine on the carbonyl carbon atom of the ester followed by the libera-

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

tion of the phenol. This mechanism is also supported by the finding in this work that no reaction takes place between the phenyl orthoesters in Table 1 and ethylenediamine. On the other hand, nucleophilic attack by amines would be possible in the aryloxysilanes. These compounds have been shown to undergo exchange reactions, which are assumed to proceed through a nucleophilic mechanism with intermediate addition compounds [7].

The necessary qualifications for a ready reaction between ethylenediamine and an aryloxysilane thus seemed to be met, and this suggested the possibility of a quantitative determination of the aryloxysilanes. The result of the application of the Glenn and Peake method to the aryloxysilanes, however, was not that expected. The consumption of potassium methoxide was invariably too high (see Table 1). Thus, while the tetraaryloxysilanes should consume 4 equiv. of potassium methoxide per mole, values between 4.85 and 4.96 equiv. per mole were obtained. The aryloxytrialkoxysilanes should consume 1 equiv. of potassium methoxide according to theory, but the experimental values were 1.81 to 1.87. For the diaryloxydialkoxysilanes the corresponding values were 2.80 to 2.88 instead of 2 and the only triaryloxyalkoxysilane tested, triphenoxymethoxysilane, consumed 3.80 equiv. instead of 3. A small number of alkylphenoxysilanes were also titrated. It was found, that the excess consumption of potassium methoxide decreased as alkyl groups were substituted for phenoxy groups on the silicon atom.

From the above it is evident that the excess consumption of potassium methoxide is related to the structure of the organosilicon compound but independent of the number of aryloxy groups linked to the silicon atom. The reason of the high values is evidently to be sought in the organosilicon compounds present in the solution after the aminolysis of the aryloxysilanes. By analogy to the reaction between phenolic esters of carboxylic acids and ethylenediamine it can be assumed that phenols and aminosilanes are formed in the aminolysis of aryloxysilanes. An aminolysis of alkoxy groups, if such are present, might also take place. Thus in the case of the tetraaryloxysilanes the end products should contain silanes in which the silicon atom is linked to four nitrogen atoms. In the case of the alkoxyaryloxysilanes the same type of compounds might be formed as well as structures in which the silicon atom is linked to both oxygen and nitrogen. The carbon-silicon bonds in the alkyl-aryloxysilanes can be assumed to be unchanged after the aminolysis which thus results in structures with carbon and nitrogen atoms linked to the silicon atom. Finally, during the titration the methyl alcohol which is present in the reaction medium might react with the aminosilanes resulting in an exchange of methoxy groups for amino groups. Obviously, it is impossible to predict with any certainty the exact structure of the compounds formed.

We will now consider the question as to why these compounds consume potassium methoxide. The ability of certain organosilicon compounds to add reagents with electron-donor atoms with the formation of penta- and hexa-covalent compounds is well known *. While it has been possible to isolate addition compounds between halogenosilanes and amines or amides [9-12], no similar adducts between organosilicon compounds and oxygen bases have

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* For a detailed discussion of these types of compounds see Stone and Seyferth [8].

been recorded so far (see, however, Ref.[13]). However, they have been assumed to occur as intermediates in several reactions. In the base-catalyzed rearrangement of organopolysiloxanes, bases, such as potassium methoxide, were found to be effective [14]. It was postulated that the first step in the base-catalyzed reaction is the coordination of the oxygen atom in the base to a silicon atom in the siloxane. The alcoholysis of alkoxysilanes in the presence of sodium alkoxides has been assumed to proceed via pentacovalent silicon intermediates formed from the alkoxysilane and alkoxide ion [15]. In a study of the hydrolysis of triphenylsilyl fluoride Swain et al.[16] obtained kinetic evidence of the formation of intermediate adducts between this compound and water. Other similar examples exist [17,18].

The obvious conclusion to be drawn from this discussion is that the "excess" potassium methoxide is used up by addition to the silicon atom. We may consider the organosilicon compounds in question as Lewis acids which are neutralized by the base present. This assumption is in accordance with the decrease in excess base consumption in the series $(CH_3)_nSi(OC_6H_5)_{4-n}$ when n increases from 0 to 3. Replacement of a phenoxy group by a methyl group should cause a decrease in L-acidity from inductive as well as steric reasons *.

Not only aryloxysilanes can be titrated with potassium methoxide in ethylenediamine. This method was also found applicable to alkoxysilanes. Thus tetraethoxysilane in two runs used up 0.98 and 1.00 equiv. of potassium methoxide per mole and methyltriethoxysilane 0.72 and 0.73 equiv. per mole. Trimethylethoxysilane consumed less than 0.01 equiv. per mole and tetraethylsilane did not react at all with potassium methoxide **. Here only L-acidity is present while in the case of the aryloxysilanes the sum of the H-acidity and L-acidity is obtained. It is unsettled whether the alkoxysilanes remain unchanged or an aminolysis of the alkoxy groups takes place. A sharp decrease in acidity as ethoxy groups are replaced by methyl groups is clearly shown. It was not the purpose of this paper to investigate the reaction between alkoxysilanes and potassium methoxide in ethylenediamine. The few results presented here are, however, promising from a practical as well as a theoretical point of view. This reaction might find valuable application for identification and quantitative analysis of organosilicon compounds and also for studying the relationship between the structure of the latter and their ability to react with electron donating compounds.

The results of the analysis of 19 aryloxysilanes are summarized in Table 1. It is seen that compounds for which the bromination method failed, as thymoxytriethoxy- and carvacryloxytriethoxysilane, can be titrated readily (Nos. 17 and 18). On the other hand the method failed for aryloxysilanes with a tertiary butoxy group linked to the silicon atom (Nos. 8 and 10). For these compounds the modified bromination procedure was applicable. The two methods thus complement each other. The variation of the excess base consumption (due to the L-acidity of the organosilicon compounds) makes the

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* As pointed out previously it is not the L-acidity of the phenoxysilane that is measured but of a reaction product the exact structure of which is unknown.

** This is in accordance with the fact that the coordination number of silicon rises above four only when it is bonded to highly electronegative elements [8].

Table 1. Quantitative analysis of aryloxysilanes and phenyl orthoesters.

No.	Compound	Bromide-bromate titration					Potassium methoxide titration					
		Ml of glacial acetic acid	Equiv. weight				Equiv. weight			Base consumption equiv. per mole of silane		
			Found	Mean value	Calc.	% Error	Calc.	Found	Mean value	Total	Due to H-acidity	Due to L-acidity
1	Tetraphenoxysilane	5	16.68 16.70	16.69	16.69	0	100.1	82.7 82.7	82.7	4.84	4.00	0.84
2	Tetra-o-cresoxysilane	20	28.46 28.56	28.51	28.54	0.1	114.1	92.0 92.0	92.0	4.96	4.00	0.96
3	Tetra-m-cresoxysilane	20	19.14 19.07	19.11	19.02	0.5	114.1	92.7 92.9	92.8	4.92	4.00	0.92
4	Tetra-p-cresoxysilane	20	28.53 28.61	28.57	28.54	0.1	114.1	93.9 94.2	94.1	4.85	4.00	0.85
5	Triphenoxymethoxy-silane	5	18.57 18.60	18.59	18.80	1.1	112.8	88.8 89.4	89.1	3.80	3.00	0.80
6	Diphenoxydimethoxy-silane	5	23.03 23.04	23.04	23.03	0	138.2	98.9 98.4	98.7	2.80	2.00	0.80
7	Diphenoxydiethoxy-silane	5	25.36 25.32	25.34	25.37	0.1	152.2	106.3 106.3	106.3	2.86	2.00	0.86
8	Diphenoxydi-*tert*.but-oxysilane	5	30.31 30.42	30.32	30.04	0.9	—	—	—	—	—	—
9	Di-o-cresoxydiethoxy-silane	20	41.30 41.31	41.31	41.56	0.6	166.2	115.6 116.1	115.9	2.87	2.00	0.87
10	Di-o-cresoxy-di-*tert*. butoxysilane	20	48.18 48.66	48.42	48.57	0.3	—	—	—	—	—	—
11	2,6-Xylenoxytrieth-oxysilane	20	140.6 140.8	140.7	142.21	1.1	284.4	152.4 152.3	152.4	1.87	1.00	0.87
12	Di-2,6-xylenoxydietho-xysilane	20	90.32 90.27	90.30	90.13	0.2	Not analyzed					
13	Phenoxytrimethoxy-silane	5	35.75 35.71	35.73	35.72	0	214.3	116.4 116.5	116.5	1.84	1.00	0.84
14	Phenoxytriethoxy-silane	5	42.72 42.77	42.75	42.73	0.1	256.4	137.8 137.6	137.7	1.86	1.00	0.86
15	o-Cresoxytriethoxy-silane	20	67.70 67.61	67.66	67.60	0.1	270.4	144.2 144.3	144.3	1.87	1.00	0.87
16	p-Cresoxytriethoxy-silane	20	67.59 67.47	67.53	67.60	0.1	270.4	148.4 149.0	148.7	1.82	1.00	0.82

Table 1. Continued.

17	Thymoxytriethoxy-silane	—	—	—	—	—	312.5	168.2 168.2	168.2	1.86	1.00	0.86
18	Carvacryloxytrieth-silane	—	—	—	—	—	312.5	166.8 167.2	167.0	1.87	1.00	0.87
19	Methyltriphenoxy-silane	5	17.92 17.97	17.95	17.91	0.2	107.5	87.6 88.0	87.8	3.67	3.00	0.67
20	Dimethyldiphenoxy-silane	5	20.43 20.49	20.46	20.36	0.5	122.2	103.1 103.2	103.2	2.37	2.00	0.37
21	Trimethylphenoxy-silane	5	27.79 27.81	27.80	27.72	0.3	166.3	155.5 157.5	156.5	1.06	1.00	0.06
22	Triethylphenoxysilane	5	34.92 34.99	34.96	34.73	0.7	208.4	201.0 203.0	202.0	1.03	1.00	0.03
23	Phenyl diethyl ortho-formate	5	32.85 32.91	32.88	32.71	0.5	—	—	—	—	—	—
24	Phenyl diethyl ortho-acetate	5	35.10 35.16	35.13	35.04	0.3	—	—	—	—	—	—

potassium methoxide method less accurate than the bromination method. However, the reproducibility for one and the same compound is generally very good under identical conditions *. It is possible that a separate measurement of the H-acidity and L-acidity can be attained potentiometrically, thus increasing the accuracy of the method.

PROCEDURE, REAGENTS AND SOLUTIONS

The aryloxysilanes were prepared in this laboratory. The synthesis of some of them was previously described [7].

Potassium methoxide, 0.1 N. The procedure of Fritz and Keen [19] was used in the preparation of the potassium methoxide solution. About 4 g of potassium were dissolved in 20 ml of absolute methanol and 50 ml of benzene in a loosely stoppered flask. Methanol was added until the solution became homogeneous, then benzene until the solution became cloudy, then it was cleared again with methanol and so on until 1 liter of clear solution was obtained. It was standardized using phenol or one of the cresols.

Indicator. o-Nitroaniline, 1.5 g, was dissolved in 100 ml of benzene.

Titration procedure. About 0.5 mequiv.** of the sample was weighed into a small glass tube. To 25 ml of anhydrous ethylenediamine in a 100 ml Erlenmeyer flask were added 2 drops of indicator solution. The flask was stoppered with a cork with a hole fitting the tip of a 10 ml burette. Potassium methoxide solution was added until the yellow colour changed to orange-red. Then the tube with the sample was added and the titration continued to the reappearance of the orange-red colour. During the titration the solution was rapidly stirred using a magnetic stirrer. To obtain reproducible results it was necessary to use a colour standard. A recommended procedure is to add the theore-

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* The quality of the ethylenediamine seems to be of some significance for the results.
** On the basis of the aryloxy groups present.

tical amount of titrant to a phenol sample and use this solution as a colour standard. However, the colour fades rather rapidly. It is better to prepare a second standard of the same colour intensity as the first using methyl orange and the appropriate amounts of acid and alkaline water solutions. This standard is stable for months.

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