NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF ESTERS IN THE PRESENCE OF ALUMINIUM CHLORIDE

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A method has been suggested for quantitative determination of esters in nitrobenzene solution containig aiuminium chloride. The method which is based on the application of NaF may be used for avoiding the interfering effect of $AlCl_3$ by transforming it into a water-soluble complex (Na_3AlF_6) making possible the alkalimetric determination of esters.

In order to follow FRIES reactions and FRIEDEL—CRAFTS reactions of phenols, respectively, it may be necessary to determine the ester-content of the reaction mixtures. Methods used so far all agree in the first step being the isolation of ester from the mixture decomposed with dilute acid. Then ester isolated was either directly measured quantitatively, or it was hydrolysed and the products were determined in a suitable way [1]—[4]. Without the isolation of ester a number of interfering factors emerge generally when determining alkalimetrically the esters. In this case the medium is heterogeneous and this fact renders difficult the titration or boiling. Also the aluminium chloride content of the system may be the source of different problems, since it undergoes hydrolysis even in neutral medium and the precipitate formed makes uncertain the detection of the end points of titrations. Nor is the isolation of esters a simple task, for it is a lengthy one and since it consists of more steps, due to the inevitable losses, its accuracy is unsatisfactory.

To eliminate these difficulties a new method has been evolved by the authors, which renders possible the determination of the ester content relatively rapid, with an error less than 2%. Using this method the isolation of ester from reaction mixture hydrolysed is not necessary. The method is based on the transformation of aluminium chloride with aqueous solution of sodium fluoride into a water-soluble complex (Na_3AlF_6). This reaction has already been used in analytical chemistry in the determination of aluminium [5]—[8]. Under the suggested conditions in the presence of ethanol the well-known alkalimetric determination of esters can be performed in homogeneous medium. Using this method, resins and tars, being always present in such reaction mixtures which cause some trouble in other cases, do not disturb. It is a great advantage of this method that the determination of ester can be connected with the isolation of products formed during the reaction

giving in an easier way products less contaminated than those obtained without applying sodium fluoride [9]. When applying the proposed method care must be taken that in the presence of Na_3AlF_6 complex the acid or alkali content of aqueous solutions cannot be exactly determined in one step by titration, at least in the concentration range of our measurements, applying phenolphtalein as indicator. *E. g.* when determining the acid content of such a solution by titration with alkali, the acid content measured is less than the real one. The cause of this may be that the rate of neutralisation reaction greatly decreases near the equivalence point. This error of the determination can be eliminated by measuring blank value and taking it into consideration. Results of measurements carried out by this method, as well as examples for its application (determination of thymylacetate) are given in the experimental part.

Experimental

A) *Materials*

Solutions. 0,1 *N* and 0,75 *N* carbonate-free NaOH solution, 0,1 and 1 *N* HCl solution, neutral NaF solution of 3,4—3,9%.

Nitrobenzene. Twice distilled, held over $CaCl_2$.

Ethanol. Commercial grade of 96%.

Aluminiumchloride. VEB. Feinchemie z. synth.

Thymylacetate. Prepared according to A. SPASOV's method [10]. Its ester content was found, by measuring the amount of NaOH needed for saponification, to be of 99,14%.

B) *Quantitative determination of thymylacetate*

The method was applied in kinetical investigations of Fries reaction of thymylacetate as follows: from a reaction mixture, being the initial concentrations both of aluminium chloride and thymylacetate in nitrobenzene solution 0,5 mole/l, 2 ml was removed and poured into a 100 ml conical flask with ground neck, containing 2 ml of ethanol. To the homogeneous solution 0,3 ml 1 *N* of HCl solution, 2 drops of phenolphtalein indicator, pumice, 12 ml of NaF solution and at last 6 ml distilled water were added. Should the indicator change its colour when adding NaF solution the determination must be repeated giving more hydrochloric acid. The mixture, already consisting of two phases was shaken two minutes, it was allowed to stand for about 2 minutes, four drops of phenolphtalein were introduced and the mixture neutralized with 0,1 *N* NaOH till attained 3 minutes' standardization of colour. (To take care of the period is very necessary.) After pipetting 2 ml of 0,75 *N* NaOH and adding 17 ml of ethanol, the solution was boiled for 45 minutes under a reflux condenser (during boiling the mixture became homogeneous), then the hot solution was estimatedly neutralized with 0,1 *N* hydrochloric acid adding at the same time 2 ml excess (altogether "*a*" ml). The change of the indicator was hardly noticeable, due to coloured sideproducts of FRIES reaction which are soluble in medium containing ethanol. After adding new pumice, in order to expel carbondioxide, the solution was

boiled for 3 min. and then cooled at room temperature. The content of the flask was poured into a measuring flask of 100 ml volume, filled at mark (because of 2 ml nitrobenzene present the volume of the solution was considered to be 98 ml), then transferred into a glass cylinder of 2,5 cm diameter, in which it was allowed to stand for about an hour. During this time both nitrobenzene and colourized materials disturbing the titration separated. 50 ml of the clear solution was removed and adding 4 drops of indicator titrated with 0,1 N NaOH till standard colour was obtained ("c" ml). The result of the determination was calculated on the basis of equation (1) where "b" signifies the blank value

$$\text{thymylacetate mmole} = 1{,}5 + \frac{9{,}8}{50} c - 0{,}1\ a - 0{,}1\ b. \tag{1}$$

C) Determination of blank value

From a solution containing the same quantity of aluminium chloride as that mentioned above, 2 ml was removed and exactly the same procedure performed as with the reaction mixture, described under B). The value of the blank ("b" ml) was calculated from equation (2), where c_b and a_b mean the corresponding acid and alkali consumption, respectively, at the determination of the blank

$$b = 15 + \frac{98}{50} c_b - a_b. \tag{2}$$

At analyses of reaction mixtures of different concentrations of aluminium chloride (A_0) to use quantities of materials in Table I seemed to be the most purposeful.

Table I

A_0 mole/l	1 N HCl ml	NaF solution ml	Water ml	Ethanol ml
0,25	0,2	6	10	17
0,50	0,3	12	5	17
0,75	0,4	18	—	20
1,00	0,5	24	—	20
1,25	0,6	30	—	24
1,50	0,7	36	—	30

D) Controlling of reliability of the method

Into conic flask of 100 ml volume thymylacetate was measured with 0,1 mg accuracy, then nitrobenzenic aluminium chloride solution of corresponding amount and concentration was pipetted into it. Further the procedure was the same as described above. Carrying out a number of measurements it was concluded that the average error of the determination is less than 2% and never greater than 4%.

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