Determination of Xanthogenates by Titration with Perchloric Acid

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During recent years, the titration of weak acids and bases in non-aqueous medium has been greatly developed. Whilst working on the titration of weak bases with perchloric acid, we observed that xanthogenates can be rapidly and quantitatively titrated in this way. Hirschkind [1] determined potassium ethyl xanthogenate by titration with hydrochloric acid according to the equation:

$$C_2H_5OCSSK + HCl = C_2H_5OH + CS_2 + KCl$$

and determined the excess hydrochloric acid by titration with sodium hydroxide. Linck [2] found that this method was not generally applicable to other xanthogenates.

In the determination of the equivalent weight of an unknown alcohol, the potassium xanthogenate is prepared and titrated with iodine as described by Whitmore and Lieber [3]. This method has not been satisfactory in all cases, and Linck has suggested the addition of barium chloride to the solution of the xanthogenate to remove by-products and decomposition products, as some of these consume iodine during the titration.

In our method we dissolve the xanthogenate in glacial acetic acid and titrate directly with a solution of perchloric acid in the same solvent. The titration can be carried out both visually and potentiometrically. The process can be represented as follows:

$$HClO_4 + CH_3COOH = CH_3COOH_2^+ + ClO_4^-$$

$$ROCSS^- + CH_3COOH_2^+ = ROCSSH + CH_3COOH$$

This is probably not the only reaction which occurs. According to Cranendonk's experiments [4] the xanthogenates decompose rapidly in acid medium and the decomposition takes place *via* the free xanthogenic acid:

$$ROCSSK + CH_3COOH = ROCSSH + CH_3COOK$$

$$ROCSSH = ROH + CS_2$$

We have found that a solution of potassium ethyl xanthogenate in glacial acetic acid (1 %) decomposes very rapidly. Approximately 50 % was decomposed after 4 minutes and approximately 95 % after 6 hours. The course of the decomposition was followed by pipetting at regular intervals a certain quantity of the solution into water and immediately titrating with 0.1 *N* iodine.

We have attempted to recrystallize the potassium ethyl xanthogenate by dissolving in a little glacial acetic acid and subsequent addition of ether. Precipitation occurred immediately but the substance did not contain sulphur and was analyzed as a compound containing potassium acetate and acetic acid. At the same time we observed the smell of carbon disulphide. This also indicates that the decomposition proceeds as mentioned above.

Furthermore, our experiments have shown that the potentiometric titration curve for potassium ethyl xanthogenate is identical with the titration curve for potassium acetate.

An *equivalent* quantity of potassium acetate is produced when the xanthogenate is decomposed, and it is chiefly this compound which is titrated with perchloric acid:

$$CH_3COO^- + CH_3COOH_2^+ = CH_3COOH + CH_3COOH$$

Table 1. Analysis of Xanthogenates.

ROCSSK	Amount g	ml $HClO_4$ 0.1000 *N*	Mol. weight		Relative error %
			calc.	found	
methyl	0.3292	22.42	146.3	146.8	0.3
ethyl	0.2005	12.48	160.3	160.7	0.3
n-propyl	0.2037	11.68	174.3	174.4	–
*iso*propyl	0.2332	13.30	174.3	175.3	0.6
n-butyl	0.3148	16.68	188.4	188.7	0.2
*iso*butyl	0.2086	11.03	188.4	189.1	0.4
*sec.*butyl	0.2096	11.06	188.4	189.5	0.6
*iso*amyl	0.3146	15.58	202.4	201.9	0.3
allyl	0.2566	14.98	172.3	171.3	0.6
cyclo-hexyl	0.1958	9.10	214.4	215.2	0.4
benzyl	0.2288	10.22	222.4	223.9	0.7
β-methoxy-ethyl	0.3136	16.53	190.3	189.7	0.3

It is therefore possible to titrate the xanthogenate quantitatively even though it is partially decomposed in acid medium. Concurrent with the iodometrical determination of the course of the decomposition, samples were withdrawn at intervals and titrated with perchloric acid as described below. The observed consumption of perchloric acid was constant, regardless of the decomposition of the xanthogenate.

EXPERIMENTAL: Preparation and purification of the xanthogenates. The xanthogenates are prepared according to Whitmore and Lieber, with a few modifications as follows: About 1 g of the alcohol is weighed into a test tube and 0.5–0.6 g potassium hydroxide (approx. 0.01 mole) is added. The mixture is gently heated with constant shaking until the potassium hydroxide is dissolved. This often takes several minutes. In a few cases it may be necessary to add, at the most, 2 drops of water. The mixture is cooled whereby it sometimes becomes viscous or solid. After cooling about 1 ml carbon disulphide (approx. 0.017 mole) is added dropwise. If the liquid becomes warm it is cooled. The mixture is stirred for some minutes with a glass rod and 20 ml of ether are added. After vigorous shaking the xanthogenate produced is filtered through a Buchner funnel and washed with a few ml of ether. This is the normal routine method employed by our students when identifying alcohols.

The xanthogenate is purified by dissolving in the least possible amount of hot

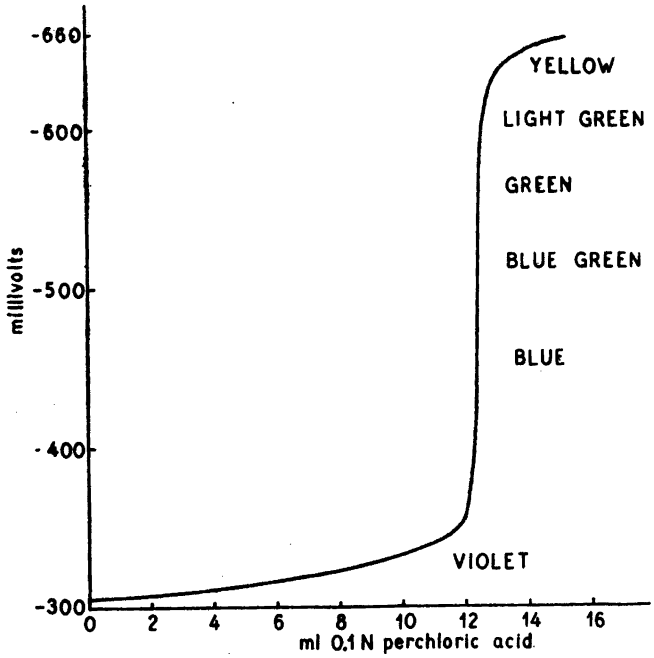

Fig. 1. Potentiometric titration curve of potassium butyl xanthogenate and colour changes of the indicator (crystal violet) during the titration.

acetone. The solution is filtered, and after cooling the xanthogenate is precipitated by addition of 20 ml anhydrous ether. The derivative is filtered off and washed with a few ml of anhydrous ether. The ether is allowed to evaporate spontaneously and the final drying is effected by means of infrared radiation.

The xanthogenates prepared in this manner are stable for several months.

Titration of the xanthogenates. Reagents used: Glacial acetic acid, not less than 99.7 % CH_3COOH. 0.1 *N* perchloric acid in glacial acetic acid. Crystal violet indicator, 0.5 g crystal violet dissolved in 100 ml glacial acetic acid. The 0.1 *N* perchloric acid is prepared and standardized according to Markunas and Riddick [5].

Procedure: About 0.200 g of the purified xanthogenate is dissolved in 15–20 ml glacial acetic acid. 2 drops of crystal violet indicator are added and the solution is titrated with 0.1 *N* perchloric acid to a distinct blue colour. The subsequent colours of the solution will be blue-green and then green, and only one or two drops (0.02–0.04 ml) 0.1 *N* perchloric acid are required to produce the colour changes from blue to blue-green and from blue-green to green. The results are given in Table 1.

We have determined the true end point potentiometrically (Fig. 1) using a calomel electrode, fibre type, as reference and a glass electrode, connected to a pH meter (Radiometer, pH meter 22). The visual end point was determined by observing the colour change of the indicator at the true end point.

As shown by Conant and Werner [6], and later by Seaman and Allen [7], the colour of crystal violet in acetic acid solution at the end point depends to a great extent on the ionic strength of the solution,

However, in the titration of the potassium xanthogenates the ionic strength at the equivalent point will be nearly constant since the slightly soluble potassium perchlorate is precipitated during the titration, and therefore the visual end point is unaffected by the amount of xanthogenate.

SUMMARY

It is shown that the potassium xanthogenates, prepared from 12 common alcohols, can easily be titrated with perchloric acid in glacial acetic acid solution, although the xanthogenates are rapidly decomposed in this medium. The titration can be carried out potentiometrically or visually, using crystal violet as indicator. Detailed instructions for the preparation, purification and the titration are given. The method described is recommended for the determination of the equivalent weight of unknown alcohols.

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