Reductions with Nickel-Aluminum Alloy and Aqueous Alkali

Quantitative Determination of Halogens in Organic Compounds

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 $\begin{array}{c} \textbf{A} \quad \textbf{RECENT publication (3) from these laboratories described} \\ \textbf{the dehalogenation of organic compounds by a nickel-aluminum alloy and aqueous alkali.} \end{array}$

Reduction as a method for the dehalogenation of organic compounds has been known for many years. The application of reduction methods for the quantitative determination of halogen in organic compounds is based on the conversion of halogen into salts of the halogen acids and the subsequent estimation of the halogen by standard analytical procedures. For this conversion, molecular hydrogen developed, for example, from zinc and acid is not generally applicable, since only a limited number of organic halogen compounds quantitatively undergo the halogen displacement when treated in this manner.

The introduction of catalytically activated hydrogen as an analytical tool for the dehalogenation of organic compounds was first described by Busch and Stove (1), who used a palladinized calcium carbonate catalyst which was prepared by heating an aqueous suspension of freshly prepared calcium carbonate with palladium chloride. The organic compound was dissolved in alcohol or water and then shaken at room temperature with the catalyst and hydrogen and sufficient alkali to neutralize the halogen acid formed. Later, Kelber (2) reported a similar procedure using a reduced nickel catalyst. Recently, the simultaneous reduction and dehalogenation of chloro-substituted azo compounds were reported to occur in the presence of Raney's nickel catalyst and hydrogen at room temperature and pressures varying from 1 to 3 atmospheres (4). All these methods when adapted for analysis require the use of hydrogen gas, a reduction catalyst prepared especially for the reaction, and the usual apparatus for catalytic reduction.

It was observed that on treatment with aqueous alkali and a nickel aluminum alloy, quantitative dehalogenation of organic compounds takes place (3). This reduction method has been very advantageously used for the quantitative determination of halogen in many aliphatic, aromatic, alicyclic, and heterocyclic compounds. The simple procedure and the fact that only the usual laboratory apparatus is required in carrying out the analysis give it a definite advantage over the other reduction methods for the determination of halogen in organic compounds. In addition, the results obtainable with this reduction method (100 \pm 0.3 per cent) compare favorably in both accuracy and precision with those by any of the other reduction methods. Its advantages over the Carius method of heating with nitric acid in a sealed tube or the peroxide oxidation in a Parr bomb are obvious.

Procedure for Analysis

FOR ALKALI-SOLUBLE COMPOUNDS. A 0.3-gram sample of the substance is dissolved in 100 ml. of 5 per cent sodium hydroxide in a tall 500-ml. beaker. Using a watch glass to cover the beaker, 3 grams of Raney nickel-aluminum alloy, in three or four portions, are added in the course of 10 minutes. The beaker must be covered with the watch glass at all times during the reduction to prevent loss of the solution by the fine spray caused by the liberation of hydrogen. The alloy may be added by simply sliding the watch glass just over the lip of the beaker, dropping the charge into the solution, and restoring the watch glass to its original position. When the reaction has subsided, the solution is heated on a steam bath for 15 minutes, the condensate on the watch glass is quickly washed into the beaker, and the solution is heated for about one hour at 90° C. to 95° C. At this stage, the nickel settles out and a clear colorless solution is obtained.

The condensate on the watch glass is again washed into the beaker and the alkaline solution is decanted from the nickel into a 200-ml. volumetric flask. The residual nickel is washed three times by decantation with hot water, the solution and washings are combined, and allowed to cool, and the volume is adjusted to the mark. A 100-ml. aliquot, or a fraction thereof, is acidified to Congo red paper with 10 per cent nitric acid and the halogen determined by any standard procedure. If the halogen is to be determined gravimetrically, the acidified solution is cooled and filtered if necessary, and the halide is then precipitated.

FOR ALKALI-INSOLUBLE COMPOUNDS. The sample is weighed into a 250-ml. Erlenmeyer flask equipped with a condenser. After adding 10 ml. of 95 per cent ethyl alcohol and 3.5 grams of alloy, the condenser is set in place and the flask cooled in an ice bath. Seventy-five milliliters of cooled 10 per cent sodium hydroxide are added through the condenser and, after the initial reaction has subsided, the ice bath is removed and the flask heated with a low flame until all the alloy has reacted (1.5 to 2 hours). It is not advisable to heat the mixture too rapidly since the initial reaction is vigorous and solution may be lost through the condenser. Any excessive foaming, during the reflux period, is controlled by the addition of a few drops of octyl alcohol. When the reduction is completed, the condenser is washed down with water and the determination completed as described for the alkali-soluble compounds.

TABLE I. DETERMINAT	TION OF HALOGEN	
Halogen Compound	Theory	Found
	%	%
3,5-Diiodo-4-hydroxyphenylacetic	62.84	62.15
acid ^a β -(3,5-Diiodo-4-hydroxyphenyl)- α -	51.40	51.61
α-(3,5-Diiodo-4-hydroxyphenyl)-β-	51.40	51.60
N-methyl-3,5-diiodochelidamic	56.57	56.54
acida β-Bromopropionic acid	52.21	$56.44 \\ 52.38 \\ 52.06$
Dibromolevulinic acida	58.32	58.00
Bromobenzene	50.85	51.01 50.87
2-Bromopyridine p-Bromoacetophenone	$\begin{array}{c} 50.61 \\ 40.17 \end{array}$	50.76 40.17
2-Bromocholestanone ^a	17.17	40.40
Cholesterol acetate dibromide ^a	27.35	$ \begin{array}{r} 16.59 \\ 27.56 \\ 27.36 \end{array} $
m-Chlorobenzoic acid	22.67	23.04
<i>p</i> -Nitrochlorobenzene	22.52	23.06
β -(p-Chlorobenzoyl)-propionic acid ^a	16.73	17.01
2-Chloropyridine	31.25	$16.81 \\ 31.02$
" Compounds prepared in the authors' Kodak chemicals purified by distillation a	laboratory; others ind/or recrystallizat	were Eastmar ion.

Summary

A simplified procedure for the determination of halogen in organic compounds is described. Quantitative displacement of halogen by catalytically activated hydrogen occurs when the organic compound is treated with a nickel-aluminum alloy in an alkali hydroxide solution. The halogen is obtained in the form of the alkali salt of the halogen acid and can easily be estimated by any standard procedure. The method is accurate, rapid, and adaptable to routine analysis, requiring only the simplest of laboratory glassware and no special reagents.

Acknowledgment

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Analysis of Ethanol for Minor Amounts of **Esters and Aldehydes**

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LTHOUGH often of a routine nature, the estimation of igaa esters and aldehydes in 95 per cent alcohol is fraught with difficulties. Furfural, acidity, and permanganate-time tests are rather readily made while specific gravity determination requires only careful attention to detail. Higher alcohols present some difficulties not considered here.

Esters

The ester content of pure ethanol usually lies between 1 and 5 parts per 100,000 volumes calculated as ethyl acetate on a 100proof basis. By the A. O. A. C. method for esters in distilled liquors (1) on a 50-ml. sample, this would be equivalent to 0.05 to 0.3 ml. of 0.1 N alkali. In distilled liquors except gin the amount is usually about 10 times that cited.

The usual chemical glassware is not sufficiently alkali-resistant to be used in the determination of such small quantities of esters. The alkali used to saponify the esters attacks the glass to such an extent that the alkali so consumed far exceeds that necessary to saponify the esters. Consequently the blank determinations are too high for accurate work. Furthermore, such blanks vary with the age of the glassware used.

A few pieces of old glassware were found in this laboratory which gave small blanks, probably owing solely to usage; they are used in pairs, giving similar blanks. An old expedient of using silver flasks involves washing out the contents into a clean flask after saponification and before titrating, using freshly boiled and cooled distilled water.

Recent studies of the chemical resistance of borosilicate glasses sold as Pyrex, Kimble, and Glasbake (3) show that dilute potassium hydroxide solutions attack such glass to a lesser degree than dilute sodium hydroxide solutions. Therefore, potassium hydroxide is used. Special alkali-resistant Pyrex, while not fully satisfactory, is preferable to the usual chemical glass.

PROCEDURE. Measure 50 ml. of 95 per cent ethanol and dilute to 100 ml, with freshly boiled and cooled distilled water. Exactly neutralize any free acidity with 0.02 N potassium hydroxide solution, using phenolphthalein as indicator. Add exactly 10.0 ml. of 0.1 N potassium hydroxide solution and reflux gently for 30 minutes. Wash down the condenser with neutral distilled water, stopper and cool the flask and contents in a water bath, remove the stopper carefully, and wash down. Add exactly 10.0 ml. of 0.1 N hydrochloric acid solution and titrate the excess acid with 0.02 N potassium hydroxide solution. Run a blank determination under identical conditions, substi-tuting 100 ml. of freshly boiled and cooled distilled water for the diluted alcohol. Each milliliter of titration is equivalent to 0.00176 gram of ethyl acetate. The usual titration will therefore fall between 0.6 and 2.9 ml. of direct titration after subtraction of the blank.

Aldehydes

The volumetric A. O. A. C. method, involving titration of excess bisulfite with standard sodium thiosulfate, is simple and sufficiently accurate when used for one or two samples. As a special distillation is required for each sample for multiple determinations, a colorimetric method is preferred for economy of time.

In the most commonly used colorimetric method (2) aldehydefree alcohol is prepared by distillation from metaphenylenediamine hydrochloride. Unless freshly prepared with great care, error is easily introduced, and the alcohol is rarely completely aldehyde-free. This may be due in part to contact with air in redistillation and in storage, even in a cold, dark place. Redistilled synthetic methanol is consistently aldehvde-free and has been used largely to replace the ethyl alcohol in this determination for several years. While distilled liquors except gin are apt to contain 4 to 12 parts per 100,000 of aldehyde, the amounts in alcohol are of the order of 0.05 to 0.2 part per 100,000.

PROCEDURE. To 2.5 ml. of the alcohol sample add 2.5 ml. of water and 15 ml. of 50 per cent by volume redistilled synthetic methanol. Add 5 ml. of fresh Schiff's reagent prepared according to A. O. A. C. standards, and mix at once. All solutions must be at 60° F. and, after mixing, maintained at that temperature for 20 minutes to develop the meximum color due to the prepared for 20 minutes to develop the maximum color due to the presence of aldehyde.

Prepare standards as follows: To 5 ml. of 50 per cent aldehyde. hyde-free alcohol add 15 ml. of 50 per cent synthetic methanol plus 0.02, 0.025, 0.03, 0.05, and 0.075 ml. of freshly diluted acetaldehyde solution containing 0.0001 gram per ml. Such small quantities can be measured with a sufficient degree of accuracy by using a 1-ml. pipet graduated in 100 parts. Vary these standards to suit specific needs. To each of the above add 5 ml. of the Schiff's reagent, mix at once, and treat as with the sample. Pyrex test tubes (25-ml.), thoroughly cleaned with chromic acid-sulfuric acid solution and efficiently rinsed, are convenient comparison tubes.

Compare the samples and the standards, all made at approxi-mately the same time, after standing for 20 minutes at 60° F.

Summary

In the accurate determination of 1 to 5 parts per 100.000 of esters in 100-proof ethanol it is necessary to have either well-aged glassware which gives a small blank, or silver flasks. Many difficulties in the determination of 0.1 part per 100,000 of aldehyde are eliminated by substituting redistilled methanol for the major part of the aldehyde-free ethanol.

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