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A New Rapid Titration Method for Determining the Halogen Ratio of Wijs Solution and of Iodine Monochloride

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Abstract

The free iodine in Wijs solution is titrated directly, in strong hydrochloric acid solution, with standard potassium iodate solution. From this titration and the usual sodium thiosulfate titration for total halogen, the iodine/chlorine ratio is calculated. Results agree closely with those obtained by the longer chlorine-water method of Lopes. The halogen ratio of reagent grade iodine monochloride, a convenient material from which to prepare Wijs reagent directly, is also determined by the new titration method.

Introduction

THE PREPARATION OF WIJS solution is described in the AOAC Official Method Cd 1-25, April 1956, Iodine Value, Wijs Method. The solution is prepared by (a) chlorinating a 0.1 *N* iodine solution in glacial acetic acid, or (b) much more conveniently by adding iodine monochloride to glacial acetic acid. The ratio of iodine to chlorine in Wijs solution must be about 1.1. The determination of this halogen ratio involves two steps: 1) titration of total halogen with $Na_2S_2O_3$ solution; and 2) titration of total iodine by the method of Lopes (1). The second step is rather inconvenient because it involves preparing a saturated solution of chlorine in water, adding the Wijs solution, and boiling for 10 min. Up to now, no simple and rapid means has been available for checking the iodine/chlorine ratio of reagent grade iodine monochloride.

Experimental

In our laboratory, Wijs solution has always been prepared from iodine monochloride, by merely pipetting 5 ml into a liter of glacial acetic acid and mixing. For this method of preparation, it is essential that the ICl itself has the correct I/Cl ratio of about 1.1. Unfortunately, a recent lot of commercial ICl was received with an I/Cl ratio of less than one. It was necessary to grind iodine crystals, weigh out the required amount, and then dissolve them in the Wijs solution to boost the ratio to 1.1.

This necessitated running a number of total iodine determinations by the somewhat tedious chlorine water procedure of Lopes. A more rapid and direct method for titrating the free iodine is described by Kolthoff and Belcher (2). In strong HCl solution, the following reaction with KIO_3 takes place.

$$2I + KIO_3 + 6HCl \longrightarrow KCl + 5ICl + 3H_2O$$

The Wijs solution is added to a mixture of 1:1 HCl and CCl_4 in a flask and shaken, whereby the free iodine present is extracted into the CCl_4 layer, coloring it violet. The mixture is then titrated with 0.04 *N* KIO_3 solution, to a colorless end point, as a measure of the free iodine.

As a confirmatory test, the foregoing KIO_3 method was first applied to a mixture of acetic acid, 1:1 HCl, and CCl_4 containing a known amount of free iodine. Excellent results were obtained using 10-ml and 15-ml portions of iodine solution. Using 10-ml portions of one iodine solution, the amount of iodine present was 0.1218 g and the amounts found by titration with 0.0642 *N* KIO_3 were 0.1217 g and 0.1220 g. Using 15-ml portions of another iodine solution, the amount of iodine present was 0.1938 g and the amounts found by titration with 0.03962 *N* KIO_3 were 0.1936 g and 0.1940 g.

The iodine/chlorine ratio was then determined on a Wijs solution using both the method of Lopes and the KIO_3 procedure: the I/Cl ratio by the Lopes method was 1.10 and 1.12; by the KIO_3 method, it was 1.11 and 1.11. Both methods give the same answer.

The detailed new procedure for determining the iodine/chlorine ratio of Wijs solution, and also of reagent grade iodine monochloride, is described in the next section.

Determination of Halogen Ratio of Wijs Solution

Reagents

1) Potassium iodate solution, 0.04 *N*. Dry ACS reagent grade KIO_3 for one hour at 110C. Weigh 2.1402 g of the dried salt, dissolve in water, dilute to one liter in a volumetric flask, and mix.

2) Hydrochloric acid, 1:1. Dilute 37% HCl with an equal volume of water.

3) Potassium iodide solution, 15%. Dissolve 150 g in distilled water and make up to a liter.

Procedure

Measure 50 ml of 1:1 HCl and 50 ml of CCl_4 into a 500-ml iodine flask. By means of a pipet, transfer 25.00 ml of the Wijs solution to the flask, and shake. Titrate the free iodine in the violet-colored CCl_4 layer with the KIO_3 solution to a colorless end point using vigorous shaking.

On a second 25.00 ml portion of the Wijs solution, determine the total halogen by adding 150 ml of water, 15 ml of 15% KI solution, and titrating with standard $Na_2S_2O_3$ solution to a starch end point.

Calculate the I/Cl ratio as follows:

Calculation

$(T + F)/(T - F) =$ iodine/chlorine ratio

where $T =$ ml. $Na_2S_2O_3 \times N$ required for total halogen
$F =$ ml. $KIO_3 \times N$ required for free iodine

Derivation

$(T - F) =$ ml of N $Na_2S_2O_3$ required for the ICl
$(T - F)/2 =$ ml of $Na_2S_2O_3$ required for the Cl or the I in the ICl

$$\frac{(T - F)/2 + F}{(T - F)/2} = (T + F)/(T - F)$$

Determination of Halogen Ratio of Iodine Monochloride

It is necessary first to prepare a Wijs solution from the iodine monochloride and then determine the halogen ratio by the foregoing procedure. The iodine monochloride must contain a slight excess of free iodine so that its I/Cl ratio is about 1.1.

Procedure

Pipet 5 ml of reagent grade iodine monochloride into a liter of glacial acetic acid, and mix to form Wijs solution.

Determine the free iodine and the total halogen, using 25.00-ml portions by the foregoing procedure described under Halogen Ratio of Wijs Solution, and calculate the iodine/chlorine ratio.

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Analysis of Alpha Olefins Using a Gas Chromatograph-Mass Spectrometer Combination[1]

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Abstract

The gas chromatograph-mass spectrometer (GCMS) combination with and without catalytic hydrogenation is the most effective way to obtain detailed analysis of commercial alpha olefin mixtures. Previous descriptions of this technique presented examples only up to C_{10} alpha olefins. We have extended this technique to include alpha olefins up to C_{20}. The complete analysis of a C_{11}–C_{14} alpha olefin mixture is given as an example.

Introduction

THE COMPLETE ANALYSIS of a mixture of olefins is complicated by the large number of possible isomers. Commercial alpha olefins contain between 85 and 95% straight chain alpha olefins and varying amounts of internal, branched, and cyclic olefins; normal, branched, and cyclic paraffins; and diolefins.

Gas chromatography is a useful tool for analyzing alpha olefins, and several techniques have been reported (1,2). However, a more detailed analysis of the minor components can be obtained by using the gas chromatograph-mass spectrometer combination (GCMS).

Gohlke (3) used a gas chromatograph connected to a time-of-flight mass spectrometer for the characterization of complex mixtures. Lindeman and Annis (4) of this laboratory used a gas chromatograph with a magnetic deflection mass spectrometer to analyze the C_5–C_8 hydrocarbons in a California naphtha. Lindeman (5) subsequently analyzed an olefin fraction from a light catalytic cracked gasoline using the GCMS with catalytic hydrogenation before and after the gas chromatograph.

In this paper we present an analysis of a commercial C_{11}–C_{14} alpha olefin mixture using the GCMS with catalytic hydrogenation. The experimental technique involves separating the olefin mixture by gas chromatography and passing the eluted components into the mass spectrometer directly from either the chromatograph or the catalytic hydrogenator. The mass spectral records are then interpreted and the components determined. The amounts of the components are calculated from the gas chromatograph record. In cases of multicomponent peaks, the distribution of the components is estimated from the mass spectral records.

Experimental

Instrumentation

The gas chromatograph is a specially built dual-column chromatograph with two temperature program modes, 1C and 0.5C per minute. The thermal conductivity detectors are coupled to a 1-mv recorder modified to print time marks.

The gas chromatograph columns used in these experiments are 50-ft by ¼-in. bifilar-wound copper tubes packed with 15% Ucon LB 550X, 0.2% Alkaterge T, and 0.2% Span 80 on 60–80 mesh firebrick.

The mass spectrometer is a Consolidated Electrodynamics Corporation Model 21-103C equipped with an Applied Physics Model 36 vibrating reed amplifier and modified for fast, repetitive scanning. The time constant in the scan circuit of the mass spectrometer has been decreased to allow a mass range of 50 to 200 to be scanned in 40 sec. A resetting interval timer is used to constantly repeat the scan. Valve V-6 (Fig. 1) is a Nuclear Products all-metal bellows valve added to the instrument to isolate the spectrometer from the chromatograph when necessary.

The output from the mass spectrometer is fed to an Adage Mass Spectrum Digitizer (6), which prints mass numbers and peak heights and supplies the timing signal to the chromatograph recorder. The conventional light beam galvanometer mass spectrum

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