# **Dehydrogenation and Nitration of Hydrocarbons** of the Cyclopentane Series

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**THE** reviewer of the paper by Berl and Koerber (1) raised the question of how cyclopentane and its derivatives react under the conditions of the dehydrogenation and nitration described. Zelinsky (2) has stated that hydrocarbons of the cyclopentane series are not dehydrogenated using palladium, as are those of the cyclohexane series. In his second publication (3), he found that with platinum, only members of the cyclohexane series can be dehydrogenated, but not those of the heptamethylene series.

|  | Table I. | Dehydrogenation | AND | NITRATION |
|--|----------|-----------------|-----|-----------|
|--|----------|-----------------|-----|-----------|

| Expt.<br>No. | Material                               | Tempera-<br>ture<br>° C. | Dehydro-<br>genation | Used<br>Cc. | Found<br>Cc.        |
|--------------|--|--------------------------|----------------------|-------------|---------------------|
| 1            | Cyclo-                                 |                          | None                 | 2           | 1.89 Original mate- |
| $^{2}$       | Cyclo-                                 |                          | None                 | $2\int$     | 1.94 hydrogenation  |
| 3            | Cyclo-                                 | 320                      | 3 times              | 2)          | 1.87                |
| 4            | Cyclo-                                 | 320                      | 3 times              | 2           | 0.15 After dehydro- |
| 5            | Cyclo-                                 | 385                      | 4 times              | 2           | 1.90 genation       |
| 6            | pentane<br>Methyl<br>cyclo-<br>pentane | 390                      | 4 times              | 2 ]         | 1.95                |

Several experiments were carried out to prove the correctness of Zelinsky's investigations (Table I).

To be sure that the catalyst was not poisoned, experiment 4 was carried out, and shows that no poisoning took place.

These experiments show that cyclopentane and methylcyclopentane are practically unattacked by mixed acid A, and that, contrary to the behavior of hydrocarbons of the cyclohexane series, they show practically no dehydrogenation when submitted repeatedly to the Zelinsky dehydrogenation treatment at 325° and 385° C. This last-mentioned treatment at increased temperature was made to find out if the stability of cyclopentane and its derivatives would not be decreased with increased dehydrogenation temperature. The high stability of the 5-carbon ring compounds is in accordance with the Baeyer strain theory.

### Acknowledgment

The authors are indebted to Edgar Clarke, Pennsylvania State College, and the Shell Development Corporation, San Francisco, Calif., for putting cyclopentane and methylcyclopentane at their disposition.

#### Literature Cited

- (1) Berl, E., and Koerber, W., IND. ENG. CHEM., Anal. Ed., 12, 175-6 (1940).
- (2) Zelinsky, Ber., 44, 3124 (1911).
  (3) Ibid., 45, 3678 (1912).

# **Cerimetric Determination of Small Amounts** of Arsenic

# After Reduction with Hypophosphite Reagent

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THE volumetric determination of arsenic, after its reduction to the elementary state, with a reagent of high oxidation potential has particular advantages in the analysis of microquantities. The equivalent weight of arsenic under these conditions is equal to 5. In the present work the authors have made use of a hypophosphite solution in hydro-chloric acid for the reduction of As<sup>III</sup> or As<sup>V</sup> to As<sup>0</sup> and of ceric sulfate for the oxidation of As<sup>0</sup> to As<sup>V</sup>. Recently, Evans (1) made use of the same reducing agent, but he oxidized the precipitated arsenic with dilute iodine and backtitrated with thiosulfate. He made use of his procedure in the determination of arsenic in various metals and alloys. According to his data his procedure gives results accurate to about 1 per cent with amounts of arsenic greater than 1.5 mg.; with smaller amounts relatively large errors are reported—12 to 16 per cent with 0.375 mg.

The method of Evans requires boiling the arsenic solution with hypophosphite reagent with the use of a reflux condenser, but by changing the concentration of hydrochloric acid in the hypophosphite solution the authors were able to eliminate the reflux condenser. After collecting and washing the arsenic they oxidized the element to the quinquevalent state with an excess of ceric sulfate and back-titrated with

standard arsenious trioxide. The advantage of both reagents is that they are stable for a long time.

# **Reduction of Arsenic with Hypophosphite**

The amount of calcium hypophosphite present during the reduction was found to be of no consequence, as long as a large excess was used. The concentration of hydrochloric acid during the reduction was of greater importance, as the speed of reduction of the arsenious or arsenic acid increases with increasing hydrochloric acid concentration. The authors could confirm Evans' statement that a 3 N concentration of acid during the reduction was sufficient to give a quantitative separation of arsenic. However, the reduction is fairly slow and the use of a reflux condenser is required to prevent the volatilization of arsenious trichloride.

Working with 2 mg. of arsenic in the form of trioxide in an open Erlenmeyer flask and boiling for 5 minutes, they found a loss of 25 per cent; but when the hypophosphite-arsenite mixture was 6 N in hydrochloric acid they found after boiling 3 minutes or longer a loss of only 0.2 per cent. As a matter of fact, with the higher concentration of hydrochloric acid the speed of reduction is so great that boiling is not necessary. When the solution is heated on a hot plate at about 80° C.

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for 10 minutes (or longer) the reduction is complete. After the heating, the suspension must be boiled in order to coagulate the arsenic. With quantities of arsenic of the order of 1 mg., 2 minutes' boiling was found sufficient to get a readily filterable precipitate of desirable characteristics. Longer boiling after the arsenic has completely coagulated is not recommended, as larger lumps are formed which are difficult to dissolve. Moreover, a film may be formed on the surface of the glass and of the liquid which is difficultly wetted afterwards by the oxidizing reagent. With quantities of arsenic of the order of 0.1 mg. longer boiling is necessary to coagulate the precipitate completely.

#### **Collecting the Arsenic**

A suction filtering device is desirable for collecting and washing the precipitate. For quantities of arsenic from 0.75 to 10 mg. the filter tube shown in Figure 1, a, was practical.

It is made from a tube 5 cm. wide and 1-mm. capillary tubing. On the bottom is placed a cotton pad which is covered by an as-bestos pad (the asbestos should be free of reducing material). After filtration and washing, a stirring rod is used for removing the pads from the funnel, and the pads are placed in the flask in which the precipitation has been carried out. The tube is then wiped clean with a piece of dry cotton which is also trans-The tube is ferred to the flask. Instead of a filter tube an ordinary funnel can be used, as shown in Figure 1, b.

For quantities of arsenic less than about 0.5 mg. a filter stick is used with advantage. In most of their work, the authors used a simple self-made filter stick as shown in Figure 2. While a glass bead is shown as the support of the asbestos, cotton or glass wool can also be used. After the filtering and washing are complete the wad is loosened with a glass pick, and the filter stick, wad, and pick are returned to the flask.

The use of cotton filters involved the possibility of an error in the treatment of the precipitate and filtering material with ceric sulfate. Blank experiments were carried out in which 0.3 gram of cotton was heated for 5 minutes at 60° C. with 25 ml. of 0.0044 N ceric sulfate. The latter was back-titrated with standard arsenic trioxide. The loss of ceric sulfate was 0.25 per cent or less. The effect of cotton in the procedure is negligible, since the precipitated arsenic is dissolved at a temperature of 40° C.

A peculiar effect of the cotton, for which a correction has to be made, was noticed. If a dilute arsenic trioxide solution is titrated with ceric sulfate using ferrous phenanthroline as indicator until the red color has just disappeared, the red color returns upon addition of cotton. Apparently the red form of the indicator is adsorbed on the cotton. A trace of ceric sulfate is necessary to remove the red color, the amount being proportional to the amount of cotton present, and found equal to 0.13 ml. of 0.0044 N ceric sulfate per gram of cotton. The phenomenon described does not occur when a solution of the red form of the indicator is shaken with cotton; in the presence of cerous cerium and acid the surface of the cotton becomes slightly red. Since the error for which a correction can be applied is very small, the cotton was not removed by filtration after solution of the arsenic.

#### Stability of 0.044 N Ceric Sulfate

In agreement with other workers it was found that a stock solution of 0.044 N ceric sulfate in 1 N sulfuric acid kept its stability for over 8 months. The 0.0044 N solution prepared by dilution of the stronger solution with 1 N sulfuric acid decreased in strength upon standing: 0.1 per cent after 1 day, 0.5 per cent after 2 days, and 1.5 per cent after 3 days. Apparently, traces of reducing substances present in the water and the acid used in the dilution are responsible for the decrease in strength. Another solution was made, using conductivity water distilled over potassium permanganate. One day after the preparation the normality had decreased 0.2 per cent, after 2 days 0.4 per cent, after 4 days 0.85 per



cent, and after 7 days 1.3 per cent. After this time the solution remained stable for a month. Apparently, traces of reducible material are oxidized after a week of standing, and the dilute ceric sulfate solution itself is stable. When working with very dilute ceric solutions, it seems desirable to allow them to stand for a week after preparation before standardization. Such solutions are also stable when heated for short periods, whereas the freshly prepared solutions decrease in strength on heating to 40° to 100° C. After heating a freshly prepared solution for 5 minutes at 80° C., the strength had decreased by 0.75 per cent, at 100° C. by 1 per cent.

# Standardization of About 0.005 N Ceric Sulfate

The solution is standardized against 0.005 N arsenic trioxide using 0.25 per cent osmium tetroxide as a catalyst (2) and ferrous phenanthroline as indicator. Using 25 ml. of 0.005 N arsenic trioxide, the amounts of ceric sulfate required to the end point were the same with amounts of 0.25 per cent osmium tetroxide varying between 0.1 and 2.0 ml. The amount of ceric sulfate used depends upon the amount of indicator added, and an indicator correction has to be applied. In most of their work the authors used a 0.08 per cent (saturated) solution of ferrous phenanthroline perchlorate in water. The indicator blank was found to be proportional to the amount of indicator used and in their case was equal to 0.4 ml. of 0.0044 N ceric sulfate for 2 ml. of indicator solution at varying acidities.

#### Reagents

CALCIUM HYPOPHOSPHITE SOLUTION. Two hundred grams of calcium hypophosphite dissolved in 6 N hydrochloric acid and

made up with the acid to 1 liter. STOCK SOLUTION OF 0.05 N ARSENIC TRIOXIDE (STANDARD SUBSTANCE). The solution is neutral or slightly acid and prepared by the usual method. From it 0.005 N and 0.001 N ar-

pared by the usual method. From 10,005 N and 0.001 N ar-senic trioxide are made by dilution. STOCK SOLUTION OF 0.05 N CERIC AMMONIUM SULFATE IN 1 N SULFURIC ACID. Ceric sulfate solution, 0.005 N, is pre-pared from the stock solution by dilution with 1 N sulfuric acid. The solution is allowed to stand for a week and standardized (if necessary also in the presence of the same amount of cotton wool as used in the filtration of the arsenic). INDICATOR SOLUTION. A saturated solution of ferrous phenan-

throline perchlorate in distilled water.

CATALYST SOLUTION. Osmium tetroxide, 0.25 per cent, in dilute sulfuric acid.

#### Procedure

Place 25 ml. of the unknown, containing less than 2.0 mg. of arsenic, in a 250-ml. Erlenmeyer flask, and add 10 ml. of hypophosphite reagent and 35 ml. of concentrated hydrochloric acid. Heat the solution for 10 minutes on a hot plate near 80° to 90° C. but do not allow it to boil. After no further darkening is ob-

| ABLE I. D   | ETERMINATION | OF 0.1  | то 2.0 М.G. | OF ARSENIC |
|-------------|--------------|---------|-------------|------------|
| 0.0044 N    |              |         |             |            |
| Ceric       |              |         |             |            |
| Sulfate     | Volume       |         |             |            |
| Used in     | of           |         |             |            |
| Dissolving  | Indicator    | Arsenic | Arsenic     |            |
| Precipitate | e Added      | Found   | Present     | Error      |
| Ml.         | Ml.          | Mg.     | Mg.         | %          |
| 50.0        | 2            | 1.950   | 1.950       | 0          |
| 50.0        | 2            | 1.946   | 1.950       | -0.2       |
| 50.0        | 2            | 1.950   | 1.950       | 0          |
| 50.0        | 2            | 0.974   | 0.973       | +0.1       |
| 50.0        | 2            | 0.968   | 0.973       | -0.5       |
| 50.0        | 2            | 0.980   | 0.973       | +0.7       |
| 50.0        | 2            | 0.971   | 0.973       | -0.2       |
| 10          | 0.4          | 0.198   | 0.193       | +2.5       |
| 5           | 0.4          | 0.191   | 0.193       | -1         |
| 5           | 0.2          | 0.079   | 0.078       | +1         |

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0.079 TABLE II. DETERMINATION OF ARSENIC IN PRESENCE OF TIN AND ANTIMONY ADDED AS CHLORIDE

| aken, 0.375 m | g. of As)  |  |
|---------------|--|--|
| Amount of     | Arsenic  | From   |
| Gram          | Ma.  | 2010   |
| 0.5           | 0.374  | -0.3   |
| 0.5           | 0.372  | -0.8   |
| 0.5           | 0.373  | -0.5   |
| 0.5           | 0.371  | -1.0   |
| 1             | 0.372  | -0.8   |
| 1             | 0.371  | -1.0   |
| 1             | 0.377  | +0.5   |
| 1             | 0.369  | -1.5   |
|               | aken, 0.375 m<br>Amount of<br>Metal Added<br><i>Gram</i><br>0.5<br>0.5<br>0.5<br>0.5<br>1<br>1<br>1<br>1 | $\begin{array}{llllllllllllllllllllllllllllllllllll$ |

served, bring it to a quiet boil and keep it at boiling temperature for about 5 minutes, until all the arsenic has just coagulated. Remove the flask from the hot plate, allow it to cool slightly, and filter (see Figures 1 and 2). After filtering is complete, rinse the flask three or four times with water and allow this to go through the filter. Remove the pad and the precipitate from the funnel with a small glass rod, and transfer them to the Erlenmeyer flask in which the precipitation had been carried out. Wipe the funnel and the stirring rod with a cotton or asbestos wad and place this in the flask. If a filter stick is used these manipulations can be omitted.

Add a measured quantity (at least 25 to 50 per cent in excess) of standard 0.004 to 0.005 N ceric sulfate to the flask and swirl to break up the precipitate. Heat the solution to about 40° to

50° C. for 2 to 3 minutes to hasten solution of the arsenic and continue to swirl the flask as it cools, until dark spots of arsenic are no longer visible. Add to the cool solution 0.1 ml. of osmium catalyst and 2 ml. of indicator per 50 ml. of ceric sulfate added and titrate with 0.005 N arsenic trioxide to the first appearance of a reddish color, or better add a slight excess and back-titrate with 0.005 N ceric sulfate to the disappearance of the red color. With quantities of 0.1 to 0.5 mg. of arsenic, add the ceric sulfate from a microburet and back-titrate with 0.001 N arsenic trioxide or with the 0.005 N solution, using a microburet. Apply the indicator correction and if necessary the cotton correction. One cubic centimeter of 0.005 N ceric sulfate used corresponds to 0.075 mg. of arsenic.

Some of the results are given in Table I. Amounts of arsenic of the order of 1 mg. can be determined with an accuracy of 0.5 per cent, and amounts of 0.1 mg. with an accuracy of 1 to 2 per cent.

#### **Interfering Elements**

Evans (1) states that with his procedure tin, antimony, and mercury interfere, but that other ions such as lead, copper, iron, and bismuth do not interfere. According to the authors' procedure no interference was observed with tin and antimony, as is evident from the results given in Table II.

#### Summary

A procedure has been developed according to which arsenic from its solutions in the tri- or quinquevalent form is reduced to the element by calcium hypophosphite in about 6 N hydrochloric acid. The arsenic is dissolved in an excess of standard ceric sulfate and the excess back-titrated with arsenic trioxide. Satisfactory results have been obtained with amounts of arsenic varying between 2 and 0.1 mg. Tin and antimony do not interfere.

#### Literature Cited

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(2) Gleu, K., Z. anal. Chem., 95, 305 (1933).

# **Improvements in Determination of Iodine in Blood**

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THE catalytic effect of iodides on the reduction of ceric L sulfate by arsenious acid is admirably suited for the determination of blood iodine, especially when used in conjunction with the wet oxidation of the organic material by chromic acid. First described by Sandell and Kolthoff (6)it has the advantage of great sensitivity and under the proper conditions an accuracy of 2 to 4 per cent is attainable.

In order to find the optimum conditions for accuracy, the various factors controlling the catalytic action were studied carefully: concentration of reagents, acidity of reacting medium, temperature, and presence of interfering ions.

A preliminary study showed that the rate at which ceric sulfate is reduced is proportional to the quantity of iodide ion present, and that the reaction follows the monomolecular reaction law. Thus in 5 cc. of solution, for example, 0.1 microgram of iodide ion will cause a reduction of about 50 per cent of the ceric sulfate present every 5 minutes.

Since in the later stages of the reduction the amounts of ceric sulfate present are very small, it has been found more convenient and accurate to determine the ceric sulfate remaining after a given period of time than to wait for the complete reduction. The determination of the concentration of ceric sulfate is made by photoelectric measurement of the intensity of the yellow color.

The following conditions have been found satisfactory:

To 4 cc. of the iodide solution in a test tube, 1 cm. in diameter, are added successively 0.5 cc. of 0.2 N arsenious acid and 0.5 cc. of 0.1 N ceric sulfate. The test tube is kept at 30° C. in a constant-temperature water bath, and exactly 5 minutes after adding the ceric sulfate, the test tube is placed in the photoelectric colorimeter, and the per cent transmission read, using a blue filter (Corning No. 554). If the amount of reduction is slight, the tube is replaced in the water bath and read after 10. 20, or 40 minutes.

Figure 1 shows the relationship between ceric sulfate concentration and the optical density, D, for the 1-cm. test tubes using the blue filter. The optical density is calculated