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AEC RESEARCH AND DEVELOPMENT REPORT

1181

Y-1704

Chemistry

MASTER

ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION
OF ISOTRUXENE IN AUTOCLAVE-PRODUCED
INDENE POLYMERS

N. J. Williams

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the ATOMIC ENERGY COMMISSION under U. S. GOVERNMENT Contract W-7405 eng 26

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Date Issued: January 13, 1970

Document Y-1704

TID-4500

UNION CARBIDE CORPORATION
Nuclear Division

Y-12 PLANT

Contract W-7405-eng-26
With the US Atomic Energy Commission

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ABSTRACT

A spectrophotometric method has been developed for determining the content of isotruxene in truxene-isotruxene mixtures produced by the autoclave polymerization of indene. The accuracy of the method is not precisely known due to the uncertainty of the impurity level in the isotruxene standard; however, it is estimated to be ± 3.4 percent absolute assuming the purity of the isotruxene is 97 ± 2 percent absolute.

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SUMMARY

A spectrophotometric method has been developed for determining the content of isotruxene in truxene-isotruxene mixtures produced by the autoclave polymerization of indene. The method, based on the measurement of the 3375-angstrom isotruxene absorption peak, obeys Beer's Law over the 0 - 97 percent isotruxene range using a constant 20 $\mu\text{gs/ml}$ sample concentration. Based on measurements of a typical sample, the limit of error of a single result (95% confidence level) is ± 1.4 percent absolute. The accuracy of the method is not precisely known due to the uncertainty of the impurity level in the isotruxene standard; however, it is estimated to be ± 3.4 percent absolute assuming the purity of the isotruxene is 97 ± 2 percent absolute.

INTRODUCTION

An ultraviolet spectrophotometric method for determining isotruxene in isotruxene-truxene mixtures was needed by the Y-12 Development Division to measure the isotruxene-truxene ratio in autoclave-produced indene polymers. The method was required to have sufficient accuracy and precision to allow correlations of product composition with induced reaction variables. The ultraviolet spectrophotometric method meets these requirements; and, in addition, is a simple and rapid method that is well suited to process control.

SPECTROPHOTOMETRIC METHOD FOR ISO TRUXENE

EXPERIMENTAL PROCEDURE

Apparatus

The following special apparatus was used:

Model-14 recording spectrophotometer or equivalent double-beam instrument.

Matched one-centimeter quartz cells with ground glass stoppers.

A five-place analytical balance.

Spex mixer mill (Spex Industries, Inc) or equivalent mixing device.

Reagents

Special reagents used in the analysis were: reagent-grade chloroform, pure α -truxene (truxene), and pure β -truxene (isotruxene). Figure 1 gives the structural formulas for truxene and isotruxene.

Figure 1. STRUCTURAL FORMULAS FOR THE ISOMETRIC TRUXENES.

The truxene and isotruxene were prepared by the Development Division. They were isolated from autoclave-produced indene polymers and were separated and purified by differential solubility in chloroform, by column chromatography, and by sublimation.

Preparation of the Calibration Standards

The truxene-isotruxene calibration mixtures (20 μ gs/ml) were prepared volumetrically from stock solutions of truxene and isotruxene in chloroform according to the following schedule:

Stock Solutions: Truxene (TX) $0.01000 \text{ gm} \rightarrow 100/10 \rightarrow 50 = 20 \text{ } \mu\text{gs/ml}$
 Isotruxene (ITX) $0.01005 \text{ gm} \rightarrow 100/10 \rightarrow 50 = 20 \text{ } \mu\text{gs/ml}$

Percent ITX	Volume ITX (mls)	Volume TX (mls)	Concentration ITX ($\mu\text{gs/ml}$)	Absorbance 3375 A vs Chloroform
0	-	Stock Solution	0	0.070
19.4	5	20	4	0.378
38.8	10	15	8	0.690
48.5	10	10	10	0.840
58.2	15	10	12	0.975
77.6	20	5	16	1.303
97	Stock Solution	-	20	1.617

Figure 2 presents the calibration curve.

Preparation of the Samples

Samples were received as dry powders after having been previously separated from the autoclave reaction mixture. In order to insure sample homogeneity, the total sample ($\sim 2 - 3$ grams) was transferred to a 10-milliliter plastic vial containing two plastic balls and mixed on a Spex mixer for thirty seconds. A single 50-milligram aliquot was weighed into a tared 50-milliliter beaker on a five-place analytical balance. Approximately 30 milliliters of chloroform was added and the mixture warmed gently to dissolve most of the sample. The mixture was then transferred to a 250-milliliter volumetric flask, made to about 200 milliliters with chloroform, and warmed in a steam bath until all the sample dissolved, giving a clear solution. After cooling to room temperature, and making to volume with chloroform, ten milliliters were diluted to 100 milliliters for the ultraviolet absorbance measurement. (The absorbance of the solution should be measured within eight hours after preparation, as the solution is not stable.)

Figure 2. ISOTRUXENE CALIBRATION CURVE.

Measurement of the Absorbance

A detailed description of the instrument and its operating procedure is given in an operating and service manual provided by the manufacturer.^(a) Optimum operating conditions were determined according to procedures described in a

(a) Instructions for Cary Spectrophotometer Model 14; Cary Instruments, Monrovia, California.

Cary application report, AR-14-2.(a) The instrument settings used in this method were as follows:

Dynode Voltage	Tap 2
Slit Control	20
Scan Speed	5 A/sec
Chart Speed	1 inch/min
Pen Period	1

Matched one-centimeter-path-length quartz cells (with ground glass stoppers) were used. Tightly fitting stoppers were necessary due to the volatility of the chloroform solvent.

Both cells were fixed with solvent and a blank scan made to insure that the baseline was straight in the 4000 - 3200-angstrom region. If the baseline was not straight, the multipots or baseline trim potentiometers were adjusted to give a straight baseline. The sample cell was then rinsed and filled with the solution to be measured and scanned from 4000 to 3200 angstroms.

DISCUSSION

As seen in Figure 3, isotruxene has two absorption peaks, located at 3240 and 3375 angstroms, which do not appear in the truxene spectrum. Truxene has a slight absorbance in this region, but no distinct absorption peaks. The 3375-angstrom peak was chosen as the basis for the method because the two peaks are not completely resolved. The 3375-angstrom peak is the further removed of the two from possible interference by the more intense peaks below 3200 angstroms that are common to both compounds. The method requires that the sample mixture be free from other reaction products which absorb in the 3375-angstrom region. Truxene and isotruxene mixtures produced by the autoclave polymerization of indene have been analyzed by mass spectrometry and have been found to contain only trace amounts of compounds other than truxene and isotruxene.

The absorbance of a truxene-isotruxene solution depends on two main variables other than instrument parameters and cell thickness: (1) the truxene-isotruxene ratio, and (2) the solution concentration. By holding the sample concentration constant, the main variable affecting absorption at 3375 angstroms is the

(b) Optimum Spectrophotometer Parameters, Application Report AR-14-2; Cary Instruments, Monrovia, California.

Figure 3. TRUXENE AND ISOTRUXENE ABSORPTION SPECTRA. (Path Length = 1 cm)

truxene-isotruene ratio. As a matter of convenience, a sample concentration of 20 $\mu\text{g}/\text{ml}$ was chosen, since this concentration of pure isotruene will have an absorbance less than 2.0 and will be within the range of the Cary-14 recorder.

From the data given in the preparation of the calibration standards, the slope and intercept of the linear calibration curve were calculated. Percent isotruene was calculated from the absorbance of the sample solution using the slope and intercept of the calibration curve.

CALCULATIONS

In order to increase the precision and accuracy of the method, the isotruxene concentration of sample solutions was calculated using the slope and intercept of the linear calibration curve rather than by reading a graph. As described under DISCUSSION, the method was set up using a constant sample concentration of 20 $\mu\text{gs/ml}$. This concentration was achieved by diluting 50-milligram samples to an effective volume of 2,500 milliliters in a two-step dilution. In practice, however, exact 50.00-milligram samples cannot be readily weighed out, so an appropriate correction factor based on sample weight was applied to the absorbance reading of each sample solution. The calculation method is best described by means of an example:

Sample Weight: 49.35 mgs

Absorbance at 3375 A = 0.954

Dilution: 49.35 mgs $\rightarrow$ 250/10 $\rightarrow$ 100

$$\text{percent ITX} = \left(\frac{a - b}{c} \right)^d \times \left(\frac{50.00}{e} \right)^f,$$

where:

- a represents the absorbance of the sample solution at 3375 angstroms,
- b the intercept of the calibration curve,
- c the slope of the calibration curve,
- d the percent isotruxene uncorrected for sample concentration,
- e the sample weight in milligrams, and
- f the sample concentration correction factor. Exactly 50.00 milligrams are required at this dilution to give the desired 20 $\mu\text{gs/ml}$ sample concentration.

Then:

$$\text{percent ITX} = \left(\frac{0.54 - 0.070}{0.01595} \right)^d \times \left(\frac{50.00}{49.35} \right)^f = 56.2.$$

RESULTS

The method as originally requested was to cover the entire 0 to 100 percent isotruxene range with an accuracy of ± 4 percent absolute and have a precision of ± 2 percent absolute. The calibration covered this range; however, most of the samples contained between 30 and 80 percent isotruxene.

The accuracy of the method is directly proportional to the purity of the truxene and isotruxene calibration standards, the purity of which cannot, at present, be accurately determined by known analytical procedures. The standards used, however, were of the highest purity available. Based on the melting points and mass spectrographic analyses of previous preparations, the isotruxene was assumed to be 97 ± 2 percent pure and the truxene to be 100 percent pure. These assumptions do not affect the usefulness of the method as a means of comparing the relative amounts of isotruxene in reaction mixtures produced under different reaction conditions.

Based on measurements of a typical sample in the 30 to 80 percent isotruxene range over a two-month period (see Table 1), the precision of the method is represented by a limit of error of a single result (95% confidence level) of ± 1.4 percent absolute. The accuracy of the method is estimated to be ± 3.4 percent absolute, including precision and calibration uncertainty due to the nature of the standards.

Table 1
PRECISION MEASUREMENT USING A TYPICAL SAMPLE

Date	Corrected Net Absorbance at 3375 A	Percent ITX
5-26-69	0.980	57.1
7-8-69	0.977	56.9
7-12-69	0.961	55.9
7-18-69	0.972	56.6
8-1-69	0.966	56.2

CONCLUSIONS

The ultraviolet spectrophotometric method for determining percent isotruxene as described in this report is sufficient for preliminary work; however, this method should be refined for more precise work. The main areas of improvement would be in measuring the purity of the calibration standards and in calibration over a more narrow concentration range based on the anticipated isotruxene content of the material to be analyzed.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to W. E. Smith of the Development Division for preparing the truxene and isotruxene standards used in the development of the method.