Figure 2 shows the temperature dependence of the rate of isomerization. Only the runs at the highest pressures have been used. The activation energy is found to be 46,000 ± 1000 cal., which is somewhat higher than those obtained earlier for other *cis–trans* isomerizations involving phenylethylene groups.[1] With this value for the activation energy, the reaction rate constant at high pressures receives the form

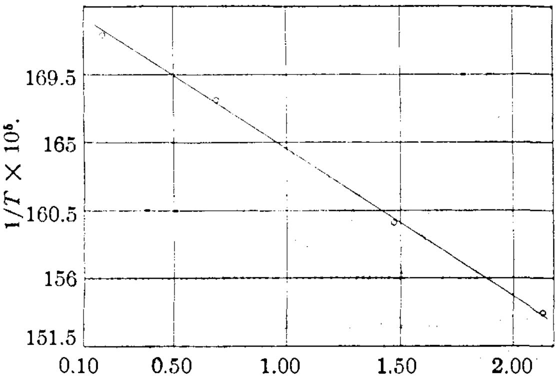

Fig. 2.—Log $k$–$1/T$ plot of the first order isomerization rate constant.

$$k = 10^{11.6 \pm 0.4}\,e^{-(46,000 \pm 1000)/RT}$$

Little new can be added to the comments which were made in earlier papers on the *cis–trans* isomerization, but we wish to point out once more that apparently in all reactions involving rotations of heavy groups, the "A" factor is considerably lower than the "normal" value, $10^{13}$, to be expected from statistical considerations.

The Eyring[7] theory, which in a simplified version, possibly applicable to the present case, gives the rate constant as

$$k = \nu e^{-E/RT}$$

$\nu$ being here presumably the frequency of the torsional vibration around the double bond, leads to values of this frequency which are of the order of 1–10 cm.$^{-1}$, hence rather too small.

## Summary

1. The rate of isomerization of $\beta$-cyanostyrene has been studied and found to be of the first order. The velocity constant at higher pressures is given by

$$k = 10^{11.6 \pm 0.4}\,e^{-(46,000 \pm 1000)/RT} \text{ sec.}^{-1}$$

2. The equilibrium mixture at 352° contains 63% high boiling (*trans*) isomer. The equilibrium composition appears to be practically independent of temperature.

(7) Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

CAMBRIDGE, MASS. RECEIVED OCTOBER 7, 1936

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RHODE ISLAND STATE COLLEGE]

# Some Characteristics of the Residue from the Cracking of Castor Oil[1]

BY ARTHUR A. VERNON AND HALKEY K. ROSS

Much work has been done to determine the chemical nature of castor oil and the results of Krafft,[2] Walden[3] and Kasansky[4] have shown that it consists mainly of the glyceride of ricinoleic acid. More recently Eibner and Münzing[5] have shown that the fatty acid content of castor oil is 95%; 80% is ricinoleic acid and the remaining 15% is a mixture of oleic, linoleic, stearic and dihydroxystearic acids. The structural formula indicates that the probable place of breaking under the influence of heat would be between the twelfth and thirteenth carbon to yield an aldehyde as is the case with hydroxy acids. The glyceryl portion of the molecule[6] should rupture readily to give acrolein and such is experimentally found to be true on this basis. The third product of decomposition should be undecylenic acid but in actual practice the residue from atmospheric cracking, after removal of heptaldehyde and acrolein, is a complex mixture. Perkins and Cruz[7] found that the distillation at 400° under a pressure of 50 mm. produced a distillate composed of about 40% heptaldehyde and 20% of undecylenic acid. Roy[8] studied the changes in castor oil when heated to 140° in the presence of oxygen and nitrogen. The viscosity, iodine number, acid number and index of refraction were found to

(1) From a thesis submitted by Halkey K. Ross to the faculty of Rhode Island State College in partial fulfilment of the requirements for a Master of Science degree.

(2) Krafft, *Ber.*, **10**, 2034 (1877).

(3) Walden, *ibid.*, **27**, 3471 (1894).

(4) Kasansky, *J. soc. phys. chim. russe*, **32**, 149 (1901).

(5) Eibner and Münzing, *Chem. Umschau Fette, Öle, Wachse Harze*, **32**, 166–176 (1925).

(6) Charles D. Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, Chapter 15.

(7) Perkins and Cruz, THIS JOURNAL, **49**, 1073 (1927).

(8) Roy, *Compt. rend.*, **196**, 1423–1424 (1933).

increase in the presence of oxygen. It was felt that an investigation of the properties of the products of the pyrolysis of castor oil might give information concerning the mechanism of the breakup under the influence of heat and therefore an investigation was made of the acid value, saponification value, acetyl value and iodine number of the residue. Barbot[9] has suggested a molecular rearrangement as the way in which the molecule may break up under the influence of heat and the results of this work may be of value for his interpretations.

**Apparatus.**—The castor oil was allowed to flow at a constant rate into a heated silica tube 65 cm. long and 2 cm. inside diameter and the product condensed in a water-cooled condenser. The temperature inside the tube was measured with a chromel–alumel thermocouple enclosed in glass.

***Material.***—The castor oil was Baker chemical grade with these constants: acid value, 12.5; saponification number, 178.3; acetyl value, 152.1; iodine value, 87.13.

**Procedure.**—The tube was heated to the desired temperature and the oil allowed to flow into the tube at a rate of 505 g. per hour. The first 10–15 cc. of the cracked product was discarded and then about 150 cc. of the material was collected.

This substance was steam distilled until the removal of heptaldehyde was complete. The remaining material was washed, then dried with anhydrous sodium sulfate in an oven at about 100°. According to Woodman[10] this is the customary method of drying oils and fatty acids. Samples were then analyzed to determine the chemical constants.

The acid and saponification values were determined according to the A. O. A. C. Book of Methods.[11] The acetyl values were made according to the method of Andre-Cook.[12] The iodine numbers were found according to the Wijs Method.[11]

The results of the determinations are summarized in Table I.

TABLE I

DATA CONCERNING THE RESIDUE

| Temp., 0° | Acid number | Saponification number | Acetyl value | Iodine value |
|---|---|---|---|---|
| 299 | 3.46 | 178 | 151.0 | 85 |
| 340 | 12.40 | 176 | 140.0 | 92 |
| 405 | 55.30 | | 130.5 | 107 |
| 410 | | 164 | | |
| 450 | 148.80 | 82 | 93.8 | |
| 475 | 155.50 | 79 | 41.3 | 113 |
| 510 | 170.00 | 70 | 33.2 | |
| 540 | 171.20 | | | 117 |
| 620 | 187.50 | 48 | 23.5 | 119 |
| 675 | 217.00 | 42 | | 124 |
| 750 | | | | 123 |

The results of the acid number, saponification number and acetyl value determinations are plotted in Fig. 1 to show how these three characteristics vary with the temperature of pyrolysis.

It was noted that dark brown fumes were emitted and that there was no smell of acrolein in the distillate above 800°. A decomposition took place above 800° which resulted in the production of some aromatic compounds.

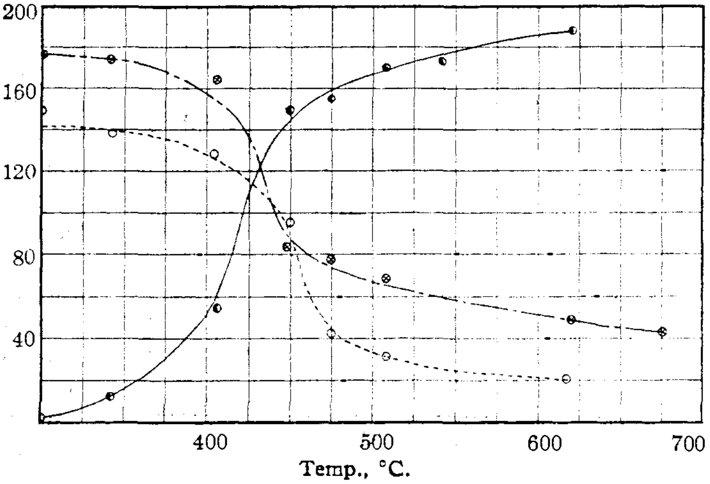

Fig. 1.—Variation of characteristics of castor oil residue with temperature of pyrolysis: ◐, free acid value; ⊗, saponification number; ○, acetyl value.

In order to determine the place of undecylenic acid in the pyrolysis, a test was made in which it was subjected to the same temperatures as castor oil at the same rate of 505 g. per hour, and the iodine value of the residue was determined. The results of this experiment are shown in Table II.

TABLE II

IODINE VALUE OF UNDECYLENIC ACID

| Temp., °C. | Iodine value |
|---|---|
| 135 | 126.6 |
| 214 | 127.2 |
| 280 | 126.9 |
| 355 | 129.0 |
| 505 | 127.8 |
| 565 | 135.0 |
| 640 | 142.0 |
| 735 | 113.6 |

A plot of the values of Table II appears in Fig. 2 together with the determinations of the iodine number of cracked castor oil.

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(9) Barbot, *Compt. rend.*, **197**, 65–67 (1933).

(10) A. G. Woodman, "Food Analysis," McGraw-Hill Book Co., Inc., New York, 1931, p. 174.

(11) Association of Official Agricultural Chemists, Book of Methods, Second Edition, XX, 19–20, 288 (1925)

(12) Andre-Cook, *J. A. O. A. C.*, 326 (1927)

## Discussion of Results

Figure 1 shows a sharp drop in saponification value at about 425° and this would indicate that the glyceryl portion of the molecule is broken off at this temperature. Figure 1 also shows an increase in the acid value at the same temperature, which is added evidence for the formation of free acid. It would seem from this that the first pyrolytic action to occur is the decomposition of the glyceryl portion and the production of acrolein. Figure 1 further shows that the acetyl value drops at 465°, which means that the hydroxyl grouping of the castor oil disappears at this point. This would indicate the formation of heptaldehyde and undecylenic acid. A valuable check on this hypothesis can be made if the characteristics of the residue after the removal of heptaldehyde and acrolein can be shown to be similar to the characteristics of the product of the pyrolysis of undecylenic acid alone. If the acetyl value of the castor oil residue is taken at some temperature and the amount of undecomposed castor oil is calculated, then the amount of iodine number contributed by that undecomposed castor oil can be calculated. If the remainder of the iodine value is attributed to undecylenic acid and its decomposition products, this value can be obtained from Fig. 2 at the corresponding temperature. The sum of these two values should agree with the corresponding iodine value of the castor oil residue.

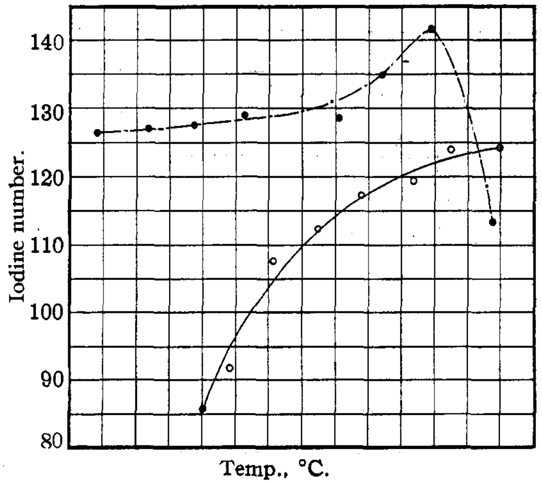

Fig. 2.—Variation of iodine number with temperature of pyrolysis: ⊗, undecylenic acid; O, castor oil.

The agreement shown in the table is within the precision of the iodine number determinations.

TABLE III

CALCULATED AND OBSERVED IODINE VALUE OF THE CASTOR OIL RESIDUE

| Temp., °C. | Calcd. iodine value of residue | Observed value of residue |
|---|---|---|
| 300 | 85 | 85 |
| 450 | 104.7 | 110 |
| 475 | 115.7 | 113 |
| 500 | 117 | 115 |
| 550 | 123.4 | 118 |
| 600 | 126.6 | 120.5 |
| 650 | 130 | 122 |
| 700 | 125 | 123 |
| 725 | 114.5 | 121 |

Ho, Wan and Wen[13] have shown that the iodine value is influenced by the amount of excess iodine solution used for a given sample. The weight of the sample taken for these determinations was always approximately the same, and the iodine solution added was always the same. Since the unsaturation of the samples varied, therefore the iodine excess must have been greater in some samples than in others. This undoubtedly influenced the values obtained. Part of the discrepancy might be attributed to the 20% of the other substances present in castor oil.

The most favorable yield of heptaldehyde obtained was 28.9% by weight of castor oil while the theoretical yield would be 34%.

Work is at present in progress to determine quantitatively the amounts of acrolein and heptaldehyde which are produced at various temperatures. It is hoped that in this way a careful check can be made on the possible mechanism which seems to be indicated by the results obtained. These would be valuable since Shepard[14] has stated that ricinoleic acid has not been cracked successfully to give heptaldehyde. However, the conditions of the pyrolysis in the cracking of castor oil may not be the same as the chemical condition when ricinoleic acid is pyrolyzed.

## Summary

1. Castor oil was submitted to pyrolysis at various temperatures in a heated silica tube. The acrolein and heptaldehyde were removed and the iodine number, acetyl value, saponification value and acid value of the residue was determined.

2. Undecylenic acid was submitted to pyrolysis under the same conditions.

3. The results may be explained by assuming

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[13] K. Ho, C. S. Wan and S. H. Wen, *Ind. Eng. Chem., Anal. Ed.*, **7**, 97 (1935).

[14] M. G. Shepard, private communication.

that acrolein splits off first and then the molecule breaks down to give heptaldehyde. The latter reaction requires a higher temperature.

KINGSTON, R. I. RECEIVED JULY 21, 1936

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MISSOURI, AND THE NEW MEXICO NORMAL UNIVERSITY]

# The Lead-Uranium Ratio of Henvey Cyrtolite[1]

BY O. B. MUENCH

In September, 1931, Dr. H. V. Ellsworth of the Department of Mines, Canada, sent a lump of cyrtolite obtained from the Besner Mine, Henvey Township, Ontario, to the University of Missouri. At that time work on the Hybla Cyrtolite[2] was planned and partly under way, so it was found impossible to do more than a little preliminary work on the Henvey Cyrtolite. Work on this cyrtolite was carried to definite results during the summer of 1935. A lead-uranium ratio on this cyrtolite is interesting for comparison with the one on a Besner Uraninite[3] which has been available for some time.

The occurrence of this cyrtolite and its mineral associates are described by Spence[4] and also Ellsworth[3] (p. 173).

**The Sample.**—The sample was mostly in one large piece with feldspar at one end. It was very homogeneous, of black pitchy luster and seemed to be altered very little, if any. Only the black homogeneous part was taken, and pulverized in an iron mortar until all of it passed through an 80-mesh sieve. This sieve had no solder from which contamination might be derived. The pulverized sample of cyrtolite weighed 242 g.

## Methods of Analysis

In general, the procedure followed in the determination of the uranium, after the sample was in solution was as follows. The zirconium and hafnium were removed as phosphates in acid solution, and then after the removal of the iron, etc., as sulfides in ammonium carbonate solution, the uranium was precipitated as the phosphate in a solution slightly acid with acetic acid. The phosphate method was used because phosphate had been introduced in the removal of the zirconium and hafnium and it was therefore the most direct method to follow. The thorium, after the sample was in solution, and the zirconium and hafnium had been removed by precipitation as phosphates in sulfuric acid solution, was precipitated as the oxalate in oxalic acid solution. Two different methods were followed from this point on. In the peroxide method, the oxalate was converted to the nitrate and the thorium precipitated with hydrogen peroxide from a neutral solution of ammonium nitrate. The precipitate on ignition changes to the oxide. In the iodate method, the oxalate was first converted to the nitrate, and then precipitated with potassium iodate in strong nitric acid solution. The iodate precipitate was dissolved in hydrochloric acid and the thorium precipitated with ammonium hydroxide. Finally this precipitate was dissolved in hydrochloric acid and then the thorium precipitated with oxalic acid. The oxalate was ignited to the oxide and weighed. The lead was determined by the usual procedure of separation as a sulfide, conversion to a sulfate, extraction with ammonium acetate and final precipitation as a chromate.

**Uranium.**—One-gram samples were fused with sodium peroxide (which oxidized all the carbon) in a nickel crucible. The fused samples were then dissolved in hydrochloric acid, baked in a porcelain dish, taken up with dilute hydrochloric acid and filtered. The residue, after volatilization with hydrofluoric and sulfuric acids, was added to the filtrate. The solution was made alkaline with pure ammonium hydroxide. After three precipitations with pure ammonium hydroxide, the precipitate was dissolved in 30 ml. of concd. sulfuric acid. From this point on, the procedure as given in the paper, "The Age of a Canadian Cyrtolite,"[2] near the bottom of p. 489 was followed.

**Thorium.**—Five-gram samples were taken for analysis. The method as given in the above

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[1] This work is a portion of a project assisted financially in part by a grant from the National Research Council.

[2] Muench, *Am. J. Sci.*, **25**, 487 (1933).

[3] Ellsworth, "Rare-element Minerals of Canada," Geological Survey, Department of Mines, Canada, Series, No. 11, 1932, p. 268.

[4] Spence, *Am. Min.*, **15**, 11, 513 (1930).