the vapor volume can be expressed as a function of reduced temperature and liquid volume along the saturation line, namely

$$\ln v_g/v_l = k \frac{(1 - \tau^2)^m}{\tau^n} \quad (5)$$

$$v_g = v_l \exp. k \frac{(1 - \tau^2)^m}{\tau^n} \quad (12)$$

2. The constant k of the suggested equation is almost identical with the critical coefficient K_{cr}, their ratio being nearly equal to unity for most substances investigated.

The critical coefficient is not a constant but varies from substance to substance, increasing with the order of curves ($\ln v_g/v_l$) in the coördinate system.

3. There seems to be a definite similarity in the mechanism of evaporation of substances as shown by the fact that the respective expansion curves can be expressed by one and the same equation and that the constants of this equation have values very close to each other for substances of the most diverse chemical and physical properties.

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The Kinetics of Thermal Cis-Trans Isomerization. VI

BY G. B. KISTIAKOWSKY AND WALTER R. SMITH

In one of the earlier papers[1] of the present series, evidence was presented indicating that the first order rate of isomerization of methyl cinnamate began to fall off at a pressure of 6 mm. Unfortunately, due to the analytical method employed, it was not feasible to study the reaction at still lower pressures. This compound and dimethyl maleate[2] have been the only two in a series of geometric isomers in which this phenomenon, characteristic of unimolecular reactions, has been observed.

In β-cyanostyrene the number of contributing degrees of freedom could be expected to be appreciably less than in methyl cinnamate, because of substitution of a CN group for the COOCH₃ group. Hence, with β-cyanostyrene the rate might begin to fall off at a higher pressure and an extensive study of the rate–pressure dependence could be made.

The present paper describes a number of experiments on the rate of isomerization of β-cyanostyrene performed at various temperatures and over an extensive range of pressures.

Experimental Details

Preparation of β-Cyanostyrene.—The nitrile was prepared according to the method of Ghosez[3] by the condensation of benzaldehyde and cyanoacetic acid in the presence of pyridine. Sixty per cent. of the theoretical yield was obtained.[4]

The resulting mixture of the geometric isomers was distilled in an all glass still 3 m. tall and 18 mm. in diameter, packed with Pyrex glass spirals.[5] A 20–1 reflux ratio was used. Two fractions were obtained, one boiling at 139.1° at 30 mm. and the other at 152° at 30 mm. The high boiling fraction was further purified by freezing and allowing it to melt at 20°. The solid portion remaining was distilled at 122° at 2 mm. in a Claisen flask. The weight ratio of high to low boiling isomers was 62:38. Ghosez[3] obtained 63% high boiling compound.

The high boiling isomer melted at 22° and had $n^{20.2}$D 1.6031. For the low boiling isomer the melting point was −4.4° and $n^{20.2}$D 1.5843. According to Ghosez and in conformity with other evidence[6] the low boiling isomer must be assigned the cis configuration. This is also in agreement with equilibrium data presented below.

Analytical Method.—The appreciable difference in the refractive indices of the two isomers provided a rapid and convenient method of analyzing the reaction mixtures. An Abbé refractometer, thermostated to 20.2° and employing a sodium vapor lamp, was calibrated with a series of known mixtures of the isomers. A strictly linear relationship between composition and refractive index was found. It was possible to detect 0.5% of either isomer.

The melting points of these mixtures were also determined by means of a single junction copper–constantan thermocouple. The couple was used sometimes to check the values obtained from the refractometer, as described below.

The apparatus was of the usual static type. Both it and the experimental procedure have already been described elsewhere.[2]

Some of the earlier runs were analyzed both by the refractive index method and the freezing point. In all cases the two methods gave analyses agreeing to 1%, which is to be regarded as indicating the absence of side reactions.

The reaction was further established by connecting the nitrile to cinnamic acid. The product from a run on the

(1) Kistiakowsky and Smith, THIS JOURNAL, **57**, 269 (1935).

(2) Kistiakowsky and Nelles, Z. physik. Chem., Bodenstein Festband, 369 (1931), and THIS JOURNAL, **54**, 2208 (1932).

(3) Ghosez, Bull. soc. chim. Belg., **41**, 477 (1932).

(4) We are greatly indebted to Dr. George F. Wright for preparing the compound for us.

(5) Kistiakowsky, et al., THIS JOURNAL, **57**, 877 (1935).

(6) Wright, ibid., **57**, 1993 (1935).

high boiling isomer gave a refractive index indicating the presence of 21% low boiling isomer; 1.69 g. of this product was refluxed for twenty-four hours with 25 cc. of an aqueous 7% sodium hydroxide solution. The solution was then neutralized with dilute hydrochloric acid and the precipitated cinnamic acid was washed free of chloride ion and dried. An 82% yield was obtained. The product melted at 133°. A sample of pure high boiling isomer gave a yield of 81% cinnamic acid, melting at 133°. This evidence, together with the agreement of the refractive index and the melting point methods, indicates clearly that the reaction studied is primarily isomerization.

Experimental Results

No real pressure change could be noted in any of the runs. The product of all runs, except those at the lowest pressure, was clear and colorless. In the latter case a slight grayish turbidity appeared. This settled out on standing and did not interfere with the refractometer readings.

The position of thermal equilibrium at 352° was determined by heating known mixtures of the isomers, in the gas phase, for varying lengths of time. The results of these experiments are reproduced in Fig. 1. At 352° equilibrium exists at 63% high boiling isomer.

A few runs on the low boiling isomer at 352° and at a pressure of 390 mm. gave average velocity constants of 4.03×10^{-5} sec.$^{-1}$. The average constant for the high boiling isomer at these conditions is 2.89×10^{-5} sec.$^{-1}$. The equilibrium concentration of 60% high boiling isomer obtained from these values is in satisfactory agreement with the more accurate value obtained above. Since these values are nearly identical with the value obtained in preparing the compound at temperatures lower than 100°, it is obvious that the value of ΔH is too small to be determined by studying the equilibrium over any convenient temperature range.

The results of all runs on the high boiling (*trans*) isomer are presented in Table I. The velocity constants have all been calculated allowing for equilibrium at 63% high boiling isomer.

Runs were made over a pressure range of 450 to 20 mm. At the lower pressures there is a marked increase in the velocity constants. At the lowest temperature this increase is nearly threefold. At the highest temperature the constants are nearly identical at all pressures. Runs in a packed flask with about six times the surface gave a marked increase in the constants at the lowest pressure, while such an increase was not noted at the higher pressures.
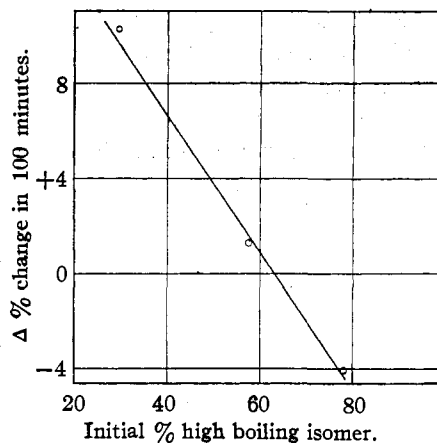

Fig. 1.—Equilibrium composition at 352°.

It is evident that at the lower pressure a wall reaction occurs to some extent. It does not interfere with the rate measurements of the homogeneous reaction at higher pressures, but makes very uncertain the detection of a possible falling off of the rate constant with pressure. Hence the originally intended study of the falling off was abandoned and only the high pressure rate studied.

TABLE I

Run	Temp., °K.	Press., mm.	Time, min.	% HB isomer	k corr. sec.$^{-1}$
6	581.3	372	1020	89.8	1.52×10^{-6}
7	581.3	380	1371	89.0	1.59
32	597.4	413	960	79.0	5.30×10^{-6}
31	597.0	399	1031	78.0	5.40
34	596.0	154	1180	78.4	4.58
35	596.3	155	1266	75.8	5.17
36	597.4	20.1	1119.5	64.6	17.3×10^{-6}
38	598.0	19.0	1180	64.0	18.9
12	626.4	364	91	84.2	3.78×10^{-5}
10	625.0	391	109	84.8	2.99
8	623.7	379	195	81.0	2.28
9	625.0	390	338	71.0	2.80
13	626.9	36	213	72.8	3.85
11	625.1	36	399	66.2	3.79
21	625.2	17.5	163	75.0	4.02
19	625.2	18.2	229	69.0	4.90
20	624.6	18.6	258.5	66.8	5.43
23	650.2	446	34.5	80.6	1.33×10^{-4}
24	650.6	458	21.0	84.2	1.64
41[a]	651.2	334	63.0	69.4	1.72
25	650.6	153	61.0	73.1	1.31
26	651.2	156	31.5	82.8	1.22
27	651.0	37	31.5	77.4	1.85
28	651.0	38	64.0	68.3	1.87
29	651.2	19.5	32.5	77.4	1.79
30	650.2	20.0	60.5	73.1	1.32
39[a]	650.2	21.0	30.8	74.8	2.29
40[a]	651.2	20.0	66.5	66.8	2.11

[a] Six times surface.

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
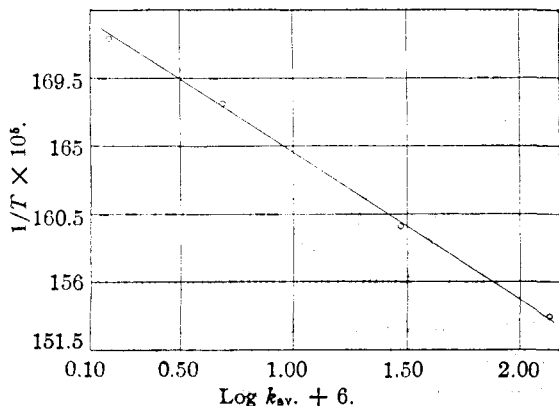

Fig. 2.—Log k–1/T plot of the first order isomerization rate constant.

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

$$k = 10^{11.8 \pm 0.4} \, e^{-(46,000 \pm 1000)/RT}$$

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

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

ν 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 β-cyanostyrene has been studied and found to be of the first order. The velocity constant at higher pressures is given by

$$k = 10^{11.8 \pm 0.4} \, e^{-(46,000 \pm 1000)/RT} \text{ sec.}^{-1}$$

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).

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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 Harse, **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).