

The Hydrogen Bromide Catalyzed Isomerization of *n*-Butenes. I. Equilibrium Values

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Equilibrium values in the *n*-butene system have been measured over the temperature range 363–724°K. Equilibrium over the lower part of the range (363–526°K.) was obtained by a heterogeneous isomerization on phosphotungstic acid, while in the upper part of the temperature range a predominantly homogeneous isomerization with hydrogen bromide was used. The derived thermodynamic data for the systems *butene-1* \rightleftharpoons *trans-butene-2* and *cis-butene-2* \rightleftharpoons *trans-butene-2* are compared with data in the literature.

Introduction

Evidence for the isomerization of *n*-butenes in the presence of hydrogen bromide was obtained in a study of the elimination of hydrogen bromide from *sec*-butyl bromide¹ and in the hydrogen bromide catalyzed dehydration of *sec*-butyl alcohol.² An investigation of the kinetics of this isomerization (to be reported later) necessitated a knowledge of the equilibrium values for the *n*-butenes, and, as the values calculated from thermodynamic properties listed in the American Petroleum Research Project 44 (A.P.I.) tables³ did not correspond with the values approached kinetically, a preliminary investigation of the equilibrium values was undertaken. The present paper reports this investigation.

Experimental

Materials. Butene-1 (Phillips research grade, 99.7%) and *cis*- and *trans*-butene-2 (National Chemical Laboratories (N.C.L.) samples, 99.4 and 99.98%) were used without further purification. Vapor phase chromatographic (v.p.c.) analysis showed approximately 0.6% *trans*-butene-2 in the *cis*-butene-2 (confirming the N.C.L. calibration) but did not detect any other impurities (limit of detection \sim 0.1%). A mixture of *n*-butenes was obtained by dehydrating *n*-butyl alcohol over alumina and was purified by vacuum distillation.

Hydrogen bromide was prepared by dropping bromine onto freshly distilled tetralin; the product was bubbled through tetralin and a trap at -40° and was collected in a trap immersed in liquid oxygen. It was further purified by trap-to-trap distillation on the vacuum line through a trap at -70° and was stored under vacuum. Phosphotungstic acid (B.D.H. laboratory reagent) was heated at 400° for 2 hr. immediately before use.

The v.p.c. column used was 20 ft. \times 0.25 in. of 20% 2,5-hexanedione on 60/80 "G-Cel" and was operated

at 0° . Hydrogen was used as a carrier gas (flow rate 1.65 l./hr.), and a thermistor, thermal conductivity detector in a standard Wheatstone bridge gave complete separation of the butenes (retention times: butene-1, 6.0; isobutene, 6.8; *trans*-butene-2, 8.1; *cis*-butene-2, 9.8 min. measured from the air peak).

Procedure. Equilibration was carried out in a standard static vacuum system with a 200-ml. Pyrex reaction vessel heated in an aluminum block furnace. The temperature was controlled to $\pm 0.1^\circ$ by a Sunvic RT2 controller and measured to $\pm 0.1^\circ$ with a platinum-13% rhodium-platinum thermocouple. Pressures in the reaction vessel were measured on a mercury manometer separated from the reaction vessel by a glass diaphragm null gauge.⁴

In the lower part of the temperature range (363–526°K.) equilibration was obtained heterogeneously on phosphotungstic acid suspended on glass wool. In the upper part of the temperature range (to 724°K.) equilibration was obtained, predominantly homogeneously, with hydrogen bromide.

After an appropriate time (varying from 5 min. to 5 days), the equilibrium mixture was expanded from the reaction vessel, hydrogen bromide was removed (where necessary), and the products were mixed before being sampled for the v.p.c. At least three v.p.c. samples of each run were analyzed and agreed to $\sim \pm 2\%$ in each proportion (e.g., $19.0 \pm 0.4\%$ butene-1). Calibration by v.p.c. of known mixtures prepared by pressure measurement also gave agreement to $\sim \pm 2\%$.

Table I. Equilibrium Concentrations of *n*-Butenes

Temp., °K.	% butene-1	% <i>trans</i> - butene-2	% <i>cis</i> - butene-2
400.0	7.4	55.6	37.0
424.6	8.7	54.5	36.8
444.8	10.0	54.0	36.0
458.0	11.3	52.3	36.4
497.6	14.3	50.7	35.0
525.7	16.0	48.7	35.3
567.3	18.5	46.4	35.1
585.3	19.9	43.4	36.7
602.3 ^a	20.8	45.2	34.0
620.7	22.1	43.3	34.6
634.6	23.0	42.5	34.5
640.8	23.4	45.6	31.0
696.1	26.7	38.6	34.7
724.0	28.2	39.0	32.8

^a Values calculated from A.P.I. tables 15.0, 52.7, 32.3.

At each temperature investigated at least three separate determinations were made, one starting from butene-1, one from *trans*-butene-2, and one from the

(4) An adaption of the gauge described by E. S. Swinbourne, *Australian J. Chem.*, **11**, 314 (1958).

(1) A. Maccoll and R. H. Stone, *J. Chem. Soc.*, 2756 (1961).

(2) R. L. Failes and V. R. Stimson, *ibid.*, 653 (1962).

(3) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, G. C. Pimental, *et al.*, Ed., Carnegie Press, Pittsburgh, Pa., 1953, pp. 715, 737, 759.

Table II

	butene-1 \rightleftharpoons <i>trans</i> -butene-2		<i>cis</i> -butene-2 \rightleftharpoons <i>trans</i> -butene-2	
	ΔH° , kcal.	ΔS° , cal. deg. ⁻¹	ΔH° , kcal.	ΔS° , cal. deg. ⁻¹
This work ^a	-3.03	-3.54	-0.44	-0.25
B and B ^b , ^c	-3.1 \pm 0.2	-3.6 \pm 0.4	-0.50 \pm 0.20	0.00 \pm 0.4
V and M ^d , ^e	-2.92	-3.1	-0.53	0.14
A.P.I.	-2.66	-2.18	-0.60	0.00

^a Temperature 363–724°K. ^b S. W. Benson and A. N. Bose, *J. Am. Chem. Soc.*, **85**, 1385 (1963). ^c Temperature 508–573°K. ^d H. H. Voge and N. C. May, *J. Am. Chem. Soc.*, **68**, 550 (1946). ^e Temperature 473–903°K.

mixture of *n*-butenes. In general, these separate determinations agreed to $\pm 5\%$. The handling procedure was shown to have no isomerizing effect.

Results

The results are shown in Table I.

Plots of $\log K$ against T^{-1} are shown graphically in the Figure 1. The $1 \rightleftharpoons 2$ and $1 \rightleftharpoons t2$ lines are best fit, least-squares straight lines, there being no evidence of curvature within the limits of experimental error over this range. The $1 \rightleftharpoons c2$ and $c2 \rightleftharpoons t2$ lines are calculated from the above two lines, but the $c2 \rightleftharpoons t2$ experimental points are shown.

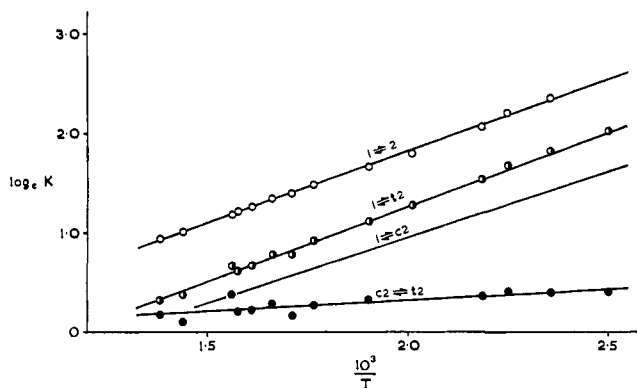


Figure 1. Equilibrium constants for *n*-butenes.

The derived ΔH° and ΔS° values for the equilibria butene-1 \rightleftharpoons *trans*-butene-2 and *cis*-butene-2 \rightleftharpoons *trans*-butene-2 are shown in Table II, which also contains data from two experimental determinations and data calculated from the A.P.I. tables.

Discussion

Benson and Bose have recently reported⁵ equilibrium measurements in the *n*-butene system using iodine

(5) See footnote *b*, Table II.

to obtain equilibration and v.p.c. to determine the proportions. Their results, obtained at 508 and 573°K., are in substantial agreement with the present work, and their experimental spread (about 5% difference between results starting from butene-1 and butene-2) is similar to that reported above. Their derived results are shown in Table II, along with their own estimated errors. The largest difference between the present work and that of Benson and Bose lies in the *cis* \rightleftharpoons *trans* isomerization. Their equilibrium constants are 1.63 at 508°K. and 1.55 at 573°K. compared with 1.45 at 498°K. and 1.32 at 567°K. in the present investigation. It can be seen from Figure 1 that the experimental spread in our work is largest in the *cis* \rightleftharpoons *trans* figures so there must remain some doubt about the correct values.

Our results are in almost perfect agreement with Benson and Bose's main finding, namely, that the A.P.I. entropy values (probably for butene-1) are in error. Also shown in Table II are figures calculated from Voge and May's investigation⁶ using an infrared technique to measure the equilibrium values. These are also within experimental error of the more recent work. The values calculated from the A.P.I. tables are also shown. Our errors are probably not greater than ± 0.1 cal. deg.⁻¹ for ΔS° in the butene-1 \rightleftharpoons *trans*-butene-2 figures, but probably no better than Benson and Bose's estimated error for the *cis* \rightleftharpoons *trans* figures, this greater uncertainty in our *cis*-*trans* figures being caused by our method of obtaining the $\log K$ vs. T^{-1} plot as a difference of two other plots.⁷

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(6) See footnote *d*, Table II.

(7) NOTE ADDED IN PROOF. D. M. Golden, K. W. Egger, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5416 (1964), in a paper submitted after the present paper, present equilibria data (368.0–605.2°K.) for the *n*-butenes obtained using iodine catalysis for equilibration. Their butene-1-*trans*-butene-2 data are just within experimental error of those reported here, their *cis*-*trans* data are even further from our data than their previous data,⁵ but the general conclusions still agree.