Isomerization Equilibrium Constants of *n*-Butenes

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Equilibrium constants for isomerization of *n*-butenes were measured over the temperature range between 679–883° K. Equilibrium was established utilizing a commercial-grade chromia-alumina catalyst. The constants obtained in the present investigation were compared with those of published literature. Thermochemical data, $\Delta H^\circ_{f,298}$ and S°_{298}, were also obtained from the equilibrium constants among the three isomers. The values of ΔH°_f and ΔS°_f were estimated for the above temperature range: for 1-butene–*cis*-2-butene, $\Delta H^\circ = -2.54 \pm 0.49$ kcal/g-mol, $\Delta S^\circ = -3.04 \pm 0.69$ cal/g-mol, ° K; for 1-butene–*trans*-2-butene, $\Delta H^\circ = -2.96 \pm 0.40$ kcal/g-mol, ° K, $\Delta S^\circ = -3.20 \pm 0.60$ cal/g-mol, ° K; and for *cis*-2-butene–*trans*-2-butene, $\Delta H^\circ = -0.65 \pm 0.09$ kcal/g-mol, $\Delta S^\circ = -0.20 \pm 0.12$ cal/g-mol, ° K.

Accurate values of isomerization equilibrium constants of butenes systems are of importance for the kinetic analyses of the isomerization reactions as well as for the determination of basic thermodynamic functions. Although the thermodynamic equilibrium constants among three isomers have been experimentally determined by several investigators (*2, 4, 6, 7, 9, 11*), some uncertainty still exists among the constants reported. This is particularly true for the system of *cis*-2-butene and *trans*-2-butene. This uncertainty in equilibrium data seems to become more pronounced with increase in temperature. As pointed out by Benson and co-workers (*2, 7*), equilibrium values calculated from the API data (*10*) are unreliable at temperatures higher than about 600° K.

In this investigation an attempt was made to obtain more accurate values of equilibrium constants for the *n*-butenes system over the temperature range between 679° and 883° K. Isomerization reactions of butenes on chromia-alumina catalyst at high temperatures are so fast that equilibrium is reached quite readily. This affords an excellent method for obtaining butene isomerization equilibrium data at high temperatures.

EXPERIMENTAL

Materials. For all experiments, Matheson CP grade 1-butene, *cis*-2-butene, and *trans*-2-butene were used with a minimum purity of 99% of corresponding butene. Analysis of *n*-butene showed that the main impurities were isobutylene and remaining isomers of *n*-butenes.

The catalyst, 20% chromia (Cr_2O_3) on alumina, is manufactured by the Houdry Process Corp. and is designated as Type A50. Typical properties are:

Surface area	55 m²/g
Total pore volume	0.31 cc/g
Pellet density	1.42 g/cc
Size	14–20 mesh
Calculated average pore diameter	225 Å

Apparatus. The measurements were carried out in a flow reactor, illustrated in Figure 1, consisting of a stainless steel tube that provides for a catalyst chamber 1 in. in diameter by 3½ in. long. Six thermocouples inserted into a ¼ in.-thermocouple well running down the center of the catalyst bed and three others located on the circumference of the bed, measure the complete temperature profile of the reaction. The highest temperature gradient in the catalyst bed was 8° C. This gradient was observed when the feed contained predominantly 1-butene. During the ordinary runs in which the compositions of feeds were closer to the equilibrium compositions, the overall temperature gradients in the bed were not higher than 3° C. Ports located immediately before and after the catalyst chamber draw samples of the gases entering and leaving the catalyst chamber. These ports also measure the pressure within the chamber and the pressure drop through the catalyst bed.

Provision is made for introducing into the catalyst chamber, as required, *n*-butenes feed, nitrogen for purging the reactor system, air for regeneration of the catalyst, and hydrogen for pretreatment of the catalyst. More complete description of experimental procedure is given elsewhere (*8*). Each stream is filtered, dried with a column packed with Drierite and Ascarite, and metered by means of calibrated rotameters before entering the reactor. Two preheaters are used to preheat the feed to proper reaction temperature. The heaters are programmed to minimize hydrocarbon decomposition before it enters the reaction zone of the reactor. An electrically heated aluminum-bronze

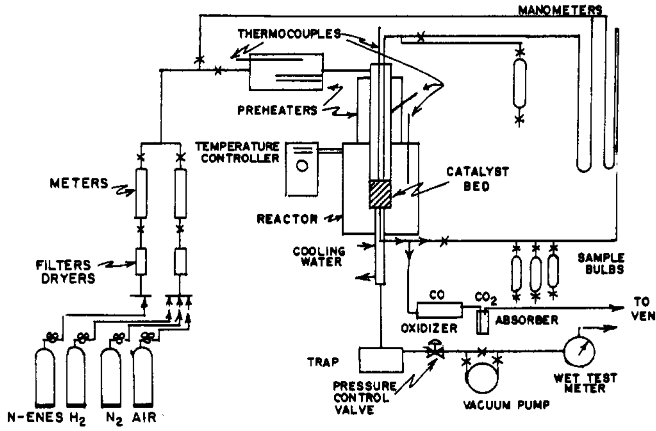

Figure 1. Flow diagram of isomerization equipment

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block serves as a heat sink which provides adequate temperature control to the catalyst bed.

Analysis. Analysis of 3-ml normal temperature and pressure (NTP) samples of hydrocarbon gases was carried out by gas-liquid chromatograph at 25° C using a Model A Varian Aerograph gas chromatograph. A 25-ft column filled with 20% by weight tributyl phosphate on 40–60-micron chromosorb B was used with helium as carrier gas flowing at a rate of 50 ml/min. Some 12 components can be quantitatively determined including methane, ethane, ethylene, propane, propylene, isobutane, *n*-butane, 1-butene, *cis*-2-butene, *trans*-2-butene, and 1,3-butadiene. The procedure analyzing the chromatograms was checked extensively using a standard calibrating mixture and mass spectroscopy. The calibrating mixture was purchased from the Matheson Co., and the analyses of the mixture supplied by the company were 1-butene 50.05 ± 0.5%, *cis*-2-butene 25.03 ± 0.2%, *trans*-2-butene 24.90 ± 0.2%.

Experiments. A standard method of pretreatment was developed to ensure constant catalyst activity. The procedure consisted of three steps. First, air was passed over the catalyst for a period of 22 hr at a rate of 0.02 standard ft^3/min (SCFM) to regenerate the catalyst to a constant oxidized state. Hydrogen was then used to reduce the catalyst. The hydrogen pretreatment was studied, and an optimum period of 2 hr at a rate of 0.115 SCFM was determined. The experimental run then follows. This procedure was cyclic and repeated without interruptions. Standard runs were conducted at the beginning and at the end of a series of runs. The results of these standard runs were matched within an accuracy of ±5%.

A butene mixture was fed into the reactor at a rate of 0.15 g-mol/min at atmospheric pressure for 10 min. The weight of the catalyst used was 35 grams. We designate this flow condition as the standard condition. During each run, samples were taken at 4, 6, and 10 min. The analyses of these samples showed no appreciable deviations in butene concentrations. This indicated that the catalyst retained the same level of activity during the course of the experiments.

EXPERIMENTAL RESULTS

To test that the equilibrium conditions were virtually attained for the isomerization of *n*-butenes, we conducted two kinds of experiments: (1) experiments with each of three isomers as a starting material, (2) experiments with different residence time of reactant gas.

Table I shows the equilibrium constants, K_{BC}, K_{BT}, and K_{CT} obtained by the first kind of test. At about 700° K the equilibrium was attained by approaching from three butene mixtures of extreme compositions: either predominantly 1-butene, *cis*-2-butene, or *trans*-2-butene. Similar experiments were also conducted at approximately 670° and 680° K by using the same flow rate of *n*-butenes. The resulting three equilibrium constants agreed to within an accuracy of ±6%. For temperatures higher than 710° K, we did not perform these equilibrium-testing experiments. Rather we assumed that at the higher temperatures all isomerization rates involved in the system are fast enough so that the equilibrium conditions are reached more easily than at lower temperatures.

Wei and Prater (*12*) have studied in detail the kinetics of monomolecular reaction systems and in particular the isomerization of *n*-butenes. Significant results of their study are that the reaction paths do not spiral about the equilibrium point during convergence to equilibrium and that these paths *only intersect* at the equilibrium point, regardless of the composition of starting material. Our experimental results listed in Table I show that the values of K_{BC}, K_{CT}, and K_{BT} are essentially identical. In light of the conclusions obtained by Wei and Prater our results indicate that thermodynamic equilibria were indeed established. The second kind of test was also performed for our equilibrium study. In addition to the runs with standard flow condition, we conducted a test with a flow rate which is about half of the standard condition. However, no substantial changes were observed in the extent of the isomerization reaction. With these experimental findings in mind, we concluded that our experimental conditions employed here were adequate for the complete attainment of equilibrium conditions. Table II summarizes the equilibrium data collected between 679° and 883° K.

Figures 2 through 4 compare our data with those obtained by Benson's research group (*2*, *7*). As can be seen from these figures, all the experimentally obtained values of K_{BC}, K_{BT}, and K_{CT} agree and are quite reproducible for an extended temperature range. In fact, the Benson data taken in the low temperature region can be extrapolated smoothly to project our experimental data gathered in the high-temperature region. Voge and May (*11*) in their pioneering work determined the thermodynamic equilibrium constants among the three isomers at the temperature ranges between 400° and 900° K. At low temperatures, their K_{CT} values deviate significantly from those reported by Benson. Additionally the K_{CT} values of Voge and May increase with increasing temperatures at temperatures higher than 800° K. This is quite improbable. More recently, Maccoll and Ross (*9*) reported thermodynamic equilibrium constants for *n*-butenes. Their values of K_{CT} are substantially different from those of Benson. Presumably some systematic errors are involved in the concentration measurements of either *cis*-2-butene or *trans*-2-butene. On this ground, the data of Voge and May and those of Maccoll and Ross were

Table I. Equilibrium Constants from Three Different Feeds

Feed	Temp, °K	Equilibrium constants K_{BC}	K_{CT}	K_{BT}
1-Butene	710	1.20	1.36	1.64
		1.22	1.35	1.63
		1.21	1.36	1.66
cis-2-Butene	702	1.21	1.35	1.64
		1.19	1.35	1.61
		1.24	1.33	1.65
cis-2-Butene	709	1.21	1.41	1.70
		1.20	1.38	1.66
		1.18	1.42	1.67
trans-2-Butene	698	1.20	1.43	1.70
		1.20	1.44	1.79
		1.22	1.44	1.75

K_{BC}, K_{CT}, and K_{BT} are, respectively, the thermodynamic equilibrium constants for 1-butene $\rightleftarrows$ *cis*-2-butene, *cis*-2-butene $\rightleftarrows$ *trans*-2-butene, and 1-butene $\rightleftarrows$ *trans*-2-butene system.

Table II. Isomerization Equilibrium Constants for *n*-Butenes

Temp, °K	Equilibrium constants K_{BC}	K_{CT}	K_{BT}
679	1.17	1.48	1.74
684	1.25	1.44	1.81
696	1.18	1.44	1.70
698	1.20	1.44	1.75
702	1.21	1.35	1.63
710	1.21	1.36	1.64
712	1.06	1.46	1.55
719	1.20	1.40	1.68
733	1.06	1.40	1.49
779	1.00	1.37	1.38
787	0.98	1.37	1.38
824	0.88	1.32	1.17
826	0.88	1.35	1.18
883	0.79	1.35	1.10

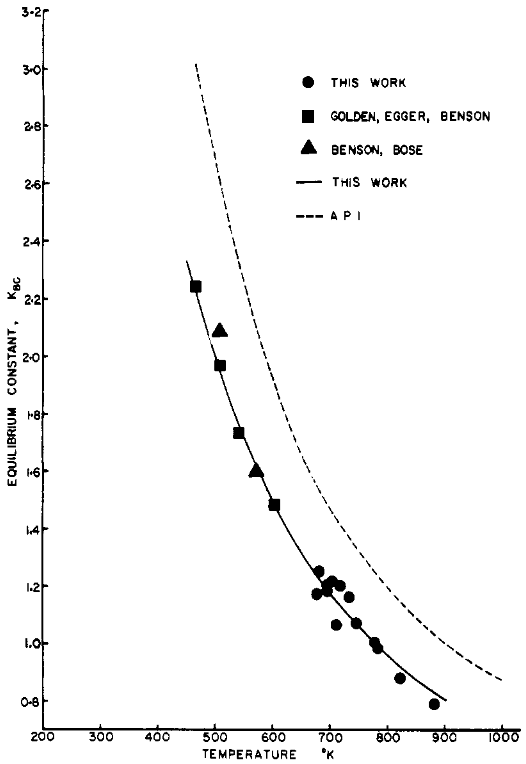

Figure 2. 1-Butene–*cis*-2-butene equilibrium constant and temperature

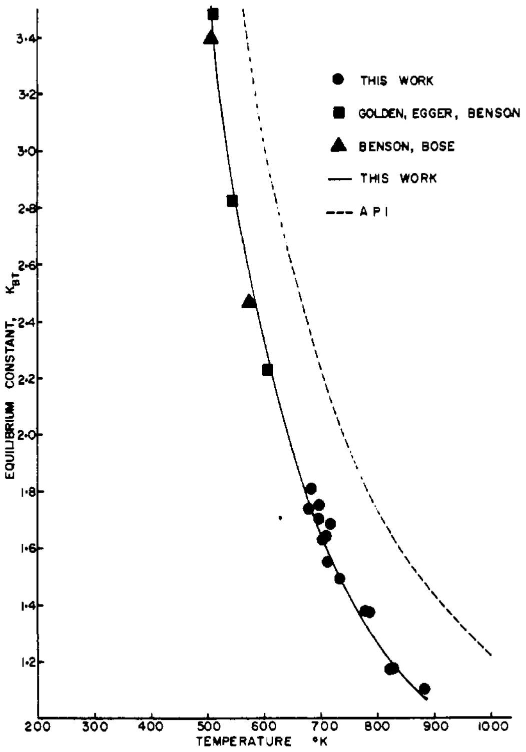

Figure 3. 1-Butene–*trans*-2-butene equilibrium constant and temperature

not employed for the computations of thermochemical parameters.

ESTIMATION OF THERMOCHEMICAL PARAMETERS

The thermodynamic equilibrium constant, K_T, and thermochemical quantities are correlated by the following relationships:

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \int_{298}^{T} (\Delta C_p^\circ) dT \qquad (1)$$

$$\Delta S_T^\circ = \Delta S_{298}^\circ + \int_{298}^{T} (\Delta C_p^\circ / T) dT \qquad (2)$$

where

$$\Delta H_{298}^\circ = \Delta H_f^\circ,\ \text{products, 298} - \Delta H_f^\circ,\ \text{reactants, 298}$$

$$\Delta S_{298}^\circ = S^\circ,\ \text{products, 298} - S^\circ,\ \text{reactants, 298}$$

and

$$\Delta C_p^\circ = C_p^\circ,\ \text{products} - C_p^\circ,\ \text{reactants}$$

$$\ln K_T = -\Delta H_T^\circ / RT + \Delta S_T^\circ / R \qquad (3)$$

With the thermodynamic equilibrium constants measured as a function of temperature the use of Equation 3 provides the enthalpy and entropy *changes* for the reaction system. However, it should be clearly noted that ΔH_T° and ΔS_T° are assumed to be constant over the temperature range of interest. For the temperature range between 679° and 883° K the values of ΔH_T° and ΔS_T° were calculated utilizing our equilibrium data. Equation 3 is nonlinear with respect to the parameters ΔH_T° and ΔS_T°. Thus, the Gaushaus nonlinear regression program (*5*) was applied. Table III presents the resulting estimates of ΔH_T° and ΔS_T° along with the approximate 95% confidence intervals.

From Equations 1 through 3, it can be seen that the estimates of ΔH_{298}° and ΔS_{298}° for the reactions and subsequently those of $\Delta H_{f,298}^\circ$ and S_{298}° for both reactants and products may be obtained, provided that the heat capacity functions of reactants and products are available for the system. For the *n*-butenes system, a total of six values of $\Delta H_{f,298}^\circ$ and S_{298}° were calculated combining our equilibrium data and those reported by Benson. The calculated values were only considered parameters for correlations of these high temperature data. For the estimation, an objective function given by Equation 4 was minimized by adjusting the six parameters of $\Delta H_{f,298}^\circ$ and S_{298}°.

$$S = \sum (K_{BC} - \hat{K}_{BC})^2 + \sum (K_{BT} - \hat{K}_{BT})^2 + \sum (K_{CT} - \hat{K}_{CT})^2 \qquad (4)$$

Here $\hat{K}_{BC}$, $\hat{K}_{BT}$, and $\hat{K}_{CT}$ are, respectively, the calculated thermodynamic equilibrium constants of 1-butene–*cis*-2-butene, 1-butene–*trans*-2-butene, and *cis*-2-butene–*trans*-2-butene system. Employing these estimates, we computed the predicted values of the equilibrium constants of *n*-butenes. They are presented by solid lines in Figures 2 through 4. The broken lines in these figures are the equilibrium constants computed from the free energy function and standard heat of formation at 0° K which are listed in the API data (*10*). Values of $\Delta H_{f,298}^\circ$ and S_{298}° are reported in the API data (*10*) and, furthermore, Benson (*1, 3, 6*) recently developed a method for obtaining accurate estimates for these thermochemical constants. However, use of these constants in conjunction with the API specific heat data does not result in a correct prediction of the equilibrium constants for the isomerization at high temperature. The estimation method presented in this report would provide accurate estimates of $\Delta H_{f,298}^\circ$ and S_{298}° when precise C_p° functions are available. A better method for estimation of low temperature values of $\Delta H_{f,298}^\circ$ and S_{298}° would be provided by determination of the equilibrium constants at 298° K.

CONCLUSIONS

Accurate data for thermodynamic equilibrium constants among *n*-butenes were experimentally obtained at high temperatures. These data were smoothly connected with the

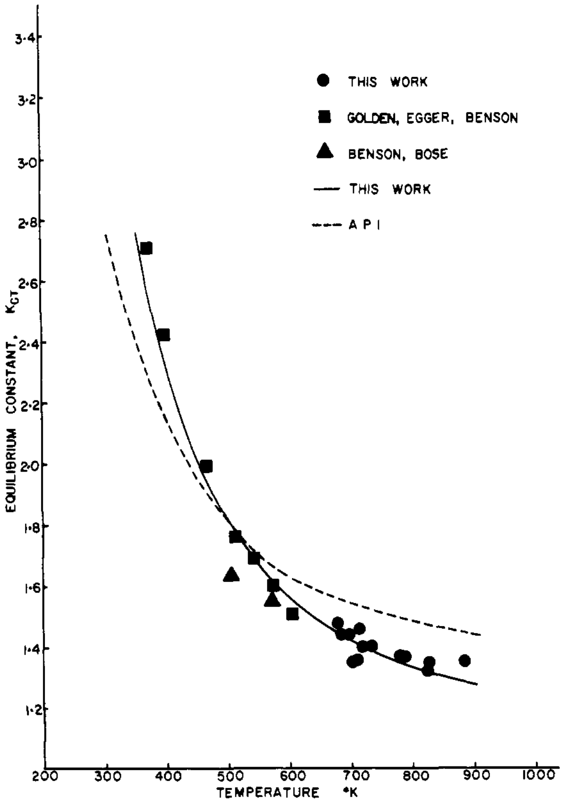

Figure 4. *cis*-2-Butene–*trans*-2-butene equilibrium constant and temperature

Table III. Estimates of ΔH° and ΔS° Utilizing Data Obtained in This Study

(Temperature range 679–883° K)

Isomerization system	ΔH°_T kcal/g-mol[a]	ΔS°_T cal/g-mol, °K[a]
1-Butene-*cis*-2-butene	−2.54 ± 0.49	−3.04 ± 0.69
1-Butene-*trans*-2-butene	−2.96 ± 0.40	−3.20 ± 0.60
cis-2-Butene-*trans*-2-butene	−0.65 ± 0.09	−0.20 ± 0.12

[a] ± signs represent approximately 95% confidence limits.

Benson data which had been gathered for the lower temperature region. The resulting estimates were compared with the values presented by the API report. A number of discrepancies exist between our estimates and the API values. Because of these differences, the sole use of the API values, in the temperature region of 400–900° K, produces significant errors in estimating equilibrium constants for the *n*-butenes system.

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