# Thermodynamics of *n*-Butene Isomerization

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**Abstract:** Equilibrium constants for the isomerization of *cis*-2-butene and 1-butene to *trans*-2-butene have been measured between 251 and 357°K by allowing various linear $C_4$ hydrocarbons to react with hydrogen over a palladium catalyst. The values were included with literature data at higher temperatures to provide thermodynamic properties of isomerization from 250 to 900°K. The cis–trans values lie within experimental error of the original API data at all temperatures; the 1-ene–trans values indicate a revision of the API data for the entropy of 1-butene is called for. The old value of 73.04 eu at 298.16°K should be replaced by 74.46 eu.

As a follow-up of studies on the hydrogenation of 1,3-butadiene[1] on palladium–alumina, we have investigated the ratios of the *n*-butenes in the product mixture as the reaction nears completion. These ratios remain constant beyond the addition of about 1.5 mol of $H_2$ per mole of butadiene, presumably reflecting the attainment of equilibrium among 1-butene and the cis and trans forms of 2-butene.

While several studies of the equilibrium composition of the *n*-butenes as a function of temperature have been published,[2–7] the results vary considerably. (After comparison of the cis–trans equilibrium constants produced by three investigators[3–5] using different methods, one author[5] has suggested that kinetic effects of the equilibrating agent may make it very difficult to find a true equilibrium by any chemical means.) In a very recent paper, Happel[6] considers the work of Benson[3] to be the most reliable at temperatures below 600°K and extends the data to 883°K. Prior to the work of Akimoto, *et al.*,[7] which was carried out at the same time the present work was being done, there were no data below 368°K. Our goal was to extend the data to lower temperatures; the data presented in this paper range from 360 down to 251°K. One of the consequences of the equilibrium studies to date has been a certain skepticism concerning the validity of the *n*-butene data in the API tables.[8]

## Experimental Section

The catalyst was 0.03% palladium on alumina, reduced overnight at 300–350° in a batch reactor and flushed with $H_2$ immediately before use. All gases were purchased from Matheson Co. and were used without purification. For the 1,3-butadiene experiments the $H_2$ to hydrocarbon ratio was 2:1; for the butene experiments it was 1:1. Product analyses were performed *via* glc, using a 3:8 by weight dimethyl sulfolane on Chromosorb P column 25 ft long, at 17°. Separation of the three isomers was complete, and ratios of the weights of cut-out peaks agreed with the ratios of corresponding partial pressures of synthetic mixtures (corrected for impurities) well within experimental error. Because different sensitivities were used in recording each peak, the nominal values of the gas chromatograph attenuator settings were checked against a Rubicon potentiometer. The maximum deviation from nominal for the ratio of two readings was 0.2%. Temperatures were measured with a mercury in glass thermometer calibrated against an NBS certified platinum resistance thermometer. The bath was controlled to ±0.2°.

## Results

The values of the equilibrium constants for 1-ene to trans and cis to trans at several temperatures are presented in Table I. Each entry is the average of several analyses as indicated in the table. The average deviation for each $K$ is given in parentheses.

**Table I**[j]

| $T$, °K | Feed | $K_{T/1}$ | No. of samples[i] | $K_{T/C}$ | No. of samples[i] |
|---|---|---|---|---|---|
| 250.8 | T, C[a] | 65.5 (±2.0) | 7 | 4.59 (±0.04) | 6 |
| 273.2 | T, C[a] | 41.1 (±1.2) | 9 | 3.72 (±0.08) | 8 |
| 273.2 | BD | 41.1 (±2.4) | 8 | 3.72 (±0.14) | 8 |
| 273.2 | 1 | 29.2 (±1.8)[e] | 7 | 3.70 (±0.16) | 10 |
| 273.2 | 1 | 30.8 (±1.9)[e] | 8 | 3.69 (±0.17) | 8 |
| 288.6 | BD | 31.6 (±1.7) | 7 | 3.45 (±0.11) | 6 |
| 303.8 | BD | 22.4 (±1.3) | 6 | 2.99 (±0.06) | 9 |
| 318.5 | BD | 18.5 (±1.6) | 8 | 2.84 (±0.10) | 10 |
| 333.6 | BD | 14.7 (±0.7) | 9 | 2.62 (±0.05) | 9 |
| 346.5 | BD | 12.3 (±0.9) | 8 | 2.41 (±0.05) | 6 |
| 355.2 | T, C[b] | 11.3 (±0.2) | 7 | 2.55 (±0.10) | 7 |
| 357.2 | T, C[c] | 12.1 (±0.7)[e] | 6 | 2.52 (±0.14) | 10 |
| 357.2 | 1 | 10.8 (±0.6) | 7 | 2.46 (±0.09) | 7 |
| 357.2 | 1 | *f* | | 2.47 (±0.05) | 5 |
| 357.2 | C | 11.2 (±1.4) | 7 | *f* | |
| 357.7 | C | *f* | | 2.35 (±0.13) | 5 |
| 358.2 | C | 10.7 (±0.9) | 6 | 2.23 (±0.15)[g] | 5 |
| 358.7 | T, C[c] | 12.4 (±0.6)[e] | 5 | 2.48 (±0.12) | 7 |
| 358.7 | 1 | 10.1 (±1.0) | 5 | 2.43 (±0.12) | 5 |
| 359.2 | T, C[c] | 12.8 (±1.0)[e] | 5 | 2.45 (±0.04) | 4 |
| 360.4 | 1[d] | 10.6 (±0.7) | 6 | 2.36 (±0.04) | 5 |
| Overall av deviation | | 6.6%[h] | | 3.6% | |

[a] T:C ratio = 1:1. [b] T:C ratio = 3.46:1. [c] T:C ratio = 3.12:1. [d] Isomerization *via* thermal generation of I·. [e] The low and high values obtained for 1 and T,C feeds respectively are explained by a starting mixture too far removed from equilibrium. These values are not included in the fits. [f] Data trending, indicating nonequilibrium. [g] Rejected from quadratic fit, found to be beyond four times the average deviation for these data. [h] At our temperatures, the 1-butene peak is the smallest, hence least precisely measured, leading to a larger error in the determination of $K_{T/1}$. [i] Number of samples refers to sequential analyses as the simultaneous hydrogenation and isomerization reactions proceed. [j] BD = 1,3-butadiene, T = *trans*-2-butene, C = *cis*-2-butene, 1 = 1-butene.

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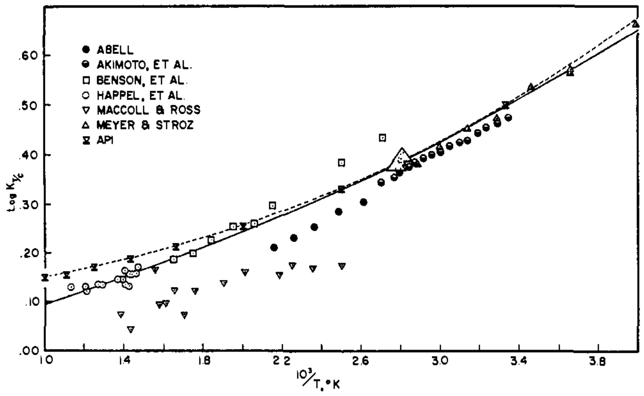

Figure 1. Solid line represents the best quadratic fit of the data of Happel, Benson, and the present work. The two low-temperature points of Benson were not included, for reasons given in the text. The dashed curve represents the API data.

The observation that the ratios of the butenes remain constant as their hydrogenation proceeds is an indication of equilibrium but could reflect the presence of a steady state, since in these experiments the butenes are intermediates rather than final reaction products. Consequently, several experiments were performed starting with butene compositions widely different from those characteristic of the 1,3-butadiene experiments. (At the point where isomerization of the butenes commences, the butene composition is about 53:42:5 for 1-ene:trans:cis.[1]) Values of $K$'s agreed within experimental error with those obtained in the butadiene runs, except as noted in Table I.

## Discussion

Plots of log $K$ *vs.* $10^3/T$ are presented in Figures 1 and 2. We have included only data obtained by authors who used gas-liquid chromatographic (glc) analysis of the equilibrated butenes. There is serious scatter for the cis-trans data of various authors, while there is very little for the 1-trans data. This indicates a possible difficulty in separating the cis and trans elution peaks for accurate analysis. It is a fact that the 1-butene peak is eluted well before those of the 2-butenes, and the latter are close together. At the lower temperatures, the trans peak is much larger than the cis, making the cis the less reliable of the two. Since each group states that calibration of known mixtures was accomplished as part of the analytical procedure, it is difficult to say which cis-trans data are reliable.

For the cis-trans isomerization, our data stand in excellent agreement with the original API data and with all but the low-temperature values of Benson, *et al.*[3] For the two lowest temperature points, these workers used a tungsten lamp to dissociate $I_2$ because thermal dissociation alone provided too slow a reaction rate. There is evidence that this may have introduced an upsetting effect on the equilibrium in question. Benson[3] reports one experiment in which the lamp was used with an unusually low partial pressure of $I_2$. The results were discarded because they were not consistent with those obtained at higher $I_2$ pressures; yet the value of $K_{T/C}$ is within experimental error of ours at the temperature in question (360°K). In addition, we have placed 1-butene and solid $I_2$ together in the dark at this temperature, and after 3 days the cis-trans ratio agreed with that obtained in our 1,3-butadiene runs. After 5 days, the contents of the flask were sampled again with the same results.

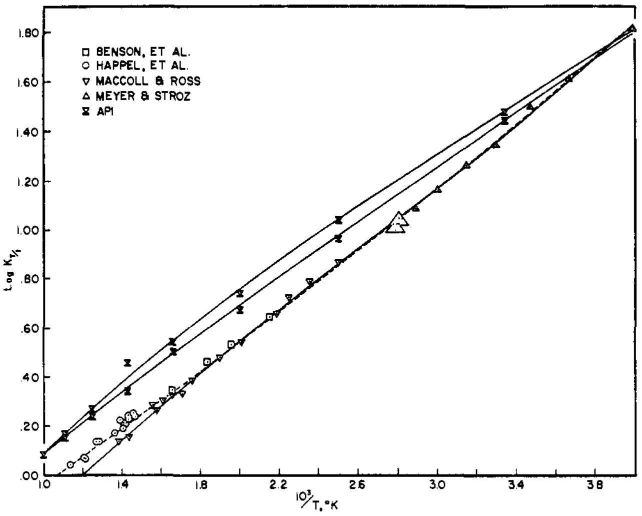

Figure 2. The dashed curve represents the best quadratic fit of all experimental points on the graph. The lowest solid curve is a cubic fit of the data excluding Happel's work. (See text.) The upper two curves are based on the API data tabulated for log $K$ and derived from the tabulated values for $\Delta H$ and $\Delta S$.

The results of Happel, *et al.*,[6] fit nicely onto the curve containing the present data and Benson's higher temperature data but cause it to drop slightly below the API curve at high temperatures (see Figure 1).

The values of $K_{T/C}$ produced by Akimoto, *et al.*,[7] lie consistently about 5% below ours. Since these authors state a maximum possible error of 3%, and our overall precision is about 3% also, the results of the two laboratories are in agreement within the limits of error. The discrepancy is systematic, however, indicating that one set of data is more accurate than the other.

We have chosen to include the data of Happel,[6] Benson,[3] and the present work to define a curve covering the temperature range from 251 to 883°K for the following reasons. The data of Maccoll and Ross[4] show a degree of scatter far worse than any of the other authors. In the light of their much better precision for the 1-ene to trans data, it seems likely that separation of the cis and trans isomers on the glc column was incomplete, as discussed at the beginning of this section. Any tailing of the trans into the cis would result in a $K_{T/C}$ which is too small. Since $K_{T/C}$ increases at lower temperatures, this effect leads to a larger discrepancy in this direction in accord with the behavior of Maccoll and Ross's data in Figure 1.

Both Benson, *et al.*,[3] and Abell[5] used the same liquid phase for analysis of the butenes. The former used a 50-ft column at 0°, whereas the latter used a 25-ft column at 25°. Clearly, Benson's chromatograms must have exhibited higher resolution of the cis and trans peaks. In addition, Benson's experimental section is very explicit regarding analysis and treatment of data, indicating a strong concern for accuracy. The observation that Abell's data fall below those of Benson, and that Akimoto, *et al.*'s, fall below ours, is consistent with the idea of incomplete separation of the cis and trans isomers in the case of the low values.

**Table II**

| $T$, °K | 250 | 300 | 400 | 500 | 600 | 700 | 800 | 900 |
|---|---|---|---|---|---|---|---|---|
| | | | | Cis $\longrightarrow$ Trans | | | | |
| $\Delta G°$ | | | | | | | | |
| API | | −0.69 | −0.61 | −0.59 | −0.59 | −0.61 | −0.64 | −0.66 |
| MBH[a] | −0.74 | −0.68 | −0.61 | −0.56 | −0.53 | −0.50 | −0.48 | −0.47 |
| ASP[b] | | −0.66 | | | | | | |
| $\Delta H°$ | | | | | | | | |
| API | | −1.00 | −0.81 | −0.66 | −0.56 | −0.47 | −0.41 | −0.34 |
| MBH | −1.11 | −0.99 | −0.84 | −0.75 | −0.69 | −0.65 | −0.62 | −0.59 |
| ASP | | −1.08 | | | | | | |
| $\Delta S°$ | | | | | | | | |
| API | | −1.04 | −0.49 | −0.15 | +0.05 | 0.18 | 0.28 | 0.35 |
| MBH | −1.48 | −1.02 | −0.59 | −0.39 | −0.28 | −0.21 | −0.17 | −0.14 |
| ASP | | −1.42 | | | | | | |
| | | | | 1-ene $\longrightarrow$ Trans | | | | |
| $\Delta G°$ | | | | | | | | |
| API[c] | | −2.04 | −1.92 | −1.72 | −1.51 | −1.28 | −1.01 | −0.72 |
| CE[d] | −2.11 | −1.90 | −1.58 | −1.27 | −0.93 | −0.55 | | |
| QE[e] | −2.10 | −1.91 | −1.57 | −1.26 | −0.96 | −0.67 | −0.39 | −0.11 |
| $\Delta H°$ | | | | | | | | |
| API | | −2.64 | −2.63 | −2.64 | −2.68 | −2.71 | −2.74 | −2.77 |
| CE | −3.46 | −2.97 | −2.79 | −2.91 | −3.07 | −3.24 | | |
| QE | −3.10 | −2.99 | −2.85 | −2.77 | −2.72 | −2.68 | −2.65 | −2.62 |
| $\Delta S°$ | | | | | | | | |
| API | | −2.18 | −2.09 | −2.16 | −2.22 | −2.27 | −2.31 | −2.35 |
| CE | −5.40 | −3.57 | −3.02 | −3.28 | −3.58 | −3.84 | | |
| QE | −4.00 | −3.60 | −3.20 | −3.02 | −2.93 | −2.87 | −2.82 | −2.79 |

[a] From curve based on the present data, Benson's excluding two low-temperature points, and Happel. See text. [b] The choice of Akimoto, Sprung, and Pitts[7] as the most reliable values at 298°K. It is based on their data and those of Abell[5] and Voge and May.[2] [c] Based on $\Delta H° - T\Delta S°$. There is a small discrepancy between this value and the one based on the $\Delta G_f°$ values. See Figure 2. [d] Based on the cubic equation discussed in the text. [e] Based on the quadratic equation fit to all data.

Happel, *et al.*,[6] checked the accuracy of their glc analyses using mass spectroscopy, lending to their values a somewhat higher degree of reliability.

Least-squares fit of these data (excluding the two low-temperature points of Benson) results in the equation

$$\log K_{T/C} = 0.01947(10^3/T)^2 + 0.08663(10^3/T) - 0.006692$$

The average deviation is 0.008 in $\log K_{T/C}$. Values of the derived thermodynamic properties are presented in Table II. The thermodynamic properties for cis → trans at 298°K of Akimoto, *et al.*,[7] are included for comparison. The only significant discrepancy is in the entropy change, manifested in Figure 1 as a downward shift from the line we have chosen, brought about presumably by incomplete resolution of cis and trans as already discussed.

For the 1-trans isomerization the data of four different laboratories, involving five different chemical methods, both homogeneous and heterogeneous, stand in extremely good agreement. It is obvious from Figure 2 that the API data for this system need revision. As Benson[3] has suggested, it is likely that the absolute entropy of 1-butene used in compiling the API tables is about 1 eu too low. The present work strengthens this suggestion by supporting the original API data for the 2-butenes at moderate temperatures. These data had been brought into question by Happel[6] after consideration of his own data and those of Benson (see Figure 1).

When all the data between 251 and 883°K are fitted to a quadratic curve by least-squares analysis, the resulting curvature is of opposite sign from the API curvature. A check of experimentally measured heat capacity data[9,10] indicates that $\Delta C_p$ for the 1-trans isomerization changes sign at 357°K. Thus we should expect an inflection point in the curve of Figure 2 at this temperature ($10^3/T = 2.80$), with positive curvature to the right and negative to the left of 2.80.

While the scatter in the data makes it difficult to justify fitting the data to a cubic equation, the presence of an inflection point within the range of available data makes the attempt defensible. Such a fit to all the data produces the inflection at a negative absolute temperature. If the data of Happel, *et al.*,[6] are excluded, however, the inflection occurs at $10^3/T = 2.59$, remarkably close to 2.80, and the fit has the proper curvature at higher and lower temperatures. In addition, the curve produced (see Figure 2) is very nearly parallel to the API curve at high temperatures, where the statistical thermodynamic calculations involved are most reliable. (The downward shift of the line produced in this work from the API line is believed to be the result of an erroneous value for the entropy of 1-butene as discussed below. The curvature of the line is independent of this value, however.)

In spite of these arguments, there appears to be no experimental reason for excluding the data of Happel, *et al.*[6] Consequently, while we include both the quadratic and cubic fits, we emphasize that complete objectivity makes the former curve the one of choice.

The dotted line in Figure 2 represents a quadratic fit of all the data, and the solid line is the cubic fit excluding Happel's data. The corresponding equations (and average deviation in $\log K_{T/1}$) are, respectively

$$\log K_{T/1} = 0.01825(10^3/T)^2 + 0.5326(10^3/T) - 0.5884\ (\pm 0.016)$$

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$$\log K_{T/1} = 0.02409(10^3/T)^3 - 0.1874(10^3/T)^2 + 1.096(10^3/T) - 1.081\ (\pm 0.011)$$

The former equation covers the temperature range from 251 to 883°K; the latter, from 251 to 724°K. Thermodynamic properties derived therefrom are presented in Table II.

Benson[3] discusses the sources and reliability of the thermodynamic data in the API tables and points out that the entropy values for 1-butene are least reliably known. This is the result of estimations used in assignment of low-frequency vibrations upon which the thermodynamic calculations were based. The good agreement of all authors for the 1-trans isomerization should allow more accurate assignment of these frequencies and permit extension of reliable calculations to lower temperatures.

Because of the agreement among the data of different investigators for the 1-ene to trans isomerization, it is worthwhile making a quantitative estimate of the absolute entropy of 1-butene to replace the value used in compiling the API data. To be completely objective, the curve including the data of all authors should be used. When this is done, the value of $\Delta S$ at 298.16°K is $-3.60$ eu. Using the API value for *trans*-2-butene of 70.86, we find the value for $S°_{298}$ for 1-butene to be 74.46 eu. The accuracy of this number is determined by the error in $S°_{298}$ for *trans*-2-butene.

In the case of the cis–trans isomerization, the values of $\Delta H°$ and $\Delta S°$ in Table II are within the limits of error of the API data at all temperatures.

For all the equilibrium constants presented in Table I, it was assumed the gases behave ideally. This assumption was checked for 250°K using the second virial coefficient data of Roper quoted by Dymond and Smith.[11] The ratio of fugacity coefficients for the cis–trans as well as for 1-ene–trans isomerization is 0.998. Application of these refinements is not justified by the experimental error in the equilibrium constants.

## Conclusion

Recent work questioning the validity of the API data for the 2-butenes has not been substantiated. The most reliable data for equilibrium constants provide thermodynamic properties in agreement with the API values up to 900°K, and the present work extends them down to 250°K. On the other hand, the original API value for the standard entropy of 1-butene at 298.16°K is definitely erroneous. The old value of 73.04 eu should be replaced by 74.46 eu with an error determined by the accuracy of the absolute entropy of *trans*-2-butene.

**Acknowledgment.** The gas chromatograph used in this work was a gift of the Richardson Company; the platinum resistance thermometer and Mueller Bridge used for temperature calibration were purchased with financial assistance from the Research Corporation. We are grateful to Drs. Akimoto, Sprung, and Pitts for permission to use their data prior to publication.

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# Heats of Formation of Protonated Cyclopropane, Methylcyclopropane, and Ethane

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**Abstract:** Equilibrium constants have been measured for proton transfer reactions between protonated methanol or protonated formic acid with propylene, *trans*-2-butene, cyclopropane, methylcyclopropane, and ethane. The single ion source of a mass spectrometer was used as reactor. From the free energies of reaction and assuming negligible entropy change, proton affinities have been determined for the above compounds assuming $\Delta H_f(i\text{-}C_3H_7^+)$ to be 191.7 kcal/mol. Heats of formation of the various protonated ions calculated from these values show that protonated cyclopropane and methylcyclopropane have heats of formation different from that of the propyl or butyl ions showing that the ring structure for these ions is maintained. The heat of formation of $C_2H_7^+$ is about 0.2 kcal/mol less than that of $C_2H_5^+$. This is in accord with the postulated instability of $C_2H_7^+$.

This research has been directed toward establishing thermodynamic properties of certain interesting hydrocarbon positive ions for which no suitable values have yet been determined. Several investigators have postulated protonated cyclopropane or methylcyclopropane as intermediate in the solvolysis of norbornyl derivatives,[1] in the addition of acids,[2–4] acetyl chloride,[5] and bromine[6] to cyclopropane, and in the reaction of cyclopropanecarboxylic acids.[7] Recently, Ausloos, *et*

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