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Thermodynamics of the geometrical isomerization of 2-butene and 2-pentene

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The use of two different catalysts for the metathesis of alkenes, active in adjoining temperature regions, allowed an accurate determination of the equilibrium constant for the gas-phase *cistrans* isomerization of both 2-butene and 2-pentene over the temperature range 250 to 823 K. Because of this broad temperature range, thermodynamic functions of these reactions, *viz*. $\Delta G^{\circ}(\mathbf{g}, T), \Delta H^{\circ}(\mathbf{g}, T), \Delta S^{\circ}(\mathbf{g}, T)$, and even $\Delta C_{p}^{\circ}(\mathbf{g}, T)$, could be evaluated with a higher precision than from thermochemical tables (API, NBS) or from other equilibrium studies. Moreover, the use of recent spectroscopic quantities for 2-butene results in calculated values of thermodynamic functions which are more in agreement with our experimental results than the values in the API tables.

1. Introduction

Accurate values of the thermodynamic equilibrium constant for *cis-trans* isomerizations are valuable for kinetic studies of these reactions as well as for the determination of related thermodynamic functions.

Several authors have reported experimental equilibrium constants for the *cis-trans* isomerization of 2-butene,⁽¹⁻⁷⁾ and 2-pentene.^(4,7,8) These individual studies, however, cover mostly a temperature range smaller than 100 K. At overlapping temperature regions often large discrepancies exist. Nevertheless, some authors combine these quantities to obtain a correlation for the equilibrium constant to be valid over the whole temperature range covered by these different studies.^(2,5,7)

In view of the need for accurate values of the equilibrium constant for the *cis-trans* isomerizations of these alkenes for our kinetic studies⁽⁹⁾ on the catalytic metathesis of alkenes,⁽¹⁰⁾ and of the uncertainties in the literature data, we performed equilibrium studies on the geometrical isomerization of both 2-butene and 2-pentene by means of the metathesis reaction. The latter reaction not only yields new alkenes by interchange of alkylidene groups (equation 1), but also effectuates a rapid *cis-trans* isomerization *via* the same mechanism.⁽¹⁰⁾

$$2\mathbf{R}\mathbf{C}\mathbf{H} = \mathbf{C}\mathbf{H}\mathbf{R}' = \mathbf{R}\mathbf{C}\mathbf{H} = \mathbf{C}\mathbf{H}\mathbf{R} + \mathbf{R}'\mathbf{C}\mathbf{H} = \mathbf{C}\mathbf{H}\mathbf{R}'.$$
 (1)

The use of two highly selective metathesis catalysts, viz. $(\text{Re}_2O_7 \text{ on } \delta\text{-Al}_2O_3)$ and $(WO_3 \text{ on } SiO_2)$, which are active in adjoining temperature regions, enabled us to

obtain equilibrium measurements over a wide temperature range (250 to 823 K). This provided a good basis for the calculation of thermodynamic functions.

2. Experimental

cis-2-Butene (Matheson CP, 0.12 per cent *trans*-2-butene), *trans*-2-butene (Matheson CP, 0.21 per cent *cis*-2-butene), and a mixture of (0.38cis-CH₃CH=CHCH₃ + 0.62*trans*-CH₃CH=CHCH₃) (Matheson CP) were purified before use over (Cu on Al₂O₃) (BASF R3- 11) and molecular sieves (Merck 3A) to remove oxygen and water, respectively. *cis*-2-Pentene (Fluka, 0.44 per cent *trans*-2-pentene) and *trans*-2-pentene (Fluka, 0.25 per cent *cis*-2-pentene) were freeze-distilled three times and stored with activated molecular sieves.

The catalyst (Re_2O_7 on δ -Al₂O₃) was prepared by impregnation of δ -Al₂O₃ (Ketjen CK-300) with an aqueous solution of NH₄ReO₄ (Merck), followed by drying at 390 K, and calcining in a stream of dry oxygen during 4 h at 830 K. Samples of 12, 14, and 15 mass per cent (Re_2O_7 on δ -Al₂O₃) (activated for 4 h in a stream of dry air at 830 K, followed by rinsing with helium for 2 h at the same temperature), were used in the temperature range 250 to 523 K. The other catalyst (WO₃ on SiO₂) was prepared by impregnation of SiO₂ (Davison Grace 62) with an aqueous solution of ammonium metatungstate (Koch-Light Laboratories), dried, and calcined overnight in oxygen at 823 K. Samples of 6, 12, and 20 mass per cent (WO₃ on SiO₂) (activated for 15 h in a stream of dry and oxygen-free helium at 823 K) were used in the temperature range 513 to 823 K.

Three different reaction systems were used to cover the whole temperature range.⁽¹¹⁾ An all-glass batch reactor (cooled or heated with ethanol) was used in the temperature range 250 to 305 K. The reactant gases were recirculated through the catalyst bed by an external membrane pump. To avoid condensation of the reactants, the partial reactant pressure was kept below half the saturation pressure of the lowest boiling cis-isomer at 250 K (10 kPa for 2-butene, and 5 kPa for 2-pentene). By diluting with helium the total system pressure was kept at 0.1 MPa. The temperature was measured just above the catalyst bed with calibrated mercury thermometers (accuracy 0.1 K). The catalyst (Re_2O_7 on δ -Al₂O₃, 1.0 g) was activated externally in a tubular reactor and transferred to the all-glass reactor under nitrogen. In the second batch reactor (stainless steel) the catalyst (Re_2O_7 on δ -Al₂O₃, 1 to 2 g) was activated in situ. The gases were recirculated internally by a magnetically driven fan (Philips Ticonal 500 magnets). The temperature range studied with this system was 300 to 523 K. The third reactor, a micro-catalytic fixed-bed flow reactor, was used in the temperature range 323 to 823 K. The catalyst (either Re_2O_7 on δ -Al₂O₃ or WO₃ on SiO_2 , 5 to 6 g) was activated in situ. The temperature in the latter two reactors was measured just under and above the catalyst bed with calibrated chromel-to-alumel thermo-elements (accuracy 0.5 K). The reactant pressure in these reactors was kept below 0.1 MPa, total pressure 0.35 MPa (dilution with helium).

The gaseous reaction mixture was sampled directly using a Carle microvolume gas sampling valve (30 mm³), placed in the recirculation loop of the glass reactor, and in the outlet of the other two reactors. The reaction mixture was analysed on a gas

chromatograph (Hewlett-Packard 5750 B), equipped with a flame ionization detector. The isomers were completely separated at room temperature on a $6 \text{ m} \times 6.4 \text{ mm}$ column packed with 30 per cent *bis*-2(2-methoxyethoxy)ethyl ether on Chromosorb P (0.18 to 0.25 mm), using nitrogen as carrier gas. The g.c. signal was real-time processed by a PDP 11/10 minicomputer system, equipped with a g.c. signal-integrating program.⁽¹²⁾ The standard error of the peak areas was less than 0.06 per cent. Further processing was performed on a CDC-7300 computer system.

3. Equilibrium measurements

The equilibrium constant for the gas-phase reaction cis = trans is defined by $K_{CT} = (p_{trans}/p_{cis})_{eq}$ and was calculated directly from the results. (At the temperatures and pressures used no corrections had to be made for gas non-ideality.) In the batch systems equilibrium was assumed to be attained when the composition of the reaction mixture did not vary any more, and in the flow reactor when lowering the flow rate through the reactor did not result in a change in product composition. It was carefully verified that this effect was not caused by mass-transfer limitations.⁽¹¹⁾ The results of at least six analyses were averaged to obtain one value of the equilibrium constant, after which another temperature was chosen. To approach equilibrium from two sides, both isomers were used as sole reactant (or major component). In the



FIGURE 1. Equilibrium constant for the *cis-trans* isomerization of 2-butene(g) as a function of the temperature. -, Calculated from polynomial correlation. \bigstar , This work; \bigcirc , Meyer and Stroz;⁽⁶⁾ \bigstar , Happel *et al.*;⁽⁵⁾ \bigstar , Akimoto *et al.*;⁽⁷⁾ \blacktriangledown , Benson and Bose;⁽¹⁾ Golden *et al.*;⁽²⁾ \blacklozenge , Abell;⁽⁴⁾ \blacksquare , Macoll and Ross.⁽³⁾



FIGURE 2. Equilibrium constant for the *cis-trans* isomerization of 2-pentene(g) as a function of the temperature. -, Calculated from polynomial correlation. \bigstar , This work; $\textcircled{\bullet}$, Akimoto *et al.*⁽⁷⁾ \bigstar , Egger and Benson⁽⁸⁾ \blacklozenge , Abell.⁽⁴⁾

batch systems this two-sided approach was also obtained by raising or lowering the reaction temperature. In this way the activity of the catalyst could also be checked, since blank runs with inactive catalysts gave no indication that changes in composition were caused by adsorption or desorption effects of reactants when the temperature was changed. To avoid too much 2-pentene being transformed by metathesis into 2-butene and 3-hexene, we added 2-butene to suppress this reaction. The catalysts used were highly selective for metathesis; only above 700 K were 1-butene and 1-pentene (<1 per cent) detected.

The values obtained for the equilibrium constant for the gas-phase *cis-trans* isomerization of both 2-butene and 2-pentene are plotted in figures 1 and 2, respectively, together with the literature data. The standard deviation of K_{CT} for 2-butene, estimated from replicated results, is less than 0.5 per cent below 430 K, and less than 1 per cent at higher temperatures (accuracy and reproducibility). For 2-pentene this error amounts to less than 1 per cent below 320 K and less than 2 per cent at higher temperatures.

In our opinion the systematic deviations of the literature data from our results can be ascribed to the way of sample preparation, an incomplete separation of the isomers in the g.c. analyses, and the use of less advanced methods to evaluate the peak areas.⁽¹¹⁾ Only the results for 2-butene of Benson and Bose,⁽¹⁾ Happel *et al.*,⁽⁵⁾ and Meyer and Stroz,⁽⁶⁾ and the results for 2-pentene of Akimoto *et al.*,⁽⁷⁾ are compatible with our results.

4. Analysis of results

Our experimental results were analysed by means of functions expressing $\ln K_{CT}$ as a function of the temperature by minimizing the sum of squares of residuals, *i.e.* the differences between the experimental and calculated values of $\ln K_{CT}$, using the percentage error as a weighing factor. These functions were linear in the coefficients to be estimated, so the minimization could be done by linear regression. By statistical analysis of the regression results⁽¹³⁾ (lack-of-fit test, residual analysis, test on parameter significance, and test on the significance of the individual terms in the linear function) a third-order polynomial in (1/T) was selected:

$$\ln K_{\rm CT} = A_0 + A_1 (100 \text{ K/T}) + A_2 (100 \text{ K/T})^2 + A_3 (100 \text{ K/T})^3, \qquad (2)$$

valid over the temperature range 250 to 823 K. The parameter values, together with their 95 per cent confidence limits, are given in table 1. A combined regression on our results and the relevant literature $data^{(1,5-7)}$ did not result in a more accurate correlation.

We calculated with our correlation the standard Gibbs energy change $\Delta G^{\circ}(g)$, the standard enthalpy change $\Delta H^{\circ}(g)$, the standard entropy change $\Delta S^{\circ}(g)$, and the standard heat capacity change $\Delta C_{p}^{\circ}(g)$ of the reaction as a function of the temperature (figures 3 and 4). The 95 per cent confidence intervals of these functions were calculated from the variance-covariance matrix of the parameter estimates.⁽¹³⁾

5. Discussion

As can be seen from figures 1 and 2, the experimental K_{CT} values vary smoothly as a function of the temperature. The two-sided approach to chemical equilibrium, and the use of different reactor systems or different catalysts gave an accurate and consistent set of results. This allowed the calculation of related thermodynamic functions with a high precision over the whole temperature range. Moreover, the small error limits of $\Delta C_p^{\circ}(T)$ show that it is possible to obtain acceptable values of the second derivative of the present K(T) values.

TABLE 1. Parameter estimates together with 95 per cent confidence limits for the polynomial correlation of K_{CT} and T

	2-butene	2-pentene	
Points	72	59	
A	0.076 ± 0.058	0.69 ± 0.20	
A_1	0.54 ± 0.37	-1.92 ± 1.29	
A,	9.56 ± 2.91	16.9 ±10.4	
A_3	-5.12 ± 3.60	-10.4 ± 6.6	



FIGURE 3. Thermodynamic functions for the *cis-trans* isomerization of 2-butene(g) as a function of the temperature. (a). Standard Gibbs energy change (\bigstar , experimental values). (b). Standard enthalpy change (\diamondsuit , from enthalpies of combustion).⁽²⁵⁾ (c). Standard entropy change. (d). Standard heat-capacity change. – – – , Calculated from polynomial correlation, with 95 per cent confidence limits indicated by -----; – – – – , API values;⁽¹⁴⁾ – – – , NBS values;⁽¹⁵⁾ when omitted, figures 3(c) and 3(d), these are the same as the API values.



FIGURE 4. Thermodynamic functions for the *cis-trans* isomerization of 2-pentene(g) as a function of the temperature. (a). Standard Gibbs energy change (\bigstar , experimental values). (b). Standard enthalpy change (\blacksquare , from reference 25; \bigstar , from reference 29). (c). Standard entropy change. (d). Standard heat-capacity change. ———, Calculated from polynomial correlation with 95 per cent confidence limits (----); ———, API values.⁽¹⁴⁾ = - -, NBS values.⁽¹⁵⁾

2-Butene(g). The old API⁽¹⁴⁾ and NBS⁽¹⁵⁾ tables, having large error bounds, $[\approx 2 \text{ kJ} \cdot \text{mol}^{-1} \text{ for } \Delta G^{\circ}(T) \text{ and } \Delta H^{\circ}(T), \text{ and } \approx 2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \text{ for } \Delta S^{\circ}(T) \text{ and }$ $\Delta C_{a}^{\circ}(T)$], all fall outside our 95 per cent confidence limits (figure 3). The maximum in the $\Delta G^{\circ}(T)$ function of the API and NBS is not validated by the experimental results, and the $\Delta S^{\circ}(T)$ function does not change sign within our temperature range. These functions are mainly determined by the external rotations, hindered internal rotations, and molecular vibrations. By using more recent spectroscopic information⁽¹⁶⁻²¹⁾ and structural parameters⁽²²⁾ (table 2) it should be possible to calculate better values of these functions, as recently has been done by Chao and Zwolinsky.^(23,33) In such calculations often input quantities like vibrational wavenumbers, ΔH_{f}° , etc., are adjusted so as to bring the calculated and experimental values into reasonable agreement.[†] Although this kind of adjustment is arbitrary and empirical, for practical purposes it is valid and justified since the simple molecular model, *i.e.* that based on the rigid-rotor and harmonic-oscillator approximation, in the statistical-mechanical calculations causes these discrepancies. In this respect it is noted that the temperature dependency of ΔS° (table 3) is mainly determined by the difference in hindered internal rotation of the methyl rotors in the two 2-butenes. Chao⁽²³⁾ treated each $-CH_3$ top as independent of the presence of the other $-CH_3$ top in the molecule, each top having independent contributions to the entropy. Durig et al.,⁽¹⁶⁾ however, adopted a semi-rigid model in which the -CH₃ rotors do have coupling terms. This explains the different values for the energy barriers V_3 and possibly the smaller temperature dependency of Chao's ΔS° values (table 3).

In table 4 a comparison is given of $\Delta H^{\circ}(298.15 \text{ K})$ and $\Delta S^{\circ}(298.15 \text{ K})$ values in the literature, since these are frequently used as reference values for the calculation of thermodynamic functions at higher temperatures. Our values have the highest accuracy and fall within all of the error bounds of the listed values. The recent API value for $\Delta H^{\circ}(298.15 \text{ K})$, calculated from the enthalpies of combustion of the two isomers, is strikingly low. Obviously, it is very difficult to obtain high accuracy by this method.

	$10^{115} \frac{I_A I_B I_C}{g^3 \cdot cm^6}$	σε	$\frac{V_{\rm eff}}{\rm kJ\cdot mol^{-1}}$	$10^{40} \frac{I_r}{g \cdot cm^2}$	σ_{i}	Reference
Trans	13.8114	2	8.54	4.326	3	16, 22
Cis	17.8687	2	3.64 ^b	4.946	3	16 to 18

TABLE 2. Values of molecular properties of the 2-butenes(g)^a

^a $I_A I_B I_C$, product of the principal moments of inertia of the molecule; I_r , reduced moment of inertia of the $-CH_3$ group; σ_e , external symmetry number of the molecule; σ_i , symmetry number of the $-CH_3$ group; V_{eff} , effective energy barrier for internal rotation of the $-CH_3$ group.

^b From microwave spectroscopy a value of $3.13 \text{ kJ} \cdot \text{mol}^{-1}$ has been obtained.^(17,18) In these studies, however, no coupling between the two methyl rotors was taken into account.

† Instead of the vibrational wavenumbers⁽²²⁾ 224 and 261 cm⁻¹. Chao used the values 269 and 371 cm⁻¹ for *trans*-2-butene, so that the calculated value $S^{\circ}(g) = 288.55 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ at 274.04 K is consistent with the experimental entropy reported by Guttmann and Pitzer.⁽²⁴⁾

$-\Delta S (g)/(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$				$-\Delta S^{(g)}(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})$			
T/\mathbf{K}	Experimental	Chao ⁽²³⁾	API/NBS	T/\mathbf{K}	Experimental	Chao ⁽²³⁾	API/NBS
298.15	5.10±0.12	4.87	4.40	600	1.18±0.12	3.00	- 0.20
300	5.05 ± 0.12	4.84	4.40	700	0.74 ± 0.18	2.79	-0.80
400	3.01 ± 0.11	3.83	2.10	800	0.44 ± 0.24	2.65	-1.20
500	1.87 ± 0.06	3.31	0.60				

TABLE 3. Comparison of $\Delta S'$ (g) values for the *cis-trans* isomerization of 2-butene at different temperatures

TABLE 4. Standard enthalpy and entropy change for the *cis-trans* isomerization of 2-butene (2s error limits) at T = 298.15 K

References	$\frac{-\Delta H^{\circ}(\mathbf{g})}{\mathbf{k}\mathbf{J}\cdot\mathbf{mol}^{-1}}$	$\frac{-\Delta S^{\circ}(g)}{J\cdot K^{-1}\cdot \mathrm{mol}^{-1}}$	References	$\frac{-\Delta H^{-}(g)}{kJ \cdot mol^{-1}}$	$\frac{-\Delta S^{2}(g)}{J\cdot K^{-1}\cdot mol^{-1}}$
This work ^{<i>a</i>} Kistiakowski et al. ⁽²⁶⁾ Prosen et al. ⁽²⁷⁾ Golden et al. ^{(2) d}	$\begin{array}{r} 4.34 \pm 0.04 \\ 3.97 \pm 0.59^{h} \\ 3.14 \pm 1.55^{\circ} \\ 5.0 \pm 0.6 \end{array}$	5.10 ± 0.12 5.2 ± 1.4	Akimoto et al. ⁽⁷⁾ Meyer and Stroz ^{(6) e} API 1972 ⁽²⁵⁾ Chao ^{(23) f}	$\begin{array}{r} 4.18 \pm 0.17 \\ 4.14 \pm 0.20 \\ 5.4 \pm 2.0 \\ 4.18 \end{array}$	$4.85 \pm 0.60 \\ 4.27 \pm 0.70 \\ 4.87$

^{*a*} Values of $\Delta H^{\circ}(g)$ and ΔS (g) are not independent.

^b Calculated from the enthalpies of hydrogenation of the butenes.

^c Calculated from the enthalpies of combustion at 298.15 K.

^d These values are extrapolated from the values at 500 K by Golden *et al.*, assuming that $\Delta C_p(g, 400 \text{ K}) = 0$. ^e Error limits estimated.

^f Error limits estimated to be +0.2 to 1.0 per cent, according to Chao.⁽²³⁾

2-Pentene(g). Due to lack of molecular properties, calculation of thermodynamic functions of the two 2-pentenes is not possible. Therefore, Kilpatrick et al.⁽²⁸⁾ approximated these functions by an incremental method, based on those of the lower alkenes. In this way an accumulation of errors is likely to occur, so it is not surprising that the deviation of the API and NBS values from our results (figure 4) is larger than for 2-butene. Since the NBS $\Delta C_n^{\circ}(T)$ reasonably fits our results, the temperature dependence of the related other functions also corresponds well. The constant difference for the $\Delta H^{\circ}(T)$ and $\Delta G^{\circ}(T)$ functions is caused by the $\Delta H^{\circ}(298.15 \text{ K})$ reference value, based on the enthalpy-of-formation tables of the two 2-pentenes. The API values were based on the enthalpy of hydrogenation at 355 K of an unknown cis-trans mixture of 2-pentene.⁽²⁶⁾ To use this latter value for the calculation of ΔH_{f}° , Prosen and Rossini⁽²⁹⁾ assumed questionably (compare figures 3b and 4b) that the enthalpy difference between the two 2-pentene isomers equals that of the 2-butenes at 355 K. The $\Delta H^{\circ}(298.15 \text{ K})$ NBS value (table 5) was calculated from the tabulated enthalpies of combustion of the two 2-pentenes.⁽¹⁵⁾ If these enthalpies of combustion had been applied in the ΔH_f° tables an excellent agreement of the $\Delta G^{\circ}(T)$ and $\Delta H^{\circ}(T)$ functions with our experimental results would have been obtained. It is obvious from figure 4 that the API compilation for 2-pentene is very poor. This might be explained by the fact that, among others, 1-butene was used to calculate the properties of the two 2-pentenes. The thermodynamic functions of 1-butene, however,

are the most badly determined ones of the *n*-butenes. Based on isomerization studies corrections for the API entropies have already been suggested.^(2, 5, 6) The good correspondence between $\Delta H^{\circ}(500 \text{ K})$ of the API and of Egger and Benson⁽⁸⁾ (3.05 kJ·mol⁻¹), as mentioned by these authors, should be considered as purely accidental since at this temperature the API compilation intersects our correlation (figure 4b). Therefore, this result cannot be considered as a support for the API compilation. The $\Delta H^{\circ}(298.15 \text{ K})$ and $\Delta S^{\circ}(298.15 \text{ K})$ values of Egger and Benson⁽⁸⁾ deviate considerably from our values, because they used an inaccurate ΔC_p° to extrapolate their results to 298.15 K. The 298.15 K reference values of Akimoto *et al.*⁽⁷⁾ correspond well with our results, as could be expected from the compatibility of their values with ours. Only the value of Coops *et al.*⁽³⁰⁾ based on the combustion of the liquid pentenes, combined with ΔH_{vap}° from the API tables, does not agree within the error limits with our values.

Although new values for the thermodynamic functions of the 2-butenes have been calculated by using more accurate values for the energy barrier to internal rotation of the methyl groups, moments of inertia, and frequency assignments,⁽²³⁾ these newly calculated functions still do not correspond well with our experimentally obtained values. The main problem remains the description of the hindered internal rotation, which was made by means of the energy function:⁽³¹⁾

$$V = \frac{1}{2}V_3 \{1 - \cos(3\alpha)\}.$$
 (3)

Solutions of the wave equation will yield the energy levels from which the contributions for the hindered internal rotation can be calculated. This has been done for propene, $^{(32,33)}$ and 2-butene, $^{(23)}$ assuming no coupling between the methyl rotors. More definite values can be obtained by an extended energy function and taking into account the coupling between the two methyl rotors in the butene molecule. ⁽¹⁶⁾ In re-evaluating the tabulations for the 2-pentenes, the NBS compilation offers the best starting points. The main problem is again the description of the internal rotations in the 2-pentene molecules. Since the temperature dependence of $\Delta S^{\circ}(T)$ is mainly determined by the hindered internal rotation, our results might provide a good basis for the correction of the description of the internal rotation.

As is shown in this study for the calculation of $\Delta C_p^{\circ}(T)$, second derivatives can be

TABLE 5. Standard enthalpy and entropy change for the *cis-trans* isomerization of 2-pentene (2s error limits) at T = 298.15 K

References	$\frac{-\Delta H^{\circ}(\mathbf{g})}{\mathbf{kJ}\cdot\mathbf{mol}^{-1}}$	$\frac{-\Delta S^{\circ}(g)}{J\cdot K^{-1}\cdot \mathrm{mol}^{-1}}$	References	$\frac{-\Delta H^{\circ}(g)}{kJ\cdot mol^{-1}}$	$\frac{-\Delta S^{\circ}(g)}{\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1}}$
This work ^a API ⁽¹⁴⁾ NBS ^(15, 29) API 1972 ⁽²⁵⁾	$\begin{array}{r} 4.90 \pm 0.08 \\ 3.7 \ \pm 2.5 \\ 4.5 \ \pm 3.0^{b} \\ 4.1 \ \pm 2.5^{b} \end{array}$	$\begin{array}{r} 3.56 \pm 0.28 \\ 5.9 \ \pm 4.0 \\ 4.0 \ \pm 4.0 \end{array}$	Akimoto et al. ⁽⁷⁾ Egger and Benson ^{(8) c} Coops et al. ⁽³⁰⁾	4.81±0.25 3.8±1.2 0.88±0.75 ^b	3.39 ± 0.84 -1.7 ±1.3

^{*a*} $\Delta H^{\circ}(g)$ and $\Delta S^{\circ}(g)$ are not independent.

^b Calculated from enthalpies of combustion.

^c Extrapolated values.

calculated from unequally spaced tabulated quantities by least-squares correlation, provided that these quantities are accurate and cover a sufficiently wide range of the independent variable.

A listing of the experimental K_{CT} values for 2-butenes and 2-pentene, together with the experimental conditions, and tables of the calculated thermodynamic functions of the 2-butenes can be obtained from the authors.

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