

Nitric Oxide and Iodine Catalyzed Isomerization of Olefins.

VI. Thermodynamic Data from Equilibrium Studies of the Geometrical and Positional Isomerization of *n*-Pentenes¹

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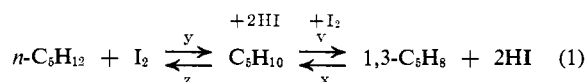
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Abstract: The equilibrium of the iodine catalyzed gas phase isomerization of 1-pentene and 2-pentene has been studied over a temperature range from 114.5 to 335.3°. The measured values for constants of both the positional ($K_{3,4}$) and the geometrical ($K_{5,6}$) isomerizations yield straight lines when plotted vs. $1/T$ (°K.). Least-square fits of data to linear equations using a standard computer regression program yield with standard errors (for a mean temperature of 500°K.): $\Delta H_{3,4}^\circ = -2.59 \pm 0.08$ kcal./mole and $\Delta S_{3,4}^\circ = -1.37 \pm 0.02$ gibbs/mole; $\Delta H_{5,6}^\circ = -0.73 \pm 0.07$ kcal./mole and $\Delta S_{5,6}^\circ = 0.40 \pm 0.14$ gibbs/mole. Our data can be equally well fitted to both linear and quadratic equations, indicating that $\Delta C_p^\circ_{3,4}$ (400–600°K.) and $\Delta C_p^\circ_{5,6}$ are very close to 0. Our data for the heats of isomerization are in very good agreement with the values of $\Delta H_{3,4}^\circ(500^\circ\text{K.}) = -2.72 \pm 0.5$ kcal./mole and $\Delta H_{5,6}^\circ(500^\circ\text{K.}) = -0.49 \pm 0.36$ kcal./mole calculated from the data on the heat of formation reported by Prosen and Rossini^{2a} and quoted in the API tables.^{2b} The entropy differences between the isomers obtained from our direct experimental data agree reasonably well with the comparative estimates of Kilpatrick, *et al.*,³ of $\Delta S_{3,4}^\circ(500^\circ\text{K.}) = -1.64$ gibbs/mole and of $\Delta S_{5,6}^\circ(500^\circ\text{K.}) = -0.09$ gibbs/mole. Values for partial group contributions and corrections thereof have been calculated from the data of this work and results reported earlier from related studies on *n*-butenes and 1,3-pentadienes.^{4a–d} They are in excellent agreement with earlier estimates.⁵

A series of previous studies^{4a–e} on iodine and nitric oxide catalyzed gas phase isomerizations of olefins has demonstrated the value of this method in determining precise differences in the thermodynamic properties of olefins by measuring the composition of equilibrated mixtures of the isomers. Applying this method to the isomerization of the normal pentenes yields not only the direct values for the differences in the enthalpies and entropies of these isomers but, when combined with our earlier measurements on *n*-butenes, yields more reliable, experimentally substantiated group contributions (increments) involved.⁵ Variable amounts of *n*-pentane and 1,3-pentadiene are formed as the only distinctly recognizable side products in our system.

This is in agreement with the reported formation of *n*-butane and butadiene in the isomerization of *n*-butenes.^{4b} The over-all reaction scheme for the formation of these side products is given by



The equilibrium $K_{v,x}$ is almost instantaneously established. It furnishes the HI for the much slower reaction *z*. Depending on the experimental conditions used, up to 40% of the final equilibrated isomer mixture consists of *n*-pentane (compare Table I). As has

previously been shown,^{4d} 1,3-pentadiene is not stable under these conditions, owing to the iodine catalyzed dimerization and cyclization reactions. As a consequence, large amounts of our initial iodine pressure are used up during the first minutes of the reaction, forming HI. The subsequent formation of *n*-pentane thus enhances the isomerization rate of the pentenes by regenerating iodine. The amount of *n*-pentane formed increases with increasing conversion and initial amount of iodine present (compare Table I).

Experimental Section

A. Procedure and Apparatus. The method and experimental setup used in the "thermal" experiments have been described in detail earlier.^{4a} Iodine or NO was added to the reaction vessel first, then the hydrocarbon. Reactions where iodine atoms have been generated photochemically were carried out in an oven with a built-in, very fast air circulation system. The temperature was controlled using a proportional controller and had a measured variation of within $\pm 0.2^\circ$. A 200-w. tungsten bulb, placed inside the oven, illuminated the 200-ml. Pyrex glass, sealed sample tubes containing the pentene-iodine mixtures. The sample tubes were constructed in such a way as to avoid any contact of the hydrocarbons and iodine in their condensed phases while preparing the sample mixture. This avoids the formation of iodides and subsequent side products. Rather small amounts of iodine were used (20–80 mg.). The reaction was quenched by connecting the hot sampling tubes to our regular "thermal" reaction system and withdrawing the sample through a break-off seal. In all our experiments the hydrocarbon fraction was separated from I_2 and HI by passing the gaseous mixture first through a glass wool filled trap at -15° , which removed all of the higher-boiling hydrocarbons (pentadiene dimers and eventually some stable iodides), together with iodine. The second trap at -15° , filled with glycine, removed any remaining condensable materials and most of the HI. The third trap was kept at room temperature and was filled with glycine, to remove the remaining HI. The hydrocarbons were then condensed over liquid nitrogen in a fourth trap and transferred to a sampling bulb for analysis.

The reaction vessel used in our "thermal" experiments was a Teflon-coated^{4d} glass vessel of 800-ml. volume.

B. Materials. The pentenes were obtained from Phillips Petroleum Co., Bartlesville, Okla. 1-Pentene was of "pure grade" (99.4%), and *cis*-2-pentene was of "technical grade" (96.5%). Analysis of the mixture of 2-pentene of "pure grade" (99.8%)

(1) This work has been supported in part by Grant No. AP-00353-01 from the U. S. Public Health Service Air Pollution Division to Stanford Research Institute.

(2) (a) E. J. Prosen and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **36**, 269 (1946); (b) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953.

(3) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **36**, 559 (1946).

(4) (a) D. M. Golden, K. W. Egger, and S. W. Benson, *J. Am. Chem. Soc.*, **85**, 1385 (1963); (b) K. W. Egger, D. M. Golden, and S. W. Benson, *ibid.*, **86**, 5420 (1964); (c) S. W. Benson, K. W. Egger, and D. M. Golden, *ibid.*, **87**, 468 (1965); (d) K. W. Egger and S. W. Benson, *ibid.*, **87**, 3311 (1965); (e) *ibid.*, **87**, 3314 (1965).

(5) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 662.

Table I. Composition of Equilibrated Mixtures of Pentene Isomers

Temp., °C.	Starting compound			Catalyst pressure, torr	Time, min.	<i>n</i> -Pentane ^b of total C ₅ , %	Final equilibrium ratios		
	1 or 2	Isomer ^a [<i>t</i> / <i>l</i>] ₀	Pressure, torr				[<i>t</i> / <i>c</i>] _t = <i>K</i> _{3,4}	[<i>t</i> / <i>c</i>] _t = <i>K</i> _{5,6}	
114.5		14.49	1.14	239	~15 ^d	1.8	12.51	3.25	
		9.97	1.14	214	~15 ^d	2.5	12.67	3.19	
141.9		...	2.63	70.4	31.4	17.3	7.61 ^c	2.86	
182.0		14.49	1.14	321	~26 ^d	1540	10.6	8.40	2.60
		10.30	1.29	100.0	~9 ^d	300	12.6	9.92 ^c	2.88
184.1		9.97	1.14	368.5	~9 ^d	1625	2.9	8.87	2.54
		14.51	1.14	218.2	32.8	4080	13.5	8.70	2.89
		9.97	1.14	109.9	34.1	1352	5.0	9.36	2.66
210.3		13.0	1.32	145.9	53.1	5455	32.1	7.45	2.98
246.5	1			151.2	17.8	145	0.8	2.11 ^c	2.44
	1			68.5	3.6	946	2.4	4.28 ^c	2.37
	1			66.8	10.2	335	1.0	4.02 ^c	2.32
	2		1.16	85.2	21.0	3110	16.1	7.59 ^c	2.37
246.3	2		1.16	100.9	55.6	1424	13.6	6.84 ^c	2.43
		2.66	1.11	92.8	35.6	1849	22.5	6.27	...
		5.47	1.14	121.8	14.6	117	2.8	6.10	2.46
		7.48	2.13	48.4	20.0	944	17.5	6.14	2.50
299.4		5.47	1.14	83.8	28.0	1105	15.3	6.38	...
		1.75	1.16	346.5	61.7	149	12.3	4.66	2.38
	2		1.16	114.7	15.8	944	42.3	4.83	2.36
		5.56	1.16	226.1	25.8	150	11.1	4.83	2.30
335.3	2		1.16	107.1	34.6	973	24.4	4.68	2.36
	2		1.16	74.0	20.8	1575	43.2	4.74	2.45
	1			56.6	14.8	1215	31.1	4.80	2.27
	1			59.3	16.8	15	0.8	2.71 ^c	2.36
	2		1.16	100.7	37.8	207	20.7	4.93	...
	2		1.16	90.0	3.8	700	26.2	4.60	2.11
	2		1.16	154.1	33.7	117	30.0	4.20	2.43
	2		1.16	54.9	25.7	89	18.3	4.43	2.23
		2.66	1.11	56.7	12.9	6	1.9	4.30	2.49
		2.66	1.11	176.4	5.5	14	1.6	4.18	2.23
	2.66	1.11	180.5	21.4	30	9.3	4.14	2.41	
	2.66	1.11	209.5				2.92 ^c	1.98 ^c	
	5.47	1.14	141.4		175.4	120	0.7	4.79 ^c	2.08
	5.47	1.14	106.9	15.6	207.9	933	1.6	4.79 ^c	2.08
	5.47	1.14	100.8	2.4		21	5.3	4.41	2.09
						17	1.2	4.68	2.10

^a 1, 2, *t*, and *c* stand for 1-pentene and 2-pentene and *trans*- and *cis*-2-pentene, respectively. ^b Result from gas chromatographic analysis. ^c Did not reach equilibrium, the conversion being too small. ^d Generation of iodine atoms photochemically.

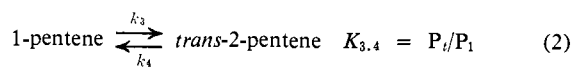
showed a *trans/cis* ratio of 1.16. Reagent grade resublimed iodine was used.

C. Analysis. Analysis of our mixtures was carried out by gas-liquid chromatography, using a Model 720 F and M gas chromatograph with TC-detector and a 6-ft. 0.25-in. column of ethylene glycol, saturated with silver nitrate, coated (17%) onto Chromosorb P (45/60 mesh).⁶ The column was operated at 10–12° using a helium flow rate of 40 ml./min.

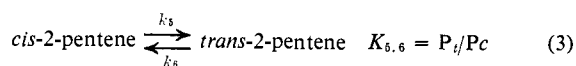
A disk chart integrator gave peak areas. We measured the following retention times after the air peak: (*trans*-2-pentene ≡ 1.0) *n*-pentane, 0.257; *trans*-2-pentene, 1.0; 1-pentene, 2.78; *cis*-2-pentene, 3.28; *trans*-1,3-pentadiene, 9.6; and *cis*-1,3-pentadiene, 1,4-pentadiene, and cyclopentene, between 18.3 and 18.5. The last three components are in part irreversibly retained at this temperature but can be quantitatively eluted at 30°. The same column of Dow Corning silicone oil 710 used in the studies of 1,3-pentadiene^{4d,e} was used to identify the 1,3-pentadienes and cyclopentene.

Results

In accord with our notation for the isomerization of butene,^{4a-c} the equilibrium constants for the positional and geometrical isomerization are denoted as



and



(6) B. Smith and R. Ohlson, *Acta Chem. Scand.*, **16**, 351 (1962).

The results from measurements of the equilibrium constants *K*_{3,4} and *K*_{5,6} for temperatures ranging from 114.5 to 335.3° are given in Table I. The values of the equilibrium constants are quite consistent and reproducible. The iodine pressure was varied up to 16-fold and the hydrocarbon pressure about 6-fold. The ratio of hydrocarbon to iodine pressure covered a range between 2.1 and 42. The same isomer ratios are obtained, starting from either side of the composition of an equilibrated mixture.

The data are consistent, using either NO or thermally or photochemically generated iodine atoms as catalysts. The values of *K*_{3,4} show maximum deviations between ± 3.6% at the highest temperature and ± 1.1% at low temperatures. This is just about what one expects, given an uncertainty in the analysis of ± 1% (maximum deviation). The values of *K*_{5,6}, on the other hand, show a much larger scatter than one expected from the uncertainties in the analysis alone (~ ± 1.5% maximum). While the maximum errors are still reasonable at 573°K. (± 4.9%) and at 520°K. (± 3.9%), they are as much as ± 11% at 609°K. Besides the fact that the scatter in the data increases strongly as we go to high temperatures, there seems to be no other dependence on any of the known and controllable experimental parameters. The fact that the *K*_{3,4} values based on the same analysis are consistent shows that the handling of the sample cannot

Table II. Thermodynamic Data for a Mean Temperature of 500°K. from the Analysis of the Equilibrium Constants $K_{3,4}$ and $K_{5,6}$ between 400 and 600°K.

Data used ^a	Equation	MC _{3,4} ^b	MC _{5,6} ^b	$\Delta S^{\circ}_{3,4}$	$\Delta H^{\circ}_{3,4}$	$\Delta H^{\circ}_{5,6}$	$\Delta S^{\circ}_{5,6}$	$\Delta C_p^{\circ}_{3,4}$	$\Delta C_p^{\circ}_{5,6}$
All	Linear	0.9912	0.8851	-1.01 ± 0.01	-2.39 ± 0.07	-0.73 ± 0.07	0.40 ± 0.14		
	Quadratic	0.9933	0.8861	-1.07 ± 0.05	-2.44^c	-0.72^c	0.41 ± 0.10	-4.0 ± 1.8	0.9 ± 2.0
Reduced	Linear	0.9899	0.8299	-1.37 ± 0.02	-2.59 ± 0.08	-0.65 ± 0.08	0.54 ± 0.16		
	Quadratic	0.9916	0.8305	-1.79 ± 0.2	-2.78^c	-0.66^c	0.51 ± 0.12	$+9.1 \pm 5.3$	1.0 ± 3.3
Normalized	Linear	0.9931	0.9415	-0.86 ± 0.09	-2.31 ± 0.04	-0.75 ± 0.04	0.35 ± 0.09		
	Quadratic	0.9959	0.9467	-1.09 ± 0.02	-2.46^c	-0.69^c	0.45 ± 0.03	-5.3 ± 1.0	2.4 ± 1.2
Kilpatrick, <i>et al.</i> ³				-1.64	-2.72 ± 0.5	-0.49 ± 0.4	-0.09	-0.67	1.52

^a Compare text. ^b MC stands for multiple correlation coefficient and is a measure of the accuracy of the fit to the given equation. For ideal fit MC equals 1.0000. ^c Error smaller than 0.01.

be responsible for these differences. We can therefore conclude that some kind of stereospecific side reaction seems to affect primarily the *cis*-2-pentene. The large scatter could probably have been avoided, at least in part, if separate experiments had been carried out for the equilibrium studies of the positional and the geometrical isomerization, as the geometrical equilibrium is established very much faster.

Figures 1 and 2 show Van't Hoff plots of the logarithm of the equilibrium constants vs. $1/T$ (°K.) for the data listed in Table I. The data have been fitted to both quadratic and linear equations, using a regular least-squares fit regression program on a Burroughs 5500 computer. In order to obtain the best physical representation of our experimental measurements, we analyzed our data three times by giving them different relative statistical weight. For the results given in the first two columns of Table II we used the complete set of data, giving every measurement the same statistical weight. This treatment gives very little weight to the few low-temperature data obtained from photochemical experiments. The values in the middle column are obtained when disregarding the photochemical experiments at 114.5° but still giving the same relative weight to the remaining bulk of the data. Finally, we computed the data by disregarding the single points at 210.3 and 141.9° and attributing the same weight to every set of data at any of the given temperatures. This last method emphasizes the low-temperature photochemical experiments. The error limits quoted in Table II are standard deviations, calculated from the computed standard errors in the coefficients of the linear or quadratic equation. Where no value is given, the error is smaller than 0.01. The multiple correlation coefficient (MC) listed in Table II is a direct measure of the overall accuracy of the fit of our data to either a linear or quadratic equation. In the case of an ideal fit, MC equals 1.0000.

The values of MC_{3,4} and MC_{5,6} clearly show that, for all three selections of our data, the fit to a linear equation is equally as good as the one to a quadratic equation. The representation of our data with a linear equation and its implication of $\Delta C_p = 0$ (400–600°K.) is therefore justified. The consistently lower values for MC_{5,6} reflect the previously mentioned larger scatter in the $K_{5,6}$ data. The thermodynamic values for the geometrical isomerization, listed in Table II, are practically unaffected by the different statistical weight applied to the data. The thermodynamic values for the positional isomerization show a dependence on the statistical treatment of the equilibrium constants.

This is a consequence of the different weight attributed to the two photochemical experiments at 114.5°, which gave equilibrium constants that are ~15% lower than expected from the calculated value using a linear equation. The same effect can be seen in the values of $\Delta C_{p3,4}$. Disregarding the two low temperature measurement results in a change in $\Delta C_{p3,4}$ from negative to positive values. We take this to mean that for some reason these data are too low.

The ΔC_p values, quoted in Table II, are obviously unreasonably large and have only limited significance. All it means is that our data do not warrant a distinction between $\Delta C_p(T) = 0$ and $\Delta C_p(T) \approx 0-2$ cal./deg. mole, which would be a physically reasonable value from all that is known about the differences in heat capacities of the isomers in the *n*-olefin series.^{2b}

The most reasonable representation of our data for the positional isomerization is the reduced linear form. For the geometrical isomerization we can use all the data to compute the thermodynamic values using a linear equation (Figures 1 and 2)

$$2.303R \log K_{3,4} = -(1.37 \pm 0.02) + (2590 \pm 80)(1/T)$$

$$2.303R \log K_{5,6} = (0.40 \pm 0.14) + (732 \pm 70)(1/T)$$

As mentioned in the introduction, large quantities of *n*-pentane are formed as the major and only detectable side product in the final hydrocarbon fraction (using our standard v.p.c. procedure). The driving force for the formation of such large quantities of *n*-pentane is the equilibrium of $K_{v,x}$ (eq. 1), which is measured to be established within seconds up to a few minutes, depending on the temperature used. The source of the 1,3-pentadiene is the very fast unimolecular elimination reaction of HI from 3-iodo-1-pentene⁷ which in turn originates by I₂ scavenging of the initially formed secondary pentenyl radicals.

The presence of 1,3-pentadiene in the initial stages of the reaction and to a smaller extent at the end of the experiment was followed by g.l.c. (using a Dow 710 column^{4d,e}) on a few separate nonequilibrium runs. In the final reaction mixtures large quantities of substituted cyclohexenes (dimer) as well as some cyclic pentenes have been found.

These results seem to indicate that 1,3-pentadiene is depleted from the equilibrium system, mainly *via* a dimerization route and significantly slower by cyclization.⁸ For some experiments over-all mass balances

(7) Results from studies on HI-olefin systems will be reported in a separate communication.

(8) K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 241 (1966).

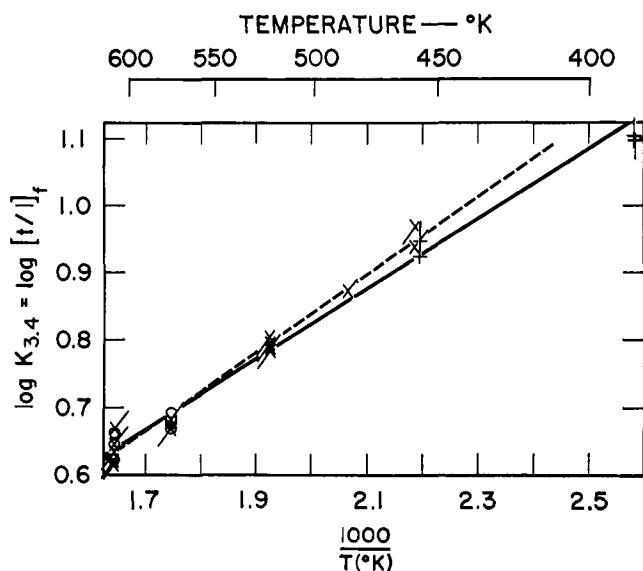


Figure 1. Van't Hoff plot of the equilibrium constant ($K_{3,4}$) for the positional isomerization of *n*-pentene. Equilibrium values are indicated with ● starting with 1-pentene, ○ starting with 2-pentene. × or + is used for a starting isomer mixture rich in *trans*-2-pentene, × or + for a mixture rich in 1-pentene. × or × are used where iodine atoms are thermally generated, ++ for photochemical experiments. The best fit to our data is shown using a solid line, values taken from the API tables are represented with a dashed line.

have been measured which checked out reasonably well with the analysis of the pentene isomers and *n*-pentane and the initial and final iodine concentration.

Discussion

There are only very few values for $K_{3,4}$ and $K_{5,6}$ available in the literature.⁹⁻¹¹ From liquid phase base-catalyzed isomerization studies, Schriesheim and Rowe⁹ obtained a value for $K_{5,6}$ at 55° of 4.35 ± 0.4 , which compares to 3.76 ± 0.36 predicted from this work. Using data from heterogeneous gas phase isomerization studies reported by Ewell and Hardy¹⁰ and by Moore, *et al.*,¹² we calculate $K_{3,4}$ to be 3.8 (364°) and 3.4 (510°), respectively. These values compare with our extrapolated data of 4.0 and 2.7. In view of the rather crude measurements, all these data are consistent with the results of this work. Very few calorimetric measurements on pentenes have been reported. Kistiakowsky, *et al.*,¹³ reported the heat of hydrogenation for a mixture of uncertain *cis/trans* composition of 2-pentene. They tentatively assigned values to either of the geometrical isomers, assuming an equilibrium mixture of the isomers at 36.5° of $P_t/P_c = 1.86$, based on the same value for the equilibrium of *trans*- and *cis*-2-butene.¹⁴ We calculate $K_{5,6}$ (310°K.) for the geometrical isomers of the 2-pentene to be 4.02 instead.

(9) A. Schriesheim and C. A. Rowe, *Tetrahedron Letters*, **10**, 405 (1962).

(10) R. H. Ewell and P. E. Hardy, *J. Am. Chem. Soc.*, **63**, 3460 (1941).

(11) W. O. Haag and H. Pines, *ibid.*, **82**, 387 (1960).

(12) L. D. Moore, J. R. Kaiser, and R. C. Odioso, Preprints, Division of Petroleum Chemistry, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, Vol. 6, No. 4, p. C-47.

(13) (a) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 137 (1936); (b) *ibid.*, **57**, 876 (1935).

(14) The correct value for $K_{5,6}$ (310°K.) is 3.74 instead.^{4a}

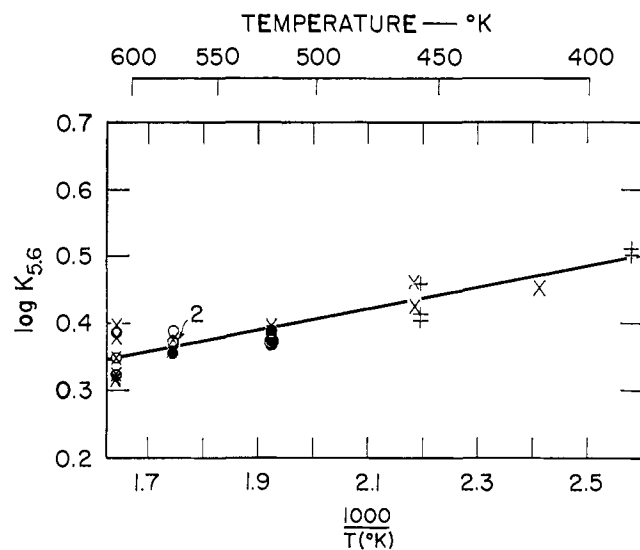


Figure 2. Van't Hoff plot of the equilibrium constant ($K_{5,6}$) for the geometrical isomerization of 2-pentene. Equilibrium values are indicated with ● starting with 1-pentene, ○ starting with 2-pentene ($t/c = 1.16$). × or + are used for a starting isomer mixture rich in *cis*-2-pentene, and indicate thermal or photochemical generation of iodine atoms, respectively (numbers indicate overlapping points).

Using Kistiakowsky's data and our value for $K_{5,6}$ and taking the difference in the heat of formation of the isomers as $\Delta H_f^{\circ}{}_{5,6}(300^{\circ}\text{K.}) = -0.93$ kcal./mole,¹⁵ we obtain for the heats of hydrogenation and the heats of formation of the isomers

$$\Delta H_h^{\circ}(298^{\circ}\text{K.}) \text{ trans } -27.21 \pm 0.2 \quad (-27.41 \pm 0.2)^{2a}$$

$$\text{ cis } -28.14 \pm 0.2 \quad (-28.49 \pm 0.2)^{2a}$$

$$\Delta H_f^{\circ}(298^{\circ}\text{K.}) \text{ trans } -7.63 \pm 0.2 \quad (-7.59 \pm 0.3)^{2a}$$

$$\text{ cis } -6.70 \pm 0.2 \quad (-6.51 \pm 0.3)^{2a}$$

The values given in parentheses refer to the values calculated by Prosen and Rossini,^{2a} based on the same experimental data and using the equilibrium value reported by Kistiakowsky, *et al.*^{13a} They assumed the difference of $\Delta H_f^{\circ}{}_{5,6}$ (298°K.) in the 2-pentenes to be the same as that for the 2-butene isomers, for which they used 1050 cal.¹⁶

The differences in enthalpies and entropies given by Kilpatrick, *et al.*,³ and quoted in the API^{2b} tables are shown in Table II for a temperature of 500°K. These data are based on no direct experimental data except for the reported heats of hydrogenation of Kistiakowsky, *et al.*^{13a} Comparative estimates and the values for the butenes and other homologs were used as a basis to derive structural increment values, to compute the higher hydrocarbons in a given series. While our direct experimental data essentially substantiate the estimates of Kilpatrick, *et al.*, it should be pointed out that the values for the *n*-butenes which they used to derive the *n*-pentene data have shown rather large discrepancies, especially in the $\Delta S^{\circ}{}_{\text{isom}}$ (~ 1 cal./deg. mole) when compared with direct experimental data.^{4a}

Using the method of iodine or nitric oxide catalyzed isomerization of olefins we obtained in independent

(15) The data of this work yield $\Delta H_f^{\circ}{}_{5,6}$ (500°K.) = -0.73 ± 0.07 . If we assign $\Delta C_p^{\circ}{}_{5,6}$ (400°K.) $\sim +1.0$ cal./deg. mole we obtain the quoted value.

(16) More recent data from equilibrium studies give a value of 1250 cal. instead.^{4c}

Table III. Thermodynamic Data from Equilibrium Measurements of the Iodine or Nitric Oxide Catalyzed Isomerization

	ΔH_f° , kcal.	ΔS_f° , e.u.
[<i>trans</i> -2-Butene]-[1-butene]	-2.8 ± 0.2	-3.1 ± 0.4
[<i>trans</i> -2-Butene]-[<i>cis</i> -2-butene]	-1.2 ± 0.15	-1.25 ± 0.2
[<i>trans</i> -2-Pentene]-[1-pentene]	-2.6 ± 0.2	-1.4 ± 0.1
[<i>trans</i> -2-Pentene]-[<i>cis</i> -2-pentene]	-0.9 ± 0.15	$+0.4 \pm 0.15$
[<i>trans</i> -1,3-Pentadiene]-[<i>cis</i> -1,3-pentadiene]	-1.0 ± 0.20	-0.1 ± 0.43

studies the thermodynamic data listed (for 25°)^{4a,d} in Table III.

Based on these values one can generate partial group contributions (increments) for the estimation of entropies and heats of formation of geometrical and positional isomers (gas phase, 25°, 1 atm.), in accordance with ref. 5. Using the symbolism defined by Benson⁵ in Table D-3 the group contributions and *cis* corrections have been calculated as shown in Table IV. These values are arrived at as follows.

Table IV

	S° , e.u.	ΔH_f° , kcal.
[C _d (C _d)(C)(H) + C(C _d)(H) ₃] _t <i>n</i> -Butene	37.6	-1.43
<i>n</i> -Pentene	38.3	-1.30
Average	37.9	-1.37
Correction for <i>cis</i> isomer		
2-Butene	+1.2	1.0
2-Olefins (C ₅ and higher)	0	1.0
3-Olefins	-1.2	1.0

For the geometrical isomers, the difference in the heats follows directly from Table III. For the entropy calculation *trans*-2-butene is taken as a standard.

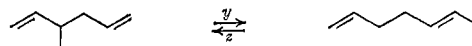
The fact that the *cis* form of the molecule has more entropy and thus more motion reflects the net result of

compensating and superimposed fractional contributions to the entropy. Changes in entropy differences of the geometrical isomer pairs in any given series of olefins has to arise essentially from differences in the barriers to free rotation of the end groups.

One can assume that the *trans* configurations of the various olefins will in general have very closely the same barriers to free rotation, whereas the barrier in the *cis* configurations depends on the restriction to internal rotation exercised by the end groups. Methyl groups will be less hindered than ethyl groups, and no differences are expected between ethyl and bulkier *n*-alkyl groups.

It is therefore reasonable to base all group contribution values involving geometrical isomers of olefins on the *trans* form and apply *cis* corrections. The intrinsic group values for the entropies are arrived at, taking symmetry contributions in the molecules into account. The values for group increments reported in this paper using the recent thermodynamic data obtained from equilibrium studies are in excellent agreement with the values calculated by Benson,⁵ which are further substantiated by this work, and their uncertainty has been reduced.

To test these partial group contributions we use the equilibrium data reported by Amano and Uchiyama¹⁷ for the isomers 1,5-heptadiene and 3-methyl-1,5-hexadiene. Correcting for $\Delta C_{p,y,z}^\circ = -3.2$ e.u. (ref. 5) and making the *gauche* correction⁵ of +0.7 kcal. to the 3-methyl-hexadiene, we calculate for the equilibrium constant of the isomerization reaction for the *trans* isomer



$K_{y,z}(500^\circ\text{K.}) = 3.84$, for the *cis* isomer 1.40 kcal. This yields $K_{\text{eq}} = 5.24$ in excellent agreement with the experimental value of 5.4 reported by Amano.¹⁷

(17) A. Amano and M. Uchiyama, *J. Phys. Chem.*, **69**, 1278 (1965).