Nitrogen Dioxide Catalyzed Geometric Isomerization of 2-Butene and 2-Pentene. A Precise Method for Determining the Enthalpies and Entropies of Geometric Isomerizations

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Abstract: NO_2 catalyzes geometric isomerization of olefins without concomitant positional isomerization. Therefore, temperature-dependent equilibrium data obtained by NO_2 catalysis may be used to calculate very precise values of the 298°K enthalpy and entropy changes accompanying the isomerization. From equilibrium constants determined over the temperature range 298–370°K for 2-butene and 298–400°K for 2-pentene, values of $\Delta H°_{r,298}$ and $\Delta S°_{r,298}$ were determined to be -1.00 ± 0.02 kcal mol^{-1} and -1.16 ± 0.07 cal mol^{-1} deg^{-1} for 2-butene and -1.15 ± 0.03 kcal mol^{-1} and -0.81 ± 0.10 cal mol^{-1} deg^{-1} for 2-pentene. These values are consistent with most previous determinations and are of substantially increased precision.

Recently we reported[1] the results of a kinetic study of the NO_2-catalyzed thermal isomerization of *cis*-2-butene to *trans*-2-butene. We found that the reaction proceeded smoothly at moderate pressures (0.1–30 Torr) and temperatures (300–380°K) with no detectable consumption of 2-butene. These results suggested that NO_2-catalyzed geometrical isomerization of olefins might provide a convenient and precise method for determining the enthalpy and entropy changes accompanying the isomerization. In this paper we present the results of our studies of the NO_2-catalyzed cis–trans isomerization of 2-butene and 2-pentene. As expected, the 298°K enthalpy and entropy changes calculated for these reactions are more accurate than previously published values.[2]

Experimental Section

Chemicals. *cis*-2-Butene (Matheson research grade, 0.7% *trans*-2-butene impurity), *trans*-2-butene (Matheson research grade, 0.3% *cis*-2-butene impurity), *cis*-2-pentene (Chemical Samples, 0.8% *trans*-2-pentene impurity), and *trans*-2-pentene (Chemical Samples, $\lesssim 0.1\%$ *cis*-2-pentene impurity) were thoroughly degassed by bulb-to-bulb distillation, analyzed by glc for hydrocarbon impurities, and then used without further purification. NO_2 (Baker CP grade) was mixed with an equal pressure of O_2 (Matheson research grade used as received) and allowed to stand overnight to remove any NO and N_2O_3 impurity ($N_2O_3 \rightleftarrows NO + NO_2$; $2NO + O_2 \rightleftarrows 2NO_2$). The NO_2 was then thoroughly degassed by bulb-to bulb distillation and used without further purification.

Apparatus. The all-glass reaction system (total volume 2.7 l.) consisted of a 2.3-l. bulb with two exit arms connected by a gas circulating loop. Mounted in the circulating loop was a circulating pump driven by magnetic coupling to an external motor. The reaction system was housed in a simple oven constructed of wood and insulating board. Two fans with motors mounted outside the oven provided efficient circulation of the air within the oven. Oven temperatures were measured using ice bath referenced thermocouples. The oven had a temperature range of 25–125° and a temperature stability of $\lesssim 0.5°$. The reaction system was serviced by a conventional high vacuum line. Greaseless O-ring stopcocks were used throughout the reaction system and the high vacuum line. Reaction system pressures were measured, using an MKS Baratron gauge (0.1–300 Torr).

Analysis. The gaseous reaction mixture was directly sampled using a Carle microvolume gas sampling valve (sample loop volume ~200 μl) connected through a greaseless O-ring stopcock to the circulating loop of the reaction system. Glc analyses for cis and trans olefin were performed on a 10% NaCl on alumina column (3 ft, $^1/_8$ in.; 100–120 mesh, acid washed, activated alumina) operated at ~75°. The Varian Aerograph gas chromatograph was equipped with a flame ionization detector. Glc peaks were displayed on a 1-mV potentiometric recorder equipped with a Disc integrator. The response and linearity of the entire analytical train (gas sample valve, gc, recorder) were calibrated, using standard gas mixtures prepared using the Baratron gauge. The combined precision of the gc analyses and calibrations was better than ±1%.

Results

For reaction 1 the equilibrium constants (K) for the

$$\begin{tikzcd} \text{cis olefin} + NO_2 \arrow[r, shift left, "k_1"] & I \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] \arrow[d, "{k_3[NO_2]}"] & \text{trans olefin} + NO_2 \arrow[l, shift left, "k_{-2}"] \\ & \text{by-products} & \end{tikzcd} \qquad (1)$$

isomerization may be accurately calculated as

$$K = ([\text{trans}]/[\text{cis}])_{\text{eq}} \qquad (2)$$

provided that the rate of by-product formation ($R_3 \cdot [NO_2][I]$) is negligible compared to the rates of the steps involved in maintaining the isomerization equilibrium. In reaction 1, because the two isomeric intermediate *cis*- and *trans*-nitroalkyl radicals are in rapid equilibrium,[1] they are jointly symbolized as I. In eq 2 and throughout the rest of this paper trans and cis will be used to denote trans and cis olefin.

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(1) J. L. Sprung, H. Akimoto, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **93**, 4358 (1971).

(2) (a) "Selected Values of Properties of Hydrocarbons," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1953; (b) F. D. Rossini, K. S. Pitzer, W. J. Taylor, J. P. Ebert, J. E. Kilpatrick, C. W. Beckett, M. G. Williams, and H. G. Weiner, *Nat. Bur. Stand. (U. S.), Circ.*, 461 (1947); (c) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969; (d) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970; (e) H. H. Voge and N. C. May, *J. Amer. Chem. Soc.*, **68**, 550 (1946); (f) G. M. Bristow and F. S. Dainton, *Proc. Roy. Soc., Ser. A*, **229**, 525 (1955); (g) D. M. Golden, K. W. Egger, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5416 (1964); (h) A. Maccoll and R. A. Ross, *ibid.*, **87**, 1169 (1965); (i) P. I. Abell, *ibid.*, **88**, 1346 (1966); (j) K. W. Egger and S. W. Benson, *ibid.*, **88**, 236 (1966); (k) K. W. Egger, *ibid.*, **89**, 504 (1967); (l) J. L. Holmes and L. S. M. Ruo, *J. Chem. Soc. A*, 1925 (1969); (m) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969). (n) After this paper was accepted for publication two papers [J. Happel, M. A. Hnatow, and R. Mezaki, *J. Chem. Eng. Data*, **16**, 206 (1971), and E. F. Meyer and D. G. Stroz, submitted for publication to the *J. Amer. Chem. Soc.*] both dealing with the cis–trans isomerization of 2-butene were brought to our attention. Since a general treatment of 2-butene geometric isomerization data is in progress, the results of these two papers have not been included in this paper.

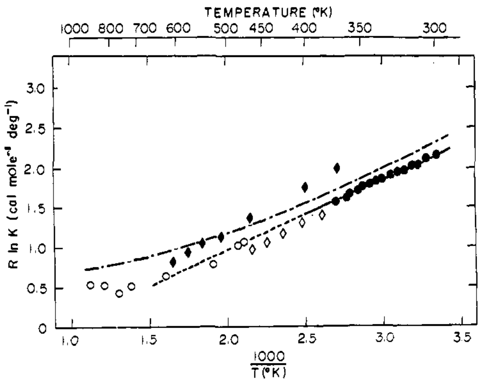

Figure 1. Van't Hoff plots of 2-butene equilibrium data: (●) this work; (◆) Golden, Egger, and Benson (ref 2g); (◇) Abel (ref 2i); (○) Voge and May (ref 2e); (- · -) API-NBS (ref 2a,b).

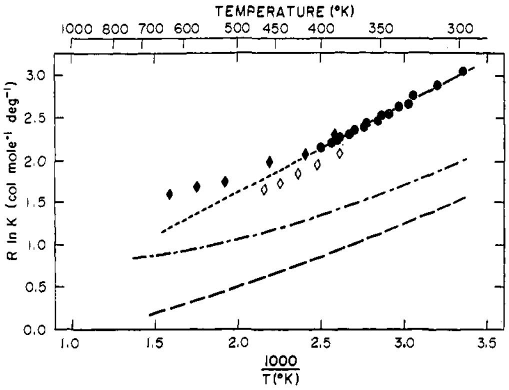

Figure 2. Van't Hoff plots of 2-pentene equilibrium data: (●) this work; (◆) Egger and Benson (ref 2j); (◇) Abel (ref 2i); (- · -) NBS (ref 2b); (- - -) API (ref 2a).

By following the ratio [trans]/[cis] until it attained its stable equilibrium value, we have determined values of K at several temperatures for the NO_2-catalyzed geometric isomerization of 2-butene (298–370°K) and 2-pentene (298–400°K). Depending on the reaction conditions, equilibrium was reached in periods of time ranging from a few hours to several days. To demonstrate that equilibrium was really being attained, initial pressures of cis and trans olefin were chosen so that equilibrium was approached from opposite directions an equal number of times. Table I and Figures 1 and 2 present our experimental results. They also show that the direction of approach to equilibrium had no significant effect on the final equilibrium position.

Table I. Equilibrium Data for the Cis–Trans Isomerization of 2-Butene and 2-Pentene

Run	Temp, °K[a]	Starting pressures, Torr Trans	Cis	NO_2	K[b]
		A. 2-Butene			
1	298.7	2.0	3.0	2.0	2.977
2	304.8	3.0	1.0	2.0	2.909
3	309.6	3.0	1.0	1.0	2.850
4	313.0	2.0	3.0	3.0	2.781
5	318.6	2.0	3.0	1.0	2.688
6	322.4	3.0	1.0	1.0	2.663
7	327.6	2.0	3.0	1.0	2.620
8	332.4	2.0	3.0	1.0	2.541
9	337.8	3.0	1.0	1.0	2.512
10	342.3	3.0	1.0	1.0	2.464
11	348.0	2.0	3.0	1.0	2.422
12	351.9	3.0	1.0	1.0	2.370
13	357.8	2.0	3.0	1.0	2.320
14	360.9	2.0	3.0	1.0	2.253
15	370.0	3.0	1.0	1.0	2.203
		B. 2-Pentene			
16	298.0	4.4	0.6	4.0	4.648
17	312.0	4.4	0.6	4.0	4.278
18	327.3	3.5	1.5	4.0	4.022
19	331.2	4.4	0.6	4.0	3.842
20	337.0	3.5	1.5	2.0	3.771
21	343.4	4.4	0.6	4.0	3.624
22	349.0	3.5	1.5	2.0	3.587
23	351.7	4.4	0.6	3.0	3.479
24	360.0	3.5	1.5	2.0	3.427
25	362.0	4.4	0.6	3.0	3.343
26	369.8	3.5	1.5	1.0	3.305
27	374.0	4.4	0.6	1.0	3.216
28	382.9	3.5	1.5	1.0	3.168
29	383.6	4.4	0.6	1.0	3.116
30	389.7	3.0	2.0	1.0	3.064
31	399.9	3.0	2.0	1.0	2.978

[a] Temperatures are accurate to at least ±0.5°. [b] K = $([\text{trans}]/[\text{cis}])_{eq}$. Values of K are accurate to better than ±0.01. Each value of K is the average of at least five replicate analyses.

For most of our experiments a small decrease (0.1–0.5 Torr) in total pressure was observed to occur during the course of the experiment. The magnitude of this fall in pressure was measured for eight of the fifteen 2-butene runs. Generally the decrease was larger for runs near room temperature because they took longer to reach equilibrium. Simple calculations showed that about one-third of the pressure drop was due to withdrawal of gaseous samples for gc analysis. The remainder was due to by-product formation, presumably by the following reaction.[3]

 (3)

$$\text{I} + NO_2 \xrightarrow{k_3} \text{R}\overset{NO_2}{\text{CH}}\overset{NO_2}{\text{CH}}\text{R}' \text{ or } \text{R}\overset{NO_2}{\text{CH}}\overset{ONO}{\text{CH}}\text{R}' \quad (3)$$

For the NO_2-catalyzed geometric isomerization of *cis*-2-butene, it has been shown[1] that $k_2 \approx k_1$ and $k_{-2} \approx k_{-1}$. Therefore, for small conversions of olefin to by-product a steady state treatment of reaction 1 yields the following expression for the apparent rate constant (k_p) for by-product formation from 2-butene

$$k_p = k_3[2k_{-1}/(2k_1 + k_3[NO_2]^2)] \quad (4)$$

If one attributes all of the measured decrease in pressure to by-product formation and also makes the unlikely assumption that 2,3-dinitrobutane and 2-nitrobutyl nitrite, the by-products of reaction 3 using 2-butene, are volatile at room temperature, then a maximum value for k_p can be calculated for each of the eight experiments with 2-butene for which the pressure fall was measured. The average of these eight values of k_p = 55 ± 15 l.^{2} mol^{-2} sec^{-1} which gives a 3σ upper limit for k_p of 100 l.^{2} mol^{-2} sec^{-1}. At 300°K reasonable values[1] for k_1 and k_{-1} are $k_1 = 10^{2.7}$ sec^{-1} and $k_{-1} = 0.24$ l. mol^{-1} sec^{-1}. Therefore, by taking k_p = 100 l.^{2} mol^{-2} sec^{-1}, a maximum value of $k_3 = 2.1 \times 10^5$ l. mol^{-1} sec^{-1} may be calculated from (4) by iteration. Routine kinetic and mathematical analysis then indicates that the deviation of the measured equilibrium ratio $([\text{trans}]/[\text{cis}])_{eq}$ from the true value of K, which would be obtained were $k_3 = 0$, must be no greater than 3% and is probably less than 0.5%. Clearly the effect of by-product formation on

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[3] (a) N. Levy and C. W. Scaife, *J. Chem. Soc.*, 1093 (1946); (b) P. Gray and A. D. Yoffe, *Quart. Rev., Chem. Soc.*, 9, 362 (1955); (c) H. Schechter, *Rec. Chem. Progr.*, 25, 55 (1955).

the position of the geometric equilibrium is wholly negligible.

Were NO_2 able to abstract the allylic hydrogens of alkyl-substituted ethylenes, then there would exist a plausible mechanism for the isomerization by NO_2 of 2-olefin to 1-olefin.

$$\mathrm{RCH{=}CHCH_3 + NO_2 \rightleftarrows R\dot{C}H{-}CH{-}\dot{C}H_2 + HNO_2 \rightleftarrows RCH_2CH{=}CH_2 + NO_2} \quad (5)$$

Because our alumina column did not separate trans 2-olefin from its 1-olefin isomer, the isomerization of either cis or trans 2-olefin to 1-olefin would not have been detected by our analytical procedures. Although the unusually weak H-N bond of HNO_2 makes this hydrogen abstraction most unlikely, we tested this possibility experimentally. When 5 Torr of 1-butene was mixed at 60° with 1 Torr of NO_2 and equilibrated for 3 days, no detectable amount of *cis*-2-butene was observed (a conversion of $\gtrsim 0.1\%$ would have been detected). Therefore, reaction 5 does not occur.

Figures 1 and 2 present Van't Hoff plots ($R \ln K$ *vs.* T^{-1}) of our data for 2-butene and 2-pentene together with the data from several other relevant studies. In both figures, whenever a study made replicate determinations of the value of an equilibrium constant, for clarity only its average value was plotted.

The Van't Hoff equation

$$R \ln K = -\Delta H^\circ_{r,T}/T + \Delta S^\circ_{r,T} \quad (6)$$

relates the equilibrium constant (K) of the geometrical olefin isomerization to the changes in enthalpy [$\Delta H^\circ_{r,T} = \Delta H^\circ_f(\text{trans}) - \Delta H^\circ_f(\text{cis})$] and entropy [$\Delta S^\circ_{r,T} = S^\circ(\text{trans}) - S^\circ(\text{cis})$] accompanying the isomerization. For temperature intervals of up to 100°, $\Delta H^\circ_{r,T}$ and $\Delta S^\circ_{r,T}$ are usually nearly constant[4] and therefore $R \ln K$ should be linear with T^{-1}. In Figures 1 and 2 the solid line is the least-squares linear correlation of $R \ln K$ with T^{-1} using all of our 2-butene or 2-pentene data from Table I.

For temperature intervals greater than 100°, the temperature dependence of $\Delta H^\circ_{r,T}$ and $\Delta S^\circ_{r,T}$ is no longer negligible and accordingly Van't Hoff plots of data spanning temperature intervals greater than 100° generally show significant curvature.

Because $\Delta C^\circ_p = C^\circ_p(\text{trans}) - C^\circ_p(\text{cis}) > 0$ for the cis–trans isomerization of 2-butene or 2-pentene, Van't Hoff plots spanning temperature ranges greater than 100° should be convex to the reciprocal temperature axis. Figure 1 shows that a plot of our 2-butene data together with the data of Abell[2i] and of Voge and May[2e] has the requisite curvature. It also shows that relative to this plot, the data of Golden, Egger, and Benson[2g] appear to lie consistently too high. Similarly, Figure 2 shows that a plot of our 2-pentene data together with that of Egger and Benson[2j] also has the requisite curvature. This figure also shows that relative to this plot, the data of Abell[2i] lie consistently too low.

The temperature dependence of C°_p(trans) or C°_p(cis) may be conveniently written as a quadratic expression

$$C^\circ_p = a + bT + cT^2 \quad (7)$$

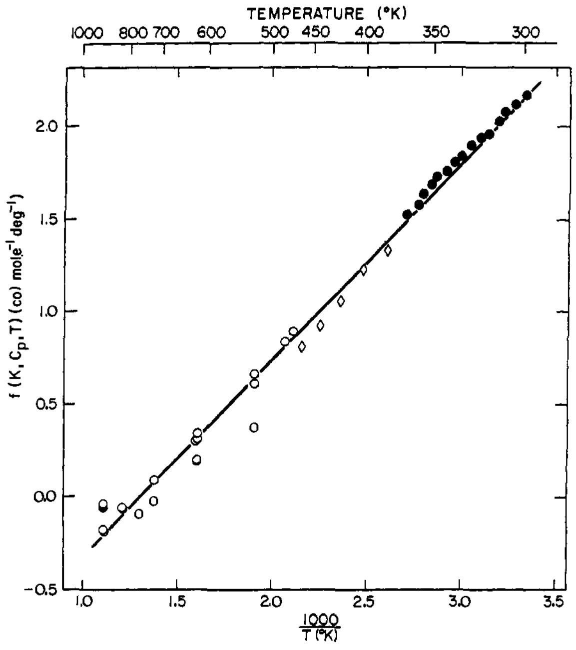

Figure 3. Plot of $f(K,C_p,T)$ *vs.* T^{-1} (see eq 5-10) for 2-butene: (●) this work; (◇) Abel (ref 2i); (○) Voge and May (ref 2e).

where the temperature coefficients a, b, and c are normally calculated from heat capacity data derived from experimental results using statistical mechanics.[5] Appropriate combination of this quadratic formulation of C°_p(trans) and C°_p(cis) with the usual temperature-dependent expressions for $\Delta H^\circ_{r,T}$ and $\Delta S^\circ_{r,T}$ yields eq 8. The left-hand side of this equation is a somewhat

$$R \ln K + \frac{1}{T}\left[\Delta a(T - T_0) + \frac{\Delta b}{2}(T^2 - T_0^2) + \frac{\Delta c}{3}(T^3 - T_0^3)\right] + \left[\Delta a \ln \frac{T}{T_0} + \Delta b(T - T_0) + \frac{\Delta c}{2}(T^2 - T_0^2)\right] = -\Delta H^\circ_{r,T_0}/T + \Delta S^\circ_{r,T_0} \quad (8)$$

complicated function of K, C_p, and T, which will be denoted hereafter by $f(K,C_p,T)$. Thus

$$f(K,C_p,T) = -\Delta H^\circ_{r,T_0}/T + \Delta S^\circ_{r,T_0} \quad (9)$$

and plots of $f(K,C_p,T)$ *vs.* T^{-1} should be linear even over extended ranges of temperature.

Figure 3 presents a plot of $f(K,C_p,T)$ *vs.* T^{-1} for our 2-butene data together with the 2-butene data of Abell[2i] and of Voge and May.[2e] The line plotted is the least-squares line calculated from all the data.[6] Figure 4 presents a similar plot of our 2-pentene data together with the 2-pentene data of Egger and Benson.[2j] Again the line plotted is the least-squares line calculated from all the data. As expected, Figure 3 shows that our 2-

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[4] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 6.

[5] In this paper all calculations employing eq 8 used temperature coefficients calculated from the 2-butene or 2-pentene heat capacity data of Kilpatrick and coworkers (ref 9). Kilpatrick's data were used because as Figure 2 shows the NBS Gibbs energy function,[2b] which is directly calculated from Kilpatrick's data, is in substantially better agreement with experimental results than is the equivalent plot based on the API modification of Kilpatrick's data.[2a]

[6] Although Abell determined each of his equilibrium constants by making replicate runs, his paper presents and of necessity we have used only the average value of each equilibrium constant. This means that in our combined 2-butene calculation (Figure 3 and ASP + A + VM in Table II) Abell's data are underweighted.

butene data correlate quite well with the data of Abell and of Voge and May, and Figure 4 that the same is true of our 2-pentene data and the data of Egger and Benson.

Table II presents the values of $\Delta H°_{r,298}$ and $\Delta S°_{r,298}$ for 2-butene and 2-pentene, which may be calculated using eq 8 from our equilibrium data (ASP)[7] and the equilibrium data of Abell (A);[2i,8] Golden, Egger, and Benson (GEB);[2g,8] Voge and May (VM);[2e,8] Egger and Benson (EB);[2j,8] and the two combinations [(ASP + A + VM)[6] and (ASP + EB)] of these different sets of data. For comparison the API[2a] and NBS[2b] values of $\Delta H°_{r,298}$ and $\Delta S°_{r,298}$ are included.

Table II[a-c]

	$\Delta H°_{r,298}$, kcal mol^{-1}	$\Delta S°_{r,298}$, cal mol^{-1} deg^{-1}
	2-Butene	
ASP	−1.00 ± 0.02, 0.02	−1.16 ± 0.07, 0.07
A	−1.21 ± 0.06, 0.05	−1.79 ± 0.16, 0.12
GEB	−1.38 ± 0.07, 0.02	−1.79 ± 0.17, 0.05
VM	−0.96 ± 0.18, 0.06	−1.24 ± 0.36, 0.10
ASP + A + VM	−1.08 ± 0.12, 0.02	−1.42 ± 0.27, 0.04
API	−1.00 ± 0.2	
NBS	−1.04 ± 0.06	−1.04 ± (0.2)[d]
	2-Pentene	
ASP	−1.15 ± 0.03, 0.02	−0.81 ± 0.10, 0.05
A	−1.23 ± 0.08, 0.03	−1.17 ± 0.22, 0.06
EB	−1.08 ± 0.15, 0.06	−0.57 ± 0.36, 0.12
ASP + EB	−1.06 ± 0.10, 0.02	−0.55 ± 0.27, 0.05
API	−0.88 ± (0.3)	−1.40 ± (0.5)
NBS	−1.08 ± (0.14)	−0.95 ± (0.5)

[a] ASP (Akimoto, Sprung, and Pitts; this work), A (Abell; ref 2i), GEB (Golden, Egger, and Benson; ref 2g), VM (Voge and May; ref 2e), ASP + A + VM (combined data of ASP, A, and VM), API (American Petroleum Institute; ref 2a), NBS (National Bureau of Standards; ref 2b), EB (Egger and Benson; ref 2j), ASP + EB (combined data of ASP and EB). [b] For equilibrium data, two error limits are given; the second is based on the scatter in the linear correlation and the first on the sum of this scatter error and the error due to the uncertainty in the heat capacity data. [c] Errors given in parentheses are estimations rather than approximate calculations. [d] Both the API[2a] and NBS[2b] compilations tabulate the same value of $\Delta S°_{r,298}$ for 2-butene.

Discussion

Estimation of Errors. In Table II for results based upon equilibrium data two error limits are given. The second of these is the scatter error in the linear correlation according to eq 8 of the equilibrium data. The first is the sum of this scatter error and the error due to the uncertainties in Kilpatrick's heat capacity data,[9] which was used to reduce the high-temperature results to 298 °K. Kilpatrick's papers[9] present no estimate of the error in his data. In the NBS compilation,[2b] the error in Kilpatrick's 2-butene $C°_{p,298}$ value is estimated to be ±0.15 cal mol^{-1} deg^{-1}. No error in $C°_p$ for 2-pentene is given for any temperature.

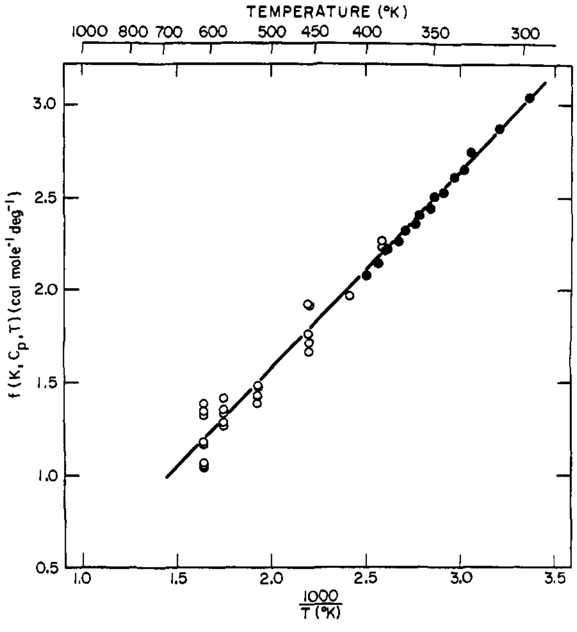

Figure 4. Plot of $f(K,C_p,T)$ *vs.* T^{-1} (see eq 5-10) for 2-pentene; (●) this work; (○) Egger and Benson (ref 2j).

Because only incomplete spectroscopic data and no appropriate calorimetric data were available, Kilpatrick's 2-pentene data were calculated by incremental methods starting from his 2-butene data. For such a calculation a reasonable estimate of the error in $C°_p$ at 298 °K for 2-pentene is ±0.3 cal mol^{-1} deg^{-1}.

Because it is likely that the percentage error in $C°_{p,T}$ does not vary greatly with temperature, the following two approximate formulas may be used to obtain the errors given in Table II for values derived from equilibrium studies. In eq 10 and 11 T_m is the midpoint of the temperature range of the equilibrium data.

$$\Delta H°_{r,298} = \Delta H°_{r,T_m} - \Delta C°_{p,T_m}(T_m - 298.15) \quad (10)$$

$$\Delta S°_{r,298} = \Delta S°_{r,T_m} - \Delta C°_{p,T_m} \ln \frac{T_m}{298.15} \quad (11)$$

Because errors in values of $C°_{p,T_m}$ for a pair of geometrical olefin isomers ought to be largely self-cancelling, the errors in $\Delta H°_{r,298}$ and $\Delta S°_{r,298}$ estimated using eq 10 and 11 are probably somewhat too large. Since as temperature increases the magnitude of the second term in eq 10 and 11 increases markedly, the errors in the values of $\Delta H°_{r,298}$ and $\Delta S°_{r,298}$ based on equilibrium data obtained at elevated temperatures are significantly larger than those based on data obtained at lower temperatures.

The error limits given in Table II for the NBS $\Delta H°_{r,298}$ values were calculated from the two σ uncertainty intervals of the 298 °K heats of hydrogenation,

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(7) From the slope and intercept of the linear correlation of our 2-butene and 2-pentene data presented in Figures 1 and 2 (solid lines), one can calculate values of $\Delta H°_{r,T}$ and $\Delta S°_{r,T}$ which are appropriate to the midpoint of our experimental temperature range. Using Kilpatrick's heat capacity data (ref 9), these values can be reduced to 298 °K giving $\Delta H°_{r,298}$ and $\Delta S°_{r,298}$ values of −1.00 ± 0.02 kcal mol^{-1} and −1.17 ± 0.07 cal mol^{-1} deg^{-1} for 2-butene and −1.16 ± 0.03 kcal mol^{-1} and −0.82 ± 0.05 cal mol^{-1} deg^{-1} for 2-pentene. Comparison with Table II shows that these values are in excellent agreement with the values obtained using eq 8.

(8) Neither Abell[2i] nor Voge and May[2e] reported 298 °K values of $\Delta H°_{r,T}$ or $\Delta S°_{r,T}$. In their 2-pentene paper, Egger and Benson[2j] report $\Delta H°_{r,298}$ and $\Delta S°_{r,298}$ values of −1.2 ± 0.15 kcal mol^{-1} and −1.25 ± 0.2 cal mol^{-1} deg^{-1} for 2-butene and −0.9 ± 0.15 kcal mol^{-1} and 0.4 ± 0.15 cal mol^{-1} deg^{-1} for 2-pentene. These values were calculated (a) by correlating their equilibrium data using a quadratic fit ($\log K = a + bT^{-1} + cT^{-2}$), (b) by calculating a value of $\Delta C°_p$ from the coefficient of the T^{-2} term of the fit, and (c) by assuming this value of $\Delta C°_p$ to be independent of temperature, which allowed their high-temperature values of $\Delta H°_{r,T}$ and $\Delta S°_{r,T}$ to be reduced to 298 °K.

(9) (a) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **36**, 559 (1946); (b) J. E. Kilpatrick and K. S. Pitzer, *ibid.*, 37, 164 (1946).

which Prosen and Rossini[10] obtained from the high temperature data of Kistiakowsky, *et al.*[11] The larger error limit for 2-pentene reflects the fact that Kistiakowsky made his measurements on a pentene sample of unknown isomeric composition, which led Prosen and Rossini to assume that at 355°K the difference in the heats of hydrogenation of 2-pentene is the same as that of 2-butene. The larger error limits of the API $\Delta H°_{r,298}$ values[2a] given in Table II reflect the fact that these values are differences in heats of formation and therefore contain an additional uncertainty, the error in the heat of formation of *n*-butane or *n*-pentane.

The error limits for the API and NBS values of $\Delta S°_{r,298}$ given in Table II are based on the error limits estimated by the NBS[2b] for the 2-butene absolute entropies given in their compilation and on reasonable estimates made by the present authors of the error limits of the 2-pentene absolute entropies. The larger error limits given for $\Delta S°_{r,298}$ for 2-pentene reflect the approximate nature of the 2-pentene absolute entropy calculations of Kilpatrick, *et al.*[9a]

Effect of By-product Formation on Values of *K*. The accuracy of the equilibrium constants obtained from catalyzed cis–trans olefin isomerizations may be strongly dependent upon the effect of catalyst-induced side reactions on the equilibrium position of the geometrical isomerization.[2e,1] Solid catalysts[2e,1,12] frequently induce polymerization, cracking, and positional isomerization at moderate temperatures and dehydrogenation at high temperatures. From unpublished results, Voge and May[2e] estimated their slowest isomerization rate to be at least ten times faster than the rate of any olefin consuming reactions occurring in their system. Consequently, despite catalyst-promoted by-product formation ranging from 2 to 30% of starting butene, they calculated that their equilibrium data were accurate to better than 10%. Although bromine atom catalysis initiates by-product formation by abstraction of hydrogen α to the olefin double bond,[21] Abell's paper on the bromine atom catalyzed isomerization of *n*-butenes and *n*-pentenes presents neither an analysis of the effects nor an estimate of the extent of by-product formation.

Benson and coworkers[2g] report that isomerization of *n*-butene catalyzed by iodine atoms yields some (0.5–6.8%) butadiene and traces (0.1–0.2%) of *n*-butane. They also suggest that some polymerization occurs at elevated temperatures. Egger and Benson[2i] report that iodine-catalyzed isomerization of *n*-pentene leads to extensive (0.8–42.3%) formation of *n*-pentene but that, due to its rapid iodine-catalyzed dimerization and cyclization, no 1,3-pentadiene is detected. Apparently due to the kinetic complexity of these systems, the authors did not attempt to calculate the effect of by-product formation on their equilibrium data. Instead they imply that, because olefin isomerization is fast compared to by-product formation, the latter can be neglected.

The present study shows that NO_2-catalyzed olefin isomerizations are largely uncomplicated by by-product formation. Because they are run at low temperatures (300–400°K), polymerization does not occur and, at least at these temperatures, NO_2 is incapable of abstracting the α hydrogens of alkyl-substituted ethylenes. Therefore, neither positional isomerization nor diene or alkane formation can occur. The system is subject to a negligible amount of by-product formation presumably due to the slow formation of α,β-dinitroalkane and β-nitroalkyl nitrite.[3] Because of the kinetic simplicity of NO_2-catalyzed olefin isomerizations, routine kinetic and mathematical analysis permits the use of 2-butene pressure decrease data to estimate that the measured equilibrium constants should be accurate to at least 3% and probably to better than 0.5%. Since an error of 3% in the equilibrium constants would alter the values of $\Delta H°_{r,298}$ and $\Delta S°_{r,298}$ by only 0.02 kcal mol^{-1} and 0.06 cal mol^{-1} deg^{-1}, respectively, the effects of by-product formation are therefore negligible.

Comparison of Values of $\Delta H°_{r,298}$ and $\Delta S°_{r,298}$. Table II shows that the 2-butene $\Delta H°_{r,298}$ values of ASP and NBS are in excellent agreement. Because of their larger limits the values of VM, API, and ASP + A + VM are in good agreement with each other and also with the more precise values of ASP and NBS. In contrast to this, the $\Delta H°_{r,298}$ values of A and GEB, obtained from halogen atom catalyzed isomerization data, are only in fair (2σ) agreement with the values of ASP and NBS. When considered together, the average of the ASP, VM, NBS, API, and ASP + A + VM values indicates a preferred 2-butene value of $\Delta H°_{r,298} = -1.0$ kcal mol^{-1}.

The 2-butene $\Delta S°_{r,298}$ values of VM, ASP + A + VM, and API–NBS are all in good agreement with each other and with the considerably more precise value of ASP. Although the $\Delta S°_{r,298}$ values of A and GEB are fortuitously in excellent agreement with each other, they are in very poor agreement with the value of ASP and by comparison to the values of ASP, VM, ASP + A + VM, and API–NBS, appear to be considerably too low. Of course, this was to be expected, since Figure 1 and Table II show that the slopes ($\Delta H°_{r,298}$ values) of the 2-butene correlations of A and of GEB are somewhat too steep. Because of the large error limits of all of the 2-butene $\Delta S°_{r,298}$ values except the value of ASP, a preferred value is not obvious. Since the values of VM, ASP + A + VM, and API–NBS are all consistent with the more precise value of ASP, a preferred 2-butene value of $\Delta S°_{r,298} = -1.2$ cal mol^{-1} deg^{-1} is indicated.

All of the 2-pentene $\Delta H°_{r,298}$ values listed in Table II, including the combined value (ASP + EB) and the less precise ($\sigma = 0.3$ kcal mol^{-1}) API value, are in good agreement. When the more precise ($\sigma \leq 0.15$ kcal mol^{-1}) values of ASP, A, EB, NBS, and ASP + EB are considered together, their average indicates a preferred 2-pentene value of $\Delta H°_{r,298} = -1.1$ kcal mol^{-1}.

Because of their large error limits, the 2-pentene $\Delta S°_{r,298}$ values of EB and ASP + EB are in good agreement with the more precise value of ASP. The rather imprecise value of NBS is also in good agreement with the value of ASP. By comparison to the values of ASP, EB, ASP + EB, and NBS, the value of A appears to be somewhat too low and that of API to be much too low. Again, because of the larger error limits of all of the $\Delta S°_{r,298}$ values except the value of ASP, the choice of a preferred value is not obvious. Because the

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(10) E. J. Prosen and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, 36, 269 (1946).

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

(12) (a) S. H. Inami, B. J. Wood, and H. Wise, *J. Catal.*, 13, 397 (1969); (b) J. L. Holmes and L. S. M. Ruo, *J. Chem. Soc. A*, 1231 (1968).

EB, ASP + EB and NBS values are all consistent with the more precise ASP value, a preferred 2-pentene value of $\Delta S^\circ_{2r.98} = -0.8$ cal mol^{-1} deg^{-1} is indicated.

Comparison of Methods. Table II shows that the precision of the 298°K values of the enthalpy and entropy changes, which accompany the cis–trans isomerization of 2-olefins, is strongly influenced by the method of measurement. When calculated from calorimetric data,[2a–d] propagation of errors occurs because for geometrical olefin isomers differences in heats of combustion,[13] heats of hydrogenation,[11] and absolute entropies[9,14] are generally quite small and therefore the percentage error of the difference is often unsatisfactorily high.

Table II also shows that when reduced to 298°K the precision of thermochemical quantities, calculated from catalytic data obtained at elevated temperatures, is markedly decreased by the limited precision of the available heat capacity data.[2a–d] Further, if the catalyst used also initiates by-product formation, in systems which are kinetically complex, such as those where positional isomerization can occur, it is exceedingly difficult to estimate the difference between the measured steady-state olefin concentrations and the true equilibrium concentrations which would result in the absence of by-product formation. In general, these problems are characteristic of solid catalysts[2e,1,12] such as aluminas, silicas, pyrolytic carbons, and noble metals and homogenous free-radical catalysts such as nitric oxide and halogen atoms.[2g,j,k] Because these catalysts require elevated temperatures, promote positional isomerization, and initiate substantial side reactions, they are kinetically complex and therefore probably unsuitable for precise determinations of 298°K values of enthalpy and entropy changes accompanying geometric olefin isomerizations.

In marked contrast to both calorimetric methods and high-temperature catalytic methods, NO_2-catalyzed olefin isomerizations are notably free from these difficulties. Because they proceed smoothly near room temperature, their precision is only minimally affected by uncertainties in heat capacity data. Since at these low temperatures NO_2 neither promotes positional isomerization nor initiates significant by-product formation, the system is kinetically simple. Accordingly, it is easy to show that the measured steady-state olefin concentrations differ from the true equilibrium concentrations by at most a few per cent. Therefore, NO_2 catalysis would seem to be the best available method for the determination of 298°K values of the enthalpy and entropy changes accompanying geometric olefin isomerizations.

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[13] E. J. Prosen, F. W. Maron, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **46,** 106 (1951).

[14] R. B. Scott, W. J. Ferguson, and F. G. Brickwedde, *ibid.*, 33, 1 (1944).