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Thermodynamics of Conformational Change in 1,3-Butadiene Studied by High-Temperature Ultraviolet Absorption Spectroscopy[1]

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Abstract: Apparent extinction coefficients were measured for 1,3-butadiene at 426–621 K and 5–15 torr at wavelengths of 237–249 nm, where only the cis isomer absorbs. In the analysis of the results, the molar extinction coefficients of the cis isomer were corrected for the effect of temperature by using an approach due to Grunwald.[5] The required normal-mode wavenumbers for the cis isomer were obtained by analysis of an IR spectrum due to Squillacote et al.[6] In the experimental temperature range, the UV band shape is Gaussian, with a temperature-independent mean and increasing width, in agreement with expectation. The following thermodynamic parameters were obtained for *s-trans-* ⇄ *s-cis-*1,3-butadiene in cal mol^{-1}: $\Delta H°_{520} = 3020 \pm 150$; $\Delta H°_0 = 3200 \pm 160$; zero-point energy difference $\Delta E_Z = 290 \pm 90$; potential energy difference (minimum to minimum) $\Delta V = 2910 \pm 180$.

The stable potential minimum for rotation about the single bond in 1,3-butadiene (C_4H_6) corresponds to the planar trans conformation, and physical properties of the *s*-trans isomer are well characterized. The position of the metastable potential minimum is less certain. The critical review and analysis by Bock, George, Trachtman, and Zanger[2] (BGTZ) indicates that there are two mirror-image *s*-gauche minimum conformations separated by a low barrier. Figure 1 shows the potential function favored by BGTZ as well as the lower torsional energy levels.[2,3] Note that the zero-point energy level in the metastable well lies above the barrier at 180° that separates the two gauche potential minima. According to accepted definitions,[4] the structure of the metastable isomer is therefore cis, and the conformational equilibrium is that shown in (1).

s-trans-C_4H_6 *s-cis*-C_4H_6

C_{2h} C_{2v}

(1)

The conformational analyses by BGTZ and by the authors whose work they reviewed are based on Raman bands assignable to the torsional mode, formal heat capacities in the range 220–320 K, and quantum mechanical calculations.[2] Since then, two developments make it seem likely that further information can be obtained from high-temperature ultraviolet (UV) absorption data. First, Grunwald[5] has analyzed the temperature dependence of UV absorption bands for orbitally allowed electronic transitions of polyatomic molecules and has clarified the dependence of molar extinction coefficients on thermal excitation of molecular normal vibrations.

Second, Squillacote, Sheridan, Chapman and Anet[6] (SSCA) have reported UV and infrared (IR) spectra of butadiene enriched in the cis isomer by equilibration at 400–900 K and trapping in an argon matrix at 20–30 K. They were able to establish the UV spectrum of the cis isomer and showed that it is shifted to longer wavelengths relative to that of the trans isomer, in agreement with structure–spectrum correlations.[7] In particular, UV absorption by the trans isomer is negligible at and above 237 nm, while that of the cis isomer is significant up to at least 250 nm. Both trans and cis absorption bands have high oscillator strengths and appear to be due to orbitally allowed transitions. (For the trans isomer, the transition has been described as $^1A_g^- \rightarrow {}^1B_u^+$.)[8]

It appears, therefore, that UV absorption measurements above 237 nm can give the mole fraction of cis. Equilibrium measurements over a range of temperatures can give thermodynamic parameters for reaction 1, provided that the temperature dependence of the molar extinction coefficients can be allowed for.

The present paper reports a critical application of the UV method to the determination of the isomerization thermodynamics of 1,3-butadiene. Apparent extinction coefficients were measured at 237–249 nm, at temperatures ranging from 426–621 K. Reactions of butadiene[9] under these conditions were negligible. The IR spectrum of the cis–trans mixture reported by SSCA[6] was analyzed. Absorption bands due to the cis isomer were identified and normal-mode wavenumbers were assigned. This provided a basis for analyzing the temperature dependence of UV extinction coefficients for the cis isomer. It also permitted omission of the assumption, commonly made in prior statistical thermodynamic analyses,[2,10] that normal-mode wavenumbers, except for the *s*-torsional mode, are identical for the *s*-cis and *s*-trans isomers.

Experimental Section

Materials. 1,3-Butadiene (Matheson, minimum purity 99.5%) was degassed by at least five freeze–pump–thaw cycles before transfer to the optical measuring cell. Gas pressures were in the range 5–15 torr and were measured to 0.2 torr with a mercury manometer. IR analysis of the gas samples revealed no impurities.

Instrumentation. An oven-type heating compartment was built to fit into the cell compartment of the Perkin-Elmer Model 323 UV spectrophotometer on which the UV spectra were obtained in order to achieve the high temperatures required for the experiments. Briefly, the heating compartment consisted of a heated inner compartment into which the quartz gas sample cell was placed and an outer casing. Both parts were made of brass. The inner compartment was heated by applying an input voltage through surrounding Nichrome wires and was well insulated from the outer casing by layers of meonite. We thank David Eaton for suggestions in the design and for construction of the heating compartment.

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[1] Supported in part by a Brandeis Career Development Fellowship to P.W.M. and by a grant from the Dow Chemical Company.

[2] Bock, C. W.; George, P.; Trachtman, M.; Zanger, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 26–34.

[3] Carreira, L. A. *J. Chem. Phys.* **1975**, *62*, 3851. Durig, J. R.; Bucy, W. E.; Cole, A. R. H. *Can. J. Phys.* **1975**, *53*, 1832.

[4] Chan, S. I.; Borgers, T. R.; Russell, J. W.; Strauss, H. L.; Gwinn, W. D. *J. Chem. Phys.* **1966**, *44*, 1103–1111. Ueda, T.; Shimanouchi, T. *Ibid.* **1967**, *47*, 4042–4047. Laane, J.; Lord, R. C. *Ibid.* **1967**, *47*, 4941–4945. Carreira, L. A.; Lord, R. C. *Ibid.* **1969**, *51*, 3225–3231.

[5] Grunwald, E. *J. Phys. Chem.* **1981**, *85*, 3409.

[6] Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657–3659.

[7] Allinger, N. L.; Tai, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4256. Giordan, J. C.; McMillan, M. R.; Moore, J. H.; Staley, S. W. *Ibid.* **1980**, *102*, 4870.

[8] Lasaga, A. C.; Aerni, R. J.; Karplus, M. *J. Chem. Phys.* **1980**, *73*, 5230.

[9] (a) Kistiakowsky, G. B.; Ransom, W. W. *J. Chem. Phys.* **1939**, *7*, 725. (b) Rice, F. O.; Ruoff, P. M.; Rodowskas, E. L. *J. Am. Chem. Soc.* **1938**, *60*, 955. (c) Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198.

[10] Aston, J. G.; Szasz, G.; Woolley, H. W.; Brickwedde, F. G. *J. Chem. Phys.* **1946**, *14*, 67. Sverdlov, L. M.; Bolotina, E. N. *Russ. J. Phys. Chem. (Engl. Transl.)* **1962**, *36*, 1502. Compton, D. A. C.; George, W. O.; Maddams, W. F. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1666.

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Table I. Apparent Molar Extinction Coefficients and Derived Parameters for 1,3-Butadiene Gas

	$10^{-2}\ \epsilon_{app}$ ($M^{-1}\ cm^{-1}$) at temperature, K										
λ, nm	298	426.3	468.0	500.3	520.0	542.4	545.6	569.2	594.3	620.7	$\Delta H°_{520}$, cal mol^{-1}
237	0.413	2.047	2.997	3.428	4.217	4.427	4.304	4.940	6.253	6.682	3130 ± 100
239	0.298	1.525	2.251	2.594	3.149	3.386	3.319	3.832	4.867	5.204	3060 ± 100
241	0.210	1.110	1.666	1.952	2.348	2.569	2.480	2.885	3.687	3.981	2930 ± 100
243	0.134	0.753	1.164	1.400	1.701	1.874	1.820	2.168	2.729	3.010	2940 ± 100
245	0.078	0.491	0.786	0.967	1.188	1.320	1.261	1.526	1.947	2.183	2900 ± 100
247	0.039	0.290	0.493	0.627	0.788	0.894	0.853	1.060	1.354	1.551	3120 ± 100
249	0.019	0.167	0.305	0.392	0.496	0.582	0.547	0.697	0.907	1.075	3050 ± 100
											av 3020 ± 90
$10^{-6}\ \sigma^2$, cm^{-2} [a]	1.89	2.34	2.56	2.72	2.77	2.90	2.85	3.01	3.04	3.22	
% error of fit	9.0	2.2	1.1	1.1	1.2	0.6	0.6	0.8	0.6	1.1	

[a] Equation 10, $m = 44\,050\ cm^{-1}$.

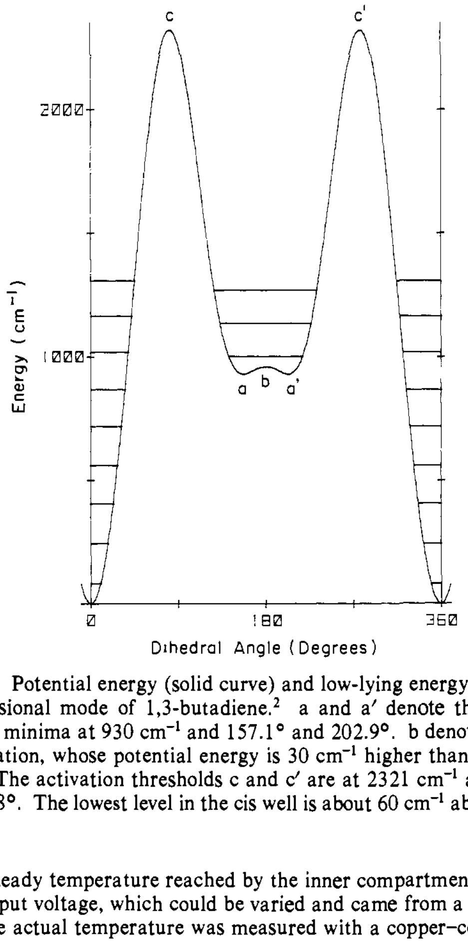

Figure 1. Potential energy (solid curve) and low-lying energy levels for the *s*-torsional mode of 1,3-butadiene.[2] a and a′ denote the gauche potential minima at 930 cm^{-1} and 157.1° and 202.9°. b denotes the cis conformation, whose potential energy is 30 cm^{-1} higher than that of a and a′. The activation thresholds c and c′ are at 2321 cm^{-1} and 82.2° and 277.8°. The lowest level in the cis well is about 60 cm^{-1} above a and a′.

The steady temperature reached by the inner compartment depends on the input voltage, which could be varied and came from a regulated line. The actual temperature was measured with a copper-constantan thermocouple whose accuracy had been checked at a number of thermometric fixed points. The quartz gas sample cell had a cross section of 1.27 × 1.27 cm^2 and a path length of 5.715 cm.

Measurement Procedure. In order to avoid prolonged heating and thus minimize reactions of 1,3-butadiene,[9] we used a relatively high input voltage (60 V) to raise the temperature quickly (3 min for 420 K to 6 min for 620 K) to approximately the desired value. The input voltage was then lowered to the appropriate value to achieve equilibrium at the desired temperature. After the steady state had been established, the UV spectrum was obtained in the range 237–249 nm. Thermocouple readings were taken before and after the UV scan and typically differed by less than 1 K. The two readings were then averaged to give the temperature of the scan.

Errors and Control Experiments. The thermocouple wire near the hot junction was shielded from temperature gradients by immersion in 2.5 cm of copper tubing. The thermal junction itself sat in a small hole inside a copper block and was in direct contact with the quartz gas sample cell. A mercury-in-glass thermometer was mounted at different heights inside the gas sample cell in order to guard further against temperature error and check for temperature uniformity. The temperature read by the mercury-in-glass thermometer was practically independent of height and differed from the thermocouple temperature by no more than 2 K at 600 K and by progressively less at lower temperatures.

In order to make sure that no significant thermal reaction occurred during the heating period, we allowed the gas sample to cool down to room temperature at the end of the series and a UV scan was subsequently taken in the range 237–249 nm. Each time the original room-temperature spectrum was recovered.

In the absorbance measurements, the heated gas was measured vs. air. Similar measurements on the evacuated gas sample cell vs. air gave 100% transmission. On the basis of the precision of values obtained for optical transmission and for butadiene concentration and of the reproducbility of results in different series, we estimate that errors in the extinction coefficients are 2% or 0.3 $M^{-1}\ cm^{-1}$, whichever is greater. Errors in temperature should be less than 2 K.

Infrared Absorption Bands of the Cis Isomer. An IR spectrum in an argon matrix at 20–30 K has been reported by SSCA[6] for a cis–trans mixture of 1,3-butadiene containing a substantial fraction of the cis isomer. Wishing to obtain normal-mode wavenumbers for the cis isomer, we made a list of all absorption bands evident in SSCA's spectrum, including the very weak ones, and identified the bands assignable to the trans isomer by using Shimanouchi's tabulation[11] as a guide. The following is a list of all bands not assignable to the trans isomer, with relative intensities and (anticipating the next section) vibrational assignments.

Wavenumber, cm^{-1} (relative intensity, vibrational assignment): 472 (m, ν_9), 475 (m, ν_{24}), 595 (m, ν_{16}), 615 (weak shoulder, $\nu_{13} + \nu_{24}$), 705 (vw, unexplained), 730 (w, $\nu_{16} + \nu_{13}$), 755 (vw, $2\nu_{13} + \nu_9$; $2\nu_{13} + \nu_{24}$), 870 (vw, $\nu_{12} + \nu_{13}$), 899 (w, ν_7), 913 (vs, ν_{15}), 995 (s, ν_{14}), 1045 (w, $\nu_{11} + \nu_{13}$; $\nu_{15} + \nu_{13}$), 1065–1090 (m, several overlapping bands, mostly due to ν_8 and ν_{23}), 1230 (vw, $\nu_{12} + \nu_{24}$), 1277 (vw, ν_{22}), 1299 (w, ν_6), 1402 (m, ν_{21}), 1425 (s, ν_5), 1470 (vw, $\nu_9 + \nu_{14}$), 1505 (w, $\nu_{10} + \nu_{24}$), 1540 (vw, $\nu_{13} + \nu_{21}$), 1580 (w, $<<uw_{14} + \nu_{16}$), 1612 (m, ν_4), 1632 (s, ν_{20}), 1655 (vw, $\nu_{12} + \nu_{15}$), 1828 (m, $\nu_{11} + \nu_{15}$), 3020 (m, centroid of C–H stretching bands).

The bands at 1045 and 1505 cm^{-1} may contain contributions from combination bands $\nu_9 + \nu_{12}$ and $\nu_{11} + 2\nu_{24}$, respectively, of the trans isomer. The 1277-cm^{-1} band does not clearly disappear when the cis–trans mixture is converted to trans.[21] The 1299-cm^{-1} band may be compared with a Raman cis band at 1309 cm^{-1}.[21]

Results and Discussion

Apparent Extinction Coefficients. Apparent (or formal) extinction coefficients (ϵ_{app}) at temperature T and wavelength λ are defined in (2), where l denotes optical path length and c is the

$$\epsilon_{app}(T,\lambda) = [\log_{10}(I_0/I)]/lc \qquad (2)$$

formal or total 1,3-butadiene concentration in moles per liter. Experimental results are listed in Table I. For the given wavelength range (237–249 nm), one is justified in assuming, on the basis of SSCA's results,[6] that the cis isomer is the sole absorbing species. Let $\alpha(T)$ denote the mole fraction of cis in the equilibrium mixture and $\epsilon_{cis}(T,\lambda)$ denote its "true" molar extinction coefficient. ϵ_{app} is then related to ϵ_{cis} and α according to (3). As a first step in deducing $\alpha(T)$, we shall consider the dependence of ϵ_{cis} on T and λ.

$$\epsilon_{app}(T,\lambda) = \alpha(T)\epsilon_{cis}(T,\lambda) \qquad (3)$$

Normal-Mode Analysis. The formal treatment of $\epsilon(T,\lambda)$ by Grunwald[5] requires a knowledge of the normal-mode wavenumbers and symmetries for the absorbing substrate. We have tried to obtain this information by consideration of published data.

Table II. Normal-Mode Wavenumber (cm^{-1}) for *s-trans-* and *s-cis-*1,3-Butadiene[a]

	nominal motion	$\bar{\nu}_{trans}$[b]	$\bar{\nu}_{cis} - \bar{\nu}_{trans}$ (calcd)[c]	$\bar{\nu}_{cis}$ (pred range)[d]	$\bar{\nu}_{cis}$, (obsd or assigned)
		A_g Symmetry		*A_1 Symmetry	
ν_1	CH_2 asym stretch	3087	−2, +5	3085-3092	(3088)
ν_2	CH stretch	3003	+8, 0	3003-3011	(3007)[j]
ν_3	CH_2 sym stretch	2992	−2, +1	2990-2993	(2992)
ν_4	C=C stretch	1630	−44, −4	1586-1626	1612 (obsd)
ν_5	CH_2 scis	1438	+5, 0	1438-1443	1425 (obsd)
ν_6	CH bend	1280	+33, + 2	1282-1313	1299 (obsd)
ν_7	C-C stretch	1196	−287, −145	909-1051	899 (obsd)
ν_8	CH_2 rock	894	+159, +7	901-1053	~1075 (obsd)[h]
ν_9	CCC deform	512	−101, −191	321-411	472 (obsd)
		*A_u Symmetry		A_2 Symmetry	
ν_{10}	CH bend	1013	+11, +26	1024-1039	(1032)[i]
ν_{11}	CH_2 wag	908	+5, +107	913-1015	915[e]
ν_{12}	CH_2 twist	522	+263, +149	671-785	742[f]
ν_{13}	C-C torsion	162	+17, +29	179-191	136[g]
		B_g Symmetry		*B_2 Symmetry	
ν_{14}	CH bend	976	−3, +36	973-1012	995 (obsd)
ν_{15}	CH_2 wag	912	+2, +12	914-924	913 (obsd)
ν_{16}	CH_2 twist	770	−270, −157	500-613	595 (obsd)
		*B_u Symmetry		*B_1 Symmetry	
ν_{17}	CH_2 asym stretch	3101	−2, −11	3090-3099	(3095)
ν_{18}	CH stretch	3055	−3, +1	3052-3056	(3054)[j]
ν_{19}	CH_2 sym stretch	2984	−2, +1	2982-2985	(2984)
ν_{20}	C=C stretch	1596	+41, +24	1620-1637	1632 (obsd)
ν_{21}	CH_2 scis	1381	+14, +41	1395-1422	1402 (obsd)
ν_{22}	CH bend	1294	−30, −25	1264-1269	1277 (obsd)
ν_{23}	CH_2 rock	990	+65, +67	1055-1057	~1085 (obsd)[h]
ν_{24}	CCC deform	301	+219, +280	520-581	475 (obsd)

[a] Symmetry species with asterisk are IR active. Values of $\bar{\nu}_{cis}$ shown in parentheses are average predictions. [b] Reference 11. [c] First entry, ref 12; second entry, ref 13. [d] $\bar{\nu}_{trans} + (\bar{\nu}_{cis} - \bar{\nu}_{trans})_{calcd}$. [e] From 1828-$cm^{-1}$ band = $\nu_{11} + \nu_{15}$. [f] Average based on the following combination bands: 1655, 870, and 1225 cm^{-1}. [g] Average based on the following combination bands: 615, 730, 755, 870, 1045, and 1540 cm^{-1}. [h] IR spectrum of ref 6 contains an unsymmetrical broad absorption band extending from 1065 to 1090 cm^{-1}. We believe that ν_8 and ν_{23} make dominant contributions. [i] This assignment is consistent with the observation of a $\nu_{10} + \nu_{24}$ combination band at 1505 cm^{-1}. [j] The centroid of CH stretching absorption of the cis isomer was observed at 3020 cm^{-1}.

trans-1,3-Butadiene belongs to symmetry species C_{2h}; *cis*-1,3-butadiene belongs to C_{2v}. For an 180° rotation about the C–C bond, symmetry species for the trans vibration correlate with those for the cis vibration as follows. $A_g \rightarrow {}^*A_1$; ${}^*A_u \rightarrow A_2$; $B_g \rightarrow {}^*B_2$; ${}^*B_u \rightarrow {}^*B_1$. (Vibrations belonging to species with an asterisk are IR active.)

For the trans isomer, we adopted the assignments by Shimanouchi.[11] To make the assignments for the cis isomer, we used a procedure that matches experiment with theoretical prediction.

Two independent theoretical calculations are available for $\bar{\nu}_{trans}$ and $\bar{\nu}_{cis}$. One is based on the CNDO/2 force method;[12] the other is based on the SCF-MO-CI method.[13] Table II lists values thus obtained for $\bar{\nu}_{cis} - \bar{\nu}_{trans}$. To the extent that the theoretical calculations disagree, they define an uncertainty range for the prediction of $\bar{\nu}_{cis} - \bar{\nu}_{trans}$. By adding the appropriate experimental value for $\bar{\nu}_{trans}$,[11] one then generates a range of prediction for $\bar{\nu}_{cis}$ for each mode (Table II).

For IR-active modes, we then compared the ranges of prediction with real absorption bands in the list for the cis isomer generated by SSCA's IR spectrum[6] presented in an earlier section. With two exceptions, we were able to find for each IR-active mode a unique absorption band whose wavenumber corresponds practically to the predicted range and whose intensity is plausible for the given vibration. One of the exceptions comprises the six C–H stretches, which are not resolved in SSCA's spectrum. However, the wavenumbers of these modes are predicted within very narrow limits and thus are not seriously in doubt. The predicted wavenumbers are also in credible agreement with the observed centroid of the C–H stretching absorption near 3020 cm^{-1}.

The second exception comprises the CCC deformation modes ν_9 and ν_{24}. SSCA's IR spectrum[6] shows no bands falling within or near the predicted ranges. The nearest observed bands are two bands of medium intensity at 472 and 475 cm^{-1}. Analysis of combination bands shows that these are separate bands, not merely branches of one and the same band.[14] We decided to assign 472 cm^{-1} to ν_9 and 475 cm^{-1} to ν_{24}.

The change in sign of $\nu_4 - \nu_{20}$ on *s*-trans ⇄ *s*-cis isomerization is consistent with empirical structure–spectrum correlations for C=C stretching wavenumbers of conjugated dienes.[15a]

Modes of A_2 symmetry are not IR active, but the theoretical predictions could be correlated similarly with wavenumbers based on combination bands. For ν_{10}, the prediction is not seriously in doubt and permits interpretation of the band at 1505 cm^{-1} as $\nu_{10} + \nu_{24}$. Concerning, ν_{11}, the trans isomer has an exceptionally strong combination band at 1820 cm^{-1}, which is assigned to $\nu_{11} + \nu_{15}$. The cis isomer has an analogous, similarly strong band at 1828 cm^{-1}, which may similarly be assigned to $\nu_{11} + \nu_{15}$.

The wavenumber listed for ν_{12} is an average based on three combination bands. That for ν_{13} is an average based on six combination bands. Both assignments seem adequately secure. The value for ν_{13} is consistent with a Raman line at 271.1 cm^{-1} assigned by Carreira to the 0–2 transition of the metastable isomer

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(11) Shimanouchi, T. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1972**, *No. 39*, 139.

(12) Panchenko, Yu. N.; Pulay, P.; Torok, F. *J. Mol. Struct.* **1976**, *34*, 283.

(13) (a) Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* **1972**, *94*, 3612. (b) After submission of the manuscript, we became aware of another independent calculation using a 4-31G basis set. The results of that calculation are in essential agreement with those listed in columns 4 and 5 of Table II. Bock, C. W.; Trachtman, M.; George, P. *J. Mol. Spectrosc.* **1980**, *84*, 243. We thank Professor Bock for calling these results to our attention.

(14) The IR spectrum contains one combination line in which a mode of ~475 cm^{-1} is in combination with a mode of B_2 symmetry and three combination lines in which a mode of ~475 cm^{-1} is in combination with a mode of A_2 symmetry.

(15) (a) Schrader, B.; Ansmann, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 364. (b) Osamura, Y.; Schaefer, H. F. *J. Chem. Phys.* **1981**, *74*, 4576.

of 1,3-butadiene.[3] It is also consistent with torsional potential functions proposed by Carreira[3] and by Durig, Bucy, and Cole.[3] BGTZ[2] have proposed that the 271.1-cm^{-1} Raman line be assigned to the 8–10 transition of the trans isomer. Their potential function (Figure 1) predicts that the 0–1 transition in the cis/gauche well should occur at ~120 cm^{-1}.

Although some uncertainties remain, it is clear that the normal-mode wavenumbers for the cis isomer differ considerably from those for the trans. Thus there is a difference of 102 cm^{-1} (290 cal mol^{-1}) in the zero-point energy ΔE_Z [$=(E_{Z,\text{cis}} - E_{Z,\text{trans}})$], which, in a statistical thermodynamic analysis, must be added to the energy difference ΔV of the potential minima.[15b] ($\Delta V = 930$ cm^{-1} in Figure 1.)

In the experimental range of 426–621 K, ΔC°_p [$=(C^\circ_{p,\text{cis}} - C^\circ_{p,\text{trans}})$] ranges from −0.44 to −0.28 cal mol^{-1} K^{-1}, the mean value being −0.35 cal mol^{-1} K^{-1}. Thus ΔH°_T changes by only −70 cal mol^{-1}, or −(2–3)%, over the entire range and may be treated as constant. As a corollary, ΔS°_T may also be treated as constant in this range. We shall use $\Delta S^\circ_{520} = -0.493$ cal mol^{-1} K^{-1}, which is the sum of rotational and vibrational entropy differences. In our calculation of the rotational entropy differences, we adopted the structure proposed by Kuchitsu et al.[16] for the trans isomer and a corresponding structure, but with the CCC bond angle widened by 2.5° as calculated by Radom and Pople,[17] for the cis isomer.

$\Delta H^\circ_T - \Delta S^\circ_0$ at the midpoint of the experimental range (520 K) is −180 cal mol^{-1}.

Effect of Temperature on Cis UV Absorption. In representing $\epsilon(T,\lambda)$ for the UV absorption band of the cis isomer as a function of T and λ, we shall use the approach of Grunwald.[5] The shapes of electronic absorption bands result from the convolution of fine-structure contributions from the various vibrational modes. For medium-sized and large molecules, the number of vibrational modes is substantial. The number of fine-structure lines then is very large, and it increases rapidly with temperature. Because of this complexity, it is necessary to treat the absorption band as an entity with characteristic statistical/average properties rather than analyze the individual fine-structure components (as one does in the spectroscopy of small molecules).

In the present we shall consider the mean wavenumber m, the variance σ^2, and the shape $\epsilon(\lambda)$ of the absorption band. For orbitally allowed electronic transitions, assuming independent contributions from s harmonic vibrations, $m(T)$ is given by (4) and $\sigma^2(T)$ is given by (5).[5] Here, primed symbols refer to the

$$m(T) = \bar{\nu}(0,0) + \sum_{i=1}^{s} \bar{\nu}_i'(a_i + b_i) + \sum_{i=1}^{s} \langle n_i \rangle (\bar{\nu}_i' - \bar{\nu}_i + 2b_i\bar{\nu}_i') \quad (4)$$

$$\sigma^2(T) = \sum_{i=1}^{s} (\bar{\nu}_i')^2[(\bar{\nu}_i' a_i/\bar{\nu}_i + 2b_i)(1 + 2\langle n_i \rangle) + 2b_i\langle n_i \rangle^2] + \sum_{i=1}^{s} \langle n_i \rangle (1 + \langle n_i \rangle)(\bar{\nu}_i' - \bar{\nu}_i + 2b\bar{\nu}_i')^2 \quad (5)$$

excited electronic state, unprimed symbols to the ground electronic state. The summations extend over all vibrational modes. $\bar{\nu}(0,0)$ is the wavenumber for the zero–zero transition and $\langle n_i \rangle$ is the mean excitation number of the ith mode at temperature T, given by (6).

$$\langle n_i \rangle = \exp(-h\nu_i/kT)/[1 - \exp(-h\nu_i/kT)] \quad (6)$$

The dimensionless parameters a_i and b_i are defined in (7) and (8), where $q_{0,i}$ denotes the equilibrium value of the ith normal coordinate in a mass-weighted coordinate system and $\delta_{q_i} = q_{0,i}' - q_{0,i}$. y_i [$=(2\pi)^{-1}(h/\nu_i)^{1/2}$] is the half-width of the ith potential well, in mass-weighted coordinates, when $n_i = 0$. $q_{0,i}$ and $q_{0,i}'$ can be different from zero only for totally symmetric modes. For *cis*-1,3-butadiene we expect, therefore, that terms involving a_i are nonzero only for modes of A_1 symmetry.

$$a_i = \frac{1}{2}\frac{\nu_i'}{\nu_i}\left(\frac{\delta q_i}{y_i}\right)^2 \quad (7a)$$

$$a_i = \frac{1}{2}\frac{\nu_i'}{\nu_i}\left(\frac{\delta q_i}{q_{0,i}}\right)^2\left(\frac{q_{0,i}}{y_i}\right)^2 \quad (7b)$$

$$b_i = [\nu_i^{1/2} - (\nu_i')^{1/2}]^2/(\nu_i\nu_i')^{1/2} \quad (8)$$

Within the constraints imposed by the basic model, eq 4–8 apply regardless of band shape.[18]

Concerning the *shape* of the electronic absorption band, there are two limiting conditions under which it becomes Gaussian.

(1) As s becomes large. The central limit theorem of statistics[18] states that the convolution of s independent probability distributions of arbitrary shapes approaches a Gaussian distribution as s becomes large. For an electronic absorption band, the modewise contributions to the absorption probability are exact analogues of probability distributions.[5]

(2) As T becomes high. With increasing temperature, the number of excited vibrational states whose population is significant increases and, as a consequence, so does the number of statistical convolutions whose resultant determines the overall band shape. As the number of such convolutions becomes large, the shape of the overall absorption band becomes Gaussian.

For *cis*-1,3-butadiene, $s = 24$. This is a moderate rather than a large number, and the UV absorption band reported by SSCA[6] at 20–30 K in an argon matrix is not Gaussian. One would expect, however, that a Gaussian shape is approached at sufficiently high temperatures, and we shall show that such shape is evident in the experimental range of 426–621 K. Before presenting that analysis, it will be useful to introduce some further considerations.

Lasaga, Aerni, and Karplus (LAK)[8] have calculated the molecular geometries of the $^1A_g^-$ and $^1B_u^+$ states of *trans*-1,3-butadiene, as well as $\bar{\nu}_i$ and $\bar{\nu}_i'$ for all vibrational modes. If their results apply to the cis isomer (at least in order of magnitude), application of eq 4 and 5 leads to the following conclusions.

(1) m is practically independent of T.

(2) σ^2 is expected to vary with T. Up to 620 K, terms involving b_i and terms involving $(\bar{\nu}_i - \bar{\nu}_i')^2$ are relatively negligible. Temperature dependence enters through the terms involving a_i. However, among the modes with A_1 symmetry, only two—ν_4(C=C stretch) and ν_7(C—C stretch)—are expected to contribute appreciably, because only for them is $q_{0,i}$ expected to change sufficiently on excitation. Equation 5 therefore simplifies approximately to (9).

$$\sigma^2(T) = \sigma_0^2 + \frac{2(\bar{\nu}_4')^3}{\bar{\nu}_4}a_4\langle n_4 \rangle + \frac{2(\bar{\nu}_7')^3}{\bar{\nu}_7}a_7\langle n_7 \rangle \quad (9)$$

Orders of magnitude of the parameters may be predicted as follows.

(1) From the UV spectrum for *cis*-1,3-butadiene at 20–30 K in an argon matrix published by SSCA,[6] we calculate that m = 43 930 cm^{-1} (227.6 nm).

(2) With the trans isomer as a model, $2a_4 \approx 2.0$ and $2a_7 \approx 1.5$, on the basis of LAK's calculations.[8] Values for the cis isomer might agree as to order to magnitude.

As a matter of fact, in the temperature range 426–621 K, the data in Table I are reproduced quite well by Gaussian band shapes. The correlations involve (10), which is obtained by introducing

$$\epsilon_{\text{app}}(T,\lambda) = \frac{\alpha(\text{T})\epsilon_{\text{cis}}^\circ}{(2\pi)^{1/2}\sigma(T)} \exp\left[-\frac{1}{2}\left(\frac{\bar{\nu} - m}{\sigma(T)}\right)^2\right] \quad (10)$$

a Gaussian function for $\epsilon_{\text{cis}}(T,\lambda)$ into (3). $\epsilon_{\text{cis}}^\circ$ is a temperature-independent constant. m is expected to be independent of T.

On fitting the data one temperature at a time, we find that m = 44 050 ± 300 cm^{-1} (227.0 ± 1.5 nm). This value, which applies to the gas phase, is in very reasonable agreement with the value of 43 930 cm^{-1} calculated from SSCA's results[6] for *cis*-1,3-bu-

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(16) Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1968**, *1*, 463.

(17) Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4786.

(18) Feller, W. "An Introduction to Probability Theory and Its Applications", 3rd ed.; Wiley: New York, 1968; Vol. 1, pp 62, 222, 230, 253-256, 266-270.

tadiene in an argon matrix, confirming that the wavelength range listed in Table I indeed measures absorption by the cis isomer.

Using $m = 44\,050$ cm^{-1}, one finds that least-squares fitting to (10) yields values for $\sigma^2(T)$, as listed in Table I. The table also includes standard percent errors of fit of ϵ_{app}, which, except at 298 K, are easily compatible with our experimental errors. At 298 K the error of fit is higher, reflecting in part the greater experimental error when ϵ_{app} is small. (The error is 2% at 237–243 nm and then increases progressively with wavelength to 15% at 249 nm.) Also, at 298 K the temperature may be too low for the assumed Gaussian band shape to be valid.

As shown in Table I, the $\sigma^2(T)$ parameters increase with T, as expected. In the approximation of (9), this variation depends on both $\langle n_4\rangle$ and $\langle n_7\rangle$. However, in the temperature range 426–621 K, $\langle n_4\rangle$ and $\langle n_7\rangle$ show a strong linear correlation; (11) fits with a correlation coefficient of 0.997. Accordingly, (9) really

$$\langle n_4\rangle = -7.41 \times 10^{-3} + 0.2170\langle n_7\rangle \qquad 426 < T < 621\ \text{K} \qquad (11)$$

contains only one independent variable. We chose it to be $\langle n_7\rangle$. The least-squares result was (12). It fits $\sigma^2(T)$ with the remarkably small standard error of 1.5%.

$$\sigma^2(T) = 1.94 \times 10^6 + (9.06 \times 10^6)\langle n_7\rangle \qquad 426 < \text{T} < 621\ \text{K} \qquad (12)$$

By comparing the parameters in (12) with those in (9) and (11), the following ranges are established: $1.94 \times 10^6 < \sigma_0{}^2 < 2.25 \times 10^6$ cm^{-2}; $0 < a_7 < 11.2$; $a_4 = (11.2 - a_7)/0.217$.

The range established for $\sigma_0{}^2$ may be compared with $\sigma^2(298)$, at which temperature the effects of thermal excitation of modes ν_4 and ν_7 are quite small. The value listed in Table I is 1.89×10^6 cm^{-2}; its statistical error is about 10%. Thus there is internal consistency.

The slope in (12) may be compared with the prediction based on a priori estimates of a_4 and a_7 for the trans isomer made earlier. The slope thus predicted for the trans isomer is 2.3×10^6 cm^{-2}, about one-fourth of the slope obtained in (12) for the cis isomer. The two values are not close, but at least they agree in order of magnitude. Perhaps that is as good as one may expect, considering that a_i depends on the *square* of the relatively small change in $q_{0,i}$ on electronic excitation, and thus is quite sensitive to changes in molecular structure and to error in its theoretical prediction. It should also be noted that ν_4 and ν_7 do not represent pure C=C and C—C stretching and conversely that contributions from other modes of A_1 symmetry may not be truly negligible.

Calculation of $\Delta H°$. Let K denote the equilibrium constant for (1). Then $K = \alpha/(1 - \alpha)$ and $\alpha = K/(1 + K)$. On introducing this in (10) and taking logarithms, we obtain (13). In the range

$$\ln \epsilon_{\text{app}}(T,\lambda) = \ln K(T) - \ln [1 + K(T)] + \ln \epsilon_{\text{cis}}{}^{\circ} - 0.5 \ln 2\pi - \ln \sigma(T) - 0.5[(\bar{\nu} - m)/\sigma(T)]^2 \qquad (13)$$

426–621 K, as has been shown, $\Delta H°$ and $\Delta S°$ for (1) may be regarded as constant and equal to their respective values at the median temperature, 520 K. Moreover, $\Delta S°_{520} = -0.493$ cal mol^{-1} K^{-1}. ln $K(T)$ is therefore given by (14). Since $\sigma(T)$ and m are known (Table I), (13) and (14) together involve only two unknown parameters, ln $\epsilon_{\text{cis}}{}^{\circ}$ and $\Delta H°_{520}$.

$$\ln K(T) = -0.249 - \Delta H°_{520}/RT \qquad (14)$$

Values for $\Delta H°_{520}$ were calculated in this way by least-squares fitting of ln $\epsilon_{\text{app}}(T,\lambda)$ as a function of T at each wavelength. Results, given with one insignificant guard figure, are listed in Table I. Their statistical errors are about 100 cal mol^{-1}. Their mean is 3020 cal mol^{-1}, and the standard deviation is 90 cal mol^{-1}. The deviations from the mean are therefore consistent with the statistical errors of the individual $\Delta H°_{520}$ values. This, together with the good fit of the Gaussian band-shape function at all temperatures in the given range, justifies the suggestion that the present treatment is free of systematic error.

On the other hand, in examining the sequence of values obtained for $\Delta H°_{520}$ with increasing wavelength, one perceives the possibility that the values vary smoothly, passing through a minimum. In the language of random sampling theory, the sequence of deviations from the mean, with increasing wavelength, contains three runs, deviations being first positive, then negative, then positive. The statistical probability that seven consecutive samples in a random distribution contain exactly three runs is 1/7.[18] In a test for randomness, that would be acceptable.

Another source of error for $\Delta H°_{520}$ is the mean wavenumber m, whose precision has been estimated as ±300 cm^{-1}. On repeating the calculations of $\Delta H°_{520}$ using different values for m, we find that an error of 300 cm^{-1} in m causes a 110 cal mol^{-1} error in $\Delta H°_{520}$. The overall error in $\Delta H°_{520}$ is therefore estimated as 150 cal mol^{-1}.

In an earlier section we had obtained values of −180 ± 30 and +290 ± 90 cal mol^{-1} for $\Delta H°_{520} - \Delta H°_0$ and ΔE_Z, respectively. On combining them with the average for $\Delta H°_{520}$ listed in Table I, we obtain the following energy quantities for (1):

$$\Delta H°_0 = \Delta E°_0 = (3020 \pm 150) + (180 \pm 50) = 3200 \pm 160\ \text{cal mol}^{-1}$$

$$\Delta V = \Delta E°_0 - \Delta E_Z = (3200 \pm 160) - (290 \pm 90) = 2910 \pm 180\ \text{cal mol}^{-1}$$

Our results may be compared with the following literature values. Carreira[3] assigned the 271.1-cm^{-1} Raman line of 1,3-butadiene to the cis isomer, partly because on raising the temperature of the gas, the line intensity increased.[19] On the basis of semiquantitative measurements at temperatures above room temperature, he estimated that $\Delta H° = 2700 \pm 500$ cal mol^{-1}.

Huber-Wälchli equilibrated 1,3-butadiene gas at 300–1000 K and then analyzed the conformational mixture by IR spectroscopy after trapping it in a cold matrix.[20] His result for $\Delta H°$ is 2500 ± 500 cal mol^{-1}. Within experimental errors, Carreira's[3] and Huber's[20] results agree with ours.

The potential energy difference ΔV for a *s*-trans → *s*-cis has been deduced experimentally, chiefly from Raman spectral data for the torsional mode.[2,3] Results deduced for ΔV *from the same data* vary from 2500 to 3290 cal mol^{-1}, depending on the details of the reasonable model chosen for interpreting the data, and thus bracket our result. The value favored by BGTZ[2] is 2660 cal mol^{-1}. We estimate its accuracy as not better than ±200 cal mol^{-1}.

Concluding Remarks

Besides strengthening our knowledge of the isomerism of 1,3-butadiene, our results—from a broader point of view—demonstrate the potential of UV absorption measurements over a wide high-temperature range as a method for measuring equilibria with small $\Delta H°$. However, it is essential in the analysis of such data to allow for the temperature dependence of extinction coefficients. The present example shows that the degree of empiricism involved in the analysis can be reduced by relating the mean and variance of the given UV absorption band to molecular vibrations of the given substrate. This approach is especially powerful when the temperature is high enough so that the shape of the UV absorption band is essentially Gaussian.

Registry No. 1,3-Butadiene, 106-99-0.

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(19) Bock et al. appear to have missed this important diagnostic observation in their interpretive review (ref 2).

(20) Huber-Wälchli, P. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 10.

(21) We thank Professor Michael E. Squillacote for this private communication.