Conformations of Conjugated Hydrocarbons. Part 1. A Spectroscopic and Thermodynamic Study of Buta-1,3-diene and 2-Methylbuta-1,3-diene (Isoprene)

By **David A. C. Compton** and **William O. George,*** Department of Science, The Polytechnic of Wales, Pontypridd, Mid Glamorgan CF37 1DL
William F. Maddams, The British Petroleum Co. Ltd., Group Research and Development Department, Epsom, Surrey

Complete vibrational spectra of both buta-1,3-diene and 2-methylbuta-1,3-diene (isoprene) have been recorded over a range of temperatures. It is indicated by spectroscopic and thermodynamic methods that both compounds exhibit an equilibrium (s-*trans* $\rightleftharpoons$ s-*cis*) and the *gauche*-conformers are not present. Measurement of intensities of selected Raman bands of isoprene over a range of temperatures leads to a value of $\Delta H^\ominus$ ± standard deviation of 4.59 ± 0.16 kJ mol^{-1} and a value of $\Delta S^\ominus$ of -0.8 J K^{-1} mol^{-1}. The complex methyl torsions of both conformers of isoprene have been assigned and the heights of the three-fold barriers calculated. Complete vibrational assignments for both conformers of isoprene have been made except for the s-*cis* C–C torsional frequency. Comparison between thermally derived thermodynamic functions and those derived by statistical mechanics leads to a value of $\Delta H^\ominus$ of 10.4 kJ mol^{-1} for butadiene, and a concentration of less than 3% s-*cis*-butadiene at normal temperatures. Using the experimental value of $\Delta H^\ominus$ obtained for isoprene new values of thermodynamic functions have been calculated over a range of temperatures, indicating a concentration of 11% s-*cis*-isoprene at normal temperature.

CONFORMATIONAL equilibria in substituted buta-1,3-dienes influence the physical and chemical properties of this class of compounds, which are of some significance in polymeric and biological structures. Buta-1,3-diene [1-5] and 2-methylbuta-1,3-diene [6-8] (isoprene) have been shown to exist predominantly in the s-*trans*-form. Thermodynamic [9] and force constant calculations have previously been made on the basis of frequency assignments based on incomplete low frequency data.

Much work [10-15] has been carried out to gain evidence of the high energy conformers of both compounds and to assign structures if possible. N.m.r. data have been interpreted in terms of a *gauche* structure [11,12] but other n.m.r. work was interpreted in terms of an s-*cis* high energy conformer [13] in line with theoretical studies.[14] Carriera has recently assigned low-frequency Raman bands to the torsional overtones of the s-*cis*-conformer of buta-1,3-diene,[15] and Kuznetsov previously assigned Raman bands in the 500—1 200 cm^{-1} regions of isoprene vapour to the s-*cis*-form.[16]

In the present work, variable temperature i.r. and Raman studies do not support many of the previous assignments, and enable revised thermodynamic functions to be calculated. Comparison between these thermodynamic functions, based on spectroscopic data, with those based on calorimetric data leads to estimation of the amount of high energy form for butadiene and to evidence that this is s-*cis* rather than *gauche*. Molecular models show that the s-*trans*-conformer of isoprene has the rotation of the methyl group hindered by its proximity to a vinylic hydrogen on the terminal carbon atom, whereas the s-*cis*-conformer shows no such steric hindrance. Hence we would expect the methyl torsion for the s-*trans*-conformer to have a higher three-fold barrier height than that for the s-*cis*-conformer. Steric factors also suggest that the enthalpy difference between conformers, $\Delta H^\ominus$, should be lower for isoprene than butadiene, which would lead to a higher concentration of s-*cis*-isoprene than of s-*cis*-butadiene.

EXPERIMENTAL

Spectroscopic grade samples of both butadiene and isoprene were supplied by B.P. Ltd. For i.r. work commercial samples were used after repeated trap-to-trap distillation on a vacuum line. Butadiene was stored at liquid nitrogen temperature on the line and isoprene was stored as a liquid over $CaSO_4$.

Raman spectra were run on a JEOL JRS S1 spectrometer using a Coherent Radiation argon ion laser. Samples were investigated in sealed Pyrex Raman tubes as liquids, or as annealed solids, using standard JEOL variable temperature equipment, and 514.5 and 488.0 nm laser lines. The spectrometer wavenumber scale was calibrated by using laser lines, and the temperature controller was calibrated by 3 f.p. measurements chosen over the range of temperatures used.

Mid-i.r. spectra were recorded on a Perkin-Elmer 521 spectrophotometer with KBr windows for gas samples in a 10 cm cell, or KRS5 windows for liquid and solid samples at various pathlengths, held in a RIIC VLT2 variable temperature unit. A high temperature gas cell of 10 cm path length was used up to 200 °C for gaseous samples. By using an Air Products AC2L cryostat a sample of isoprene was

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[14] L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4792.

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cooled in an inert argon matrix to 20 K and the i.r spectrum recorded.

Far-i.r. spectra were recorded on a Beckman RIIC FS-720 interferometer with off-line computing using apodisation. Liquids, solutions in cyclohexane, and frozen solids were held between polyethylene windows in the RIIC VLT2 unit, although slow loss of sample through the windows occurred. Vapour was distilled into a 1 m gas cell and spectra were recorded at various pressures; however, it was found particularly difficult to exclude traces of water vapour from isoprene. Various theoretical resolutions from 5 cm^{-1} for liquid and solid samples to 1 cm^{-1} for gases were used.

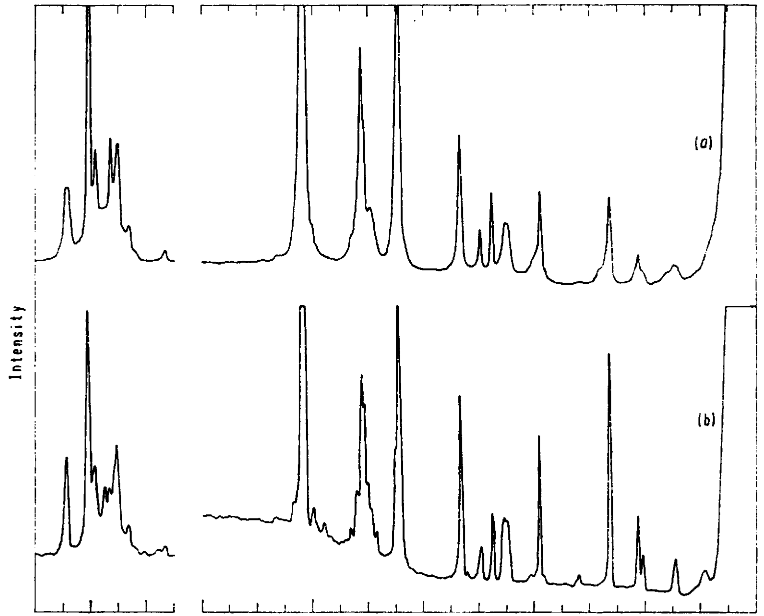

FIGURE 1 Raman spectra of isoprene, 0—3 200 cm^{-1}: (a) liquid at 20 °C; (b) solid at − 162 °C

Variable-temperature Studies.—High temperature i.r. studies have been carried out on butadiene [10,17] and isoprene,[18] and certain bands have been assigned to high energy conformers on the basis of their temperature dependence. In the present work we have extended these studies to low temperatures to avoid possibilities of decomposition and to obtain more clearly defined spectra.

Reznikova *et al.*[10] examined the i.r. spectrum of butadiene up to 130 °C and assigned bands at 462, 565, 1 125, and 1 430 cm^{-1} to the s-*cis*-conformer. A value for $\Delta H^{\ominus}$ of 7.1 kJ mol^{-1} for the s-*trans* $\rightleftharpoons$ s-*cis* equilibrium was obtained. However we found little correspondence between our results in this region and those previously reported, and so we cannot support either this value of $\Delta H^{\ominus}$, or the assignment to the s-*cis*-conformer.

For isoprene Dzessati *et al.*[18] report a marked increase in absorption at elevated temperatures in the regions 500—575, 1 210—1 290, and 1 490—1 570 cm^{-1}, and a value of $\Delta H^{\ominus}$ for the s-*trans* $\rightleftharpoons$ s-*cis* equilibrium of 6.3 kJ mol^{-1}. We examined the i.r. spectrum of isoprene up to 480 K (at which point polymerisation occurred) and observed a marked increase in intensity in the 1 250—1 290 cm^{-1} region; a series of weak shoulders increased with a weak band at 1 300 cm^{-1}. However on freezing a liquid sample these peaks do not disappear and so cannot be assigned to a high energy conformer. The 1 300 cm^{-1} band is strong in the Raman spectrum, in which no temperature dependence is apparent.

A liquid sample of isoprene at 0.5 mm pathlength was carefully examined over a range of low temperatures in the i.r. A very weak shoulder at 525 cm^{-1} increased on cooling and another very weak shoulder at 555 cm^{-1} disappeared. In the Raman a medium intensity band at 526 cm^{-1} has a weak shoulder at *ca.* 555 cm^{-1} which disappears on freezing. Figure 1 shows the Raman spectrum of isoprene in the liquid and solid phases.

According to the van't Hoff isochore equations (1) and(2) apply, where E is the concentration of a conformer and I its

$$\ln K = -\Delta H^{\ominus}/RT + \Delta S^{\ominus}/R \qquad (1)$$

$$\therefore \quad \ln(I_{\mathrm{A}}/I_{\mathrm{B}}) = -\Delta H^{\ominus}/RT + \Delta S^{\ominus}/R + \ln\,(E_{\mathrm{B}}/E_{\mathrm{A}}) \qquad (2)$$

Raman band intensity. Hence $\Delta H^{\ominus}$ may be obtained from a plot of ln $(I_{\mathrm{A}}/I_{\mathrm{B}})$ against I/T, and $\Delta S^{\ominus}$ may be calculated if ln $(E_{\mathrm{B}}/E_{\mathrm{A}})$ is known.

Hartmann *et al.*[19] showed that if a plot of integrated i.r. absorbances of the respective conformer bands gives a straight line then the ratio of extinction coefficients can be calculated. A similar expression (3) can be written for Raman band intensities. A series of 11 intensity measure-

$$I_{\mathrm{A}} = -(E_{\mathrm{B}}/E_{\mathrm{A}})I_{\mathrm{B}} + C_{\mathrm{T}}/E_{\mathrm{A}} \qquad (3)$$

ments over the range of temperatures 136.5—306 K led to a value of $\Delta H^{\ominus}$ ($\pm\ \sigma$) of 4.59 ± 0.16 kJ mol^{-1} (Figure 2). At the higher temperatures some curve resolution was necessary and this was facilitated by the high symmetry of the major

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[17] P. A. Bazhulin, Yu. A. Lazarev, and N. V. Desyatova, *Optika i Spektroskopiya*, 1962, **13**, 75.

[18] S. Dzhessati, A. R. Kyazimova, V. I. Tyulin, and Y. A. Pentin, *Vestnik Moskov Univ. Khim.*, 1968, **23**, 19.

[19] K. O. Hartmann, G. L. Carlson, R. E. Witkowski, and W. G. Fateley, *Spectrochim. Acta*, 1968, **24**, 157.

band at 526 cm^{-1}. These results are significantly different from the previous value[18] of 6.3 kJ mol^{-1}. As a plot of I_A against I_B gave a good straight line of slope -1.000 the intercept of the above plot was used to give a value for $\Delta S^{\ominus}$ of -0.84 J K^{-1} mol^{-1}, but the possible error on this is high owing to the long extrapolation required.

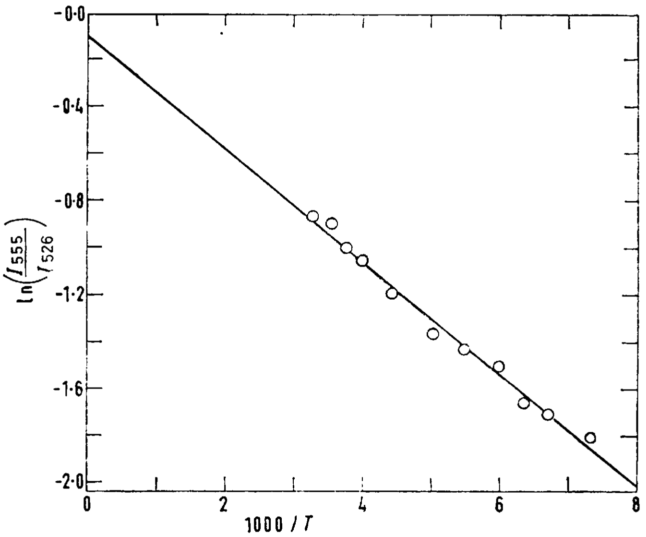

FIGURE 2 Plot of log I_{555}/I_{526} *versus* reciprocal temperature for liquid isoprene

If the high energy conformer is s-*cis* then equation (4) applies, where D is the product of the three principal moments

$$\begin{aligned}\Delta S^{\ominus} &= \Delta S^{\ominus}{}_{\mathrm{ROT}} + \Delta S^{\ominus}{}_{\mathrm{VIB}} \\ &= R\ln(D_{\mathrm{C}}/D_{\mathrm{T}})^{\frac{1}{2}} + \Delta S^{\ominus}{}_{\mathrm{VIB}} \\ &= -0.09 + \Delta S^{\ominus}{}_{\mathrm{VIB}} \qquad (4)\end{aligned}$$

of inertia (C for *cis*, T for *trans*). However if two *gauche*-conformers are present then $\Delta S^{\ominus}$ has an additional term of $R \ln 2$.

Unfortunately $\Delta S^{\ominus}{}_{\mathrm{VIB}}$ cannot be fully evaluated until the high energy C–C torsional frequency is located, but an approximate range is -1.0 to -1.5 J K^{-1} mol^{-1}. Thus the value for $\Delta S^{\ominus}$ expected for the s-*trans* $\rightleftharpoons$ s-*cis* equilibrium is -1.1 to -1.6, and that for the s-*trans* $\rightleftharpoons$ *gauche* equilibrium is $+4.6$ to $+5.1$. The experimentally determined value (-0.84) therefore supports the view that the high energy conformer is s-*cis*.

A weak shoulder at *ca.* 311 cm^{-1} on the 280 cm^{-1} band disappeared on freezing, but a very broad weak residual band underlying at *ca.* 340 cm^{-1} prevented accurate determination of $\Delta H^{\ominus}$. Bands at the same frequencies showed temperature dependence in the far i.r. but absorption of the cell windows in this region prevented accurate intensity measurements.

Other weak Raman bands at *ca.* 419, 435, and 635 cm^{-1} disappear on freezing and we have assigned them as s-*cis*-conformer fundamentals as they lie close to s-*trans*-fundamentals, but these bands were not suitable for intensity measurement. A table of the complete vibrational spectrum of isoprene is available as Supplementary Publication No. SUP 21826 (3 pp.);† i.r. torsional hot bands are given in Table 1.

Torsional Frequencies.—The torsional frequencies of butadiene and isoprene were observed by Fateley *et al.*[20] and barrier heights calculated, but the spectra were only run at low resolution. Cole *et al.*[21] examined the spectrum of butadiene at high resolution and assigned only one C–C torsion with hot bands at lower frequency. Carriera[15] located another C–C torsion at *ca.* 137 cm^{-1} by examining Raman overtones, and assigned it to the s-*cis*-conformer.

We examined the far i.r. spectrum of gaseous isoprene and found a complex spectrum below 200 cm^{-1}. Only one C–C torsion was located at 152.7 cm^{-1} with hot bands at *ca.* 150.7 and 149.6 cm^{-1}. The s-*cis* torsion could not be located. This led to a value for the barrier, V^*, of 143.2 kJ mol^{-1}, to be compared with 149.3 previously determined.

We observed two series of methyl torsions and assigned the stronger fundamental at 199.3 cm^{-1} to the s-*trans*-conformer and the weaker at 196.7 cm^{-1} to the s-*cis*-conformer. Using these $0 \longrightarrow 1$ torsions the solution of the parameter s of the Mathieu Equation[22] was calculated and two series of higher torsions were predicted. Where possible the weak torsions were tentatively assigned, but this process was hindered by the presence of traces of water vapour which we were unable to exclude. In Table 1 calculated and observed frequencies are compared, and the first two torsions of each conformer are shown in Figure 3. To confirm the assignments we reversed the $0 \longrightarrow 1$ assignments, so obtaining new values of s for each conformer, and then attempted

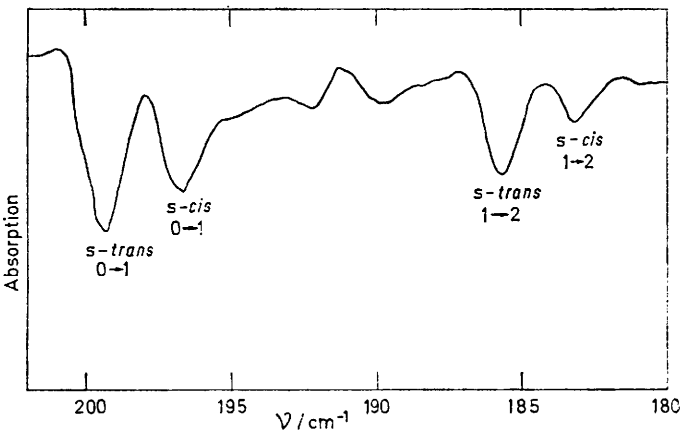

FIGURE 3 Far-i.r. spectrum of gaseous isoprene from 202 to 180 cm^{-1} showing the first two torsional frequencies of both conformers

TABLE 1

Isoprene methyl torsions

Torsion	s-*trans*		s-*cis*	
	$\nu_{\text{calc.}}$	ν_{found}	$\nu_{\text{calc.}}$	ν_{found}
$0_A \longrightarrow 1_A$		199.3		196.7
$0_E \longrightarrow 1_E$				
$1_E \longrightarrow 2_E$	185.4	185.7	182.3	183.1
$1_A \longrightarrow 2_A$	185.3		182.2	
$2_A \longrightarrow 3_A$	169.9	170.5	166.4	165.3
$2_E \longrightarrow 3_E$	168.9	168.7	166.8	164.7
$3_E \longrightarrow 4_E$	151.6	*a*	147.5	146.5
$3_A \longrightarrow 4_A$	143.2	144.7	135.2	136.1
$4_A \longrightarrow 5_A$	154.1	155.5	158.2	*b*
$4_A \longrightarrow 6_A$	195.0	*b*	189.8	189.7

[a] Absorption by C–C torsion. [b] Absorption by water vapour.

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† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin II*, 1975, Index issue.

[20] W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, 1965, **21**, 231.

[21] A. R. H. Cole, A. A. Green, and G. A. Osborne, *J. Mol. Spectroscopy*, 1973, **48**, 212.

[22] J. R. Durig, S. M. Craven, and W. C. Harris, 'Vibrational Spectra and Structure,' vol. 1, ch. 4, Dekker, New York, 1972.

TABLE 2

Isoprene

Parameter	Units	s-*trans* This work	s-*trans* Other work	s-*trans* Ref.	s-*cis* This work
I_A	10^{-40} g cm^2	97.353	98.447	6	87.009
I_B		201.367	201.055	6	216.799
I_C		293.262	294.322	6	298.349
Two-fold barrier					
I_m	10^{-40} g cm^2	14.370	14.927	10	
F	cm^{-1}	1.948	1.875	10	
ν	cm^{-1}	152.7	153	10	
V *	kJ mol^{-1}	143.2	149.3	10	
Three-fold barrier					
$rI\alpha$	10^{-40} g cm^2	5.309 9			5.169 7
F	cm^{-1}	5.271 5			5.414 4
ν	cm^{-1}	199.3	196	10	196.7
V_3	kJ mol^{-1}	11.327	10.962	7	10.798

to predict the torsions again. However this test was very sensitive: even the 1 ⟶ 2 torsions were inaccurately predicted by 2.7 and 1.3 cm^{-1} and these differences increased greatly to higher torsional levels.

The calculated barrier heights V_3 of 11.33 for s-*trans* and 10.80 for s-*cis* in Table 2 show that the s-*cis* barrier is lower by 0.5 kJ mol^{-1}, which we consider due to steric hindrance in the s-*trans*-conformer. The quoted barrier for s-*trans*-isoprene from microwave spectroscopy by Hsu [7] is 10.96 ± 0.41 kJ mol^{-1}, which is in good agreement.

Assignments.—Careful examination of the Raman and i.r. spectra of butadiene from 40 to 4 000 cm^{-1} (with special regard to depolarisation and band contour data) supported the assignments given by Panchenko.[23] The fundamental cm^{-1} values have been slightly altered, especially in the C–H stretch region, and several values have been taken from Cole *et al.*[4,21]

The isoprene molecule differs from butadiene in the replacement of one C–H by a C–Me group. The basic butadiene spectrum is altered in the following ways: (1) loss of 1 C–H stretch, 1 C–H bend, 1 *cis* wag and 1 *trans* wag; (2) gain of 2 methyl rocks (1 op and 1 ip), 1 methyl torsion (op), 3 methyl C–H stretches (1 op), 3 methyl deformations (2 asym, 1 op), 1 C–Me stretch, and several skeletal modes. Bands at 1 145 and 1 069 cm^{-1} are assigned to methyl rocking modes, and the asymmetric methyl deformations appeared close together at 1 466 and 1 442 cm^{-1} with the symmetric deformation at 1 414 cm^{-1}. There appears to be coupling of the two C–C bond stretches. Tentative assignments have been made to two polarised modes at 1 291 (strong in the Raman) and 953 cm^{-1} (weak in the Raman).

Difficulty was found in assigning the high frequency =CH$_2$ rock but a spectrum run in a cold argon matrix at 20 K showed two bands at 982 and 990 cm^{-1} which were coincident at room temperature. The former is the characteristic *trans* wag and the latter is the =CH$_2$ rock. This explains the polarised nature of the corresponding Raman band in terms of overlapping in-plane and out-of-plane vibrations.

Table 3 shows our assignments and the values for the fundamental frequencies used in the thermodynamic calculations.

Thermodynamic Calculations.—The calculation of thermodynamic parameters by statistical methods has recently been reviewed.[24] The calculated values of these parameters for butadiene and isoprene based on spectroscopic assignments to s-*trans*-conformers are lower than the values based on thermal measurements by Scott *et al.*[25] for butadiene and by Kilpatrick *et al.*[26] for isoprene. This discrepancy suggests the existence of an additional conformer which increases the energy of the system.

TABLE 3

Fundamentals

Butadiene s-*trans*	Butadiene s-*trans*	Butadiene s-*cis*	Vibration	Isoprene s-*trans*	Isoprene s-*cis*	Isoprene s-*trans*
A_g	3 102		asym. =C–H str.	3 097 *		A'
B_u	3 095		asym. =C–H str.	3 092		A'
B_u	3 056		asym. =CR–H str.			
A_g	3 028		sym. =CR–H str.	3 020 *		A'
A_g	3 008		sym. =CH$_2$ str.	2 988		A'
B_u	2 982		sym. =CH$_2$ str.	2 978		A'
			op asym. Me str.	2 956		A''
			ip asym. Me str.	2 928		A'
			ip sym. Me str.	2 910		A'
A_g	1 638		sym. C=C str.	1 638 *		A'
B_u	1 598		asym. C=C str.	1 603		A'
			ip asym. Me def.	1 466		A'
			op asym. Me def.	1 442		A''
A_g	1 438		sym. =CH$_2$ scissor	1 425		A'
			ip sym. Me def.	1 414		A'
B_u	1 384		asym. =CH$_2$ scissor	1 388		A'
B_u	1 296.2		C–H bend	1 303		A'
A_g	1 278		C–H bend			
A_g	1 203		C–C str.	1 291 *		A'
			ip Me rock	1 145		A'
			op Me rock	1 069		A''
A_u	1 013.2		op *trans* wag	990		A''
B_u	985		ip =CH$_2$ rock	990		A'
B_g	966		op *trans* wag			
			C–C str.	953 *		A'
B_g	910		op =CH$_2$ wag	903		A''
A_u	907.8		op =CH$_2$ wag	891		A''
A_g	892		ip =CH$_2$ rock	780 *		A'
B_g	753		op *cis* wag	755		A''
			ip skeletal bend	622	635	A'
A_u	524.5		op *cis* wag			
A_g	512		ip skeletal bend	523 *	555	A'
			op skeletal mode	412 *	435	A''
			op skeletal mode	401	419	A''
B_u	299.7		ip skeletal mode	288	311	A'
			Me torsion	199.3	196.7	A''
A_u	163.7	137.4	C–C torsion	152.7		A''

* Gas values from ref. 17.

Both Aston *et al.*[9] and Sverdlov and Bolotina [27] (using

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[23] Yu. N. Panchenko, *Spectrochim. Acta*, 1975, **31A**, 1201.

[24] S. G. Frankiss and J. H. S. Green in ' Chemical Thermodynamics,' Chem. Soc. Specialist Periodical Report, vol. 1, 1973, ch. 8.

[25] R. B. Scott, C. H. Meyers, R. D. Rands, F. G. Brickwedde, and N. Bekkedahl, *J. Res. Nat. Bur. Stand.*, 1945, **35**, 39.

[26] J. E. Kilpatrick, C. W. Beckett, E. J. Prozen, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, 1949, **42**, 225.

[27] L. M. Sverdlov and E. N. Bolotina, *Russ. J. Phys. Chem.*, 1962, **36**, 1502.

the method formulated by Godnev and Morozov[28]) attempted to formulate expressions for the mixing of conformers of butadiene. We consider the latter method to be inadequate. The method of Aston *et al.*[9] led to the expressions (5)—(8) if a mixture of s-*trans*-(T) and s-*cis*-(C) conformers (present in concentrations X_T and X_C, respectively) is considered where s-*trans* has the lower energy and $\Delta H^\ominus_0$ is the enthalpy difference between the conformers at absolute zero.

$$S^\ominus = X_T S^\ominus_T + X_C S^\ominus_C - R(X_T \ln X_T + X_C \ln X_C) \quad (5)$$

$$C^\ominus_P = X_T C^\ominus_{P.T} + X_C C^\ominus_{P.C} + \left(\frac{X_T X_C}{R}\right) \left[\frac{\Delta H^\ominus_0}{T} + \left(\frac{H^\ominus_C - H^\ominus_{0.C}}{T}\right) - \left(\frac{H^\ominus_T - H^\ominus_{0.T}}{T}\right)\right]^2 \quad (6)$$

$$\left(\frac{H^\ominus - H^\ominus_0}{T}\right) = X_C\left[\left(\frac{H^\ominus_C - H^\ominus_{0.C}}{T}\right) + \frac{\Delta H^\ominus_0}{T}\right] + X_T\left(\frac{H^\ominus_T - H^\ominus_{0.T}}{T}\right) \quad (7)$$

$$-\left(\frac{G^\ominus - G^\ominus_0}{T}\right) = S^\ominus - \left(\frac{H^\ominus - H^\ominus_0}{T}\right) \quad (8)$$

The entropy contribution for each component in an ideal gas mixture is given by $S_i = X_i S^\ominus_i - R X_i \ln X_i$, and so a mixture of s-*trans*- and s-*cis*-conformers leads to the expression (5) for $S^\ominus$. However if a mixture of s-*trans*- and 2 equivalent *gauche*-conformers (in concentration X_G each) is present then the expression for $S^\ominus$ becomes (9). The ex-

$$S^\ominus = X_T S^\ominus_T + 2X_G S^\ominus_G - R(X_T \ln X_T + 2X_G \ln X_G) \quad (9)$$

pressions above for $C^\ominus_P$ and $(H^\ominus - H^\ominus_0)/T$ are unchanged if *gauche*-conformers are present, if the total concentration of both-*gauche* conformers is used.

Because $S^\ominus$ and $C^\ominus_P$ are more accurately measured than enthalpy and free energy these were fitted using the above expressions, first assuming s-*cis*-conformers and secondly *gauche*-conformers. The entropy was initially fitted at each temperature by varying the concentration X of the high energy conformer and then the resultant value of X was used to fit $C^\ominus_P$ by varying $\Delta H^\ominus_0$. It was found that the values of $\Delta H^\ominus_0$ between conformers were 10.4 and 11.4 kJ mol^{-1} for *s-cis* and *gauche*, respectively.

An approximate expression for the relationship between $\Delta H^\ominus$ at any temperature T and $\Delta H^\ominus_0$ is (10). Over the

$$\Delta H^\ominus = \Delta H^\ominus_0 + T\,\Delta C_P^\ominus \quad (10)$$

range of temperatures involved $T\Delta C^\ominus_P$ is negligible (*i.e.* less than +50 J mol^{-1}), and so $\Delta H^\ominus \simeq \Delta H^\ominus_0$. Carriera[15] calculated a potential function from observed torsional modes leading to a value of 10.5 kJ mol^{-1} for $\Delta H^\ominus$. Our value of 10.4 assuming and s-*cis*-conformer is in good agreement, but the value obtained using *gauche*-conformers is not. Hence we conclude the equilibrium in butadiene to be s-*trans* $\rightleftharpoons$ s-*cis*.

The results of the calculations using the s-*cis*-conformer have yielded values of two variables X_C and $\Delta H^\ominus_0$ at each temperature which are listed in Table 4. In our calculations we used the s-*trans*-structure postulated by Kuchitsu *et al.*[5] and an appropriate s-*cis*-structure. All fundamentals including the C–C torsion were considered as harmonic oscillators. The s-*cis* C–C torsion was assigned at 137 cm^{-1} on the basis of Raman overtones observed by Carriera.[15] Owing to the low concentration of s-*cis* (or *gauche*), any errors in calculations due to uncertainty in parameters used for s-*cis*-butadiene will be negligible.

TABLE 4

Buta-1,3-diene thermodynamic functions

	$-\left(\frac{G^\ominus - H^\ominus_0}{T}\right)$/J K^{-1}/mol^{-1}		$\left(\frac{H^\ominus - H^\ominus_0}{T}\right)$/J K^{-1}/mol^{-1}		$C^\ominus_P$/J K^{-1} mol^{-1}		$S^\ominus$/J K^{-1} mol^{-1}			
T/K	Ref. 24	This work	Ref. 24	This work	Ref. 24	This work	Ref. 24	This work	X_C	$\Delta H^\ominus_0$/J mol^{-1}
173.15	200.40	203.61	43.35	40.25	52.04	52.03	243.85	243.86	0.000 7	10 400
223.15	211.97	214.20	46.31	44.12	62.37	62.35	258.28	258.32	0.006 6	10 500
233.15	214.12	216.14	46.94	44.94	64.59	64.52	261.06	261.08	0.008 0	10 600
243.15	216.22	218.05	47.60	45.80	66.91	66.87	263.82	263.85	0.010 5	10 500
253.15	218.29	219.89	48.28	46.67	69.18	69.12	266.56	266.56	0.012 5	10 500
263.15	220.31	221.72	48.98	47.59	71.56	71.58	269.29	269.31	0.016	10 400
273.15	222.30	223.51	49.71	48.51	73.89	73.89	272.01	272.02	0.019	10 300
283.15	224.11	225.26	50.46	49.44	76.27	76.29	274.71	274.70	0.022	10 400
298.15	227.10	227.83	51.63	50.90	79.89	79.88	278.73	278.73	0.028	10 300
323.15	231.70	231.99	53.71	53.39	85.90	85.86	285.41	285.38	0.039	10 300
353.15	236.96	236.80	56.39	56.53	93.04	93.09	293.35	293.33	0.056	10 400
373.15	240.30	239.92	58.30	58.67	97.64	97.69	298.60	298.59	0.069	10 400
423.15	248.09	247.49	63.45	64.03	108.24	108.26	311.54	311.52	0.106	10 300
										Av. = 10 400

Kilpatrick *et al.*[26] attempted to formulate values for the thermodynamic functions of isoprene by using values of other compounds. We attempted to fit these values by using the above method but found that the fit was poor and the value of $\Delta H^\ominus_0$ necessary to obtain the $C^\ominus_P$ results was 7.1 kJ mol^{-1}, giving an approximate value of $\Delta H^\ominus$ [equation (10)] as 6.8 kJ mol^{-1}. This disagrees with our experimental value of $\Delta H^\ominus$ and so we have recalculated the thermodynamic functions of isoprene in the following manner.

Consider the system where m equivalent low energy types of conformer A are in equilibrium with n equivalent high energy types of conformer B, *i.e.* $\{A\} \rightleftharpoons \{B\}$ where $\{A\}$ is the total concentration of all equivalent types of conformer A. The entropy change of the equilibrium must take into account the statistical weights of conformers A and B, so equation (11) follows. The free energy change involved in

$$\Delta S^\ominus = S^\ominus_B - S^\ominus_A + R \ln (n/m) \quad (11)$$

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[28] I. Godnev and V. Morozov, *Zhur. fiz. Khim.*, 1947, **21**, 799.

any reaction is given by equations (12)—(14), and the total

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} \qquad (12)$$

$$\Delta G^{\ominus} = T\left[\left(\frac{H^{\ominus}{}_{\mathrm{B}} - H^{\ominus}{}_{0,\mathrm{B}}}{T}\right) - \left(\frac{H^{\ominus}{}_{\mathrm{A}} - H_0{}^{\ominus}{}_{.\mathrm{A}}}{T}\right) - S^{\ominus}{}_{\mathrm{B}} + S^{\ominus}{}_{\mathrm{A}} - R\ln(n/m)\right] + \Delta H^{\ominus}{}_0$$

$$= T\left[\left(\frac{G^{\ominus}{}_{\mathrm{B}} - H^{\ominus}{}_{0,\mathrm{B}}}{T}\right) - \left(\frac{G^{\ominus}{}_{\mathrm{A}} - H^{\ominus}{}_{0,\mathrm{A}}}{T}\right) - R\ln(n/m)\right] + \Delta H_0{}^{\ominus} \qquad (13)$$

$$= -RT\ln K \qquad (14)$$

concentration of high energy form present is given by equation (15). From our experimental value of $\Delta H^{\ominus}$ equation

$$X_{\mathrm{B}} = K/(1 + K) \qquad (15)$$

(10) gives $\Delta H^{\ominus}{}_0$ as 4.9 kJ mol^{-1}. We have shown that the high energy conformers of isoprene is s-*cis* and hence both m and n are 1, and X_{B} becomes X_{C}. From $\Delta H^{\ominus}{}_0$, X_{C} can be calculated by using statistical values of the free energy for both conformers at any temperature. By using equations (5)—(8) new values of the thermodynamic functions of isoprene have been calculated over a range of temperatures, and are given in Table 5.

In our calculations we used the s-*trans*-structure from ref. 8 and assumed a suitable s-*cis*-structure. Contributions from the methyl torsions were calculated by using the tables of Pitzer and Gwinn reproduced in refs. 29 and 30. Any error in the values of thermodynamic functions due to the unknown s-*cis* C–C torsion will be small owing to the small concentration of s-*cis*-isoprene, which is found to be 11% at 298 K.

TABLE 5

Thermodynamic functions of isoprene †

T/K	X_{C}	$-\left(\frac{G^{\ominus} - H^{\ominus}{}_0}{T}\right)$	$\left(\frac{H^{\ominus} - H^{\ominus}{}_0}{T}\right)$	$C^{\ominus}{}_{\mathrm{P}}$	$S^{\ominus}$
273.15	0.097	247.40	59.89	96.06	307.29
298.15	0.11	252.77	63.21	102.76	315.99
300.0	0.11	253.17	63.44	103.22	316.60
400.0	0.17	273.29	76.62	128.78	349.91
500.0	0.21	291.80	89.32	151.15	381.12
600.0	0.24	309.17	101.23	170.09	410.39
700.0	0.27	325.59	112.24	186.14	437.83
800.0	0.29	341.23	122.37	199.90	463.59
900.0	0.30	356.16	131.66	211.78	487.82
1 000.0	0.31	370.47	140.20	222.07	510.67

† Units as Table 4.

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[29] Lewis and Randall, 'Thermodynamics,' rev. Pitzer and Brewer, McGraw-Hill, New York, 1961.

[30] Stull, Westram, and Sinke, 'Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.