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Infra-Red and Raman Spectra of Polyatomic Molecules

II. Cis- and Transbutene-2

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The infra-red absorption spectra of gaseous cis- and transbutene-2 have been measured with a prism spectrometer from 435 to 4000 cm^{-1} . The Raman spectra of these compounds as liquids have also been obtained. The accepted identification of the high boiling isomer with the *cis* structure is confirmed by the fact that this compound shows many more coincidences between the Raman and infra-red spectra than the other isomer, as is to be expected if the latter approximates a molecule with a center of symmetry. The observed frequencies below 800 cm^{-1} are sufficiently different for the two isomers so that it is not safe to assume that both isomers have the same vibrational entropy.

THE two isomeric butenes, cis- and transbutene-2, are interesting compounds because of their close relationship, the possibility of free rotation of the methyl groups and the fact that a considerable body of thermodynamic data concerning them has already been accumulated.¹ From the point of view of a vibrational analysis they are rather complicated, so that their spectra are somewhat difficult to interpret with any certainty until some of the simpler molecules of the same type shall have been analyzed. Nevertheless, since pure samples of these butenes were made available to us at this time,² we decided to carry out the experimental work and to postpone the analyses until later.

APPARATUS AND EXPERIMENTAL PROCEDURE

For the infra-red absorption spectra the automatic prism spectrometer described in Part I was used.³ The rocksalt prism was used to investigate the region from 750 to 4000 cm^{-1} and the KBr prism for the region from 435 to 750 cm^{-1} . The absorption cells were 20 cm long and were made of 48 mm Pyrex tubing. The windows of KBr and rocksalt were cemented to the ends

by means of clear glyptal cement. The cement was not baked. The recording was done in the manner described in Part I, with the filled cell and an evacuated dummy cell alternately in the path of the radiation. Blanks, with both cells evacuated, were taken throughout the spectrum. The absorption was recorded at intervals of three Veeder numbers throughout the entire spectrum and at least three records were taken of each band, so spaced that the spectrum was covered in steps of one Veeder number. With the NaCl prism one Veeder number is equivalent to 1 cm^{-1} at 1000 cm^{-1} and to 20 cm^{-1} at 3500 cm^{-1} . With the KBr prism 1 Veeder number corresponds to 2 cm^{-1} at 650 cm^{-1} and to $\frac{1}{3}$ cm^{-1} at 500 cm^{-1} . These intervals are much closer than are usually used. As a matter of fact, they are closer than is justified by the resolving power of the instrument, which has been designed with an eye to future improvement. The large number of points completely eliminates any advantage of the continuous type of recording, and makes more certain the positions of the minima. The slit widths in cm^{-1} are shown on Fig. 1, and varied from 6 cm^{-1} at 450 cm^{-1} to 150 cm^{-1} at 3500 cm^{-1} .

The Raman equipment is being redesigned at the present time, so that only a brief description of the apparatus used for this work will be given. The spectrograph is a rebuilt single glass prism instrument with Bausch and Lomb optics. The aperture is $f:6$ and the dispersion is 100A per mm at 4358A. The Raman tube was illuminated from four sides by four vertical quartz mercury

¹ G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.* **57**, 876 (1935). L. O. Brockway and P. C. Cross, *J. Am. Chem. Soc.* **58**, 2407 (1936). S. S. Todd and G. S. Parks, *J. Am. Chem. Soc.* **58**, 134 (1936). G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.* **58**, 766 (1936).

² We are indebted to Professor Kistiakowsky for supplying us with pure samples of these butenes. For their preparation, see reference 1.

³ H. Gershinowitz and E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 197 (1938).

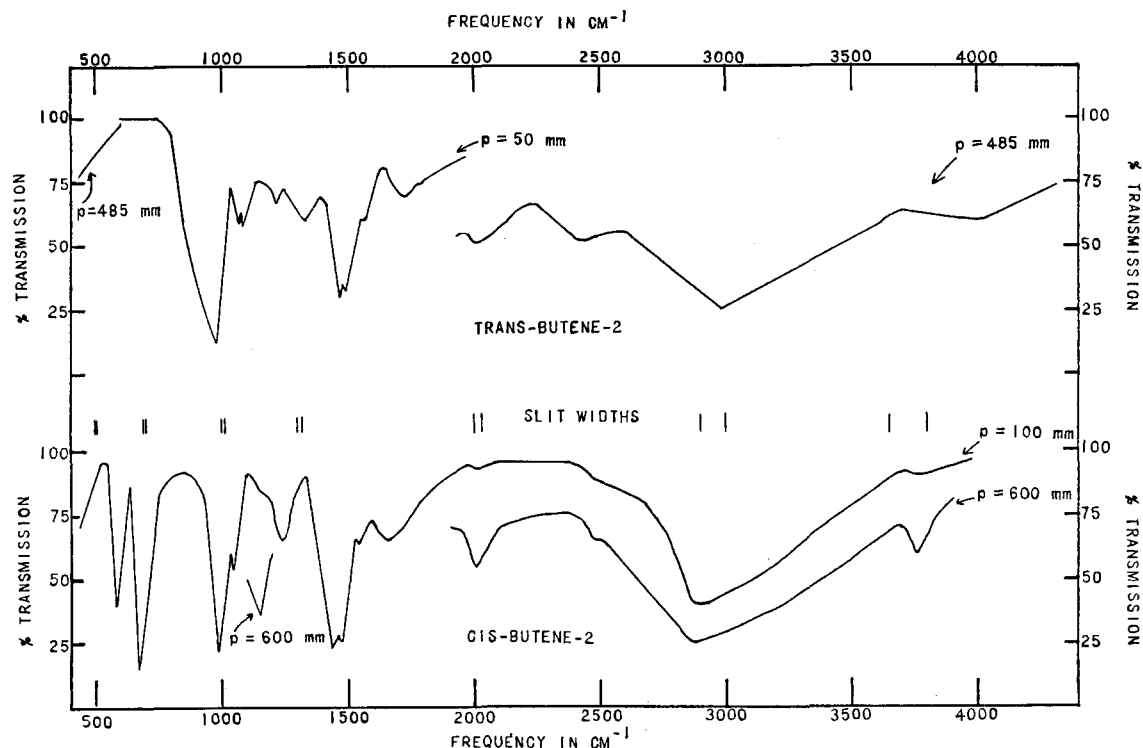


FIG. 1. Percentage transmission of cis- and transbutene-2 in the infra-red.

arcs,⁴ each operating on about 4 amp. with 25 v d.c. The lamps were provided with individual parabolic reflectors and were cooled by an air blast from a vacuum cleaner used as a blower. The liquid samples were contained in vertical Pyrex tubes of either 50- or 13 cc capacity equipped with plane Pyrex windows. A double jacketed Dewar tube surrounded the Raman cells. The inner jacket was evacuated, while the filter liquid was circulated by means of a stainless steel centrifugal pump through the outer jacket and then through a copper coil cooled with running water. Dry air was blown through a copper coil immersed in dry ice and alcohol and then up through the inside of the Dewar vessel around the Raman tube. In this way the temperature of the sample was maintained at any desired value (usually about -15°C) in spite of the large amount of heat liberated by the lamps.

Two filter solutions were used. One contained 43 g *p*-nitrotoluene and 0.06 g rhodamine 5GDN

Extra dye per liter of alcohol,⁵ and was very efficient in isolating the lines at 4358Å. The other contained the same amount of dye but only 2 g of *p*-nitrotoluene per liter and was used to transmit the 4358 and 4047Å lines while cutting out all the ultraviolet. Eastman spectroscopic plates, black backed, emulsions I-O and I-J were used. The slit width employed was usually 0.09 mm. Under these conditions the best pictures required exposures of from 1 to 2 hours.

Polarization measurements were obtained on the *trans* compound with a Polaroid cylinder, by means of the method previously described.⁵ To aid in the determination of the polarization, compensating for possible failure of the plates to obey the reciprocity law, a companion plate was taken for each Polaroid plate with weaker exciting light but the same exposure. Circumstances prevented determination of the polarization of the lines of the cisbutene-2, but we hope to have access to a sample of this compound again later, and plan to study the polarization at that time.

⁴ Much of the Raman equipment, including the arcs, was constructed by Professor G. B. Kistiakowsky for an earlier investigation.

⁵ J. T. Edsall and E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 124 (1938).

EXPERIMENTAL RESULTS

In accordance with the established structures, in the following we shall call the low boiling isomer the *trans* and the high boiling isomer the *cis* form. Fig. 1 shows the transmission curves in the infra-red for both compounds. Table I gives the positions of the minima and the relative intensities. The absorption was measured at several different pressures in order to bring out weak bands and to resolve as much of the structure as possible. The curves show the results at only two pressures for each compound, but the positions (not intensities) in the table are those obtained at the most favorable pressure for each band. The uncertainty in the position of any band is probably equal to the slit width with which it was studied. These slit widths may be estimated from those shown in the figure.

The bands in the transbutene-2 at 1072 and 1080 cm^{-1} are so close together that we are not really sure that they are distinct bands, although they appear to be such on three separate records taken at different times. Also there is some doubt about the existence of the band at 1782 cm^{-1} which appears as just a shoulder on the 1720 cm^{-1} band. The bands at 1214 cm^{-1} and 1560 cm^{-1} which appear only as slight dips in the curves may also not be real, although they are much

TABLE I. Observed frequencies in infra-red and Raman shifts with relative intensities and polarization of the trans-butene-2 Raman lines.

Cisbutene-2		Transbutene-2	
Infra-red	Raman	Infra-red	Raman
<435	304 (double)? (2)	<435	210 (3) (D)
583 (60)	402 (7)	978 (90)	507 (7) (P)
673 (85)	581 (double)? (1)	1072 (40)	746 (5) (D)
986 (80)	685 (1)	1080 (40)	870 (4) (P)
1047 (45)	881 (7)	1214 (35)	1043 (2) (D?)
1149 (15)	978 (4)	1326 (40)	1309 (8) (P)
1233 (35)	1018 (5)	1466 (70)	1389 (4) (D)
1436 (75)	1044 (4)	1488 (65)	1455 (9) (D)
1473 (70)	1267 (8)	1560 (40)	1681 (8) (P)
1541 (35)	1389 (4)	1720 (30)	2739 (2) ?
1663 (35)	1462 (7)	1782 (25)	2867 (5) (P)
2004 (5)	1669 (8)	2004 (15)	2926 (10) (D)
2481 (10)	2671 (1/2)	2427 (15)	2965 (4) (P?)
2874 (60)	2715 (1/2)	2976 (40)	3011 (2) ?
3759 (10)	2758 (1/2)	4000 (5)	
	2813 (1/2)		
	2877 (6)		
	2931 (10)		
	2979 (6)		
	3034 (8)		

more definite than that at 1782 cm^{-1} . In the cisbutene-2, the band at 1541 cm^{-1} may be doubtful.

Table II lists the frequencies (in vacuum) of the Raman lines found for each compound, with the shifts from the excitation lines to which they have been assigned. All the lines reported have been observed on at least two plates and in addition have been identified on microphotometer records made of each plate. The polarization of the lines of the *trans* compound is also listed. Table I summarizes the results of both infra-red and Raman measurements, the Raman frequencies being weighted averages of the displacements from the (k) and (e) lines of Hg.

The Raman line reported at 22728 cm^{-1} for the *trans* compound appears along the side of the 4358A Hg line and may be double. This Hg line is so broadened out that it seems that there may well be other Raman lines of shorter shifts concealed. (The line is broadened only on the lower wave number side.) Fig. 2 shows microphotometric records* of comparable plates for the *cis*

TABLE II. Observed frequencies (cm^{-1} in vacuum) with displacements from the 4047 (k) and the 4358 (e) lines of Hg.

Cisbutene-2		Transbutene-2	
ν in cm^{-1}	$\Delta\nu$ in cm^{-1}	ν in cm^{-1}	$\Delta\nu$ in cm^{-1}
23827	878 (k)	24197	508 (k)
23443	1262 (k)	23962	743 (k)
23318	1387 (k)	23843	862 (k)
23243	1462 (k)	23665	1040 (k)
22634	304 (e)	23398	1307 (k)
22536	402 (e)	23319	1386 (k)
22357	581 (e)	23251	1454 (k)
22253	685 (e)	22728	210 (e)
22055	883 (e)	22432	506 (e)
21960	978 (e)	22190	748 (e)
21920	1018 (e)	22065	873 (e)
21894	1044 (e)	21976	2737 (k)
21829	2876 (k)	21894	1044 (e)
21774	2931 (k)	21840	2872 (k)
21676	1262 (e)	21784	2921 (k)
21548	1390 (e)	21746	2959 (k)
21476	1462 (e)	21687	3018 (k) ?
21269	1669 (e)	21628	1310 (e)
20268	2671 (e)	21547	1391 (e)
20224	2715 (e)	21482	1456 (e)
20181	2758 (e)	21257	1681 (e)
20126	2813 (e)	20199	2740 (e)
20062	2877 (e)	20074	2865 (e)
20008	2931 (e)	20010	2929 (e)
19960	2979 (e)	19981	2968 (e)
19905	3034 (e)	19931	3008 (e)

* A description of the instrument used for making these records will be published shortly by Professor G. B. Kistiakowsky and Dr. W. H. Avery.

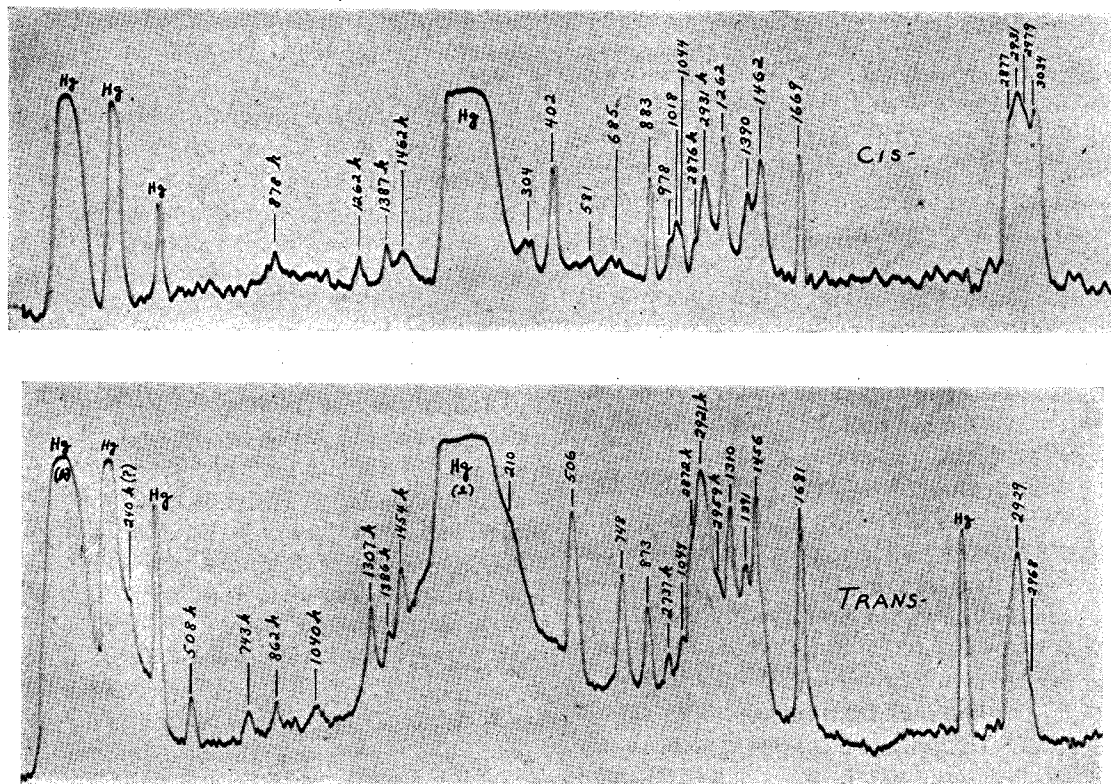


FIG. 2. Upper curve, microphotometer record of Raman spectrum of cisbutene-2. Lower curve, Raman spectrum of transbutene-2.

and the *trans* compounds which clearly show this broadening of the region about 4358 Å. This would indicate that the *trans* compound may have frequencies lower than 210 cm^{-1} . It can be seen that the mercury line at 4077 Å is similarly broadened, the line at 210 k appearing as a bump along the side. This Raman line has not been reported in the table above (the measured frequency is 24465 cm^{-1}) because it appears only on this one plate, which is the most intense one of this region.

The lines of the cisbutene-2 from 20268 cm^{-1} through 20126 cm^{-1} appear as a very faint series of sharp lines. They have, however, been identified and measured on two plates. We are uncertain whether the line at 21687 cm^{-1} in the *trans* compound is 3018 k or 1251 e , but tend to believe it is the former. The line at 304 e is quite weak but appears distinctly on four plates. The microphotometer records of this line indicate that it may be double. The line at 581 e also appears to be double.

DISCUSSION

Even without making a vibrational analysis of these molecules, it is possible to arrive qualitatively at results of interest. The transbutene-2 has a center of symmetry if the methyl groups may be considered as units. In this case there should be no coincidences between the Raman and infra-red spectra, except by accident, because the selection rules would forbid the same frequency being active in the Raman and the infra-red. For the *cis* compound, however, it should be possible to have some frequencies active in both the Raman and the infra-red. From Table I it may be seen that this state of affairs is actually realized, since there are very many more coincidences in the *cis* spectra than in the *trans*. This tends to corroborate the assigned structures.

Recently there has been much discussion about the question of whether or not methyl groups in organic molecules may rotate freely. As evidence on both sides, calculations of the entropies

pies of various molecules have been made.⁶ To make these calculations, it is necessary to know the vibration frequencies of the molecules. The isomeric butenes are among the molecules which have been studied and it has sometimes been assumed that the structure of the two isomers is so similar that they may safely be assumed to have the same vibrational entropies, at least for the purpose of such calculations. Although no certain conclusions can be drawn until the spectra of these molecules have been completely analyzed, so that all the vibration frequencies are known, from the available data it would seem that this assumption is of doubtful validity. Table I shows

⁶ K. S. Pitzer, *J. Chem. Phys.* **5**, 473 (1937); L. S. Kassel, *ibid.* **4**, 144 (1936).

that while the trans- and the cisbutenes have practically identical spectra when one considers the frequencies above 800 cm^{-1} , below that the spectra are quite different. Although this difference may be wiped out by the existence of frequencies which may not have been observed by us, such a possibility is rather remote and it would seem much more probable that there are real differences in these low frequencies. This seems not unreasonable, when one considers that in these low frequencies motions of the entire chain are involved and that these might well be different for the two compounds. It does not seem profitable, therefore, to attempt to draw definite conclusions about the existence of free rotation unless all the vibration frequencies are known.

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Separation of Gaseous Isotopes by Diffusion

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The behavior of a set of mercury diffusion pumps has been investigated and the separation factors for a number of isotopic mixtures have been determined. Formulae have been derived which give the dependence of enrichment on the choice of reservoirs. In addition, Barwich's theory for the fractionation process has been extended to the case of finite reservoirs. The solution for this problem is a slowly converging series, but a qualitative picture of the dependence of equilibrium time on various factors is obtained. The separation factors which have been found for the

Hertz diffusion pumps for bromine in CH_3Br , carbon in CH_4 , oxygen in O_2 and H_2O , Ne, and A are 1.005, 1.107, 1.045, 1.073, 1.198, and 1.154 per unit, respectively. Twelve pumps of the Hertz design, and seventeen modified units were used. The modifications were made in an attempt to improve the original design, but the factors obtained for these units are smaller. Auxiliary experiments indicate that the performance of the new units is seriously impaired by the presence of back diffusion and that increased factors can be obtained by eliminating the latter effect.

1. INTRODUCTION

IN recent years many problems in chemistry, biology, and physics have arisen whose solutions are facilitated by or dependent on the use of fractionated isotopes. There is consequently a growing interest in the more immediate problem of the separation of isotopes. Many fractionating devices, based on physical or chemical principles, have been applied to a number of isotopic elements with varying degrees of success.¹ One of the more promising methods has been that of separation by diffusion.

This method, although historically the first to be employed, gave no marked results until quite recently. The weakness of the earlier diffusion experiments lay in the fact that only one fractionating unit could be employed in a single operation. However, in 1932, G. Hertz² announced the invention of porous-walled units, so designed that a number of them could be connected in series, leading to multiple fractionation in one operation. These units have been used by a number of investigators^{2, 3} for the fractionation of neon, hydrogen, carbon and nitrogen.

² G. Hertz, *Zeits. f. Physik* **79**, 108 (1932).

¹ For recent reviews, see F. W. Aston, *Mass Spectra and Isotopes* (Edw. Arnold and Co., 1933). G. Champetier, *Bull. Soc. Chem.* **3**, 1701 (1936).

³ Harmsen, *Zeits. f. Physik*, **82**, 589 (1932); Harmsen, Hertz, and Schutze, *Zeits. f. Physik* **90**, 703 (1934); Wooldridge and Smythe, *Phys. Rev.* **50**, 233 (1936).