

InfraRed Absorption Spectra of Some C4 and C5 Dienes

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Citation: *The Journal of Chemical Physics* **15**, 131 (1947); doi: 10.1063/1.1746441

View online: <http://dx.doi.org/10.1063/1.1746441>

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Infra-Red Absorption Spectra of Some C₄ and C₅ Dienes

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(Received October 28, 1946)

The infra-red absorption spectra from 2 to 15 μ have been obtained of 1,3-butadiene, 1,2-butadiene, isoprene, and *cis*- and *trans*-1,3-pentadiene vapors. Salient features of the spectra are discussed.

I. INTRODUCTION

THE infra-red absorption spectra are given here for 1,3-butadiene, 1,2-butadiene (methylallene), 2-methyl-1,3-butadiene (isoprene), and *cis*- and *trans*-1,3-pentadiene (piperylene), all in the vapor phase. The spectrum of 1,3-butadiene has been reported previously in the literature,¹ but in general with less resolution than was obtained here.

The spectrograph, experimental details, and accuracy obtained have been discussed in the preceding article,² except that the spectrum of *trans*-1,3-pentadiene has been obtained with an absorption path of 70 cm in addition to the previously used path of 15 cm. The sources of the pure materials used are as follows:

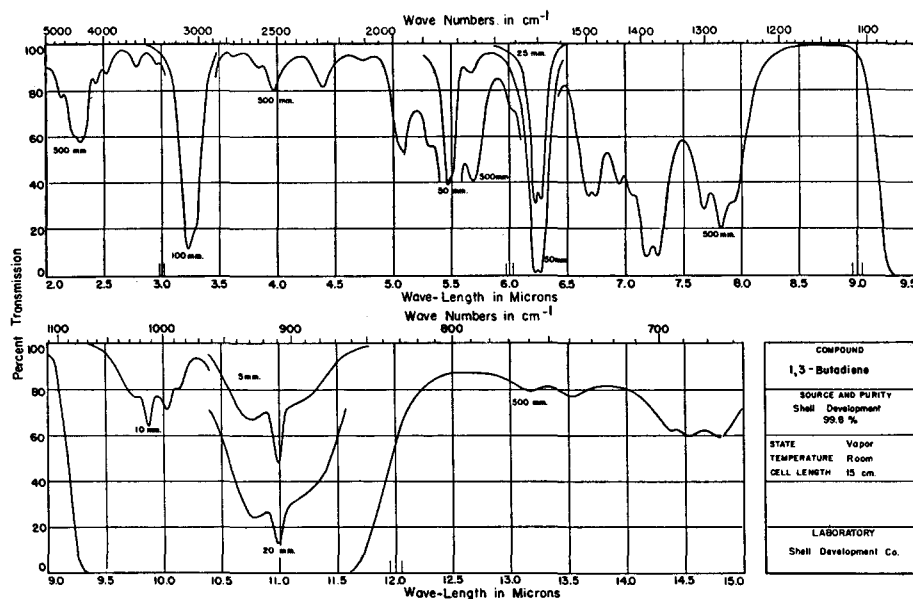
1,3-Butadiene. The 1,3-butadiene was regenerated from butadiene sulfone. Mass spectrometric analysis indicated not more than 0.2 percent butylene and not more than 0.05 percent butane.

1,2-Butadiene. The 1,2-butadiene sample was prepared from crotyl alcohol and distilled in a laboratory column. Its purity is believed to be better than 99 percent as judged from physical constants.

Isoprene. Isoprene was regenerated from recrystallized sulfone. Mass spectrometric analysis indicated no amylenes or pentane present, the only impurity being 0.03 percent acetone.

***cis*-1,3-Pentadiene.** The sample of *cis*-1,3-pentadiene was obtained through the courtesy of Dr. Craig of the B. F. Goodrich Company, Akron,

FIG. 1. Infra-red absorption spectrum of 1,3-butadiene.



¹ E. Bartholomé and J. Karweil, *Zeits. f. physik. Chemie* **35B**, 448 (1937); R. B. Barnes, U. Liddel, and V. Z. Williams, *Ind. Eng. Chem., Anal. Ed.* **15**, 83 (1943).

² R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.* **15**, 120 (1947).

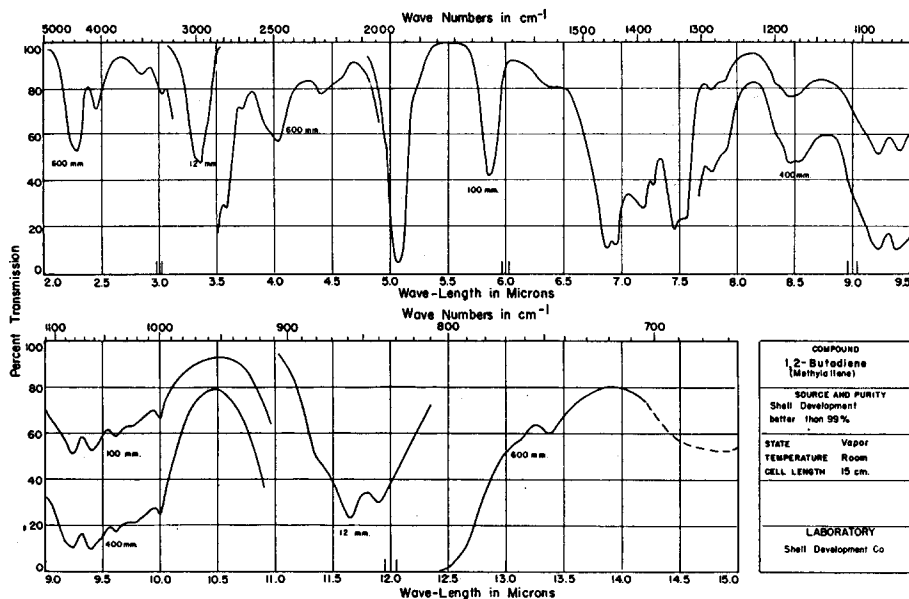


FIG. 2. Infra-red absorption spectrum of 1,2-butadiene.

Ohio.³ Mass spectrometric analysis indicated no pentane and 0.15 percent amylene. The infra-red spectrum (Fig. 4) shows some indication of the *trans*-isomer by a weak band at 12.2 μ , where the

TABLE I. Wave-lengths, frequencies, and intensities of absorption maxima (vapor spectra).

1,3-Butadiene			Isoprene			1,2-Butadiene		
$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	<i>I</i>	$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	<i>I</i>	$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	<i>I</i>
2.13	4695	0 _s	2.14	4675	0 _s	2.24	4465	0 _s
2.23	4485		2.25	4445	0 _s	2.29	4365	1
2.30	4350	1	2.30	4350	2	2.465	4055	0
2.33	4290		2.46	4065	0	2.53	3955	0
2.44	4100	0	ca. 2.59	ca. 3860	0 _s	2.85	3510	0
2.53	3955	0	3.23	3095	8	3.03	3300	0
2.795	3580	0	3.335	3000		3.32	3010	
2.97	3365	0 _s	3.61	2770	1 _s	3.37	2965	9
3.23	3095	9	3.99	2505	0	3.44	2905	
3.30	3030	0	4.11	2435	0	3.60	2775	1 _s
3.63	2755	0	4.22	2370	0	3.74	2675	0 _s
3.85	2595	0 _s	4.62	2165	0	3.94	2540	1
3.98	2515	0	4.82	2075	0	4.035	2480	
4.41	2265	0	5.065	1974	1	4.42	2260	0
4.75	2105	0	5.29	1890	7	4.59	2180	0 _s
5.06	1975	1	5.56	1799	7	5.075	1970	9
5.09	1965		5.77	1733	1 _s	ca. 5.28	ca. 1890	1
5.31	1883	0 _s	6.06	1650	1 _s	5.87	1704	5
5.47	1828	7	6.205	1612		5.91	1692	
5.50	1818		6.24	1603	10	ca. 6.35	ca. 1570	1 _s
5.69	1757	1 _s	6.57	1522	1	6.88	1453	6
6.02	1661	0 _s	6.83	1464	7	6.96	1437	
6.23	1605	10	6.89	1451		7.20	1389	2
6.275	1594		7.04	1420	4	7.29	1372	1 _s
6.68	1497	1	7.20	1389	7	7.46	1340	6
6.75	1481		7.58	1319	3	7.57	1321	
6.95	1439	0	7.675	1303		7.78	1285	1 _s
7.06	1416	0 _s	ca. 8.08	ca. 1235	0 _s	7.90	1266	0 _s
7.195	1390	5	ca. 8.55	ca. 1170	0 _s	8.35	1198	2
7.285	1373		8.73	1145	1	8.45	1183	
7.675	1303	3	9.26	1080		8.57	1167	
7.82	1279		9.33	1072	5	ca. 9.00	ca. 1110	4
7.98	1253		9.41	1063		9.235	1083	
9.76	1025		9.98	1002		9.395	1064	
9.875	1013	9	10.09	991	9	9.48	1055	
10.035	997		ca. 10.22	ca. 980		9.615	1040	
10.135	987		ca. 10.86	ca. 920		9.79	1021	
10.76	929		11.03	907	10	9.995	1001	
10.995	909	10	11.20	893		ca. 11.36	ca. 880	10
ca. 11.30	ca. 885		ca. 11.90	ca. 840	1 _s	11.645	859	
13.19	758	0	ca. 12.08	ca. 825		11.895	841	
13.54	739	0	ca. 12.96	ca. 770		ca. 13.14	ca. 760	0 _s
14.38	695		13.215	757	3	13.75	727	0 _s
14.56	687	1	13.48	742		ca. 14.90	ca. 670	1
14.81	675							

³ The preparation and properties are described in J. Am. Chem. Soc. 65, 1006 (1943).

FIG. 3. Infra-red absorption spectrum of isoprene.

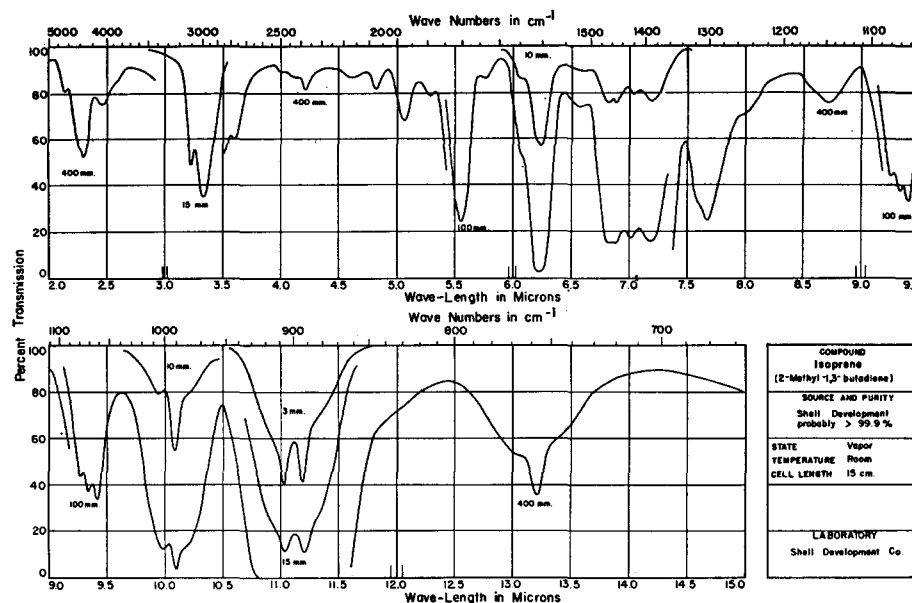


TABLE I—Continued.

<i>cis</i> -1,3-Pentadiene			<i>trans</i> -1,3-Pentadiene		
$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	<i>I</i>	$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	<i>I</i>
2.12	4715	0	2.33	4290	1
2.29	4365		3.315	3015	9
2.42	4130	0 _s	3.40	2940	
2.57	3890	0	3.64	2745	1 _s
2.70	3705	0	3.91	2560	0
2.765	3615	0	4.37	2290	0
2.92	3425	0	5.00	2000	0
3.08	3245	0 _s	5.42	1845	0 _s
3.27	3060	9	5.545	1803	6
3.36	2975		5.67	1784	0 _s
3.59	2785	1 _s	6.02	1661	7
3.80	2630	0	6.21	1610	7
3.92	2550	1	6.51	1536	
4.26	2345		6.56	1524	1
4.39	2280	0 _s	6.88	1453	7
4.67	2140	0	7.03	1422	0 _s
5.02	1992	1	7.22	1385	
5.13	1949	0	7.60	1316	3
5.22	1916	0 _s	7.70	1299	
5.36	1866	0 _s	7.81	1280	0 _s
5.50	1818	6	7.91	1266	0 _s
5.645	1771	1	8.17	1224	2
5.77	1733	1	8.50	1166	2
6.04	1656	6	9.83	1017	
6.22	1608	7	9.98	1002	9
6.26	1597		10.15	985	
6.56	1524	1	10.54	949	1
6.80	1471	1 _s	10.97	912	
6.92	1445		11.12	899	9
6.97	1435	8	11.32	883	
7.19	1391	4	12.02	832	
7.645	1308		12.195	820	5
7.735	1293	2	12.41	806	
7.94	1259				
8.00	1250	3			
8.52	1174				
8.60	1163	1			
8.85	1130				
8.935	1119	2			
9.91	1009				
10.03	997				
10.37	964	8			
10.52	951				
10.86	921				
11.035	906	10			
11.22	891				
12.22	818	0 _s			
12.73	786				
12.93	773	6			
13.20	758				
14.33	698	0			

"s" indicates shoulder on an adjacent stronger band.

trans-isomer has a strong band. If one assumes this explanation of the 12.2 μ band, the sample contains about 3 percent of *trans*-1,3-pentadiene.

trans-1,3-Pentadiene. The sample of *trans*-1,3-pentadiene was obtained by regeneration from the recrystallized sulfone. Mass spectrometric analysis showed no pentane and 0.15 percent amylene. The infra-red spectrum (Fig. 5) contains no detectable band at 12.9 μ , where *cis*-1,3-pentadiene has a strong band. From this the *cis*-content is estimated to be less than one percent.

The spectra are shown in Figs. 1 to 5, and the wave-lengths and frequencies of bands are given in Table I.

II. DISCUSSION

The general features of the spectra of olefins discussed in the preceding paper² are for the most part found as expected in the diene spectra. In the 3 μ region, 1,3-butadiene and isoprene show the band at 3.2 μ due to the olefinic CH₂ group. However, 1,2-butadiene and the 1,3-pentadienes show bands at 3.3 to 3.4 μ , with no marked shoulder at 3.2 μ .

In the 7 μ region (HCH bending vibrations), 1,2-butadiene, isoprene, and the 1,3-pentadienes have bands at both 6.8 μ and 7.2 μ as would be expected of molecules containing methyl groups. Only a single strong band in this region, at 7.2 μ , is shown by 1,3-butadiene.

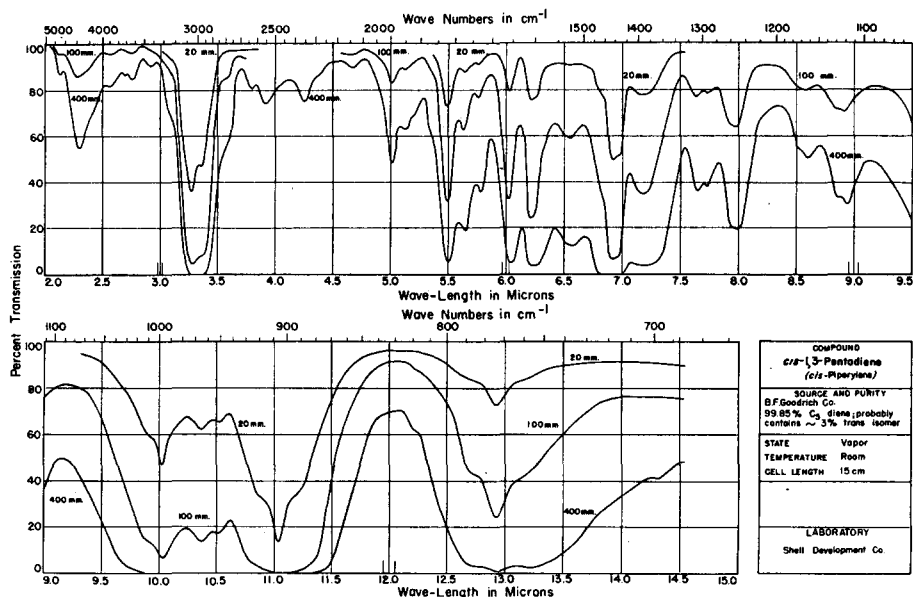


FIG. 4. Infra-red absorption spectrum of *cis*-1,3-pentadiene.

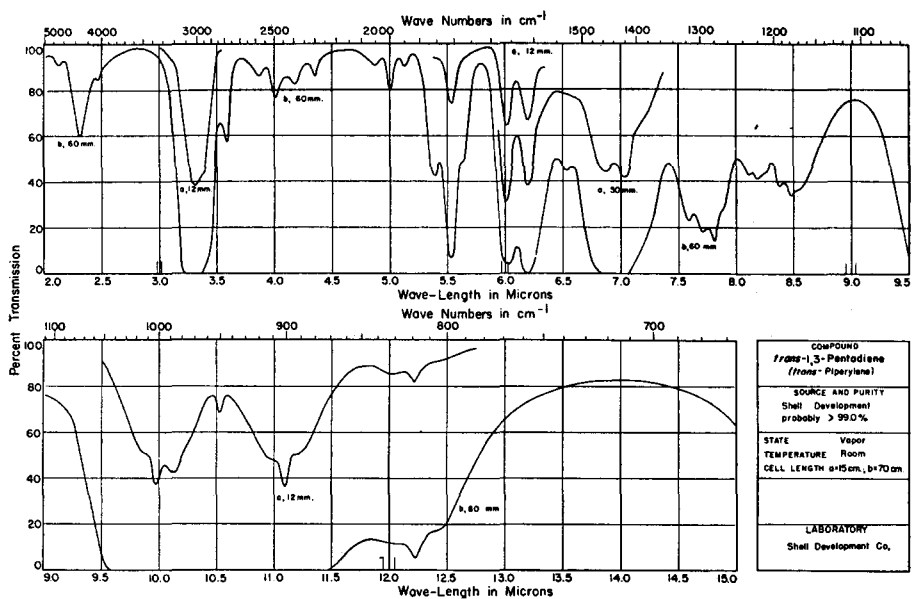


FIG. 5. Infra-red absorption spectrum of *trans*-1,3-pentadiene.

The very strong absorptions in the 10 to 12 μ region agree well with the regularities noted in the mono-olefin spectra (see Table III, preceding paper²). An exception is 1,2-butadiene, which has only a single strong band at 11.6 μ . It would, however, not be expected that allene-type compounds fit such a scheme, since the forces governing out-of-plane bending of the hydrogen atoms would be different from those in an isolated double bond. What are very probably the first overtones of the strong 10 to 12 μ bands are found

as moderately strong bands in the 5.5 to 5.8 μ region.

In the 6 μ region, 1,3-butadiene has a single strong band at 6.24 μ (1603 cm⁻¹). Since at room temperature this compound supposedly consists predominantly of the *trans*-form,⁴ this is the only C=C stretching frequency which should be observed. It is possible that the very weak band at 6.02 μ (1661 cm⁻¹) is due to one of the C=C

⁴ R. S. Mulliken, Rev. Mod. Phys. 14, 265 (1942).

stretching frequencies of the smaller amount of *cis*-form present.⁵ Isoprene also shows, surprisingly, only one strong band in this region, at 6.24μ (1603 cm^{-1}). In this case, where there are no symmetry selection rules operating, two bands would be expected for the two C=C stretching frequencies. Both *cis*- and *trans*-1,3-pentadiene are normal in this respect, each showing two moderately strong bands, at 6.03μ and 6.23μ (1658 and 1605 cm^{-1}).

The C=C stretching frequencies of 1,2-butadiene, like those of allene, would be expected to be widely separated from the normal C=C frequency region (*ca.* 1650 cm^{-1}) because of the

large amount of mechanical resonance. By analogy with the well-understood allene spectrum⁶ they appear as the bands at 5.075μ and 9.395μ (1970 and 1064 cm^{-1}).

Further interpretation of these spectra will not be attempted in view of the relative complexity of the molecules and the lack of good understanding of hydrocarbon spectra in general.

The authors gratefully acknowledge the assistance of Messrs. D. H. Merrill and P. S. Zucco and of Mrs. Z. Alcorn and Miss L. Bassi in the operation of the spectrograph and in calculation and drawing of curves for this and the preceding paper.

⁵ R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, J. Chem. Phys. 11, 432 (1943).

⁶ J. W. Linnett and W. H. Avery, J. Chem. Phys. 6, 686 (1938).

Infra-Red Absorption Spectra of Some Octenes

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(Received October 28, 1946)

The infra-red absorption spectra in the 2μ to 15μ region of 1-octene, 2-octene, 3-octene, 4-octene, 2-methyl-1-heptene, 6-methyl-1-heptene, and 2,4,4-trimethyl-1-pentene are given. Salient features of the spectra are discussed.

I. INTRODUCTION

IN continuation of the study of the absorption spectra of olefins commenced in the two preceding articles,¹ results are given here on the spectra of seven octenes. The normal octenes and methylheptenes were pure hydrocarbons obtained from the American Petroleum Institute, and were prepared under the direction of Professor C. C. Boord of the Department of Chemistry of the Ohio State University as part of the American Petroleum Institute Hydrocarbon Research Project in the Industrial Research Foundation of the University. The 2,4,4-trimethyl-1-pentene was prepared at the Shell Development Company Laboratories by repeated careful distillation from a sample of commercial di-isobuty-

lene. Its final purity, as determined from physical constants, is believed to be better than 99.5 percent. *Cis*- and *trans*-configurations are discussed in footnote 6.

The spectrograph, experimental details, and accuracy for the vapor spectra were discussed in the first article of this series.¹ However, a change in wave-length calibration was noted during the runs reported in the present paper. This was corrected as well as possible, but there were not sufficient quantities of samples to rerun the spectra and insure the accuracy claimed for the previous work. Hence the limits of error of wave-lengths are estimated to be about $\pm 0.03\mu$ for the spectra of the octenes. Because of the low vapor pressure of the octenes an absorption path of 58 cm was used in obtaining the vapor spectra. For the liquid spectra, cells were used whose design was a modification of the type described

¹ R. S. Rasmussen and R. R. Brattain, J. Chem. Phys. 15, 120, 131 (1947).