[CONTRIBUTION FROM THE SPECTROSCOPY LABORATORY AND DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Vibrational Spectra and Structure of Cyclobutene and Cyclobutene-d_6[1]

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Cyclobutene and cyclobutene-d_6 have been prepared by the method of Cope, Haven, Ramp and Trumbull.[5] The infrared absorption spectra of both vapor and liquid have been obtained in the range 250–3800 cm.$^{-1}$ and Raman spectra (including semi-quantitative depolarization factors) have been determined for the liquids. Many vibrational frequencies permitted to occur in the Raman effect by selection rules were not observed. The spectra have been interpreted in terms of a C_{2v} structure, for which the chief spectroscopic support is the number and position of infrared bands of type C. In cyclobutene the carbon–carbon double bond frequency is observed at the unusually low value of 1566 cm.$^{-1}$. The Raman line at this frequency is intense but the infrared band is so weak that it could have been ascribed to an overtone.

The cyclobutene molecule contains a C–C double bond in a four-membered ring, and offers the molecular spectroscopist an unusual example of the effect of ring strain on the double bond frequency and the carbon–hydrogen frequencies associated with a double bond. It is also useful in assisting the evaluation of vibrational frequencies of the CH_2 group in small ring compounds as a member of the series cyclopropane-ethylene oxide–cyclobutene-cyclobutane whose spectra have recently been reported together with those of the deuterium analogs.[3] Its structure apparently has not been investigated by X-ray diffraction or by microwave spectroscopy, but a recent study by electron diffraction has been carried out by Goldish, Hedberg and Schomaker.[4]

Experimental

Cyclobutene and cyclobutene-d_6 were obtained as intermediates in the synthesis of cyclobutane and cyclobutane-d_8, respectively. The synthesis was that of Cope, Haven, Ramp and Trumbull,[5] modified to adapt it to the preparation of the deuterium compound.[6] The general method having already been reported, only the purification procedure and the characteristics of the compounds obtained will be given.[7]

The crude cyclobutene (and cyclobutene-d_6 also) was purified by the addition of bromine and fractional distillation of the resultant dibromocyclobutane. Cyclobutene was then regenerated by reduction with zinc in ethanol[8] with a 97% recovery. Unfortunately the infrared spectrum of the regenerated material indicated the presence of an appreciable amount of butadiene, whose boiling point differs by only 5° from that of cyclobutene. The butadiene was removed by bubbling the impure gas four or five times through molten maleic anhydride, the extent of the removal being followed by means of the butadiene infrared bands at 997–1012 cm.$^{-1}$. It was estimated that the final concentration of butadiene was less than 0.1%. The cyclobutene was then distilled once again (at 200°K., condensed at 77°K.) and stored in the vapor phase for spectroscopic study.

Both the cyclobutene prepared in this way and the cyclobutane obtained from it by subsequent hydrogenation were subjected to careful infrared and mass spectrometric analysis.[9] The observed purity of the latter compound confirmed that the original cyclobutene was in excess of 99.9% pure chemically. The isotopic purity of cyclobutene-d_6 by both methods was 99.7 atom-% D.

Spectroscopic Procedures.—Infrared spectra were measured in the range 250–3800 cm.$^{-1}$ on the gaseous compounds and from 400 to 3800 cm.$^{-1}$ for the liquids. The spectrometer was a Perkin–Elmer 12B single-beam instrument, in which prisms of LiF, CaF_2, NaCl, KBr and KRS-5 were employed in their respective regions of optimum dispersion. The low temperature liquid cell was that designed by Lord, McDonald and Miller[10] who also have described the modified optics of the spectrometer used in this work. The liquid was cooled by Dry Ice–acetone slush, and its temperature was probably slightly above −75°.

The spectra are shown in Figs. 1 and 2 and the wave numbers (vac) of the transmission minima in cm.$^{-1}$ in Tables I and II. The precision of wave number measurement is 2 cm.$^{-1}$ or better below 2500 and 5 cm.$^{-1}$ or better above.

Raman spectra of liquid samples were photographed by standard techniques[3] with a Zeiss three-prism spectrograph. Semiquantitative depolarization factors were determined by a single-exposure method.[11] An attempt was made to photograph the Raman spectrum of cyclobutene excited by the mercury resonance line Hg-2537, but decomposition of the sample under intense ultraviolet radiation was sufficiently rapid that inferior spectra were obtained. The results of the Raman work are listed in Table III. The Raman spectrum of cyclobutene has not been reported previously, but there were available to us the results of an earlier study by Slowinski[12] on a cyclobutene sample prepared by a different method.[13] Slowinski's results agree closely with those of Table III both as to frequency and intensity, except that he reported fewer lines and the intensity of the butadiene line at 1635 cm.$^{-1}$ indicated about 5–10% of this substance in his sample. A very weak line found in spectra of some samples during the present work at about 515 cm.$^{-1}$ has been rejected as probably belonging to butadiene since it was not found in spectra from which the 1635 butadiene line was absent.

The infrared spectrum of cyclobutene obtained with the instrument used in the present work has been reported earlier by Roberts and Sauer.[13]

Discussion of Spectroscopic Results

The selection rules for the highest possible symmetry (C_{2v}) for cyclobutene permit all 24 fundamental frequencies to be Raman-active and all but five in the infrared. Thus the assignment of fundamentals has to be carried out with little help from selection-rule arguments. Fortunately the infra-

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(1) This paper is based on a thesis submitted by D. G. Rea to the Graduate Department of Chemistry, Massachusetts Institute of Technology, in partial fulfillment of the requirements for the Ph.D. degree, September, 1954. A preliminary oral account was presented at the Pittsburgh Conference on Applied Spectroscopy, March, 1954 (*Anal. Chem.*, **26**, 429 (1954)). Part of the work has been supported by the Office of Ordnance Research under Contract DA-19-020-ORD-896.

(2) Wm. S. Knudsen Fellow, 1953–1954.

(3) (a) A. W. Baker and R. C. Lord, *J. Chem. Phys.*, **23**, 1636 (1955); (b) R. C. Lord and B. Nolin, *ibid.*, **24**, 656 (1956).

(4) E. Goldish, K. Hedberg and V. Schomaker, THIS JOURNAL, **78**, 2714 (1956).

(5) A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, *ibid.*, **74**, 4867 (1952).

(6) R. C. Lord, *J. Chem. Phys.*, **21**, 378 (1953).

(7) Complete details of the synthesis are described in the Ph.D. thesis of D. G. Rea.

(8) G. B. Heisig, THIS JOURNAL, **63**, 1698 (1941).

(9) We are indebted to Dr. Fred Mohler of the National Bureau of Standards for the mass spectrometric analyses. The calibration of the infrared analysis of the high-D sample was based on the infrared and mass spectra of the low-D sample.

(10) R. C. Lord, R. S. McDonald and F. A. Miller, *J. Opt. Soc. Am.*, **42**, 149 (1952).

(11) R. C. Lord and E. Nielsen, *J. Chem. Phys.*, **19**, 1 (1951).

(12) E. J. Slowinski, Jr., Ph.D. thesis, Massachusetts Institute of Technology, September, 1949.

(13) J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949); **74**, 3192 (1952).

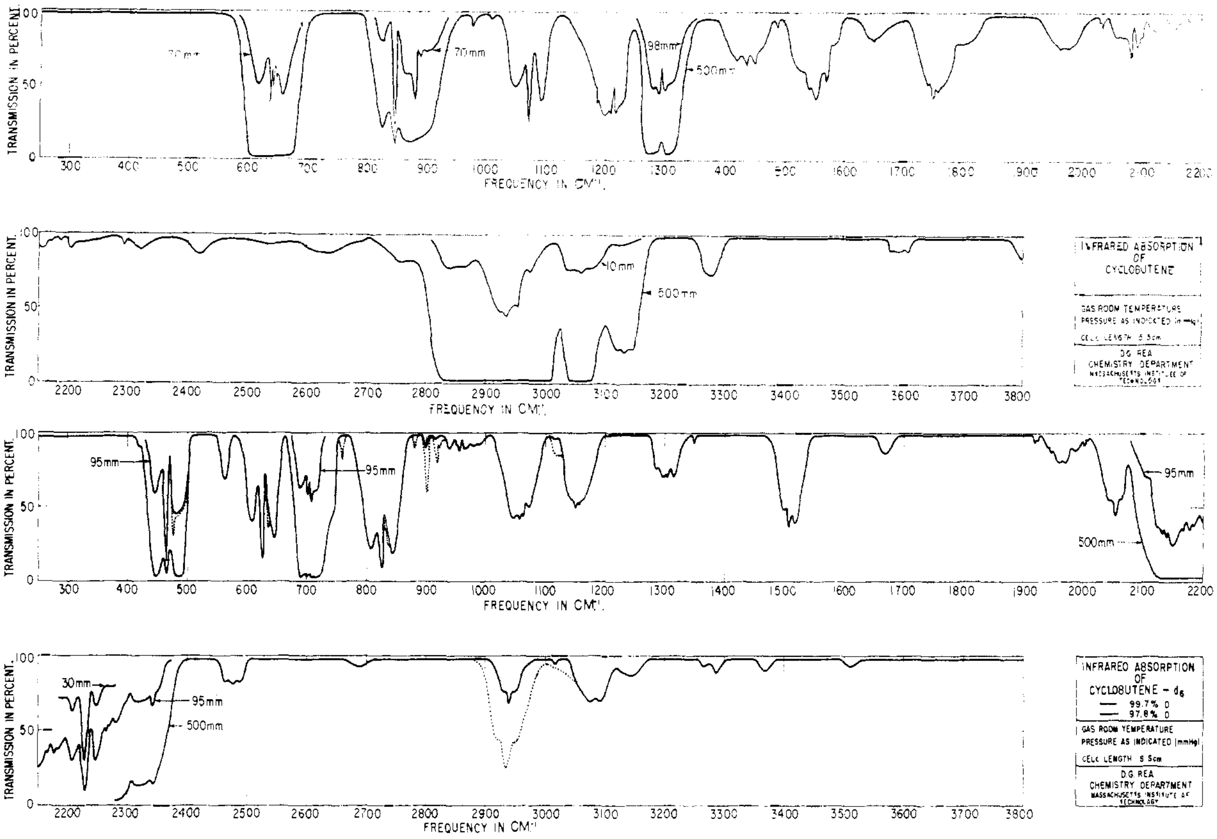

Fig. 1.—Infrared spectra of gaseous cyclobutene and cyclobutene-d_6.

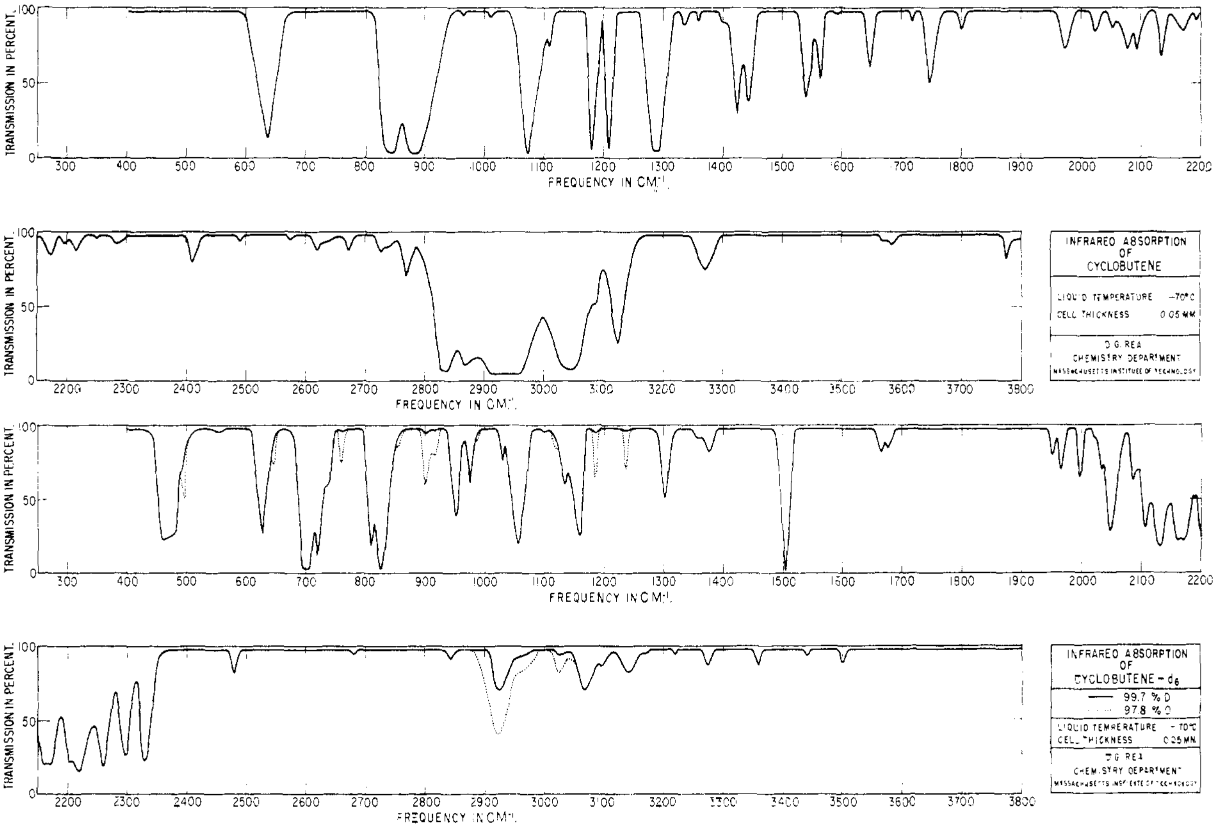

Fig. 2.—Infrared spectra of liquid cyclobutene and cyclobutene-d_6.

TABLE I

INFRARED SPECTRUM OF CYCLOBUTENE[a]

Vapor ν(cm.$^{-1}$ vac)		Liquid ν(cm.$^{-1}$ vac)	I	Assignment
3804	w			$\nu_2 + \nu_{19}$
		3775	w	$\nu_2 + \nu_{23}$
3612	w			?
3590	w	3586	w	$\nu_{21} + \nu_{24}$
		3567	w	$\nu_2 + \nu_{24}$
3278	w	3272	w	$\nu_{13} + \nu_{21}$
3134	m,B	3126	m	ν_{14}
		3085	m	?
3060	s,A	3043	s	ν_1
2975 R	s	2960		
2955 Q	s,C	↕	vs	ν_{21}
2935 Q	s,A			ν_2
2925 P	s	2900		
2862	s,B	2866	s	$\nu_4 + \nu_{16}$
2842		2839	s	$2\nu_{16}$,
		2830	s	$\nu_3 + \nu_5$
1797	w	1801	w	$\nu_8 + \nu_{24}$
1762 R	m			$\nu_{13} + \nu_{16}$,
1757	m			$\nu_7 + \nu_{24}$
1751 Q	m,A?	1747	w	$2\nu_{19}$
1740 P	m			
1649	w	1647	m	?
1582 R	m			
1570 Q	m	1565 m	m	ν_3
1554 P	m			
1540 Q	m	1539	m	$\nu_{13} + \nu_{18}$
1529 P	w			
1450	w	1443	n	ν_4
1437 Q′	w,B?	1426	m	ν_{16}
1430 Q″				
		1400	w	$\nu_{13} + \nu_{22}$
		1361	w	?
		1337	w	$2\nu_{12}$?
1304 R	s			
1297 Q′	s,B	1288	s	ν_{17}
1291 Q″				
1278 P	s			
1224 R	m			
1217 Q′	m,B	1210	s	ν_{18}
1211 Q″				
1198 P	m			
1186	m	1180	s	ν_6
1142	w			
		1109	w	ν_7
1094 R	m			
1074 Q	m,C	1073	s	ν_{22}
1054 P	m			
978	w	966	w	ν_8?
900 R				
888 Q	s,B	886	s	ν_{20}
883 Q	s,A?			
866 R	s			
846 Q	s.C	846	s	ν_{23}
828 P	s			
657 R	s			
645	s			
640	s			
635 Q	s,C	636	s	ν_{24}
615 P	s			

[a] Abbreviations: P, Q, Q′, Q″, R refer to the rotational branches of a single band and A, B, C to the band type (see text and Fig. 3). sh = shoulder, v = very, s = strong, m = medium, w = weak for cell thicknesses and pressures shown in Figs. 1 and 2. Overtones which cannot be explained as binary combinations are labeled "?." Between 1800 and 2800 cm.$^{-1}$ there are about 25 weak or very weak overtone bands in the vapor and a similar number (though not always at similar frequencies) in the liquid. For brevity these are not included in Table I. They are recorded in the thesis of D. G. Rea.

red band contours indicate the assignments for a number of frequencies and comparison with the spectra of cyclopropane and ethylene oxide and their deuterium derivatives[3] is also helpful.

The expected modes of vibration for each species are given in column 3 of Table IV. Approximate moments of inertia required for calculation of band contours and product rule values may be obtained from the geometrical parameters of the molecule as determined by Schomaker, *et al.*[4] If one takes the twofold axis (C_{2v} symmetry) as the z-axis with the x-axis perpendicular to the ring plane at the center of gravity, and adopts the values C=C, 1.34 Å.; C–C (perpendicular to C_2^z), 1.57 Å.; C–C ("parallel" to C_2^z), 1.54 Å.; C–H (CH_2), 1.08 Å.; C–H (C=C), 1.07 Å.; ∠HCH, 110°; ∠HC=C, 120°; ∠C–C–C bisected by CH_2 plane, one obtains $I_x = 123.8$, $I_y = 71.5$, $I_z = 63.0$ for cyclobutene and $I_x = 158.1$, $I_y = 95.8$, $I_z = 83.6$ for cyclobutene-d_6, all in units of 10^{-40} g.-cm.^{2}. The band contours and theoretical product-rule ratios are not sensitive to the precise values of the geometrical parameters.[14]

From these values it follows that vibrations of species A_1 (Table IV) should produce bands of type A,[15] species B_1, type B, and species B_2, type C. The shapes of the band contours for room temperature observation have been calculated by the procedure of Badger and Zumwalt[16] and it is found that in cyclobutene, type A bands should have a Q branch of medium intensity and a P–R separation of about 29 cm.$^{-1}$. Type B bands should exhibit a split Q branch (spacing about 7 cm.$^{-1}$) and P–R separation of some 30 cm.$^{-1}$. Type C bands should have a sharp, strong Q branch and P–R spacing of about 40 cm.$^{-1}$. These contours are shown for $T = 300°$K. in Fig. 3.

Assignment of Frequencies

Although in principle all twenty-four fundamentals are Raman-active, it is apparent from Ta-

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[14] The values adopted for the geometrical parameters are not exactly the same as those given by Goldish, Hedberg and Schomaker,[4] though they do lie within or close to the latters' estimates of error. It appears to us that the decreased double bond frequency implies a lower C=C force constant than usual and hence a slightly larger C=C distance. The value given by Goldish, *et al.* (1.325) is slightly smaller than their "standard" value (1.330), but their limits of error (±0.046) are wide enough to include our value of 1.34. The large value appears more reasonable to us in light of the unusually low C=C frequency (1566 cm.$^{-1}$). Quite possibly the C=C distance is even larger than 1.34.

[15] See G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945, p. 469.

[16] R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, **6**, 711 (1938).

TABLE II

INFRARED SPECTRUM OF CYCLOBUTENE-d_6[a]

Vapor ν (cm.$^{-1}$ vac)	I	Liquid ν (cm.$^{-1}$ vac)	I	Assignment
3510	w	3498	w	$\nu_1 + \nu^1$
		3439	w	?
3367	w	3357	w	$\nu_1 + \nu_5$, $\nu_6 + \nu_{21}$
3285	w	3272	w	$\nu_{15} + \nu_{18}$
		3218	w	$\nu_2 + \nu_4$
		3170	w	$\nu_7 + \nu_{21}$
3146	w	3142	w	$\nu_1 + \nu_{19}$
3094	w	3096	w	$\nu_{15} + \nu_{17}$
3077	w	3067	w	$\nu_{14} + \nu_{19}$
2688	w	2682	w	$\nu_{21} + \nu_{24}$
2480	w	2478	w	$\nu_3 + \nu_{17}$
2355 R	s			
2344 Q	s,A?	2335	s	ν_1
2315 P	s			
		2296	s	$2\nu_{18}$
2281 R	s			
2271 Q′ 2266 Q″	S.B	2261	s	ν_{14}
2248 R				
2228 Q	s,C	2221	s	ν_{21}
2210 P	s			
		2204	s	$\nu_4 + \nu_{18}$
2187 R				
2178 Q		2169	s	ν_2
2168 R				

Vapor ν (cm.$^{-1}$ vac)	I	Liquid ν (cm.$^{-1}$ vac)	I	Assignment
		2160	s	$\nu_5 + \nu_6$
2151 R	s			
2140 Q′ 2135 Q″	s,B	2129	s	ν_{15}
2106 P	s			
		2106	s	$2\nu_4$
		2087	m	$\nu_4 + \nu_5$
2064 R	m			
2055 Q	m,A	2046	m	$2\nu_5$
2045 P	m			
		2032	w	$\nu_4 + \nu_{17}$
		1676	w	$\nu_7 + \nu_8$, $\nu_4 + \nu_{23}$
1669	w	1665	w	$2\nu_{22}$
1521 R	m			
1509 Q	m,A	1504	s	ν_3
1499 P	m			
		1376	w	?
1350	w	1357	w	$\nu_8 + \nu_{23}$
1314 R	w			
1305 Q′ 1298 Q″	w,B	1302	m	$\nu_{11} + \nu_{23}$
1287 P	w			
1157 1150	m m	1155	m	ν_{18}

Vapor ν (cm.$^{-1}$ vac)	I	Liquid ν (cm.$^{-1}$ vac)	I	Assignment
		1135	w	ν_6
		1100	w	$\nu_{13} + \nu_{22}$
1074	m			
1063 R?	m			
1058 Q?	m,B?	1056	s	$\nu_4 + \nu_{16}$
1047 P?	m			
		1031 w		ν_5
991 R	w			
982 Q	w	976	m	ν_{17}
967 R 956 Q′ 953 Q″ 941 P	w,B?	955	m	ν_7
843 R	s			
826 Q	s,C	826	s	ν_{22}
808 P	s			
		810	s	ν_{19}
745 sh	m	741	m	$\nu_{12} + \nu_{31}$
		722	s	ν_8
718 R	s			
708 Q′ 703 Q″	s,B	702	s	ν_{20}
689 P	s			
642 R	m			
625 Q	m,B	624	m	ν_{23}
608 P	m			
562	vw	552	w	$2\nu_{13}$
475 R	s			
462 Q	s,C	481–453	vs	ν_{24}
446 P	s			
419	w		..	$\nu_{20} - \nu_{13}$

[a] See footnote *a* Table I. for symbols. About a dozen very weak transmission minima observed in the range 1890–2010 cm.$^{-1}$ are omitted from Table II. These can readily be assigned to combinations of the eight fundamentals observed between 810 and 1155 cm.$^{-1}$.

ble III that only a fraction of these, particularly of those expected to lie below 1500 cm.$^{-1}$, have been

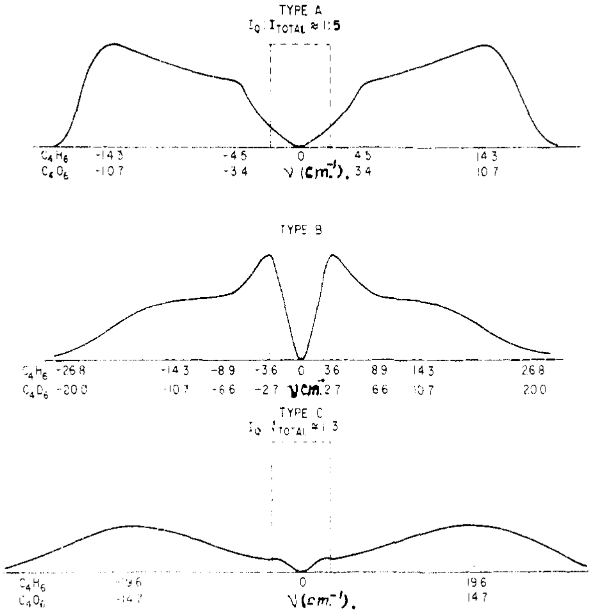

Fig. 3.– Calculated infrared band contours for cyclobutene and cyclobutene-d_6 at 300°K.

TABLE III

RAMAN SPECTRUM OF LIQUID CYCLOBUTENE AND CYCLOBUTENE-d_6

$\Delta\nu$ (cm.- vac)	I, p (estd.)	Assignment	$\Delta\nu$ (cm.$^{-1}$ vac)	I,p (estd.)	Assignment
3129	3 dp	ν_{14}			
3058	7 p	ν_1	2335	7 p	ν_1
3047	2 -	?	2297	1 -	$2\nu_{18}$
			2262	5 dp	ν_{14}
			2218	3 dp	ν_{21}
2933	9 p	ν_2	2167	7 p	ν_2
2916	6 p?	ν_{15}	2161	7 p	$\nu_5 + \nu_6$
2876	4 p	$2\nu_4$	2127	3 dp	$\nu_{17} + \nu_{18}$
2840	5 p	$2\nu_{16}$	2108	4 p	$2\nu_4$
			2047	3 p	$2\nu_5$
2494	1 dp?	$\nu_{17} + \nu_{18}$, $\nu_{16} + \nu_{22}$	1947	0 -	$2\nu_{17}$
1566	10 p	ν_3	1504	10 p	ν_3
1444	5 p	ν_4	1136	5 p	ν_6
1427	4 dp	ν_{16}	1054	0 -	ν_4, ν_{16}
1276	1 dp?	ν_5	1031	0 -	ν_5
			953	10 p	ν_7
1182	5 p	ν_6	833	1 dp?	ν_{22}
1113	10 p	ν_7	735	2 dp	$\nu_{12} + \nu_{13}$
986	8 dp	ν_8			
875	6 dp	ν_{19}	723	3 dp	ν_8
850	1 -	ν_{20}			
325	1 -	ν_{13}			

TABLE IV

SYMMETRY SPECIES, SELECTION RULES AND FREQUENCY ASSIGNMENTS FOR C_{2v} STRUCTURE OF CYCLOBUTENE AND CYCLOBUTENE-d_6[a]

Species, selection rules and product rule values	Vibn. No.	Approximate form of vibration	Assignment C_4H_6	Assignment C_4D_6
	1	CX stretching	3058	2335
A_1	2	CX_2 stretching	2933	2164
$\rho < 6/7$;	3	C=C stretching	1566	1504
Type-A bands	4	CX_2 deformation	1444	[1054]
$\tau_{calcd} = 5.365$ $\tau_{obsd} = 5.19$	5	CX in-plane bending	1276	1031
	6	Ring expansion	1182	1136
	7	Ring expansion	1113	953
	8	CX_2 wagging	986	723
	9	CX_2 stretching	(2955)	(2228)
A_2	10	CX_2 twisting	(1100)	(850)
$\rho = 6/7$; IR-inactive	11	CX out-of-plane bending	(800)	(650)
$\tau_{calcd} = 3.472$	12	CX_2 rocking	(640)	(460)
	13	Ring puckering	325	275
	14	CX stretching	3126	2261
B_1	15	CX_2 stretching	2916	2129
$\rho = 6/7$;	16	CX_2 deformation	1426	[1054]
Type-B bands $\tau_{calcd} = 4.75$	17	CX in-plane bending	1288	976
$\tau_{obsd} = 4.63$	18	Ring expansion	1210	1155
	19	Ring deformation	875	810
	20	CX_2 wagging	850	702
B_2	21	CX_2 stretching	2955	2228
$\rho = 6/7$	22	CX_2 twisting	1074	826
Type-C bands $\tau_{calcd} = 3.277$	23	CX out-of-plane bending	846	625
$\tau_{obsd} = 3.21$	24	CX_2 rocking	635	462

[a] ρ = depolarization ratio of Raman lines; τ_{calcd} = theoretical value of product-rule ratio; τ_{obsd} = product-rule ratio of observed frequencies; CX refers to olefinic CX bonds, CX_2 to aliphatic CX_2 group, X = H or D; ( ) means "estimated frequencies," [ ] means "observed frequency assigned to two fundamentals."

observed. Most of the fundamentals must therefore be evaluated from the infrared.

Species A_1.—There are six polarized Raman lines in cyclobutene and five in cyclobutene-d_6 which can be assigned readily as indicated in Table IV. The remaining two A_1 frequencies in cyclobutene are placed at 1276 and 986 on the basis of their expected locations. The former is questionably depolarized and the latter, though observed as depolarized, coincides with a source line which could have influenced the depolarization ratio under the conditions of measurement. In the deuterium compound the lines at 1031 and 1054, though so weak that their depolarization factors could not be measured, are placed in species A_1 because they lie approximately at the plates to which the CH_2 deformation and CH in-plane bending frequencies should shift in cyclobutene-d_6. The remaining frequency—723—is selected from the pair 723–735 because this region is the expected location of CD_2 wagging and the lower of the pair is more intense and gives slightly better agreement with the product rule. The pair 723–735 also occurs in the infrared of liquid cyclobutene with an intensity ratio similar to that in the Raman effect. This fact suggests Fermi resonance, and after attempts to assign 735 as fundamental encountered difficulties, it was attributed to the combination tone $\nu_{12} + \nu_{13}$, in resonance with ν_8.

Species B_1.—If the foregoing assignments are correct, most of the B_1 vibrations must be either unobserved in the Raman effect or in coincidence with A_1 frequencies. However, some of this species can be assigned from the infrared band type (B) and others can be located by elimination, *i.e.*, because their band types are not A or C. In the spectrum of cyclobutene vapor, the bands at 3134, 1294 and 1214 are rather definitely of type B and those at 1434 and 885 are probably of type B, though overlapping of other bands interferes with the identification. In cyclobutene-d_6 the distinction between band types A and B is much less clearcut and only the band at 706 is sufficiently free from overlapping to be identified as type B. However, the locations of the B_1 fundamentals in cyclobutene and the product rule assist considerably in the assignments. The ones shown in Table IV show good correlation with analogous frequencies in cyclopropane, ethylene oxide and their deuterium analogs.[3] It is interesting that the B_1 vibrations show greater intensity than the A_1 vibrations in the infrared.

Species B_2.—The infrared (type C) bands of this species in both compounds are the most intense of all. This fact together with the distinctive band shape and freedom from overlapping enables all B_2 vibrations to be identified readily. The assignment given in Table IV fits the product rule satisfactorily and correlates well with related molecules.[3]

Species A_2.—This species is inactive in the infrared. Although the A_2 vibrations are formally allowed in the Raman effect, the only observed line which cannot easily be assigned to other species is the extremely weak one at 325 in cyclobutene. This is so low that it can correspond only to the ring-puckering vibration. The analogous frequency in cyclobutene-d_6 is expected at about 275 cm.$^{-1}$, but was not detected in the Raman effect. Certain overtones in the infrared are best explained with the help of an A_2 fundamental of this frequency, and it is therefore entered in Table IV as an observed value.

All the other A_2 modes are similar to the B_2 modes and frequencies are estimated for them by analogy.

Overtones.—In various regions of the infrared spectrum many overlapping overtones are observed. The selection rules are so lax (only species A_2 is forbidden), the overlapping so extensive and the effect of anharmonicity so uncertain that the information obtainable from overtones is limited. Many of the weaker overtone frequencies have been omitted from Tables I and II. Plausible explanations are given for most of those listed in the tables.

Discussion

Since the highest reasonable symmetry for the cyclobutene molecule is C_{2v}, the structural problem from a symmetry standpoint is the rather empty one of distinguishing between C_{2v}, C_2, C_s and C_1

(no symmetry). In any of these structures, all vibrations would be both infrared- and Raman-active except for the infrared-silent vibrations of species A_2 of C_{2v}. Therefore the vibrational selection rules are unfavorable *a priori* for a structural decision, and in addition the failure of numerous vibrations to appear in the Raman effect renders firm decision impossible.

The most significant structural evidence is furnished by the type-C infrared bands. The number of these found is just that predicted for C_{2v} symmetry for both cyclobutene and cyclobutene-d_6. The frequencies and band shapes (see Fig. 3) are those expected and the frequency product ratio for species B_2 agrees with the theoretical value. To be sure, these things might happen by accident for a structure of lesser symmetry, particularly if the deviation from C_{2v} geometry were rather small. The best one can say is that there is some rather definite evidence in favor of a C_{2v} structure and nothing compelling against it. High-resolution study of the rotation–vibration spectra for bands of all three types in both molecules should furnish sufficient information to evaluate the most important geometrical parameters.

An interesting result of this study is the unusual location and intensity of the double bond frequency. Presumably the low frequency is the result of a decrease in the C=C force constant due to strain in the four-membered ring,[17] as was pointed out above. The high intensity of the double bond vibration in the Raman effect is remarkable, as is the unusually low intensity of the infrared band. The latter, which is weaker than the overtone bands at 1540 and 1760, cannot be used with assurance to indicate the presence of HC=CH in a four-membered ring, and particularly its absence from an infrared spectrum is not an indication of the absence of this group from a molecule. The Raman spectrum is a more reliable guide for this purpose.[18] Substitution of one of the hydrogens by methyl, halogen, or other group will of course affect both the frequency and intensity of the C=C infrared absorption band.

Thermodynamic Functions of Cyclobutene

So far as the authors are aware, no investigation has been made of the heat capacity and heats of transition of cyclobutene. It is therefore not possible to check the assignment given in Table IV by comparison of calculated with measured entropy, free energy or heat capacity. Calculation of these quantities has been carried out by Mr. Alfred Danti of this Laboratory and these results will be published separately.

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[17] J. O. Halford (*J. Chem. Phys.*, **24**, 830 (1956)) has shown that a considerable variation in the carbonyl frequency of ketones could result without changing the force constants simply by a change of the bond angles of the carbonyl group. Possibly a similar effect is partially responsible for the low C=C frequency in cyclobutene.

[18] D. E. Applequist and J. D. Roberts (THIS JOURNAL, **78**, 4012 (1956)) have recently published infrared spectra of methylenecyclobutene and certain related compounds. Although the exocyclic double bond of methylenecyclobutene gives a strong infrared absorption band at about 1670 cm.$^{-1}$, no band is reported near 1550 cm.$^{-1}$ for the internal double bond. In the Raman spectrum of this compound, on the other hand (M. V. Evans and R. C. Lord, unpublished results), both double bond frequencies are present, at 1673 and 1530 cm.$^{-1}$, respectively, the latter being considerably stronger.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Surface Catalysis of the Ortho- to Para- Conversion in Hydrogen under Pressure at Low Temperatures

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The surface catalysis of the ortho- to para- conversion in hydrogen was investigated on a series of catalysts consisting of 0.05 to 2.47% chromia–alumina under pressures in the range 5 to 100 atmospheres at 77°K. and on a 0.05% chromia–alumina catalyst at approximately 29 atm. in the region 55–195°K. For catalysts of lower chromia concentrations the half-life varied linearly with pressure and linearly with the reciprocal of the number of gram-atoms of chromium in the catalyst chamber. The rate data, which were first order with respect to composition, support the theory of Harrison and McDowell[2] who adapted the Wigner[3] theory to the case of conversion in a physically adsorbed hydrogen layer on a paramagnetic surface. The rate constant temperature dependency, in agreement with this theory, was positive for the case of high hydrogen surface coverage investigated in this research. This is in contrast to the negative temperature dependency of the rate constant usually observed for the case of low surface coverage. Absolute rate calculations were made for the case of high surface coverage using Harrison and McDowell's choice of reasonable values for certain constants in the rate expression. Good agreement with experiment was obtained.

Introduction

Though considerable experimental work has been done concerning the surface catalysis of the ortho–para- conversion in hydrogen at pressures of 1 atm. or less, the catalysis at higher pressures and low temperatures has been little studied since the initial experiments of Bonhoeffer and Harteck[4] and Farkas and Bonhoeffer[5] to prove the existence of the heterogeneous catalysis.

Harrison and McDowell,[2] in their study of the para–orthohydrogen conversion on the free radical α,α-diphenyl-β-picrylhydrazyl at low temperatures and pressures, concluded that the conversion takes place by interaction between hydrogen mole-

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[2] L. G. Harrison and C. A. McDowell, *Proc. Roy. Soc.* (*London*), **A220**, 77 (1953).

[3] E. Wigner, *Z. physik. Chem.*, **B23**, 28 (1933).

[4] K. F. Bonhoeffer and P. Harteck, *ibid.*, **B4**, 113 (1929).

[5] A. Farkas and K. F. Bonhoeffer, *ibid.*, Bodensteinband, 638 (1931).