[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

Vacuum Ultraviolet Absorption Spectra of Cyclic Compounds. I. Cyclohexane, Cyclohexene, Cyclopentane, Cyclopentene and Benzene[1]

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The far ultraviolet absorption spectra of the five- and six-membered ring hydrocarbons, cyclohexane, cyclohexene, cyclopentane, cyclopentene and benzene have been measured between 45,000 and 64,000 cm.$^{-1}$. Measurements of intensity have been made by a photographic method using the compounds as flowing vapors to minimize photodecomposition. Values of oscillator strength have been calculated. Applications of the results to the problem of the molecular structure of five- and six-membered ring compounds are noted.

Introduction

The molecular structure of five- and six-membered ring compounds has been a subject of much discussion and conflicting evidence. Recent articles by Pitzer[2] and co-workers have summarized the extensive studies of infrared and Raman spectra and of thermodynamic properties that have been made by many investigators and have concluded that no one of the four compounds, cyclohexane, cyclopentane, cyclohexene and cyclopentene is planar. Recent infrared and Raman measurements by Miller and Inskeep[3] have shown conclusively that cyclopentane does not have D_{5h} symmetry. The present paper concerns the spectra of these four compounds as well as that of benzene which is generally treated as a planar hexagon of D_{6h} symmetry.

The ultraviolet absorption spectra of these five compounds have been studied but in no case have intensity measurements of the vapor spectrum been reported. The present measurements have been made in the Schumann region between about 2200 and 1500 Å.

Scheibe and Grieneisen[4] studied the spectrum of cyclohexane and Klevens and Platt[5] noted that the transmission limits of a 0.13 mm. layer of liquid cyclohexane and cyclopentane were 1765 and 1725 Å., respectively.

Carr and Stücklen[6a,b] have measured the position of the bands of cyclohexene, cyclopentene and benzene in this region. Price and Tutte[6b] have shown photographs of cyclohexene and benzene and have found ionization potentials. Platt, Klevens and Price[7] have reported intensity measurements of cyclohexene in heptane solution.

The ultraviolet spectrum of benzene has been a subject of much investigation both experimental and theoretical. A careful vibrational analysis of the band system near 2600 Å.[8] has given evidence that the latter is a forbidden transition of type A_{1g}-B_{2u} allowed by an E_g vibration.

In the vacuum ultraviolet region, benzene shows moderately strong absorption near 2000 Å. and a very intense band at 1750 Å.[6a,b] as well as Rydberg series of bands.[9] Price and Walsh[10] attribute the sharp bands at 1790 Å. as the first member of one of the previously reported Rydberg series which is superimposed on an underlying region of strong absorption which is comparable to the excitation in cyclohexene. This band has been generally assigned as an A_{1g}–E_{1u} transition.

The group of diffuse bands near 2000 Å. is believed by Carr and Stücklen[11] to constitute the first member of the other Rydberg series previously reported by Price and co-workers. Nordheim, *et al.*,[12] suggest that the 2000 Å. band is a forbidden transition to a B_{1u} state. Craig[13] has recently suggested that the alternative assignment, A_{1g}–E_{2g}, mentioned by Nordheim is more reasonable. The intensity of benzene in heptane solution has been measured in this region.[14]

Experimental

The measurements were made on samples supplied by the Bureau of Standards. The maximum amount of impurity is shown in mole per cent. as follows: cyclohexane (209a-5) 0.01 ± 0.006%; cyclopentane (219-5S) 0.05 ± 0.02%; cyclohexane (522-2S) 0.023 ± 0.02%; cyclopentene (288-5S) 0.034 ± 0.021%; benzene (210a-5) 0.03 ± 0.02%.

In the case of the olefins, the sealed tubule was broken in vacuum and the sample passed directly into the absorption tube which had previously been flushed with nitrogen and evacuated. Two different samples were used of the cyclohexane, cyclopentene and benzene with agreeing results.

The method of measurement was essentially that described by Harrison[15] but was extended to shorter wave lengths. A Hilger fluorite prism spectrograph was used with a hydrogen lamp. Photographs were made of the vapor continuously flowing through a 32.5-cm. absorption cell with fluorite windows. The calculations of intensity were made from microphotometer records of plates bearing a three-minute exposure of the compound and four timed exposures of the empty cell for calibration purposes. Tests of the reciprocity relation[16] for the Ilford Q plates used showed the validity of the method under the conditions of use.

For each compound studied plates were made so that at each wave length there were two to six values of molecular coefficient calculated from measurements over a two- to threefold change of pressure. The photographic method is not one of high accuracy and in general the agreement of

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(1) This work has been supported by the ONR under Contract N8onr-74100, NR-055-160.

(2) C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947); J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, *ibid.*, **69**, 2483 (1947); C. W. Beckett, N. K. Freeman and K. S. Pitzer, *ibid.*, **70**, 4227 (1948).

(3) F. A. Miller and R. G. Inskeep, *J. Chem. Phys.*, **18**, 1519 (1950).

(4) G. Scheibe and H. Grieneisen, *Z. physik. Chem.*, **B25**, 52 (1934).

(5) H. B. Klevens and J. R. Platt, THIS JOURNAL, **69**, 3055 (1947).

(6) (a) E. P. Carr and H. Stücklen, *J. Chem. Phys.*, **6**, 55 (1938); (b) W. C. Price and W. T. Tutte, *Proc. Roy. Soc.* (*London*), **A174**, 207 (1940).

(7) J. R. Platt, H. B. Klevens and W. C. Price, *J. Chem. Phys.*, **17**, 466 (1949).

(8) H. Sponer, G. Nordheim, A. Sklar and E. Teller, *ibid.*, **7**, 207 (1939).

(9) W. C. Price and Wood, *ibid.*, **3**, 439 (1935).

(10) W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (*London*), **A191**, 22 (1947).

(11) E. P. Carr and H. Stücklen, *J. Chem. Phys.*, **7**, 631 (1939).

(12) G. Nordheim, H. Sponer and E. Teller, *ibid.*, **8**, 455 (1940).

(13) D. P. Craig, *ibid.*, **17**, 1358 (1949).

(14) C. W. Rector, G. W. Schaeffer and J. R. Platt, *ibid.*, **17**, 460 (1949).

(15) A. J. Harrison, C. L. Gaddis and E. M. Coffin, *ibid.*, **18**, 221 (1950).

(16) Reference 15; Harrison and Tannenbaum, unpublished work.

these values was such that the average deviation in log E was 0.03. Since, however, the vibrational structure of the bands caused reproducible variations of intensity within this limit, and thus values averaged from a number of plates tended to blur the details of structure, the absorption curves were plotted from selected plates rather than from average values. In no case was the difference between selected and average values considered significant. Both the slit width of the spectrograph which was somewhat large to minimize exposure time and the slit width of the microphotometer had an effect on the apparent sharpness and hence the height of the sharp bands.

The estimated error varies with the region of the spectrum. Beyond 60,000 cm.$^{-1}$ the emission lines of molecular hydrogen in the light source prevented the observation of narrow bands so that the curves beyond this point are less reliable and show only the general shape of the absorption band without fine structure. · At wave numbers below 48,000 cm.$^{-1}$ measurements were also made with the Beckman spectrophotometer using a specially constructed vapor-handling system[15] for the three compounds which absorbed in this range. The excellent agreement with the results obtained with the vacuum spectrograph shows that the vacuum method is of comparable accuracy in this region and is much superior for the study of narrow bands because the Beckman instrument requires the use of wide slits in this region.

The standards of wave length employed were the nitrogen emission lines at 1745.246 and 1742.734 Å., mercury absorption line at 1849.68 Å., the copper spectrum above 2000 Å. and the lines of molecular hydrogen.

Results

Table I shows values for the absorption maxima of benzene. The absorption curves for the five compounds are shown in Figs. 1 and 2 which give the logarithm of the molar extinction coefficient ($E = d/cl$ where d is the optical density, c is in moles/liter and l the length in cm.) plotted against the wave number.

The oscillator strength of the bands shown in Table II is calculated from the area under the curves by the formula $f = 4.32 \times 10^{-9} \int E d\nu$.

TABLE I

INTENSITY OF BAND MAXIMA OF BENZENE VAPOR

Wave length, Å.	Wave number	Pressure, mm.	Log E	Average	Average deviation
2037	49,080	0.0617	3.73		
2031	49,230	.0617	3.73		
		.0783	3.70		
		.103	3.62	3.68	0.04
2025	49,380	.0443	3.76		
		.0617	3.73		
		.0783	3.70		
		.103	3.62	3.70	0.04
1999	50,020	.0391	3.84		
		.0443	3.90		
		.0591	3.82		
		.0617	3.82		
		.0783	3.82		
		.103	3.75	3.82	.03
1964	50,920	.0391	3.78		
		.0443	3.88		
		.0591	3.80		
		.0617	3.79		
		.0783	3.80		
		.103	3.73	3.80	.03
1930	51,800	.0391	3.70		
		.0443	3.79		
		.0591	3.72		
		.0617	3.70		
		.0783	3.75	3.73	.03
1905	52,490	.0391	3.68		
		.0443	3.76		
		.0591	3.71		
		.0617	3.69		
		.0783	3.74	3.71	.03
1898	52,680	.0391	3.68		
		.0443	3.77		
		.0591	3.70		
		.0617	3.69		
		.0783	3.74	3.71	.03
1890	52,920	.0391	3.69		
		.0443	3.78		
		.0591	3.72		
		.0617	3.71		
		.0783	3.75		
		.103	3.64	3.71	.03
1879	53,220	.0391	3.67		
		.0443	3.76		
		.0591	3.70		
		.0617	3.67		
		.0783	3.73		
		.103	3.62	3.69	.03
1861	53,730	.0391	3.73		
		.0591	3.75		
1803	55,460	.00338	4.91		
		.00394	4.88		
		.00546	4.85	4.88	.02
1790	55,870	.00338	5.13		
		.00394	5.08	5.10	.03
1769	56,520	.00338	4.91		
		.00394	4.89		
		.00546	4.86	4.89	.02
1766	56,620	.00338	4.93		
		.00394	4.89		
		.00546	4.87	4.90	.02
1759	56,850	.00338	4.90		
		.00394	4.88		
		.00546	4.86	4.88	.02

TABLE II

VALUES OF OSCILLATOR STRENGTH

Substance	Wave number range, cm.$^{-1}$	f-Value
Cyclohexene	45600–51200	0.01
	51200–58100	.19
	58100–64300	.20
Cyclopentene	47600–50000	.004
	50000–64000	.32
Benzene	47500–53400	.12
	53400–60000	1.2

Since the bands are overlapping in this region of the spectrum, the calculation is made between certain frequencies as indicated.

Discussion of Results

The especial contribution of this work is considered to be in the determination of extinction coefficients and consequently of oscillator strength, since earlier measurements in vapor phase have included only qualitative estimates of intensity. The wave numbers of bands showed fairly good agreement with those previously reported[4,6a] and are not shown here. The following points seem worthy of comment. (1) The absorption band of

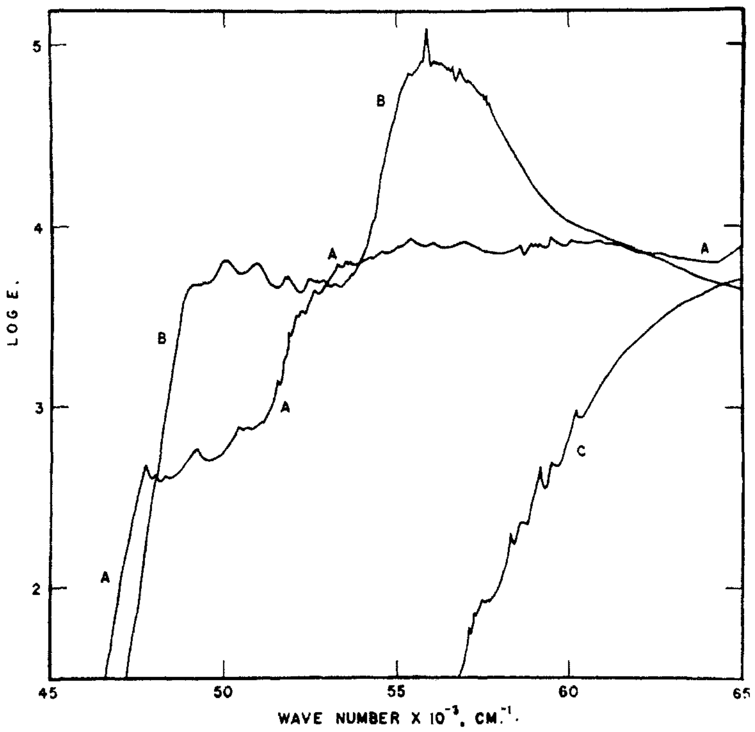

Fig. 1.—Absorption curves of: A, cyclohexene; B, benzene; C, cyclohexane.

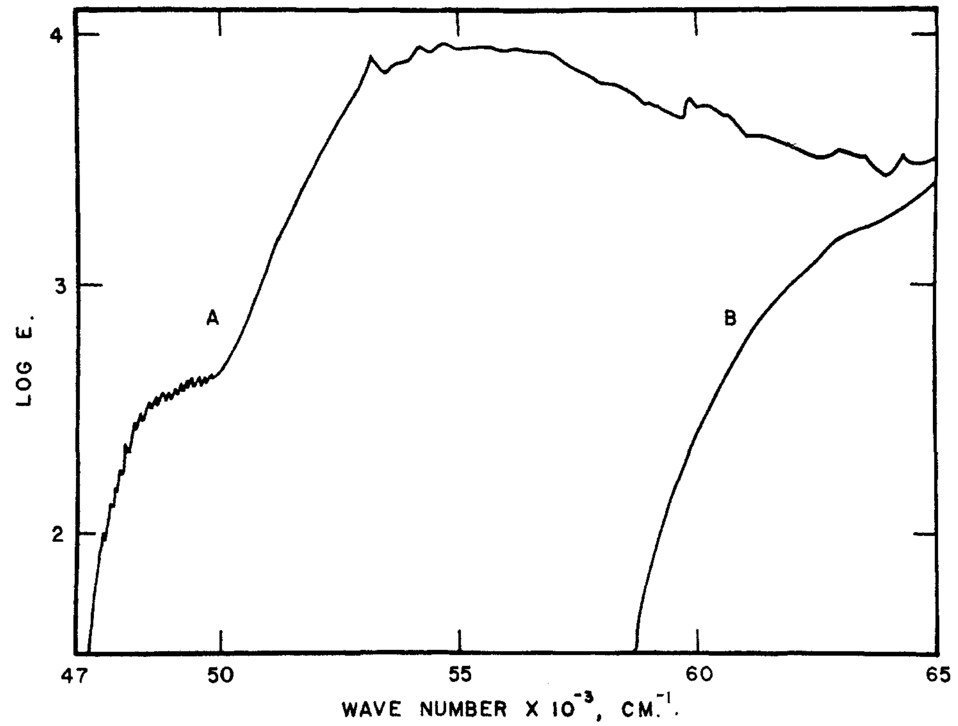

Fig. 2.—Absorption curves of: A, cyclopentene; B, cyclopentane.

cyclopentane is displaced to higher frequencies than that of cyclohexane. It seems to be without marked structure although its displacement into the region of the hydrogen line spectrum could have obscured shallow bands. Measurements of cyclopentane, which was enclosed in the absorption cell for an exposure time of three minutes at a pressure of 4 mm., showed increased general absorption and the appearance of narrow bands not observed in a comparable exposure of flowing vapor, thus indicating the effect of photodecomposition.

(2) The introduction of a double bond in the molecule, as in cyclohexene and cyclopentene, produces a marked change in the spectrum as is shown in Figs. 1 and 2. The general position and intensity of absorption in these two compounds is similar, in accord with the conclusion of Carr and Stücklen[17] that the immediate environment of the double bond determines the position of the first absorption bands. There are certainly two and probably more overlapping band systems in the region under investigation. Certain bands in cyclopentene observed by these authors[6a] and suggested by them to be due to the presence of cyclopentadiene were not observed here, thus confirming their suggestion.

(3) The oscillator strengths of the first two bands of cyclohexene vapor (0.01 and 0.19, respectively) are slightly lower than those obtained for cyclohexene in *n*-heptane solution.[7] In the latter case one smooth band "with a long wave length tail" was observed with an oscillator strength of 0.23 ± 0.05.

(4) The vibrational structure of cyclohexene and cyclopentene bands show marked differences. The first band of cyclopentene consists of a long succession of narrow shallow bands with separations averaging 130 cm.$^{-1}$ which are believed to

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[17] E. P. Carr and H. Stücklen, *J. Chem. Phys.*, **4**, 760 (1936).

represent vibrations of the ring. The structure of the corresponding band of cyclohexene is quite different with no vibrational frequencies of less than 250 cm.$^{-1}$ in evidence. However, a separation of 1485 cm.$^{-1}$ is clearly marked and doubtless corresponds to the double bond stretching frequency of 1650 cm.$^{-1}$ observed in the ground state through Raman and infrared measurements. In cyclohexene as in cyclohexane no prominent separation was observed which might parallel the ring breathing frequencies near 800 cm.$^{-1}$ which cause strong polarized Raman lines.[18]

(5) The intensity data for benzene give an opportunity for the testing of some of the controversial assignments. The band system at 50,000 cm.$^{-1}$ consists of a group of bands with a prominent separation of around 800 cm.$^{-1}$ representing a ring-breathing vibration. The first of these bands seems to be rather a group of three narrow bands and is of lower intensity as is the first band of the forbidden transition in the quartz ultraviolet. However, the intensity is not sufficiently different from the others to warrant a conclusion that it originates from a higher vibrational level of the ground state.

This conclusion was supported by a study of the spectrum of benzene vapor in a jacketed tube maintained near $-20°$. The relative intensity of the first two bands showed no measurable change from that at room temperature. Studies at lower temperatures were not feasible because of condensation of benzene.

The f value for this band measured from 47,500–53,750 cm.$^{-1}$ was calculated as 0.12. Platt and co-workers[14] found an f value of 0.1 for the corresponding band in heptane solution which seems to be displaced toward the visible by about 1000 cm.$^{-1}$. The band system at longer wave lengths undergoes a much smaller shift from vapor to solution. Both the position and the intensity of the most intense band seem quite different in vapor and in the solution measurements cited,[14] which would indicate that the solvent has a larger effect on this band than on those of longer wave length. The top of the underlying band is at an E value of about 80,000 while the strong peak at 55,870 cm.$^{-1}$ extends even higher. An over-all value of f from 53,750 to 60,000 cm.$^{-1}$ was calculated as 1.23 though this is believed to represent two transitions, one a Rydberg series overlying an N–V transition of type A_{1g}–E_{1u}.

The next papers of this series will discuss five- and six-membered ring compounds containing oxygen and nitrogen atoms, respectively.

Acknowledgment.—The authors are indebted to the Office of Naval Research, and also to the Research Corporation for the Beckman spectrophotometer used in some of the measurements.

SOUTH HADLEY, MASS. RECEIVED APRIL 25, 1951

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[18] K. W. F. Kohlrausch and H. Wittek, *Z. physik. Chem.*, **B48**, 177 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

The Vacuum Ultraviolet Absorption Spectra of Cyclic Compounds. II. Tetrahydrofuran, Tetrahydropyran, 1,4-Dioxane and Furan[1]

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The vacuum ultraviolet absorption spectra have been measured for four cyclic ethers, tetrahydrofuran, tetrahydropyran, 1,4-dioxane and furan in vapor phase. Bands are found for each of the compounds in the region between 50,000 and 60,000 cm.$^{-1}$ which are due to the excitation of the unshared electrons of oxygen. In the case of the first three compounds characteristic structure showing low frequency vibrational differences is prominent in these bands. Though the first three compounds have only low absorption at wave numbers below 50,000 cm.$^{-1}$, furan shows the broad absorption band characteristic of dienes in this region.

Introduction

An earlier paper of this series[2] discusses the spectra of five- and six-membered saturated hydrocarbon rings and the effect on the absorption of introducing unsaturation electrons in the ring in the form of one or multiple double bonds. In this paper the effect of unsaturation electrons present as unshared electrons of one or more oxygen atoms is considered. The cyclic ethers tetrahydrofuran and tetrahydropyran were chosen since they have an oxygen atom in an otherwise saturated five- and six-membered ring, respectively, while 1,4-dioxane illustrates the effect of two oxygen atoms which are sufficiently separated to have little effect on each other. In furan there are unsaturation electrons from the carbon atoms of the ring to give a conjugated system.

There has been little or no investigation of the vacuum spectra of the first three compounds. That of furan has been previously reported by Pickett[3a] and by Price.[3b] Measurements of a related compound, dihydropyran,[4] in solution have shown only a broad band with a maximum value of E of 3,800 at 51,280 cm.$^{-1}$.

Experimental

The spectral measurements were made as described in the first paper of this series.[2,5] All samples used were purified in this Laboratory and distilled in an atmosphere of nitrogen

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[1] This work was supported by the ONR, Contract N8-onr-74100; NR-055-160. This paper was presented at the Physical and Inorganic Section of the 119th Meeting of the American Chemical Society, April, 1951.

[2] L. W. Pickett, M. Muntz and E. M. McPherson, THIS JOURNAL, **73**, 4862 (1951).

[3] (a) L. W. Pickett, *J. Chem. Phys.*, **8**, 293 (1940); (b) W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (*London*), **A178**, 201 (1941).

[4] J. R. Platt, H. B. Klevens and W. C. Price, *J. Chem. Phys.*, **17**, 466 (1949).

[5] A. J. Harrison, C. Gaddis and E. M. Coffin, *ibid.*, **18**, 221 (1950).