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The Absorption Spectra of a Series of Dienes

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A SYSTEMATIC study of the ultraviolet absorption spectra of simple hydrocarbons has been in progress in this laboratory for some years as a group research project. The study involves the preparation of highly purified hydrocarbons in which the position of the double bond or bonds is known with certainty and the spectrographic examination of these compounds in vapor and liquid phases with the quartz spectrograph in the near ultraviolet and in vapor phase with the fluorite vacuum spectrograph down to 1400A. This spectrographic work demands a very high degree of purity in materials and with the exception of the 2,4-dienes[1] all of the hydrocarbons reported in this paper have been synthesized and purified in this laboratory under the direction of Dr. Mary L. Sherrill. The experimental technique for the spectroscopic measurements has been described previously.[2]

The absorption spectra of eighteen mono-olefines together with two cyclic hydrocarbons containing one double bond have been examined and certain general characteristics and relationships have been established.[3] The spectrum of each of these shows a region of low intensity absorption in the neighborhood of 40,000 cm^{-1}, followed by intense and very characteristic absorption above 43,000 cm^{-1}. Between 43,000 and 53,000 cm^{-1} there is a group of narrow diffuse bands which are superimposed upon a broad and more intense band whose maximum is near 57,000 cm^{-1} for most of the aliphatic compounds. The spectra of the two cyclic hydrocarbons cyclopentene and cyclohexene are very similar to the ethylenic derivatives in the first two regions of absorption but differ profoundly in the region above 52,000 cm^{-1} which would indicate that absorption in this latter region is determined by the structure of the molecule as a whole, while the absorption at longer wave-lengths is more closely associated with the unsaturated linkage and its immediate environment in the molecule. The position of the narrow diffuse bands is, in fact, determined by the number of alkyl groups directly bound to the carbon atoms of the double bond and is independent of the nature of the alkyl group or groups. There is a progressive shift toward the visible of 3000–4000 cm^{-1} as the hydrogen atoms of ethylene are replaced by alkyl groups and it seems probable that these bands represent an electronic transition closely related to atomic spectra and constitute the lowest member of a Rydberg series whose limit gives the ionization potential of the molecule. The electronic excitation concerns one of the "π" or unsaturation electrons of the double bond.[4]

An extensive study of these Rydberg series spectra of hydrocarbons at shorter wave-lengths has been made by Price and co-workers. Their values for the ionization potentials show a progressive decrease as alkyl groups are substituted on the carbon atoms of the double bond which parallels the shift toward longer wave-length observed in our measurements of the group of bands between 43,000–53,000 cm^{-1}. The diffuseness of the bands in question as compared with the bands identified as Rydberg series bands by Price would seem to be due to their superposition on the broad, intense band which is ascribed by Mulliken to the class of molecular electronic transitions known as $N\rightarrow V$ transitions. This identification of the two types of bands in the spectra of mono-olefines between 43,000 and 60,000 cm^{-1} is of particular interest in the interpretation of the spectra of hydrocarbons containing two double bonds.

The absorption spectra of eleven aliphatic dienes and three cyclic dienes have now been examined. Measurements of cyclopentadiene and 1,3-cyclohexadiene have already been pub-

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[1] These were furnished through the courtesy of Dr. A. L. Henne of the American Petroleum Institute Laboratory at Ohio State University.

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

[3] E. P. Carr and H. Stücklen, J. Chem. Phys. **4**, 760 (1936); **6**, 55 (1938). E. P. Carr and M. K. Walker, J. Chem. Phys. **4**, 765 (1936).

[4] E. P. Carr and H. Stücklen, J. Chem. Phys. **7**, 631 (1939); W. C. Price and W. T. Tutte, Proc. Roy. Soc. **A174**, 207 (1940).

lished[5] and detailed reports with a more complete analysis of the other compounds will be published shortly. In this brief review it is possible only to point out certain of the general relationships which the experimental results indicate.

In the work on mono-olefines and the earlier study of diolefines, Schumann plates made by Hilger were used and the emulsion on these plates was not sufficiently even to admit of photometric measurements. The absorption curves for the vapor measurements of these substances indicate only the relative intensities of bands as estimated from their appearance on the photographic plates and the pressure changes necessary to bring out the different bands. Quantitative determination of molecular extinction coefficients for the liquid and hexane solution phase in the long wave region were made by the Henri photographic method and the use of a copper-silver spark. The absorption curves for three different types of diolefines show very different characteristics depending upon whether the two double bonds in the hydrocarbon molecule are isolated as in 1,5-hexadiene, conjugated as in 1,3-pentadiene or adjacent as in ethyl allene.[6] In 1,5-hexadiene the absorption curve is almost identical with that of pentene-1, differing only in an increased intensity which corresponds approximately to an increase of twice that of the mono-olefine. Two diffuse bands near 52,000 cm^{-1} are evident only as sharp step-outs on the broad band but are in the same region as the shallow bands of the mono-olefines which have the same number of hydrogen atoms bound to the carbon atoms of the double bond.

Where the double bonds are conjugated, the spectrum is very different; the broad band of the mono-olefine is shifted toward longer wavelengths and has a maximum near 48,000 cm^{-1}. A group of narrow diffuse bands is superimposed on this band and further to the ultraviolet there is a group of very sharp discrete bands. Five conjugated dienes of this type have been examined and the spectra of all are closely analogous. In ethyl allene where the double bonds are adjacent in the molecule the spectrum shows a broad region of quite intense absorption extending from 42,000 to 60,000 cm^{-1}. Dimethyl allene has also been measured and shows a very similar spectrum. In both of these spectra there is some evidence of the narrow diffuse bands which characterize the mono-olefines and the positions of these bands in the two allenes correspond approximately with those of the mono-olefines.

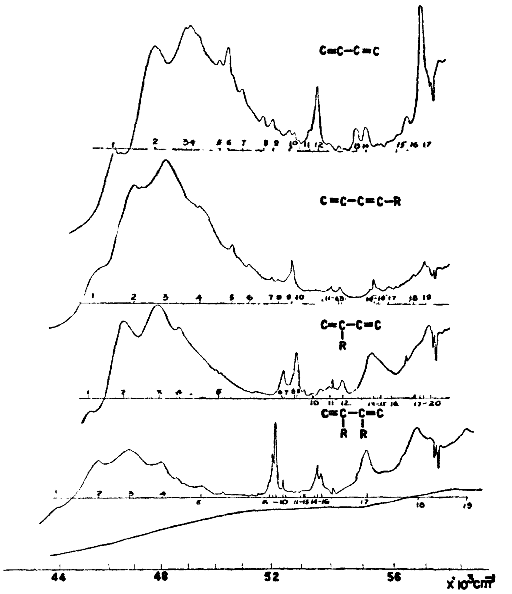

FIG. 1. Microphotometer tracings of the absorption spectra of (1) butadiene, (2) 1,3-pentadiene, (3) isoprene, (4) 2,3-dimethylbutadiene between 44,000 and 58,000 cm^{-1}, together with exposure of hydrogen lamp for comparison.

Recent study has been directed towards a more detailed study of the conjugated aliphatic dienes. The use of Ilford Q-plates in the vacuum spectrograph has made photometric measurements possible and microphotometer records of the different spectra give a more dependable basis of comparison than the earlier curves based on appearance pressures.

Figure 1 gives the microphotometer records of four dienes, whose structural formulae, omitting hydrogen atoms, are indicated. The alkyl group *R* is in each case the methyl group. The absorption spectra of three of these dienes in the vacuum ultraviolet have been examined by Price[7] and co-workers but their analysis has been concerned

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[5] Pickett, Paddock, and Sackter, J. Am. Chem. Soc. **63**, 1073 (1941); V. Henri and L. W. Pickett, J. Chem. Phys. **7**, 439 (1939); E. P. Carr and H. Stücklen, J. Chem. Phys. **6**, 55 (1938).

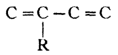
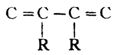
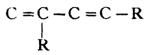
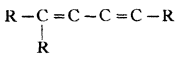
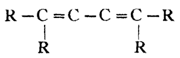
[6] E. P. Carr and H. Stücklen, *Proc. Seventh Conference on Spectroscopy* (John Wiley and Sons), p. 128.

[7] W. C. Price and A. D. Walsh, Proc. Roy. Soc. **A174**, 220–234 (1940).

primarily with the identification of Rydberg series bands in the short ultraviolet between 60,000 and 70,000 cm^{-1} and the measurements made in this laboratory extend from 43,000 to 60,000 cm^{-1}.

All of the molecules in this group except 1,3-pentadiene have both of the unsaturated linkages at the end of the chain so that each of these molecules would have two unsaturated carbon atoms with no substituent and 1,3-pentadiene would have one such carbon atom. If the interpretation of the spectra of mono-olefines in this region is correct, then it would be reasonable to expect that a Rydberg series arising from the excitation of a π electron of one of the end carbon atoms might have a higher excitation energy than one from the second or third carbon atom of butadiene.[8] In other words, the spectrum should show the origin of at least two Rydberg series in this region and by analogy with the mono-olefines which have only one alkyl substituent the higher energy transition should be in the region of 53,000 cm^{-1}. Examination of the photometer record of the spectrum of butadiene shows a sharp intense band at 53,650 cm^{-1} and another sharp but very intense band at 50,560 cm^{-1} which is superimposed on the broad diffuse band which has been interpreted as an $N \rightarrow V$ transition.[9]

TABLE I. Vibrational bands (in cm^{-1}).

	Broad bands		Group A		Group B	
$C{=}C{-}C{=}C$	1320	1340	1610	1565	1630	1535
$C{=}C{-}C{=}C{-}R$	1400	1320	1240(?)		1575	
 $C{=}\underset{R}{C}{-}C{=}C$	1305	1350	1500		1550	1530
 $C{=}\underset{R}{C}{-}\underset{R}{C}{=}C$	1370	1450	1520		1485	1490
 $C{=}\underset{R}{C}{-}C{=}C{-}R$	1320	1130			1575	
$R{-}C{=}C{-}C{=}C{-}R$	1400	1320			1650	
 $R{-}\underset{R}{C}{=}C{-}C{=}C{-}R$			1605	1560	1550	1545
 $R{-}\underset{R}{C}{=}C{-}C{=}\underset{R}{C}{-}R$			1565	1565	1560	1530

Broad bands 43000–49000 cm^{-1}
Sharp bands
Group A 46000–50000
Group B 51500–54000

On the assumption that the bands at 50,560 cm^{-1} and 53,650 cm^{-1} represent the lowest members of two different Rydberg series, the corresponding bands in the other spectra have been identified and are designated as group A and B, respectively. Because of the superposition of the A band on the broad band, the position of this band is more difficult to measure than the sharp bands of group B but it is clearly evident in each of the curves of Fig. 1. There is a vibrational pattern associated with each of these transitions which is very similar for both groups and the separation of about 1500 cm^{-1} (Table I) shows the main $C{=}C$ valence vibration.

A quantitative method for determining intensities has not been worked out but these microphotometer records give a basis for comparing intensities in a single spectrum. For example, it is significant to note that the intensity of the group B band in 1,3-pentadiene, where there is only one unsaturated carbon atom at the end of the chain, is considerably less in relation to the maximum of the $N \rightarrow V$ band than the corresponding band where each molecule has two such carbon atoms. Where there is an alkyl substituent it was found for mono-olefines that the Rydberg bands are displaced toward the visible by about 3000–4000 cm^{-1} and an analogous relation seems to exist for the dienes. If this assumption is correct the sharp bands near 52,000 cm^{-1} should disappear where there are alkyl substituents at both ends of the conjugated system.

Figure 2 gives the microphotometer tracing for three dienes where the double bonds are in the 2,4 position and consequently these molecules would have no unsaturated carbon atoms without one or more substituents. These curves differ in important characteristics from those of Fig. 1. Two records are reproduced for 2,4-hexadiene and for 2-methyl, 2,4-hexadiene, the upper one of the vapor at considerably higher pressure and the lower curve at pressures comparable with those of the 1,3-dienes of Fig. 1. In the low pressure

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[8] The classification of molecular spectra by Mulliken as of two types, Rydberg and sub-Rydberg (J. Chem. Phys. **7**, 20 (1939)), accounts satisfactorily for the general characteristics of the diene spectra observed. The interpretation of the changes in the Rydberg type spectra with slight changes in the structure of the molecule would seem to point toward a molecular model where the unsaturation electrons are associated with individual carbon atoms.

[9] R. Mulliken, J. Chem. Phys. **7**, 121 (1939).

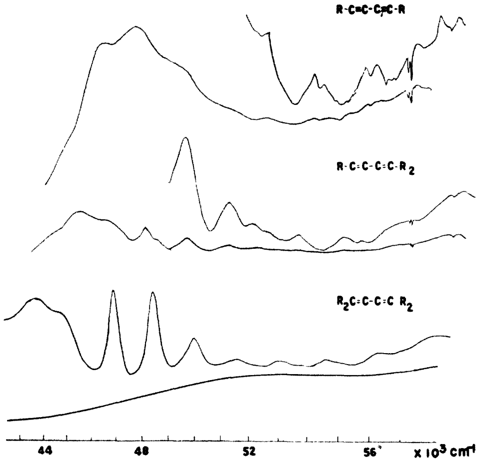

FIG. 2. Microphotometer tracings of the absorption spectra of (1) 2,4-hexadiene, (2) 2-methyl-2, 4-hexadiene, (3) 2,5-dimethyl-2, 4-hexadiene, (4) hydrogen continuum, between 43,000 and 59,000 cm.$^{-1}$

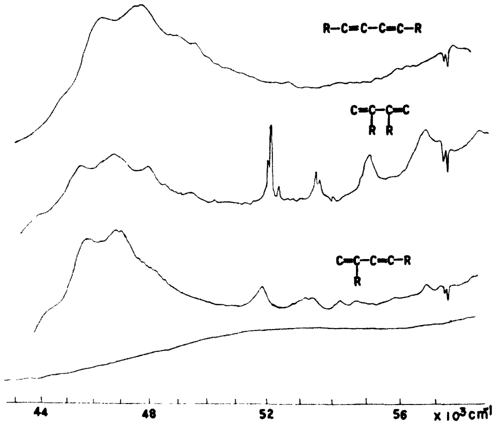

FIG. 3. Microphotometer tracing of absorption spectra of (1) 2,4-hexadiene, (2) 2,3-dimethylbutadiene, (3) 2-methyl-1, 3-pentadiene, (4) hydrogen continuum.

curves there is no evidence of the sharp narrow bands which characterize the 1,3-dienes although at pressures sufficiently high that there is complete absorption in the $N \rightarrow V$ band the hexadiene shows an absorption pattern quite similar to 1,3-pentadiene but shifted slightly to lower wave numbers. The intense $N \rightarrow V$ band would seem without doubt to be due to resonance along the carbon chain; if there is a shift of the conjugated system to the end of the chain, resulting in the formation of any of the 1,3-isomer, this would account for the appearance of the group *B* bands at high pressures.

Where a third alkyl group is substituted for hydrogen a sharply marked band system appears with the first band at 48,135 cm^{-1} and with four alkyl groups the arrangement around each double bond is similar to group III of the mono-olefines with three alkyl substituents. In this group of the mono-olefines the first band of the Rydberg series for diisobutylene, with the same number of carbon atoms in the molecule, is at 46,380 cm^{-1}; for 2,5-dimethyl 2,4-hexadiene the first sharp band is at 46,860 cm^{-1} and this is followed by two bands each separated from the preceding by 1,565 cm^{-1}, the main C=C valence vibration.

The experimental evidence would seem to justify the conclusion that the narrow bands in both mono- and di-olefines are of the Rydberg type and that the energy of the electronic transition of this type is practically unaltered by the conjugated system of double bonds whereas the $N \rightarrow V$ transition is shifted toward the visible by 9000–14,000 wave numbers as compared with mono-olefines.

The three broad diffuse bands that are found on the long wave side of the broad band in all of the conjugated dienes, irrespective of their individual molecular structure, have analogous separations in all of the compounds (Table I) but this vibration is reduced somewhat more from that of the ground state ($\sim$1600 cm^{-1}) for these bands than with the Rydberg type transitions shown by the bands of groups A and B. Because of the particular position of the broad bands of the two heavier 2,4-dienes, which are measured at the end of the photographic plate with the quartz spectrograph and at the beginning with the vacuum instrument, the maxima of these bands cannot be measured with the same accuracy of the other bands of this group and are not given in the table. Their separations seem to be of approximately the same order as in the analogous group of the other dienes.

In Table II the effect of slight structural changes in the molecule is shown by the displacement of each type of band as measured from the corresponding bands of butadiene. The last column gives the decrease of the ionization potential (in cm^{-1}) as compared with butadiene.[10] Compounds numbered 3, 4, and 5 are all hexa-

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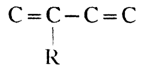
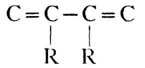
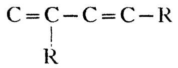
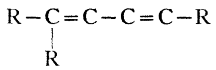
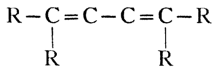
[10] W. C. Price and A. D. Walsh, Proc. Roy. Soc. **A174**, 220 (1940).

Table II. Displacement of corresponding bands in cm^{-1} in relation to butadiene.

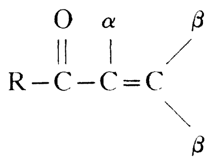
		Broad band (max.)	Group A	Group B	Limit of Rydberg Series (Price)
1	$\mathrm{C{=}C{-}C{=}C{-}R}$	780	1100	870	
2	 $\mathrm{C{=}\underset{R}{C}{-}C{=}C}$	1100	1870	800 1235	1750
3	 $\mathrm{C{=}\underset{R}{C}{-}\underset{R}{C}{=}C}$	2070	2530	1475	2855
4	 $\mathrm{C{=}\underset{R}{C}{-}C{=}C{-}R}$	2080		1845	
5	$\mathrm{R{-}C{=}C{-}C{=}C{-}R}$	1080		1030	
6	 $\mathrm{R{-}\underset{R}{C}{=}C{-}C{=}C{-}R}$	3580	2425	1550	
7	 $\mathrm{R{-}\underset{R}{C}{=}C{-}C{=}\underset{R}{C}{-}R}$	5480	3700	2200	

dienes so that the band displacements are dependent only on the structural changes within the molecule. It is significant to note the much greater shift of the maximum of the $N \rightarrow V$ band where the carbon chain is branched than in the straight chain compound (3 and 4 as compared with 5). The bands of group A in compounds 4 and 5 overlapped the broad band to such an extent that they could not be identified and measured although evidence of their existence near 48,000 cm^{-1} is shown in the photometer records of Fig. 3 which gives the three hexadienes together. The relative shifts of the group B bands in the hexadienes seem less significant than the very striking difference in the relative intensities of these bands as shown in Fig. 3. This is one of the strongest arguments in support of the assumption that the π electron involved in the transition may be localized on a particular carbon atom of the conjugated system.

Another consequence of this assumption would be that group A bands would constitute the lowest member of the series leading to the first ionization potential. The ionization potentials are reported for only three of the diolefines but it is of interest to note that those displacements parallel much more closely the ones of group A than of the two other groups (Table II).

Finally this table shows that the substitution of two methyl groups causes a shift of approximately twice that of one in the $N \rightarrow V$ band but there is a proportionally much larger shift for three or four alkyl groups in this band which is not reflected in the other groups.

Examination of the absorption spectra of a series of unsaturated ketones whose conjugated system is analogous to that of the diolefines[11] has led Woodward to make a generalization to the effect that "the position of the wave-length of maximum absorption for the intense band in the absorption spectra of α, β-unsaturated ketones reveals the extent of substitution of the carbon-carbon double bond in an α, β-unsaturated carbonyl system." The general formula for the substituted ketones as given by Woodward is



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}\overset{\alpha}{\overset{|}{C}}{=}C}\begin{smallmatrix}\diagup\beta\\ \diagdown\beta\end{smallmatrix}$$

where α and β apply to a large number of different substituents. The maximum of the intense band for a mono-substituted ketone is some 3500 wave numbers less than that of the $N \rightarrow V$ band for 2,4-hexadiene which would be the analogous compound in the diene series, but the shift of this maximum as the number of substituents is increased parallels closely the shift in the dienes with increasing number of alkyl substituents.

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[11] R. B. Woodward, J. Am. Chem. Soc. **63**, 1123 (1941).