

The Ultraviolet Absorption Spectra of Simple Hydrocarbons III. In Vapor Phase in the Schumann Region

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weak absorption band in the quartz region may be summarized as follows:

Configuration	$\log \epsilon = -2.00$
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{R}-\text{C}=\text{C}-\text{H} \end{array}$	38,000–39,000 cm^{-1}
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{R}-\text{C}=\text{C}-\text{R} \end{array}$	34,500–35,800 cm^{-1}
$\begin{array}{c} \text{R} \quad \text{H} \\ \quad \\ \text{R}-\text{C}=\text{C}-\text{H} \end{array}$	35,000–36,400 cm^{-1}



The possible theoretical significance of these results will be discussed in the following paper in connection with the study of the absorption spectra of these same compounds in the Schumann region.

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The Ultraviolet Absorption Spectra of Simple Hydrocarbons

III. In Vapor Phase in the Schumann Region

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(Received July 21, 1936)

Absorption spectra measurements between $\lambda = 2300\text{\AA}$ and 1500\AA were made for fourteen ethylenic hydrocarbons, which included four butenes, five pentenes, one hexene, two heptenes and two octenes. A comparative study of these results together with those from the earlier papers in the series has shown the existence of certain general relationships between the absorption spectra of all ethylenic derivatives. The number of alkyl groups bound to the carbon atoms of the $\text{C}=\text{C}$ bond determines the wave number of the first absorption band; there is a progressive shift toward the visible with increasing number of alkyl groups but the nature of the alkyl group has almost no influence on the position of the first band; where two alkyl groups are bound to the same carbon atom (unsymmetrical substitution) or to different carbon atoms (symmetrical substitution), the wave number of the first band is very slightly different. The first band of these derivatives is tentatively assigned to an electronic excitation corre-

sponding to the transition ${}^1A_1 \rightarrow {}^1B_1$, predicted for the ethylene molecule. Usually one, but never more than three bands of this system could be seen because of overlapping with another group of bands of higher intensity. All of the sixteen olefines have this same intensity change, showing the existence of another electronic excitation. A third group of bands corresponding to a third electronic excitation can be seen clearly in the spectra of four hydrocarbons and may possibly be present but overlapping the lower frequency group in the other compounds. The bands are too broad and diffuse to admit of analysis of vibrational structure but certain recurring separations, which are probably related to the 1350 cm^{-1} vibrational frequency of ethylene, are evident. In the molecules of higher symmetry, where fewer transitions are permitted by the selection rules, there is less overlapping and therefore more discrete bands can be seen.

INTRODUCTION

IN the description of the electronic structure of polyatomic molecules in their normal and excited states, the principle of molecular orbitals as derived from the linear combination of atomic orbitals has been applied, particularly by Mulliken, to the interpretation of the carbon-carbon double bond of organic chemistry and a detailed theoretical analysis of the orbital structure of the $\text{C}=\text{C}$ double bond in ethylene has been worked out.¹ Since the method depends primarily on the

symmetry conditions of the nuclear frame work of the molecule, a spectroscopic study of a number of closely related ethylenic derivatives should give the experimental data which are necessary to test the theoretical deductions both for ethylene and its derivatives.² For some years an extensive study of ethylene hydrocarbons has been in progress in this laboratory and this paper correlates the results of earlier measurements of six ethylenic derivatives in the Schumann region and reports the results for ten additional olefine

¹ Mulliken, Phys. Rev. **41**, 49, 741 (1932); *ibid.* **43**, 279 (1933); J. Chem. Phys. **3**, 517 (1933).

² Snow and Allsopp, Trans. Faraday Soc. **30**, Part 1, 93 (1934).

hydrocarbons. The absorption spectra of four butenes,³ five pentenes, two hexenes, three heptenes and two octenes have been measured.

The experimental set-up for these determinations was substantially the same as that described previously.⁴ The essential features of the apparatus are shown by diagram on Fig. 1. In the present study a longer absorption tube (60 cm) was substituted for those used in the earlier work in order that the partial pressure of the hydrocarbon vapor under examination might be sufficiently low to bring out more bands than were evident at higher pressures. All of the hydrocarbons which had previously been studied were reexamined and in some cases additional bands were noted. The partial pressure of the hydrocarbon in the absorption tube cannot be measured exactly but it can be estimated and pressure changes regulated by careful control of the temperature of the bath (from -78°C to room temperature) in which the bulb containing the liquid hydrocarbon was immersed, by changing the length and width of the capillary through which the stream of nitrogen saturated with gaseous hydrocarbon flowed into the absorption tube and also by control of the difference in pressure between the absorption tube and the bulb containing the liquid hydrocarbon. The partial pressure of the absorbing vapor varied from 50 mm to less than 0.1 mm. All the bands that are given in the following tables were photographed while the vapor was kept flowing through the absorption cell. This was an essential precaution since when the vapor is stationary or flowing very slowly there is considerable photochemical decomposition of the hydrocarbon which is readily evidenced by the appearance of new bands in the spectrum. In some cases these disintegration products could be identified spectroscopically (C_2H_4 , C_2H_2), but these bands were easily differentiated from those of the pure hydrocarbon under investigation. A later paper will deal with a spectroscopic study of the disintegration products of the olefines; the investigation of each hydrocarbon was made under conditions

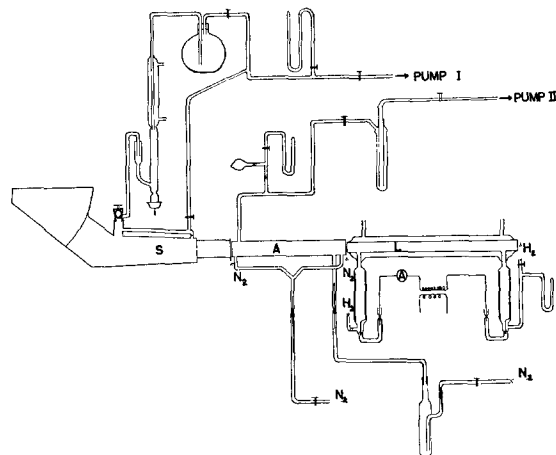


FIG. 1 shows the light source L (H_2 -lamp), the absorption tube A and the spectrograph S . Nitrogen enters the vessel containing the liquid hydrocarbon through a capillary and after being saturated with the vapor is passed through another capillary into the absorption cell. A steady current of pure nitrogen flows against both fluorite windows of the cell and avoids a contact between the hydrocarbon vapor and the sealing material at the windows. The absorption tube is connected with a pump which makes possible the continuous flow of the mixture of nitrogen and vapor. The small gap between the windows of the cell, the spectrograph and the hydrogen lamp is kept free from air by a nitrogen stream under atmospheric pressure.

which gave photochemical decomposition as well as with flowing vapor where no disintegration took place.

With the exception of three of the butenes all of the hydrocarbons studied show only diffuse absorption bands. It is possible only to measure the center of the bands and measurements on different plates may vary by $50\text{--}80\text{ cm}^{-1}$. Only a few bands in each spectrum were sufficiently sharp to obtain a higher accuracy in measuring. In general, all plates were measured, but because of variations in quality of the plates as well as in the experimental conditions certain plates gave much sharper bands and the final results were taken from one plate which seemed to give the sharpest maxima. For each compound a number of plates were taken, each having 5 exposures through the hydrocarbon at different partial pressures as well as two comparison spectra of the hydrogen discharge taken before and after the hydrocarbon was photographed. In order to study the complete spectrum from 10 to 40 plates were taken for each compound examined. In the case of a number of the olefines there was a broad continuous band adjacent on the short wave side to a set of discrete bands. The maximum of this

³ These hydrocarbons were made available for our spectroscopic work through the courtesy of Professor G. B. Kistiakowsky of Harvard University and are of the same high purity as the samples used for their hydrogenation experiments.

⁴ Carr and Stücklen, *Zeits. f. physik. Chemie* **B25**, 57 (1934).

TABLE I.

Group I							
Butene-1		Pentene-1		Heptene-1		Isopropylethylene	
λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)
1875	53330	1884	53080	1886	53020	1895	52770
1819	54970	1830	54640	1831	54610	1865	53620
1730	57800 (max. band <i>B</i>)	1740	57470 (max. band <i>B</i>)	1740	57470 (max. band <i>B</i>)	1813	55160
						1730	57800 (max. band <i>B</i>)
Group II a							
<i>cis</i> Butene-2 ¹				<i>trans</i> Butene-2 ¹			
λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)
2072	48260	1924	51970	2052	48730	1917	52160
2014	49650	1889	52940	2024	49400	1894	52800
1955	51140	1869	53500	1989	50270	1750	57140 (max. band <i>B</i>)
		1740	57470 (max. band <i>B</i>)	1964	50920		
Pentene-2				Hexene-3			
λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)
2051	48760	1911	52330	2033	49190	1851	54020
2009	49780	1859	53800	1994	50150	1792	55800
1977	50580	1770	56500 (max. band <i>B</i>)	(1958)	(51070) ²	1746	57270
1947	51360			1939	51570	1706	58620
Group II b							
Isobutene ¹				Unsym. Methyl Ethyl Ethylene			
λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)
2018	49550	1792	55800	2009	49780	1785	56020
1935	51680	1776	56310	1935	51680	1730	57800
1887	52990	1747	57240	1881	53160	1690	59170
1840	54350	1705	58650	1827	54730	1657	60350
		1671	59840				
Diisobutylene I							
λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)				
2035	49140	1906	52460				
1965	50890	1863	53680				
Group III							
Trimethylethylene				Diethylmethylethylene			
λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)
2181	45850	1861	53730	2150	46510	1842	54290
2148	46550 ³	1812	55190	2090	47850	1785	56020
2122	47120	1774	56370	2033	49190	1729	57840
2055	48660	1729	57840	1997	50070	1688	59240
1962	50970	1691	59140	1943	51470	1655	60420
1917	52160			1893	52830		
Diisobutylene II							
λ (Å)	$1/\lambda$ (cm ⁻¹)	λ (Å)	$1/\lambda$ (cm ⁻¹)				
2156	46380	1933	51730				
2040	49020	1727	57900 (max. band <i>B</i>)				
1993	50170						

¹ Some fine structure can be seen, but in this paper only the center of each group of bands is given. The analysis of the fine structure of 3 butenes will be reported later.

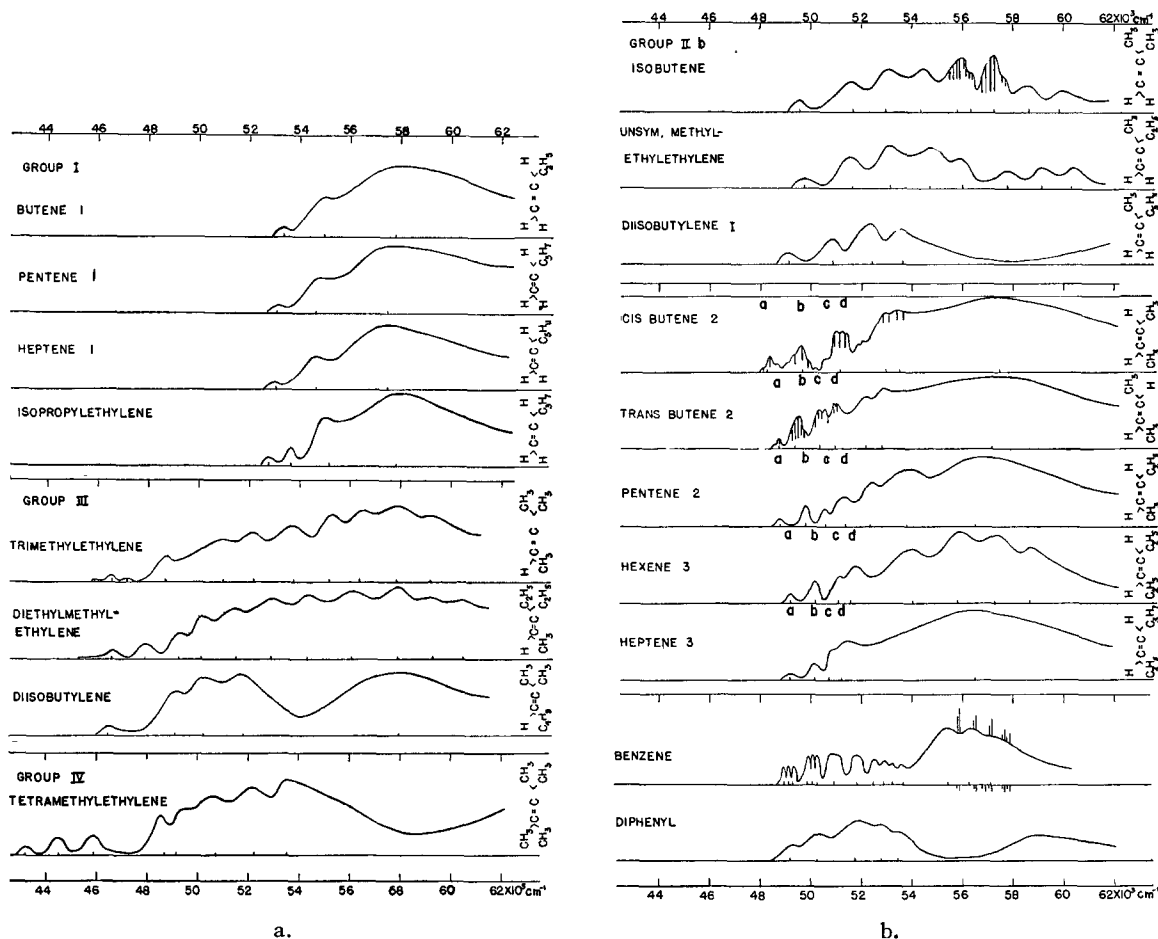
² Indicates a step-out not a discrete band.

³ Center of a band showing threefold splitting.

band could not be determined with a greater accuracy than $\pm 10\text{Å}$ ($\pm 300\text{ cm}^{-1}$).

The presence of even small amounts of peroxides in the hydrocarbons was found in absorption measurements in the liquid phase to be associated with a considerable shift of absorption toward the visible but no evidence of any such

effect could be detected in the vapor phase measurements in the Schumann region although hydrocarbons known to contain peroxide were examined. Similarly different samples of a given hydrocarbon whose absorption spectra in hexane solution showed considerable variation in the intensity of the step-out at 42,000–45,000 cm^{-1}



FIGS. 2a AND b. Absorption bands of ethylenic derivatives. The intensities are estimated from the partial pressure of the hydrocarbon and the appearance of the bands on the photographic plate. The number of the group indicates the number of alkyl groups that are substituted for the hydrogen atoms of ethylene.

showed no detectable difference in the measurements of the vapor spectra with the fluorite spectrograph.

RESULTS

In the preceding tables (Table I) wave-lengths and wave numbers of the center of the absorption bands are given for each of the hydrocarbons studied. In the curves given in Fig. 2, the relative intensities are estimated on the basis of their appearance on the photographic plates. It should be noted that the continuous background given by the light source (H_2 -lamp) diminishes toward the short wave region around 1650Å where the many-line spectrum begins. Absorption bands appearing in the region where the continuous background shows decreasing intensity would

probably show a somewhat different intensity, as estimated from the photographic plate, from that which would be obtained if the continuous background were of constant intensity throughout but it seems improbable that this factor would exert very great effect on the intensity estimates which have been made. In the region showing the many-line spectrum of hydrogen only strong bands can be identified. No discrete bands of the *pure* olefine (i.e., where no photochemical decomposition had taken place) were evident in this region but a decrease of intensity of the H_2 -lines due to continuous absorption may be easily noted by comparison with the spectrum of the lamp alone.

In order to correlate the results of absorption measurements of all the ethylenic hydrocarbons investigated in this laboratory the curves for

tetramethylethylene and 3-heptene⁵ are included in Fig. 2. Since certain similarities between the spectra of unsaturated aliphatic and aromatic hydrocarbons have been observed the curve for benzene⁴ and diphenyl⁶ are given.

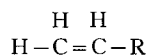
No attempt has been made to make photometric records of the plates. Although the Hilger plates which were used were extremely good, the emulsion is too uneven to justify quantitative photometric work. The curves were drawn in such a way that if a set of bands, including the minima between the bands, have higher values on the ordinate than the maxima of another band or set of bands, then the pressure necessary to bring out these stronger bands is about 1/10 the pressure for the less intense band or bands. The ordinate on the curve would represent the logarithm of the intensity rather than the intensity itself.

On the basis of earlier work in this laboratory a subdivision of the ultraviolet spectrum into four regions, called *A*, *B*, *C* and *D*, has been made. The region *A*, showing continuous absorption, included that portion below 1550Å and was ascribed to an electronic excitation related to the saturated C—C linkage; the other three regions were correlated with the unsaturated C=C bond; region *B* on the basis of the earlier experiments consisted of a broad continuous band between 1800 and 1700Å. Region *C*, between 2300 and 1800Å, consisted in general of narrow, fairly discrete bands and *D* was the quartz ultraviolet part of the spectrum. In the recent much more extensive investigation the classification into the regions *A* and *D* remain unchanged, but the *B* and *C* regions are altered somewhat. The region previously designated as *B* is not always one of continuous absorption only but may have some discrete bands; also, from a theoretical standpoint as will be developed later, it seems advisable to divide region *C* into two parts, of which the region of shorter wave-length seems more closely related to the *B* region than the long wave region of *C* and will hereafter be designated as *B*₂ while the earlier *B* region is called *B*₁.

Before taking up the detailed discussion of our results it is of interest to note the general characteristics of the various spectra in relation

to the molecular configuration of the hydrocarbon molecule. The spectra of all of the sixteen ethylenic hydrocarbons examined can clearly be divided into four groups depending upon the number of alkyl groups which have been substituted for the hydrogen atoms of ethylene. The most striking effect is the progressive shift toward the visible of the whole set of bands as the number of alkyl groups bound to the carbon atoms of the double bond is increased, while the effect of different alkyl groups as substituents is almost negligible.

Group I



The absorption spectrum in the Schumann region begins about 53,000 cm⁻¹, two bands were found in the straight-chain hydrocarbons and three in isopropyl ethylene, followed by a broad continuous band with its maximum around 57,000 cm⁻¹.^{6a}

Group IIa



In group IIa, both the *cis* and *trans* forms of 2-butene were measured while each of the other hydrocarbons of the group consisted of a mixture of the *cis* and *trans* forms.

The absorption starts between 48,000 and 49,000 cm⁻¹, and a number of discrete bands were obtained. The general similarity between the bands in the different olefines is readily apparent although certain bands may be slightly shifted. It is of interest to note the way in which band "c" is shifted toward "d" as the molecule becomes heavier until in heptene-3 this band appears merely as a "step-out" of band "d." The maximum of absorption as with Group I lies near 57,000 cm⁻¹, and it is only in hexene-3 that dis-

^{6a} In isopropyl ethylene a set of bands with fine structure was found at extremely high pressures (50 mm) in the region 46,000–47,000 cm⁻¹. The existence of absorption bands of much lower intensity in this longer wave region was suspected from the absorption curve of the solution and careful search was made for them. They were obtained with three different samples of isopropyl ethylene which had been prepared by two different synthetic methods. Further experiments are in progress to see whether analogous bands could be present in other compounds of Group I or whether they are characteristic of isopropyl ethylene which in its chemical reactivity differs considerably from the other compounds of this group.

⁶ Carr and Walker, this issue.

⁶ Unpublished work.

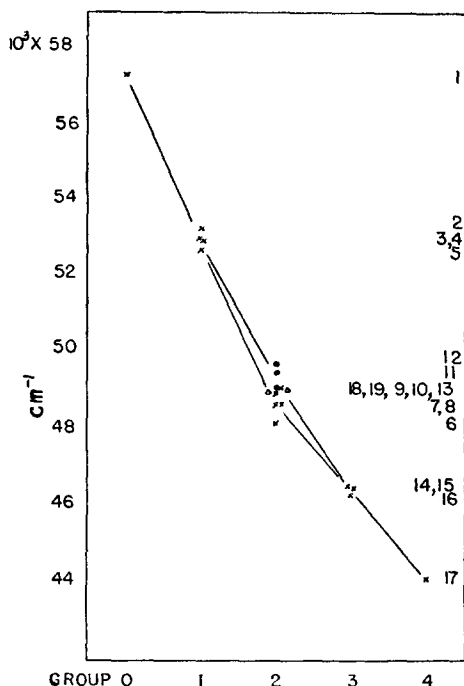


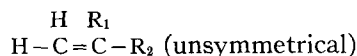
FIG. 3. Position of the first bands in the Schumann ultraviolet of ethylenic derivatives and ethylene plotted against the group number. 1, ethylene;¹ 2, butene-1; 3, pentene-1; 4, heptene-1; 5, isopropylethylene; 6, *cis* butene-2;² 7, *trans* butene-2;² 8, pentene-2; 9, hexene-3; 10, heptene-3; 11, isobutene; 12, *trans* methylethylethylene; 13, diisobutylene I; 14, trimethylethylene; 15, diethylmethylethylene; 16, diisobutylene II; 17, tetramethylethylene; 18, benzene; 19, diphenyl.

¹ Price, Phys. Rev. **47**, 451 (1935).

² Center of first group.

crete bands can be seen in this region. The curves for benzene and diphenyl are included for comparison with the ethylenic hydrocarbons of Group IIa since in these aromatic hydrocarbons the arrangement of hydrogen and carbon atoms around the double bond is analogous to this group and the curves show a marked similarity in the position of the first two bands.

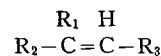
Group IIb



In Group IIb, where both alkyl groups are bound to the same carbon atom, the absorption begins between 49,000 and 50,000 cm⁻¹, and is thus shifted slightly to the ultraviolet in comparison with Group IIa. The most striking feature of the spectra of this group is the similarity of the first four bands in each of the compounds and the marked differences between these three

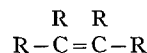
compounds in the short wave region: in isobutene a set of bands with fine structure appears, in unsymmetrical methylethyl ethylene a sharp decrease in intensity occurs and in diisobutylene I the intensity diminishes to an even greater extent and shows no distinct band.

Group III



Absorption of hydrocarbons belonging to Group III begins about 46,500 cm⁻¹, but it is much more difficult to identify analogous bands in the three hydrocarbons of this group. The sharp minimum, found in diisobutylene II at 54,000 cm⁻¹, is not found in the other compounds. With trimethylethylene there is a threefold splitting of the first band and in plotting the curve, Fig. 3, the most intense middle band is taken as the characteristic first absorption band.

Group IV

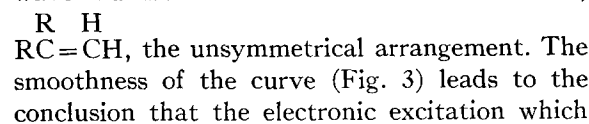
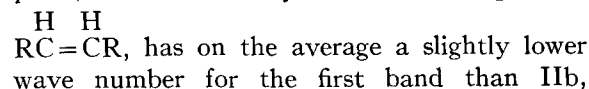


Only one compound belonging to Group IV has been examined, tetramethylethylene. As was pointed out in the previous paper the spectrum is considerably shifted towards the red in comparison with the other hydrocarbons. The first band is at about 43,100 cm⁻¹, the maximum of absorption occurring at 53,500 cm⁻¹.

DISCUSSION

The shift of absorption in the Schumann region toward the visible as the number of alkyl groups around the double bond is increased is shown graphically in Fig. 3 where the wave number of the first band is plotted against the number of alkyl groups. The value for ethylene, as Group 0, is taken from Price's measurements.⁷

In this curve, Group II is divided into two parts, IIa with the symmetrical arrangement,



⁷ Price, Phys. Rev. **47**, 444 (1935).

accounts for the first absorption band in all of the olefines must be the same for all the ethylenic derivatives and closely related to that in ethylene itself. Applying the principle of the linear combination of atomic orbitals, Mulliken⁸ has given an interpretation of the electronic configuration of ethylene according to which the lowest electronic state is an A_1 state and the first excitation would be of the type $[x+x] \rightarrow [x-x]$. This transition results in two excited levels, 3B_1 and 1B_1 , of which the 3B_1 is the lower. Since the change $^1A_1 \rightarrow ^3B_1$ involves a change in multiplicity of the term, the probability of this transition was estimated to be of the order of 10^{-4} of that for the $^1A_1 \rightarrow ^1B_1$ transition.

Snow and Allsopp⁹ have applied a similar process of reasoning to the C=C double bond in ethylenic derivatives, assuming the ground state of $R_1R_2C=CR_3R_4$ to be a 1A_1 level. Since for molecules of lower symmetry the number of upper states which are permitted is greater, it is possible, as was pointed out by Snow and Allsopp, that the absorption spectrum of ethylenic derivatives may be quite different from that of ethylene. Their study, however, of the spectra of trimethylethylene, cyclohexene and ethylene indicated a marked similarity between the upper states of ethylene and of ethylene derivatives and on the basis of their results a tentative assignment of the weak bands of cyclohexene and trimethylethylene measured in liquid and solution phase in the long wave region was made as due to the transition $^1A_1 \rightarrow ^3B_1$, whereas the much more intense bands in the region 2160–2080Å were tentatively assigned to a $^1A_1 \rightarrow ^1B_1$ transition.

Largely because of the analogous structure of the bands observed in the spectra of ethylene and its derivatives, Snow and Allsopp concluded that the band system of ethylene derivatives at about 2100Å is the same in origin as the group of bands in ethylene at slightly shorter wave-lengths (2069 to 1935Å) although the discrepancy in intensities seemed puzzling since the bands for the derivatives have intensities 100 times as great as the bands which they considered to be the corresponding bands of ethylene. On the basis of our results as shown by the curve it would seem more

probable that the band system of ethylene which corresponds to the bands of the derivatives in the 2100Å region is that observed by Price⁷ as beginning at 1744Å ($57,320\text{ cm}^{-1}$). Such a conclusion has further justification when one compares the difference in wave numbers between the beginning of absorption in the low intensity band of the liquid hydrocarbon and the first band of that compound in the Schumann region. As was pointed out in the preceding paper of this series the beginning of absorption in the quartz region as measured by the frequency corresponding to $\log \epsilon = -2.00$, is shifted progressively towards the visible with increasing number of alkyl groups attached to the carbon atoms of the double bond in the same way in which the first band in the Schumann region spectra is displaced. For the twelve hydrocarbons which were measured in both quartz and Schumann regions, the difference in wave-numbers is between 12,850 and 15,000 cm^{-1} . The difference for ethylene is $14,300\text{ cm}^{-1}$ if 1744Å is compared with 2325Å for $\log \epsilon = -2.00$, which is obtained from a short extrapolation of Snow and Allsopp's curve for liquid ethylene.

The matter of relative intensities for such an assignment of corresponding bands of ethylene and its derivatives would seem to be more consistent. Although our intensity estimates in the vapor phase measurements are only approximate it was found that for all the ethylenic derivatives a partial pressure of somewhat less than 1 mm is necessary to bring out the first band, thus indicating a close parallelism in the intensities of corresponding bands. The intensity of the ethylene band at 1744Å, according to the measurements of Scheibe and Grieneisen¹⁰ must be of the same order since this band appears when the partial pressure of the ethylene is between 1 mm and 0.1 mm.

If Snow and Allsopp's assignment of $^1A_1 \rightarrow ^1B_1$ for the bands of ethylene derivatives in the 2100Å region is correct then the first band found by Price for ethylene should be assigned to the same transition. Similarly the absorption of ethylene in the quartz region beginning about 2300Å would be assigned to a $^1A_1 \rightarrow ^3B_1$ transition. The parallelism which is evident between the shift of

⁸ Mulliken, Phys. Rev. **41**, 751 (1932); J. Chem. Phys. **3**, 517 (1935).

⁹ Snow and Allsopp, Trans. Faraday Soc. **30**, 93 (1934).

¹⁰ Scheibe and Grieneisen, Zeits. f. physik. Chemie **B25**, 52 (1934).

absorption in the quartz region and in the Schumann region when the configuration of the molecule is altered indicates a close relationship between the electronic transitions concerned and gives strong support to the correctness of Snow and Allsopp's assignment of levels for the ethylenic derivatives.

The sphere of influence of the $[x+x]$ and $[x-x]$ orbitals is localized in the neighborhood of the C=C bond according to Mulliken, and would therefore be little influenced by varying the alkyl group attached to the carbon atom and consequently the position of the first band would be independent of the nature of the alkyl group. The progressive shift toward the visible with increasing number of alkyl groups should be considered from the point of view of the decrease in the number of hydrogen atoms bound to the carbon atoms of the double bond and the consequent effect on the carbon atom or rather the $[x]$ orbitals due to the replacement of hydrogen atoms by the less electropositive alkyl groups. From this point of view a comparison of the ionization potentials of ethylenic derivatives having different numbers of alkyl groups around the double bond would be of interest. The fact that the position of the first band in the spectrum of benzene, as well as of diphenyl, should bring these hydrocarbons in Group IIa of the olefine classification seems to be more than an accidental coincidence and to imply that the relationship is of fundamental significance in the interpretation of the energy relationships of unsaturated hydrocarbons.

Although the nature of the alkyl substituent has only a very slight effect it is of interest to note that the experimental points which show the greatest deviation from the curve are those in which the alkyl groups have a branched chain which would indicate that there is a slight influence due to spatial configuration.

Fig. 2 indicates that after the first or the first few bands the intensity of absorption increases sharply. This rise in intensity is such that the partial pressure of the hydrocarbon must be decreased to one-tenth or less of its previous pressure to bring out the next set of bands on the photographic plate. In some cases there is a remarkably large gap between the last band of low intensity (region C) and the first of the high

intensity group. This change in intensity is so marked in all of the hydrocarbons that it would seem to represent a transition to another upper level and this group of bands, which was included in region C in the earlier paper⁴ has now been considered as belonging to Group B. Although this transition is characteristic of all the olefines, the point at which this band system appears varies with the different hydrocarbons and the bands overlap those of region C to such an extent that it is not possible to follow the vibrational spectrum in either group. It is perhaps premature to assign a definite transition to this group of bands but it seems probable that it is a transition which is restricted to molecules of lower symmetry than ethylene since neither Price nor Scheibe and Grieneisen report a corresponding group of bands in ethylene.

The character of the spectrum of certain olefines indicates that a subdivision should be made within the region designated as B. This shows most clearly in Group IIb, where there is a sharp change in the spectrum beginning about 55,000 cm^{-1} . In isobutene this change is marked by the appearance of bands with fine structure, in unsymmetrical methylethylethylene and diisobutylene I, by the sharp decrease in intensity. In diisobutylene II, a similar decrease in intensity is apparent and is followed by another band. This region which in these four compounds begins about 55,000 cm^{-1} has been designated as region B_1 , and the region of longer wave-length as B_2 . Whether the same subdivision is justified for the other olefines and where it should be made is uncertain, both regions may overlap to such an extent that no separation is apparent. It is of interest to note, however, that the subdivision shows most clearly in those compounds where there is unsymmetrical substitution of hydrogen atoms of ethylene. The group of bands designated as belonging to region B_1 indicates another electronic transition which like B_2 seems to have no counterpart, at least of comparable intensity in the spectrum of ethylene.

With regard to the vibrational spectra of the ethylene compounds there are certain general relationships which are of interest but no detailed analysis is possible because of the breadth and diffuseness of the bands. In the case of the three butenes in which only two methyl groups are

bound to the C=C nucleus, the single vibrations are resolved and the analysis of these spectra will be considered in a separate paper. An excitation of an electron in an $[x]$ orbital, localized in the region of the C=C bond would have little if any influence on the rest of the molecule and as a consequence the number of vibrational frequencies associated with this electronic excitation is limited. In the case of ethylene, Price reports only two different types of vibration with frequencies of 1340 and 480 cm^{-1} associated with the first electronic band and these vibrations were believed to depend mainly on the C=C linking whereas the vibrations which involve the C-H bonds are not excited. In the ethylene derivatives, some fairly constant frequency differences are evident in region C; for example, about 1350 cm^{-1} between the first bands of tetramethylethylene and between the first two of diethylethylene, but in general only one member of a series can be found in region C.

In regions B_2 and B_1 such restrictions do not seem to hold since a considerable number of band maxima may be seen although the bands are less sharp and more difficult to distinguish than in region C. Fig. 2 shows that although there is no consistent frequency difference between adjacent band maxima yet in most cases the separation of these maxima lies between 1200 and 1500 cm^{-1} . If the strongest vibration which occurs in all these molecules is one along the C=C axis and this frequency is of the same order as that in ethylene, 1350 cm^{-1} , it is quite possible that this vibration is combined with deformation vibrations of smaller frequency and lower intensity.

Since the B region is one of strong predissociation, the single vibrations give rise to fairly broad bands and these broad bands coalesce in such a way as to result in a maximum of absorption which is more or less shifted in relation to any single vibration. The maximum is therefore rather an accidental one which shows only an approximate relationship to the strongest of the excited vibrations. In bands c and d of Group IIa it is possible to follow the way in which two band maxima merge into each other as the weight of the molecule increases.

It is of interest to note that in hexene-3 and in tetramethylethylene a greater number of bands can be seen than in the more unsymmetrical molecules although the contrary would be expected from the selection rules. This must be due to the fact that with the more symmetrical molecules fewer vibrations are excited and consequently there is less overlapping and the bands show more clearly.

The intensity distribution of vibrational sequences is puzzling. A maximum of absorption is reached at the point at which the broad continuous band has its maximum, at about 57,000 cm^{-1} , but there is no evidence of a strongly absorbing 0-0 band nor of decreasing intensity of band maxima in a vibrational sequence. If the probability of transition to the B_1 and B_2 levels were very nearly the same, the absorption would overlap and thus explain in part the intensity increase toward the maximum at 57,000 cm^{-1} .

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