

The Ultraviolet Absorption Spectra of Simple Hydrocarbons I. nHeptene3 and Tetramethylethylene

Emma P. Carr and Margery K. Walker

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The Ultraviolet Absorption Spectra of Simple Hydrocarbons

I. *n*-Heptene-3 and Tetramethylethylene

EMMA P. CARR AND MARGERY K. WALKER, *Department of Chemistry, Mount Holyoke College, South Hadley, Massachusetts*

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The ultraviolet absorption spectra of *n*-heptene-3 and tetramethylethylene were measured in liquid and hexane solution phase, between 4000Å and 2100Å and in vapor phase between 2300Å and 1500Å. Curves showing the logarithm of the molecular extinction coefficient as a function of the wave number are given for the measurements in the quartz region and tables giving the regions of absorption together with the wave-lengths of the centers of bands for the measurements with the fluorite vacuum spectrograph. Comparison with earlier work shows the progressive shift toward the visible of the absorption bands in the Schumann region as the hydrogen atoms of ethylene are replaced by alkyl groups, and the parallelism between the spectra of different hydrocarbons having the same configuration with respect to the double bond.

DETAILED information regarding the spectroscopic characteristics of compounds containing the carbon-carbon double bond is of importance from the standpoint both of chemical reactivity and of theoretical understanding of the electronic configurations which constitute the ethylenic linkage. Of fundamental importance to these problems is the question of how the energy relationships of the ethylenic configuration are affected by replacement of the hydrogen atoms of ethylene by alkyl radicals.¹ Owing to the complexity of the molecules, ultimate analysis of the spectroscopic data obtained for ethylenic derivatives of this type is not yet possible. Nevertheless, much can be learned from a comparative study of the spectral characteristics of an appropriately selected series of such hydrocarbons, which will eventually contribute to a more

specific electronic description of the carbon-carbon double bond.

Systematic investigation of the light absorption of olefine hydrocarbons throughout the region $\lambda=4000\text{Å}$ to $\lambda=1500\text{Å}$ has been undertaken in this laboratory. The present paper covers two substances for which data are complete through the entire range, and for which the results are of particular interest in relation to work already published.^{1a} Similar study of several other hydrocarbons is well advanced, and an extensive program is planned which includes, in addition to simple olefines, benzene derivatives, diolefines, conjugated double bond systems, and other related groupings.

EXPERIMENTAL

The wave-length range covered by these investigations is such as to require two types of technique. The absorption in the near ultra-

¹ (a) Carr and Stücklen, *Zeits. f. physik. Chemie* **B25**, 57 (1934); (b) Snow and Allsopp, *Trans. Faraday Soc.* **30**, 93 (1934).

violet, between 3300 and 2500Å, has on the order of from one-thousandth to one ten-thousandth the intensity of that in the further ultraviolet. Because of this low intensity the pure liquid hydrocarbons and their hexane solutions were employed for this region of the spectrum rather than the materials in the gaseous state. The procedure for making this type of measurement, which has been fully described by one of us,² was followed with minor modifications. The iron electrodes were replaced by copper, and a second spark gap was introduced in series with the copper spark to make the discharge more steady. The photographic plates used were Eastman No. 40 and Eastman Ultraviolet Spectroscopic, the latter making it possible to follow the light absorption very satisfactorily to 2100Å.

The far ultraviolet absorption was obtained for the substances in the vapor state at pressures of 10 mm or less, through a column 11.5 cm long. The optical system was a Hilger E419 fluorite vacuum spectrograph. Light from a discharge through hydrogen was passed through the cell fitted with fluorite windows and containing the vapor of the compound to be studied, and thence into the spectrograph. The spaces between the ends of the absorption cell and the lamp and the spectrograph were less than 1 mm in width and were filled with nitrogen. Nitrogen was also used to carry the hydrocarbon vapors in continuous flow through the cell and to provide gaseous shields next to the fluorite ends of the absorption chamber to prevent reaction of the hydrocarbon with the white wax which held the windows in place. These experimental arrangements have been discussed in detail in a report on preceding work from this laboratory.^{1a}

DATA

The quartz ultraviolet absorption of the two substances under consideration, *n*-heptene-3 and tetramethylethylene, is reported in terms of molecular extinction coefficients, the logarithms of which, when plotted against wave numbers, give the well-known type of absorption curve. The curves in each case are based on about sixty experimental points so closely spaced as to con-

stitute an almost continuous line when plotted on the scale of the figures appearing in the text.

Earlier work in this laboratory on the absorption of ethylenic derivatives below 2300Å led to the recognition of three distinct divisions of this portion of their spectra, which were designated as regions *A*, *B* and *C*. Since the results reported in this paper admit of similar classification, the limits and characteristics of the different regions are summarized briefly. From 2300Å to about 1850Å, there is a region of narrow diffuse bands, the number and position of which depend markedly on the particular hydrocarbon concerned; this is referred to as region *C*. Below this is a region which seemed to show only a broad continuous band with a maximum in the region 1750 to 1800Å which was designated as region *B*. Because of the breadth of the band it is not possible to determine the position of the maximum with an accuracy greater than $\pm 15\text{Å}$. Region *A* consists of a second broad structureless band whose maximum cannot be determined with our spectrograph but must be below 1530Å. This band is found also in the absorption of saturated hydrocarbons and is associated with the saturated carbon-carbon linkage. The breadth of both *A* and *B* varies greatly with pressure, so that they are frequently observed to merge into one another, giving the impression of continuous absorption below 1800Å. The narrow bands in region *C* for the two compounds here reported are very shallow, i.e., they are underlaid by continuous absorption and do not exceed it greatly in intensity. This occasions considerable difficulty in obtaining good exposures of the bands and a rather higher uncertainty in their measurement than is the case, for instance, with benzene which has a much more clearly defined spectrum. Two possible sources of this background may be noted, *viz.*, the narrow bands lie sufficiently close together that their margins may overlap; or the long wave-length side of band *B* may extend throughout this entire region at the pressures necessary to bring out the *C* bands. It seems likely that both factors are operating to some extent; the former more particularly at longer wave-lengths of region *C* and the latter in the shorter wave-length portion.

The limits of accuracy of the values for the location of band centers are probably somewhat

² Carr, J. Am. Chem. Soc. **51**, 3041 (1929).

better than $\pm 75 \text{ cm}^{-1}$ at 2300Å, $\pm 60 \text{ cm}^{-1}$ at 2100Å, and $\pm 50 \text{ cm}^{-1}$ at 1850Å. It should be noted that this uncertainty is due to the difficulty in determining the exact point which is to be taken as the center of the band. No estimate of band widths are given, since these vary within fairly wide limits with the pressure of the hydrocarbon vapor. All these bands are diffuse, and within the limits of the dispersion (250 cm^{-1} per mm at 2100Å and 200 cm^{-1} at 1850Å) show no indication of heads or of fine structure. The relative intensities of bands or regions of absorption cannot be determined with precision by the method of measurement which we have used. An approximate estimate can be made, however, by comparison of the exposures taken with different pressures of the hydrocarbon vapors, and such estimates for each compound are given in the form of a curve in Fig. 2.

N-heptene-3

N-heptene-3 employed for this study was prepared in this laboratory under the direction of M. L. Sherrill.³ Fig. 1 shows the quartz ultraviolet absorption curve for this substance in the pure state and in hexane solution. With lengths of absorbing column (d) which varied from 0.2 to 7.0 cm, the absorption of the pure hydrocarbon could be followed from $\log \epsilon = -2.00$ to -0.60 . A 0.428 molar solution gave the absorption to $\log \epsilon = 0.90$, and the remainder of the curve was obtained from a second dilution to 0.034 molar. Notable features of the absorption curve (Fig. 1) are its long wave-length limit which lies at about $35,200 \text{ cm}^{-1}$, the step-out extending from the beginning of absorption to approximately $39,000 \text{ cm}^{-1}$ which indicates the presence of a low intensity band, the second wide step-out between $42,000$ and $46,000 \text{ cm}^{-1}$, which is due to another band of much higher intensity, and the final sharp rise in intensity of absorption which continues uninterrupted to $47,200 \text{ cm}^{-1}$. The absorption curve is markedly affected by the presence of so-called peroxide substances which form in most olefinic hydrocarbons. For this

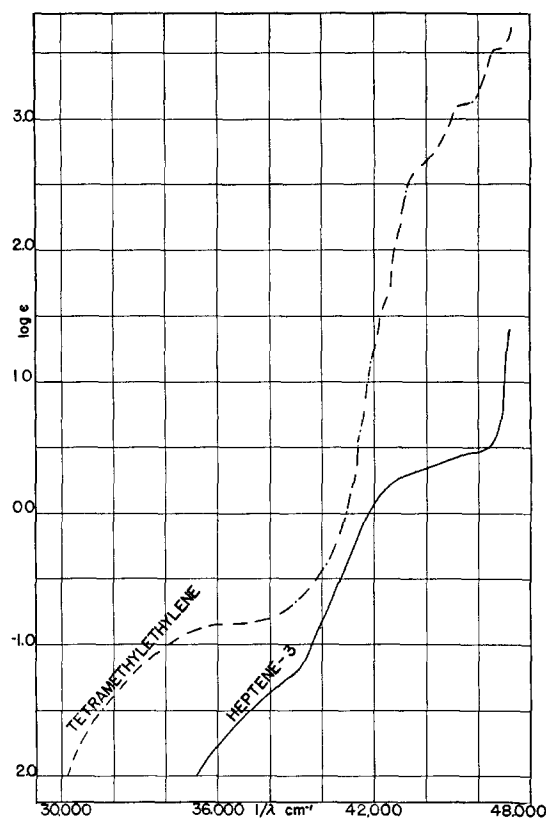


FIG. 1.

reason the absorption was studied immediately after distillation from sodium, and with minimum exposure to air during transfers and dilution. The material used for the absorption study was therefore originally peroxide free, and when tested afterwards for presence of peroxide showed only very slight traces.⁴

Absorption by gaseous *n*-heptene-3 in the far ultraviolet shows in region C three discrete bands and a fourth step-out which precedes the last band and indicates the existence of a fourth band. The position of these bands and of the step-out are given in Table I. The qualitative estimate of relative intensity of absorption in the far ultraviolet region is indicated in Fig. 2.

Tetramethylethylene

We are indebted to Professor F. C. Whitmore of Pennsylvania State College for supplying a sample of tetramethylethylene for these spectro-

³ The synthesis of 4-heptanol and the preparation of the heptene by dehydration of the alcohol with sulphuric acid was carried out by Joyce J. Wadmond. Her data on the physical constants are as follows: b.p. $95.7-95.8^\circ$ at 760 mm, d_{20}^{20} 0.7001, n_D^{20} 1.4041.

⁴ The ferrous sulphate ammonium thiocyanate test was used for determining the presence of peroxide.

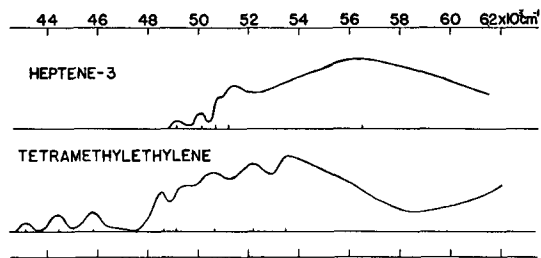


FIG. 2.

graphic investigations.⁵ Fig. 1 shows the absorption curve of this substance in the quartz ultraviolet region. The points up to $\log \epsilon = -0.4$ were obtained from the pure liquid hydrocarbon; up to $\log \epsilon = 1.00$ from a 0.34 molar hexane solution; up to $\log \epsilon = 2.00$ from a 0.034 molar solution; to $\log \epsilon = 3.00$ from a 0.0034 molar solution, and the remaining points from a 0.0004 molar solution. The beginning of absorption for this substance is at $30,200 \text{ cm}^{-1}$ from which point a broad step-out indicating a band of low intensity extends to about $39,000 \text{ cm}^{-1}$. Beyond $40,000 \text{ cm}^{-1}$ the intensity of absorption rises sharply to about $43,400 \text{ cm}^{-1}$ where lies the first of the narrow bands observed in the vapor spectrum. Three of these bands can be identified between this point and $47,300 \text{ cm}^{-1}$. This compound has the tendency already noted as characteristic of ethylenic hydrocarbons to form peroxides, and was therefore treated with the same precautions as were used for *n*-heptene-3.

In the *C* region, the absorption is characterized by the presence of six narrow diffuse bands together with a sharp step-out indicating another band, the wave-lengths and wave numbers of the centers of the bands are given in Table II. In this compound, region *B* is shifted toward the visible to such an extent that it overlaps the last three or four bands of *C* so that the measurement of these bands is somewhat more uncertain than

TABLE I. *Far ultraviolet absorption of n-heptene-3.*

A		B		C	
A	cm^{-1}	A	cm^{-1}	A	cm^{-1}
<1530	>65,400	1750-1720	57,140-58,000	2035 1995 (1972) 1953	49,140 50,120 (50,700) 51,200

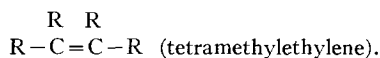
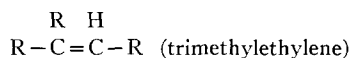
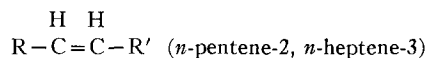
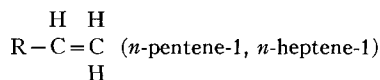
⁵ Physical constants for the material which we used are the following: b.p. $73.2-73.5^\circ$ at 760 mm; n_D^{20} 1.41198.

is the case with the other bands and the determination of the maximum of the broad band *B* is difficult.

A comparison of the positions of the three narrow bands observed in the hexane solutions of tetramethylethylene with those of the corresponding bands in the vapor spectrum is made in Table III. The wave number at which the curve of the hexane solution shows the sharp change in shape at the beginning of a step-out is chosen for comparison with the band centers in the vapor phase. Such a choice is more or less arbitrary but gives a comparable point for the three bands. The values of the extinction coefficient give a dependable basis for comparison of the intensities in the vapor phase measurements.

DISCUSSION OF RESULTS

The types of ethylenic derivatives which have been studied previously in this laboratory together with these two additional compounds are



The complete ultraviolet absorption of these six compounds can be classified into the three regions previously described together with a fourth region, designated as *D*, which includes the quartz measurements between 3300 and 2100 Å.

These four regions of absorption can be seen in all the ethylenic hydrocarbons and would indicate the existence of a similarity in their elec-

TABLE II. *Far ultraviolet absorption of tetramethylethylene.*

A		B		C	
A	cm^{-1}	A	cm^{-1}	A	cm^{-1}
<1530	>65,400	max 1870	53,480	2318 2248 2181 2056 (1995) 1973 1916	43,140 44,480 45,850 48,640 (50,110) 50,670 52,200

tronic transitions. Certain conclusions concerning the relationship of the electronic band systems of ethylenic derivatives to those of ethylene are suggested by these results but will be considered in a later paper from this laboratory. The point of special interest in the present study is the number and position of the absorption bands in region C and their relation to the structure of the hydrocarbon molecule. In the earlier study of three pentenes and one heptene^{1a} two important relationships between molecular configuration and absorption spectra were evident; (1) the spectra of *different* hydrocarbons having the same arrangement of alkyl groups around the double bond are almost identical, (2) the position of the first absorption band in the Schumann region is characteristic of the number of alkyl groups around the double bond and is shifted progressively toward the visible as the number of alkyl groups increase. The study of 3-heptene and tetramethylethylene adds one hydrocarbon of similar structure to those already studied, and one of a type not previously examined. The relationship between the bands in region C of the six aliphatic hydrocarbons and benzene are given in Fig. 3.

Comparison of the spectra of the group of olefines having the configuration $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{C}=\text{C}=\text{C}=\text{C} \end{array}$ with that of benzene shows a striking similarity in the position of the first band and points to the conclusion that this grouping, which is also common to the benzene molecule, must be an influencing factor in determining the position of

TABLE III. Comparison of ultraviolet absorption of tetramethylethylene in the vapor state and in hexane solution.

Vapor		Solution (0.0004 M)	
<i>A</i>	cm ⁻¹	<i>A</i>	cm ⁻¹
2318	43,140	2304	43,400
2248	44,480	2217	45,100
2181	45,850	2155	46,500

ABSORPTION BANDS OF OLEFINS IN THE SCHUMANN ULTRAVIOLET					
TYPE	COMPONENT	42000	46000	50000	54000cm
$\begin{array}{c} \text{C} \quad \text{C} \\ \quad \\ \text{C}=\text{C}=\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	Tetramethylethylene				
$\begin{array}{c} \text{C} \quad \text{H} \\ \quad \\ \text{C}=\text{C}=\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	Trimethylethylene				
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C}=\text{C}=\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	Pentene-2				
	Heptene-3				
	Benzene				
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C}=\text{C}=\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	Pentene-1				
	Heptene-1				
		2380	2177	2000	1852 Å

FIG. 3. (The heading of the second column should be "Compound.")

the first absorption band of benzene as well as of the aliphatic series.

The absorption spectrum of tetramethylethylene is the first hydrocarbon of the type

$\begin{array}{c} \text{C} \quad \text{C} \\ | \quad | \\ \text{C}=\text{C}=\text{C}=\text{C} \end{array}$ whose absorption spectrum has been studied in this region. The pronounced shift to longer wave-lengths of the first band is in agreement with what would be expected from the progressive displacement toward the visible which was previously found for the first absorption band of the pentenes as the hydrogen atoms around the double bond are replaced by alkyl groups.

Certain other characteristics of these vapor spectra will be taken up in a later paper when data from the study of a large number of closely related hydrocarbons are analyzed in detail.

The absorption spectra of the hydrocarbons in liquid and solution as measured with the quartz spectrograph show exactly the same relationship between the different types of groupings as are evident in the Schumann region. The absorption curve for heptene-3 parallels very closely that of pentene-2⁶ while the beginning of absorption in the different hydrocarbons as measured by the wave number corresponding to an extinction coefficient, $\log \epsilon = -2.0$ shows a progressive shift toward the longer wave-lengths in going from pentene-1 to tetramethylethylene.

⁶ M. L. Sherrill and G. F. Walter, J. Am. Chem. Soc. **58**, 742 (1936).