The Ultraviolet Absorption Spectra of Simple Hydrocarbons II. In Liquid and Solution Phase

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II. In Liquid and Solution Phase

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Molecular extinction coefficients for twelve olefine hydrocarbons have been determined between $\lambda = 3300$A and 2100A and are given in the form of curves showing the logarithm of the extinction coefficient as a function of the wave number. The beginning of absorption, as measured by log $\epsilon = -2.0$, is quite characteristic of the number of alkyl groups bound to the carbon atoms of the double bond and is only very slightly affected by the nature of the alkyl group.

IN the preparation of highly purified hydrocarbons for absorption spectra measurements in the Schumann region it has been found that the reproducibility of an absorption curve for a given hydrocarbon as measured in liquid phase and hexane solution with a quartz spectrograph, gives an excellent test for the purity of the compound as well as furnishing experimental data of importance in the spectroscopic analysis of these compounds. This paper summarizes the results of such measurements on twelve hydrocarbons, six of which have been reported previously from this laboratory.[1] Nine of the twelve compounds were prepared in this laboratory and the other three, tetramethylethylene and the two diisobutylenes were given us in very pure form by Professor F. C. Whitmore of Pennsylvania State College. Since the fundamental purpose of this investigation is to make a systematic study of the relation between the ultraviolet absorption spectra of an ethylenic hydrocarbon and the position of the double bond in the molecule it is evident that the compounds must be of the highest possible purity. Ultraviolet absorption spectra measurements were made at different stages in the purification of the compounds and purification was continued until the absorption curves after two distillations were identical.

Preparation of Compounds

The preparation and purification of the hydrocarbons has been carried out by different workers under the general direction of Professor Mary L.

Sherrill of this laboratory.[2] Four of the compounds were prepared by dehydration of an alcohol, this method being used in the case of alcohols which are least likely to give a mixture of hydrocarbons on dehydration by sulphuric acid; for example, *n*-pentene-2 from diethyl carbinol, *n*-heptene-3 from dipropyl carbinol, trimethylethylene from tertiary amyl alcohol, methyl diethylethylene from triethyl carbinol. With the exception of tertiary amyl alcohol, where the commercial product was used, the alcohols were prepared in this laboratory by Grignard syntheses. In the case of the other hydrocarbons, the brom-ether synthesis of olefine hydrocarbons, developed by Boord and co-workers,[3] has been found to be most satisfactory. A detailed description of the preparation and purification of 2-methylbutene-1 by this method has already been published.[4] The other hydrocarbons which were synthesized by the Boord method involve fewer reactions for the brom-ether preparation but the method of purification of the hydrocarbon by azeotropic distillation with alcohol through a Crismer column and subsequent fractionations of the hydrocarbon through a Fenske column has been practically the same throughout all the preparations.

In the earlier preparations, the hydrocarbons were refluxed and distilled over sodium during the final purification but the treatment with sodium has been discontinued since the hydrocarbons seemed to form peroxides more readily after distillation from sodium. The effect of

[1] Sherrill and Walter, J. Am. Chem. Soc. **58**, 742 (1936); Carr and Walker (Part I of this series).

[2] Sherrill, Otto and Pickett, J. Am. Chem. Soc. **51**, 3023 (1929); Sherrill, Mayer and Walter, ibid. **56**, 926 (1934); Sherrill and Walter, ibid. **58**, 742 (1936).
[3] Boord and co-workers, J. Am. Chem. Soc. 1930 to date.
[4] Sherrill and Walter, reference 2.

TABLE I.

Compound	b p. °C, 760 mm	n_D^{20}	d_4^{20}
Pentene-1	30.1 ±0 05	1.3710	0.6410
Pentene-2 (symmetrical methylethylethylene)	36.40±0.05	1.3797	0 6505
2-Methylbutene-1 (unsymmetrical methylethvlethylene)	31.05±0.05	1.3777	0 6504
3-Methylbutene-1[1] (isopropylethylene)	20.20±0.03	1.3675 (15°)	0.6323 (15°)
2-Methylbutene-2 (trimethylethylene)	38.42 ±0.05	1.3878	0.6620
Hexene-3[2a] (symmetrical diethylethylene)	66.70 ±0.05	1 3947	0 6785
2-3-Dimethylbutene-2 (tetramethylethylene)	73.35 ±0.10	1.41198	
Heptene-1	93.45 ±0 05	1 3991	0 6970
Heptene-3 (symmetrical ethylpropylethylene)	95.75 ±0.05	1 4041	0.7001
3-ethylpentene-2[2b] (methyldiethylethylene)	95 2	1.4140	0.7222
2-4-4-Trimethylpentene-2[3] (diisobutylene II)	105.15 ±0.05	1.4161	0 7211
2-4-4-Trimethylpentene-1[3] (diisobutylene I)	101.6 ±0.10	1.4083	0.7151

[1] Prepared by the reduction of 1-bromo-2-ethoxy-3-methylbutane with zinc. In the course of hydrogenation experiments on our hydrocarbon by Kistiakowsky and co-workers in the Harvard laboratory, freezing point measurements were attempted but the freezing point is evidently below the temperature of liquid air. Freezing point determinations of the hydrogenation product, however, gave a very sharp freezing point indicating that the isopropylethylene was a very pure product (Private communication.)
[2] Prepared, and physical constants, including absorption spectra, determined by (a) K. B. Nisbet. (b) C. Monod, in partial fulfillment of the requirements for the M.A. degree.
[3] Prepared by Whitmore and co-workers by dehydration of tertiary butyl alcohol. See J. Am. Chem. Soc. 54, 3706 (1933).

treatment with sodium is still under investigation in this laboratory. The satisfactory agreement in the physical constants of our preparations with those reported by Kistiakowsky and co-workers,[5] for which detailed descriptions of their methods are given, shows the high degree of purity obtained. Table I gives the physical constants for all the compounds whose absorption spectra are reported in this paper.

ABSORPTION SPECTRA MEASUREMENTS

The extinction coefficients were measured in the region 3500 to 2100A by the photographic comparison method developed by Henri.[6] The spectrograph is a Hilger quartz instrument (E–2) and the light source a condensed spark between copper electrodes. For the short ultraviolet region a condensed spark between a copper and silver electrode has been used recently. Uniform time of 10 seconds for the exposure through the standard, i.e., 1–2 mm thickness of spectrographic hexane in the case of the pure liquid hydrocarbons, or with the hexane solutions, the same thickness of

[5] Kistiakowsky, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. 58, 137 (1936).
[6] V. Henri, Etudes de Photochimie (Gauthier, Villars et Cie., Paris, 1919). Cf. E. P. Carr, J. Am. Chem. Soc. 51, 3041 (1929).

hexane as for the solution with which it is compared, and an exposure of 40 sec. and 60 sec. through each thickness of the hydrocarbon were used throughout. In some cases these times were lengthened for the short ultraviolet region but the same ratio was retained. Baly tubes of fused quartz were used for all the measurements, the length of the absorbing column being varied from 7 to 0.2 cm. The extinction coefficients from $\log \epsilon = -2.0$ to about -0.5 were determined with the pure liquid hydrocarbon, while hexane solutions varying in concentration from 0.8 molar to 0.0003 molar were used for the higher values of $\log \epsilon$. The photographic plates were Eastman No. 40 and Ultraviolet Spectroscopic. Each curve is based on from fifty to seventy experimental points but they are not shown on the curves since they are so closely spaced as to give almost a continuous line. The curves are plotted in the usual way with the logarithm of the molecular extinction coefficient on the ordinate and wave number on the abscissa. The absorption curves for the five pentenes are given in Fig. 1. Pentene-2 represents an equilibrium mixture of the *cis* and *trans* forms since our distilling column was not efficient enough to separate these isomers.[7] This is no doubt true of the two other hydrocarbons which can exist as geometrical isomers, *n*-heptene-3 and *n*-hexene-3.

DISCUSSION

It will be noted that all of the pentenes (Fig. 1) show somewhat similar absorption curves although there are certain characteristics which differentiate the five isomers. The existence of two step-outs, which result from the overlapping of an absorption band of lower intensity with a more intense one, is evident in each of the curves.

Whether the higher intensity step-out which comes at shorter wave-lengths is characteristic of the olefine hydrocarbons or whether it is due to a trace of an impurity, not detected by other methods, is still under investigation in this laboratory. Long refluxing over sodium, or repeated distillations from sodium, especially if the hydrocarbon has stood some weeks or months after

[7] Results of hydrogenation experiments carried out on this product by Kistiakowsky and co-workers in the Harvard Laboratory indicate it to be a mixture of the two isomers. J. Am. Chem. Soc. 58, 137 (1936).
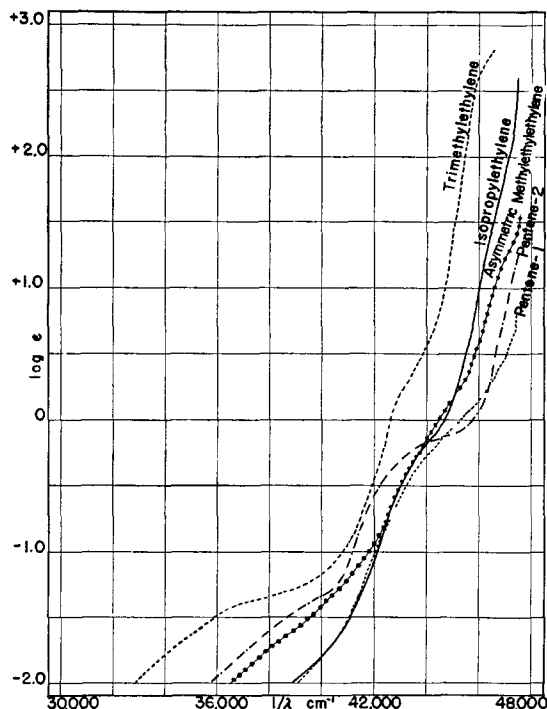
FIG. 1.

preparation, gradually lowers the extinction co-efficient at which this step-out appears although the rest of the curve shows no appreciable change in the absence of peroxides. Where peroxides are present the beginning of absorption is shifted markedly toward the visible and the intensity of the first step-out is increased. The change in intensity of the second step-out has been studied particularly with trimethylethylene; by repeated treatment with sodium curves have been obtained which show only a single broad step-out and are in excellent agreement with those obtained by other investigators,[8] but a freshly prepared sample, not subjected to long treatment with sodium always shows a step-out of somewhat higher intensity between 42,000 and 45,000 cm^{-1}. In all of the hydrocarbons this is the region of the spectra where the exact reproducibility of the curves for different samples of the same hydrocarbon is most difficult. Because of the possibility of molecular rearrangement due to prolonged heating with sodium this treatment

has been avoided and either azeotropic fractionations with alcohol or repeated fractionations of the hydrocarbon alone have been carried out until absorption curves showed no change on distillation. The reproducibility of the absorption curve is a much more delicate test for the purity of an olefine hydrocarbon than any of the other physical constants. The possibility of the presence of minute quantities of a diene has been considered and is under investigation. Because of the very great intensity of the diene band in the region 42,000–45,000 cm^{-1} [9] as little as 1 part in 10,000 would be amply sufficient to account for the increased absorption in this region and yet give no evidence in any of the other physical constants. Whether or not this step-out is characteristic of a hydrocarbon containing one C=C linkage, or is because of minute traces of a very absorptive impurity, the position of the band does not change with the different isomers as is true with the band of low intensity which gives the step-out at longer wave-lengths.

The position of the low intensity band is the most significant result of the absorption spectra studies in this region. Consideration of the curves for the pentenes shows that the position of this band is characteristic of the number and to a less extent the arrangement of the alkyl groups around the double bond. There is a progressive shift toward the visible as the number of hydrogen atoms bound to the carbon atoms of the double bond is decreased. Since in the case of a step-out there is no definite point for comparison as is true with the maximum of an absorption band, the beginning of absorption as measured at log $\epsilon = -2.00$ on our curves has been arbitrarily chosen for comparison between the different hydrocarbons. Pentene-1 and isopropylethylene with the same arrangement of hydrogen and alkyl groups around the double bond begin at exactly the same place, 39,000 cm^{-1}, but differ in the short wave region. The effect of two alkyl groups on different carbon atoms, as compared with the two groups on the same carbon atom is shown by the curves for pentene-2 and 2-methyl-butene-1 where the two curves are quite similar but that for the latter beginning slightly to the ultraviolet, 35,400 cm^{-1}, as compared with

[8] Luthy, Zeits. f. physik. Chemie **107**, 285 (1923); Allsopp and Snow, Trans. Faraday Soc. **30**, Part **1**, 93 (1934).

[9] Int. Crit. Tab. **5**, 364.

pentene-2 at 35,800 cm^{-1}. Finally when there are three alkyl groups as in trimethylethylene the absorption at log $\epsilon = -2.00$ is at 32,800 cm^{-1}.

This same relationship between the position of the low intensity absorption band and the number of alkyl groups around the double bond is shown in the absorption curves for the three hexenes and three heptenes given in Fig. 2.[10]

It is of interest to note the comparatively slight influence on the absorption curve of a change in alkyl groups which is shown by the close similarity of analogous molecular configurations; for example, pentene-1 and heptene-1, pentene-2, hexene-3, and heptene-3 and trimethylethylene and methyl-diethylethylene. The intensities at which the step-outs occur differ but the position of the low intensity band as measured by log $\epsilon = -2.00$ parallels very closely those of the corresponding pentenes, while that of tetramethylethylene is shifted toward the visible as would be
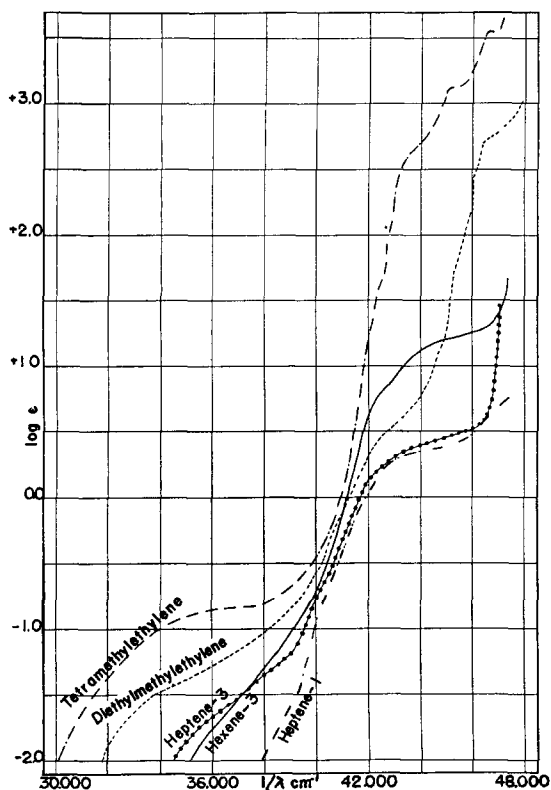

FIG. 3.

FIG. 2.

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[10] Curves for tetramethylethylene and heptene-3 are reproduced from the earlier paper in this series. See Carr and Walker, J. Chem. Phys. this issue.

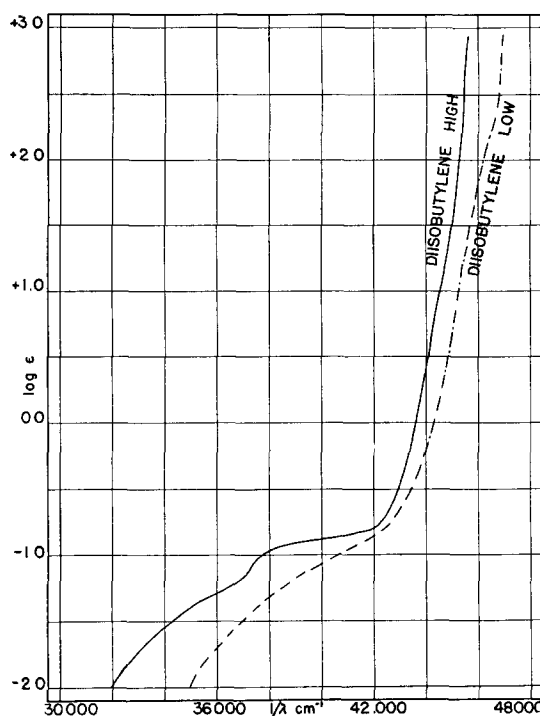expected. In Fig. 3 are given the curves for the two diisobutylenes supplied for this investigation by Whitmore and co-workers. Had the constitutional formulas not been known from chemical methods it is evident from the analogy to the curves of the other hydrocarbons, that the number of alkyl groups around the double bond could be predicted. The nature of the alkyl substituents has practically no influence in determining the position of the absorption band since the curves of diisobutylene high, with the tertiary butyl group, and diisobutylene low, with the highly branched neopentyl group, show the beginning of absorption at the same position as compounds of similar configuration having the methyl or ethyl group in the corresponding position. The difference between symmetrical and unsymmetrical substitution by two alkyl groups cannot be distinguished unless both compounds are known in which case the absorption of the unsymmetrically substituted hydrocarbon is shifted slightly to the ultraviolet in relation to the other. On the basis of these absorption curves the relation between molecular configuration and the beginning of the

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

Configuration	$\log \epsilon = -2.00$
H H R − C = C − H	38,000–39,000 cm^{-1}
H H R − C = C − R	34,500–35,800 cm^{-1}
R H R − C = C − H	35,000–36,400 cm^{-1}

R R R − C = C − H	32,000–32,800 cm^{-1}
R R R − C = C − R	30,000 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.

The Ultraviolet Absorption Spectra of Simple Hydrocarbons

III. In Vapor Phase in the Schumann Region

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Absorption spectra measurements between λ = 2300A and 1500A 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 C = 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 corresponding 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 C = 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

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[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).