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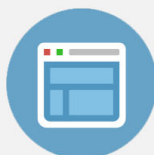
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## Absorption Intensities of Ethylenes and Acetylenes in the Vacuum Ultraviolet\*

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The spectra of three octenes, cyclohexene and 2,3-dihydropyrene, and of octyne-1 and -2 were obtained in *n*-heptane solution to 1700Å. Intensity measurements on ethylene vapor to 1550Å enable the contribution of the Rydberg bands to be separated from that of the continuum. The *f*-values in ethylene and the octenes are about 0.30, agreeing with Mulliken and Rieke's theoretical prediction within the experimental uncertainty of about 20 percent. The *f*-values of the octynes are about the same, but those of cyclohexene and dihydropyrene are about 0.20.

## INTRODUCTION

THE spectra of octene-1, octene-2-*cis* and -*trans*, of cyclohexene and of 2,3-dihydropyrene were measured in *n*-heptane solution in an 0.13 mm cell to 1700Å in order to discover the effects of substitution on the intensity of the double bond absorption peak near 1800Å. These spectra are compared with preliminary intensity measurements on the corresponding peak in ethylene vapor near 1600Å. Spectra of two substituted acetylenes, octyne-1 and octyne-2, were also obtained in *n*-heptane solution to 1700Å.

Many previous studies have been made on the absorption of various substituted ethylenes in the vapor phase, but without intensity measurements. A complete bibliography was given in an earlier article.<sup>1</sup> Absolute intensity measurements on octene-3 and some other olefinic compounds in *n*-heptane solution were reported in two earlier papers,<sup>2</sup> but the *cis-trans* composition of the octene was un-

known, and the other olefin spectra were altered by fatty acid absorption. Therefore we wished to get absolute intensity measurements and locate the absorption maxima in more primitive octenes and in a simple cyclic olefin.

A bibliography of previous work on acetylene vapor in the vacuum ultraviolet was also given in the earlier paper.<sup>1</sup> The spectrum of methylacetylene has since been obtained.<sup>3</sup> No intensity measurements on acetylenes in solution below 2000Å have been reported heretofore.

## APPARATUS AND TECHNIQUES

The apparatus and techniques for the solution studies are the same as those described earlier.<sup>2,4</sup> The uncertainty in the intensity measurements is about  $\pm 10$  percent.

The ethylene vapor plates were taken in an attempt to see whether absolute intensity measurements could be made on vapors using the same hydrogen arc source and the same plate calibration technique that we used for liquids. Ethylene has both narrow bands and a broad continuous absorption. Fortunately, the first strong narrow bands lie in the hydrogen continuum where their width and central intensity can be accurately measured (see Fig. 1); but below 1650Å, where measurements must be made using the strong but randomly spaced hydrogen emission lines, the absorption is essentially continuous.<sup>5</sup>

In taking the plates, a few mm pressure of the vapor was placed in a small gas pipette and the vapor was then released from the pipette into the spectrograph. The relative volumes of the pipette and spectrograph were known and the pressure in the spectrograph (about 20 microns) could be computed from the perfect gas law. The light path in the apparatus was 34 cm.

At first there was difficulty in obtaining repro-

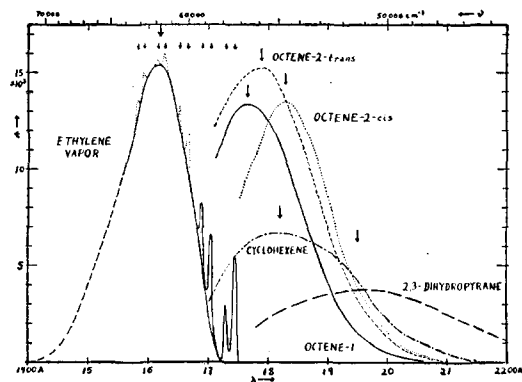


FIG. 1. Absorption of olefins.

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<sup>1</sup> J. R. Platt and H. B. Klevens, Rev. Mod. Phys. 16, 182, (1944).

<sup>2</sup> J. R. Platt, I. Rusoff, and H. B. Klevens, J. Chem. Phys. 11, 535 (1943); I. Rusoff, J. R. Platt, H. B. Klevens, and G. O. Burr, J. Am. Chem. Soc. 67, 673 (1945).

<sup>3</sup> W. C. Price and A. D. Walsh, Trans. Faraday Soc. 41, 381 (1945).

<sup>4</sup> J. R. Platt, H. B. Klevens, and G. W. Schaeffer, J. Chem. Phys. 15, 598 (1947).

<sup>5</sup> W. C. Price, Phys. Rev. 47, 444 (1935); W. C. Price and W. T. Tutte, Proc. Roy. Soc. (London) A174, 207 (1940).

ducibility, apparently because of the absorption of the vapor by stopcock greases and vacuum wax. Differences between extinction values from different plates were as great as 50 percent. Later work showed that the absorption of diene vapors is reproducible with mean deviations of about 10 percent if Silicone stopcock grease is used,<sup>6</sup> and this procedure was followed in obtaining the curves given here. With our present pumping system, additional errors may arise from traces of residual oxygen in the spectrograph as we approach the strong oxygen peak at 1450Å. Increased variations which we observed below 1550Å are probably from this cause.

The difficulties with photo-decomposition of static vapors reported by earlier workers were not troublesome, probably because in our spectrograph only about 2 percent of the vapor is in front of the spectrograph slit, exposed to the direct light of the arc.

Corrections were made for the scattered background light in the spectrograph by taking one exposure through the ethylene vapor, two exposures for intensity calibration with the spectrograph pumped out and a final exposure with air in the spectrograph so that no wave-lengths below 1850Å are present. In the last exposure, all the light which appears to be below 1850Å must be scattered light of longer wave-lengths and its contributions can be measured at the same positions as those at which the ethylene vapor absorption is measured. Corrections for scattered light were also made in the solution studies by a similar method. These corrections become appreciable only below about 1800Å where the continuum from the hydrogen arc is relatively weak.

#### SOURCE AND PURITY OF COMPOUNDS

Commercial tank ethylene was used for the ethylene vapor studies, for its absorption in this region is very intense and traces of impurities would not change the extinction values by more than the experimental error. The octene-1 and octene-2-*cis* and -*trans* were kindly supplied by Dr. W. Nudenberg. Their physical properties were:

Octene-1, b.p. 120–121°C;  $n_D^{20} = 1.4089$   
 Octene-2-*cis*, b.p. 125–125.5°C;  $n_D^{20} = 1.4146$   
 Octene-2-*trans*, b.p. 124–124.5°C;  $n_D^{20} = 1.4132$ .

The cyclohexene was obtained from Eastman Kodak Company and was distilled twice through a Podbielniak column with 50 effective plates, using the center cut from each distillation. It has a boiling point of 83.0°C,  $n_D^{20} = 1.4452$ .

The dihydropyrene was obtained from Dr. R. F. Nystrom and was fractionated and the center cut

TABLE I. Main features of spectra.

Compound	$\lambda_{\max}$	$\nu_{\max}$	$\epsilon_{\max}$	width $\text{cm}^{-1}$	f-value
ethylene	1,625	61,500	15,000	5,200	.34 $\pm$ .15
<i>N</i> → <i>V</i>	1,743	57,360	5,500	~230	.03 $\pm$ .01
Rydberg	1,729	57,840	3,000	~230	
—	—	—	—	—	
octene-1	1,770	56,400	13,000	(5,200)	.29 $\pm$ .08
octene-2- <i>trans</i>	1,790	55,900	15,000	(5,200)	.34 $\pm$ .08
octene-2- <i>cis</i>	1,830	54,600	13,000	5,200	.29 $\pm$ .08
cyclohexene	1,820	54,900	6,600	8,100	.23 $\pm$ .05
2,3-dihydropyrene	1,950	51,280	3,800	9,600	.18 $\pm$ .04
octyne-1 A	—	—	—	—	—
B	1,850?	54,000	2,200	(3,600)	.04 $\pm$ .02
C	2,225	45,000	120	(4,800)	.003 $\pm$ .002
octyne-2 A	1,775	56,300	10,000	(5,800)	.22 $\pm$ .08
B	1,960?	51,000	~2,000	(2,900)	.04 $\pm$ .02
C	2,225	45,000	160	(4,800)	.003 $\pm$ .002

taken, with boiling point of 85°C,  $n_D^{20} = 1.4391$ . After redistillation through the Podbielniak, an earlier sample of dihydropyrene had turned brown after standing a short while, so the later sample was run immediately after being put through the column and having its refractive index checked.

Octyne-1 and -2 were obtained from Dr. J. B. Jerome. Their properties were:

Octyne-1, b.p. 126.0°C,  $n_D^{20} = 1.4163$

Octyne-2, b.p. 138°C,  $n_D^{20} = 1.4761$ .

#### SPECTRA

The spectra of the olefins are shown in Fig. 1 and some main features of the spectra are summarized in Table I.

The strong allowed electronic transition in ethylene has been designated as the *N*→*V* transition by Mulliken and Rieke.<sup>7</sup> This continuum has its maximum in ethylene at about 1625Å as shown in Fig. 1. The curve above 1550Å represents the average of the two best plates. The measurements become unreliable below about 1550Å where the prism and window materials and traces of oxygen in the spectrograph begin to absorb appreciably. Below this point, the curve can be estimated with the help of Price's reproductions<sup>4</sup> which indicate that the intensity must go nearly to zero at 1400Å. This half-width of the *N*→*V* continuum is then about 5200  $\text{cm}^{-1}$ , which is close to the half-width of the more accurately measured octene-2-*cis* peak at longer wave-lengths. The  $\epsilon$ -value, or oscillator strength, of the ethylene in Table I was obtained from the area under the curve by the usual procedure. It must be regarded as uncertain to  $\pm 50$  percent. An attempt will be made to improve this value using new techniques.

Superimposed on the *N*→*V* continuum is a doublet series of narrow line-like bands which are

<sup>7</sup> See the bibliography in reference 1, especially R. S. Mulliken and C. A. Rieke, "Reports on Progress in Physics," Phys. Soc. (London) 8, 231 1941; and R. S. Mulliken, Rev. Mod. Phys. 14, 265 (1942).

<sup>6</sup> Lois E. Jacobs and J. R. Platt, J. Chem. Phys. 16, 1137 (1948).

believed to involve the first electronic state of a Rydberg series.<sup>6,7</sup> Previously it had not been known how strong the centers of these bands were, so that no estimate could be made of their oscillator strength relative to that of the continuum; it was feared they might be too narrow for accurate intensity measurements. Densitometer traces on the present vapor plates showed that the lines are quite broad, about 6Å half-width, and so the intensity measurements are straightforward. Price found five doublets forming a vibrational series with the spacing of the C=C stretching frequency. Only two of the doublets could be measured accurately in our hydrogen continuum. The peak absorptions of the first pair are given in Table I. The second pair has about 0.8 the intensity of the first, if measured using the continuous absorption underneath as a base line. The second member of each doublet has about 0.6 the intensity of the first member. The other three doublets could not be clearly seen in the hydrogen many-line spectrum, but have been sketched in on the curve in Fig. 1 in the way suggested by Price's reproductions. Probably the total *f*-value of the group of five is three or four times the *f*-value of the first doublet, or about 0.03.

(It is possible, of course, that this figure is too low because of the presence of unresolved fine structure which will produce an apparent departure from the Lambert-Beer law. With the slits used, the spectrograph will resolve  $\frac{1}{4}$ Å or about  $10\text{ cm}^{-1}$  at these wave-lengths, which is too coarse for detecting the widest rotational structure in ethylene. On the other hand, the narrow bands are quite symmetrical and show no visible evidence of heads or of branch structure. This suggests that the component lines may be naturally broadened so as to wipe out such features, in which case the procedure used will give correct *f*-values.)

The octene-1 curve is shifted about  $5000\text{ cm}^{-1}$  to the red from the ethylene vapor curve as the combined result of substitution and of solution. It is about  $1100\text{ cm}^{-1}$  to the red of the propylene vapor curve maximum as given by Price and Tutte.<sup>5</sup> The peaks of octene-2-*cis* and of cyclohexene (which must have approximately a *cis* configuration) are at substantially longer wave-lengths than the octene-2-*trans* peak. The increased intensity in the octene-2-*trans* may account for the fact that its molar refractivity is higher than that of the *cis* in spite of its shorter wave-length peak. Its absorption to the red of 2100Å is also higher than that of *cis*.<sup>8</sup> This *cis-trans* difference of about  $1200\text{ cm}^{-1}$  in peak position is larger than that given by Price and Tutte<sup>5</sup> for the vapors. They find the cyclohexene vapor peak is only about  $800\text{ cm}^{-1}$  to the red of the butene-2-*trans*. The order of the *cis-trans* peaks

here agrees with the order of the ionization potentials found by Walsh<sup>9</sup> in *cis*- and *trans*-dichloroethylenes—which were 9.66 and 9.96 electron volts, respectively. However the sequence of his strong 1900Å bands in these compounds was reversed from ours, possibly as a result of some interaction in the excited state between the two chlorines.

The octene-3 studied earlier<sup>2</sup> must have been about 70 percent *cis* judging by its curve shape and peak position. The present peak values are higher, partly because of the corrections applied here for scattering at the short wave-lengths.

The long wave-length tail on the octene spectra is much more pronounced than in ethylene and is quite probably due to the contributions of the first Rydberg states. Such long wave-length tails, or step-outs, in the vapors of substituted ethylenes have been discussed at some length in the literature.<sup>1</sup> Their effect on the "transmission limits" of these octenes has been examined in a recent paper,<sup>8</sup> which gives microphotometer traces showing the differences in absorption from 2050 to 2500Å.

The peak intensity of cyclohexene is certainly significantly lower than that of the octenes. We examined the idea that this might be due to a twist of the double bond out of its planar configuration in order to adjust the angles in the rest of the molecule to more favorable values. Inspection of a Fisher-Hirschfelder atom model confirms the likelihood of a twist of this kind. A computation using the usual bond distances shows that distortions of at least three or four degrees in all C—C—C angles would be necessary if no twist is allowed about the double bond. No doubt some of this distortion will be relieved by a few degrees of twist, the exact amount depending on the relative force constants for angle bending and for twisting. (This treatment leaves out of account the hydrogen repulsions used by Pitzer to explain the non-planarity and thermodynamic properties of cyclopentane and cyclohexene in a recent preliminary note.<sup>10</sup> Such repulsions might either favor or suppress the twist, depending in a detailed way on the exact model chosen.) Lister<sup>11</sup> concluded from thermochemical evidence that the angle of twist was zero. If the intensity followed a cosine-square law with angle of twist about the double bond, such as we found for the bands of some orthosubstituted dimethyl anilines,<sup>12</sup> the ratio of the cyclohexene *f*-number to that of the octenes would indicate an effective angle of twist (averaged over thermal motions) of about  $30^\circ$ . This is so far from Lister's prediction that we must conclude either that the change of intensity

<sup>9</sup> A. D. Walsh, Trans. Faraday Soc. **41**, 35 (1945).

<sup>10</sup> K. S. Pitzer, Science **101**, 672 (1945).

<sup>11</sup> Lister, J. Am. Chem. Soc. **63**, 143 (1941).

<sup>12</sup> H. B. Klevens and J. R. Platt, J. Am. Chem. Soc. **71** (1949), in press.

<sup>8</sup> H. B. Klevens and J. R. Platt, J. Am. Chem. Soc. **69**, 3055 (1947).

is very much faster than the cosine-square law, which seems unlikely, or that the loss of intensity is largely due to some other cause.

If twist is present it should not only decrease the intensity but should also produce red shifts. Mulliken and Roothaan<sup>13</sup> predicted strong red shifts with increasing angle of twist in ethylene. This will account qualitatively for the broadening of the cyclohexene spectrum with almost unchanged position of the peak, if we assume that under thermal motions, some molecules are almost untwisted and given an octene-2-*cis* spectrum while others are twisted various amounts and give progressive red shifts, though with progressive loss of intensity. Quantitatively, the red shift on the long-wave edge of the peak of about  $1000\text{ cm}^{-1}$  in going from octene-2-*cis* to cyclohexene would correspond to something like  $8^\circ$  angle of twist, judging from the theoretical estimates of Mulliken and Roothaan on ethylene. Of course the long wave-length tail on cyclohexene may equally well be due to displacement of the Rydberg bands in this molecule. At  $2100\text{A}$  the cyclohexene absorption is about ten times that of octene-2-*cis*. The general decrease of intensity in cyclohexene accounts in part for its low molar refractivity relative to that of the non-cyclic hexenes.

The 2,3-dihydropyran is the same molecule as cyclohexene, except that a  $\text{CH}_2$  group next to the double bond is replaced by an oxygen. Manipulation with a model suggests that the twist in this case should be less than that of the cyclohexene. The shift to long wave-lengths and the additional reduction of intensity must then be the result of the oxygen substitution, and resonance of the lone pair oxygen electrons with  $\pi$  electrons of the double bond. A similar shift occurs in vinyl chloride vapor whose peak is near  $1830\text{A}$  as compared with  $1730\text{A}$  for propylene vapor.<sup>9</sup>

The acetylene spectra are given in Fig. 2. The intensities are plotted on a log scale so as to show the relation of the bands found here to the bands of acetylene vapor itself. What appear to be corresponding bands are marked by the same letters, A, B, C, on the vapor and solution curves. The shaded vapor curve is estimated from data on appearance pressures and path lengths as reported in earlier acetylene vapor studies;<sup>1</sup> the values are uncertain by a factor of at least three. Nevertheless, there is clearly a red shift of some  $5000\text{ cm}^{-1}$

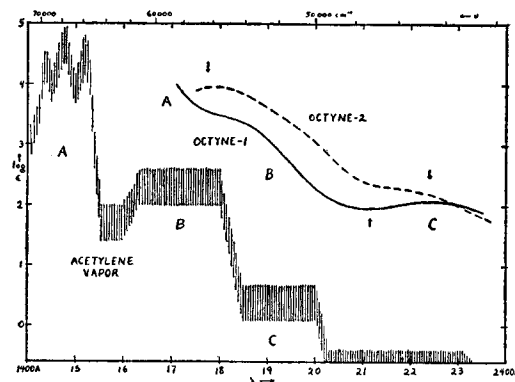


FIG. 2. Absorption of acetylenes.

in going from the simple vapor to the substituted compound in solution, just as was found with the ethylenes. Price and Walsh<sup>3</sup> found some  $2000\text{ cm}^{-1}$  red shift in going from acetylene vapor to methyl-acetylene vapor.

The spectrum of octyne-1 does not go over any clear maximum before reaching  $1700\text{A}$  but that of octyne-2 seems to do so. Very probably this maximum corresponds to the strong absorption in acetylene vapor at  $1500\text{A}$ . The peak intensity seems to be less in the solution, but this may be because of the broadening effect of the solvent, since the vapor maxima are rather sharp. Since the measurements do not extend very far down over the peak on the short wave-length side, this uncertainty in the  $f$ -value is larger than the uncertainty in the intensity measurements; but the value appears to be about 0.27, not much different from that of ethylene.

The peaks or step-outs in the octynes near  $2200\text{A}$  seem to be more intense than the  $1900\text{A}$  bands in the vapor by a factor of 10. In this region, the absorption is weak enough to be much affected by impurities, but the two solution curves agree quite well with each other, and the uncertainty in the vapor estimates is of course large.

The red shift of  $2500\text{ cm}^{-1}$  in going from octyne-1 to octyne-2 is almost twice as large as for the corresponding change in the ethylenes. It is associated with an increase in refractive index.

#### ACKNOWLEDGMENTS

We are grateful to Howard Carter, Dorothy Iker Lossy, Lois Jacobs, and Marvin Miller for technical assistance. We are indebted to the University of Michigan for the loan of the vacuum spectrograph used in this work.

<sup>13</sup> See reference 5, also R. S. Mulliken, Rev. Mod. Phys. **14**, 265 (1942); R. S. Mulliken and C. C. J. Roothaan, Chem. Rev. **41**, 219 (1947); also further unpublished calculations.