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the photographic region a clear distinction between $\parallel$ and $\perp$ bands is impossible. The reason for the diffuse nature of most of the $\parallel$ bands in this region is apparently the fact that the sub-bands no longer coincide even approximately. For this reason the assignments given in Table III for the bands in the region $3\nu_{CH}$ must be considered as decidedly tentative. No specific assign-ments are given for the bands in the regions $4\nu_{CH}$, $5\nu_{CH}$, and $6\nu_{CH}$.

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Quantitative Determination of Extinction Coefficients in the Vacuum Ultraviolet: Divinyl Ether*

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A method of determining the molar extinction coefficients of organic compounds in the vapor phase in the vacuum ultraviolet has been developed. Measurements made with a fluorite spectrograph on flowing vapor samples of divinyl ether show a precision of 3 to 8 percent and satisfactory agreement with measurements made from 2360 to 2100A with a Beckman DU spectrophotometer. The absorption spectrum of divinyl ether is completely free from fine structure. The extinction coefficient increases rapidly from a value of 10 at 42,400 cm^{-1} to a maximum of 15,900 at 49,200 cm^{-1} and decreases to a minimum value of 4000 before beginning to rise again at 56,700 cm^{-1}. The oscillator strength of the band is 0.45.

THE vacuum ultraviolet absorption studies in this laboratory have been extended to include meas-urements of molar extinction coefficients of organic compounds in the vapor phase. Such quantitative data are particularly useful for comparison with theoretical predictions concerning electronic transitions of organic molecules. The method of measurement which has been developed is somewhat similar but different in essential details from that used by Platt[1] and co-workers.

Standard spectrographic practices have been used. The reciprocity law behavior of the spectrographic plates has been studied and the results have justified the use of a simple empirical time calibration of the plates. The long-wave region of the vacuum spectro-graph corresponds to the short-wave region of the Beckman DU spectrophotometer. Measurements of several compounds have been made with both instru-ments and the results in all cases have shown satis-factory agreement. The final measurements of divinyl ether, the compound used during the development of the method, are reported here. The measurements of other compounds will be reported in papers dealing with series of related compounds.

EXPERIMENTAL

Spectrographic measurements.—The equipment con-sists of three separate systems: the spectrograph, the vapor handling system and the light source. Fluorite windows are used throughout and the narrow spaces between the windows of the separate systems are filled with flowing nitrogen. The spectrograph and the light source have been described.[2] The spectrograph is a fluorite prism instrument which has a dispersion that varies from about 10A per millimeter at 2000A to about 2.5A per millimeter at 1400A. Ilford QI plates are used. The light source is a water cooled hydrogen lamp which is operated with flowing hydrogen. Even though this lamp is only operated during the time of the plate expo-sures, its reproducibility has been repeatedly demon-strated.

A flowing vapor system in a separate absorption tube is used in preference to the introduction of vapor into the spectrograph. This reduces the probability of meas-uring the absorption of photochemical products and protects the spectrograph from the deposition of prod-ucts which might reduce the transmission of the instru-ment. The system for handling the vapor, Fig. 1, is of all Pyrex glass construction with the exception of the windows which are cemented to the absorption tube, B. The method depends upon establishing a steady rate of flow which is determined by the vapor pressure of the compound, the dimensions of two constrictions and the capacity of the pumps. The pressure in the absorp-tion tube B is controlled by controlling the vapor pressure of the compound with a temperature bath around the sample tube, A.

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[1] L. E. Jacobs and J. R. Platt, J. Chem. Phys. 16, 1137 (1948).

[2] E. P. Carr and H. Stücklen, Zeits. f. physik. Chemie B25, 57 (1934); J. Chem. Phys. 4, 760 (1936).

After the system is flushed with nitrogen and evacuated with stopcocks 1, 2, and 3 closed, two calibration exposures of t_1 and t_2 minutes are made. The nitrogen is flushed from the sample tube by alternately opening stopcocks 1 and 2 for a few seconds at a time. Stopcock 1 is then left open and an exposure of t_c minutes is made of the compound after the pressure becomes constant. The system is again flushed with nitrogen and evacuated and two more calibration exposures of t_3 and t_4 minutes are taken. The particular times used depend upon the part of the spectrum being studied and the width of the slit in the spectrograph. For this work calibration exposures of 0.50, 1.00, 1.50, and 2.00 minutes and a compound exposure of 3.00 minutes have been used.

The condensation of vapors in the McLeod gauge has been avoided by constructing a gauge with a series of gradated bulbs and nine calibration marks. With this, readings are made over a wide range of pressures without using large differences in mercury levels. A study has been made of the validity of using the pressure just beyond the absorption tube as the pressure in the absorption tube. To do this the gauge was connected through a three-way stopcock to both the entrance and exit tubes of the absorption tube and the pressure of a flowing vapor was read alternately on the two sides of the absorption tube. The variations in the readings were random and of the usual order found in setting and reading the gauge.

The study of a compound can usually be made with six to eight plates. No real difficulties have been en-

FIG. 1. Vapor system used with the vacuum spectrograph. A is a 10 ml sample tube. B is a 32.5 cm absorption tube with fluorite windows. A steady state of flow is established which depends upon the vapor pressure of the sample, the dimensions of the constrictions and the capacity of the pumps. The vapor pressure is controlled by controlling the temperature of the sample tube A.

countered with leaks and the spectra have been free from evidences of contamination by either stopcock grease or sealing compound. Since the transmission of the absorption tube gradually decreases with use the windows are occasionally removed and cleaned.

Microphotometer measurements.—A microphotometer record is made with a recording instrument. Each recording has six curves: the base line (zero response of the galvanometer); traces of the time exposures t_1, t_2, t_3 and t_4; and a trace of the t_c exposure of the compound. At a particular wave-length, the distance from the base line to each of the traces is measured and the logarithm of the distance to the calibration trace is plotted against the logarithm of t_c/t where t is t_1, t_2, etc. These points give a smooth curve which approaches a straight line. From this and the logarithm of the distance to the compound trace is read a value of $\log t_c/t$ for the compound. Within the limits of the reciprocity law, this value is the optical density, and assuming that the vapor is an ideal gas at the pressures used the molar extinction coefficient is easily calculated.

The reciprocity law for the Ilford QI plates has been checked by using vibrating copper screens. The percent transmission of these screens was determined with the Beckman DU spectrophotometer and checked with a photometer which had been calibrated by a step tablet. This step tablet had been calibrated by the Research Laboratories of the Eastman Kodak Company. Measurements with the spectrophotometer showed the percent transmission of the screen to be independent of the wave-length over the region 8000 to 2100A and it has been assumed that this percent transmission could be used for the shorter wave-lengths. Some of the screens gave a much more severe test than demanded by the actual spectrographic measurements: for example a 25-second exposure of the full light source as compared to a 305-second exposure of the light source through a screen having a 8.18 percent transmission. Comparisons which were made with the microphotometer showed the same darkening of the photographic plate. A difference of less than one percent in the photometer response would have been detectable. Jacobs and Platt[1] have reported the Schwarzschild factor of Ilford Q plates to be 0.95.

Beckman measurements.—The vapor handling system used with the Beckman DU spectrophotometer consists of a small sample tube, a one centimeter fused quartz absorption cell, a vapor chamber, an inclined mercury manometer, a McLeod gauge and a mercury vapor pump. The cell is connected to the Pyrex system through a graded seal and is carried by a wooden holder in the regular cell carriage of the spectrophotometer. A glass coil in the connecting tube allows for the movement of the absorption cell in and out of the light path.

Divinyl ether.—The divinyl ether was obtained as Vinethene from Merck and Company. It was placed over flake potassium hydroxide for several days and
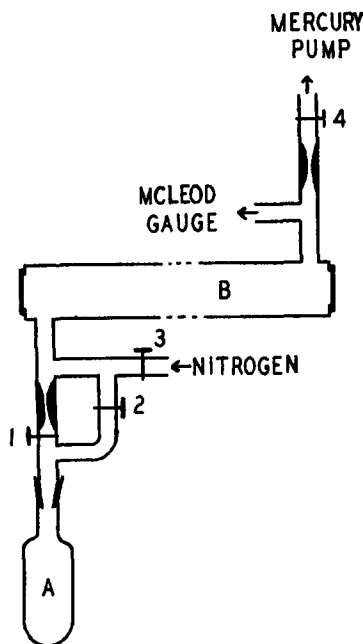
distilled through a modified Fenske column. Measurements were made on fractions having not more than 0.02°C variation in boiling point.

RESULTS

Typical values of the logarithm of the extinction coefficient, $\log \epsilon$, obtained with the vacuum spectrograph are given in Table I. In general the mean deviation in this function is of the order of 0.01 to 0.03. This corresponds to a mean deviation of three to eight per-

TABLE I. $\log \epsilon$, vacuum spectrograph measurements.

Wave number	Plate 73 (0 089 mm)	Plate 74 (0.047 mm)	Plate 75[a] (0.043 mm)	Plate 77 (0.025 mm)	Plate 78[b] (0.029 mm)	Plate 79 (0 032 mm)
46,260	3.68	3.71	3.74	3.71	—	3.64
49,180	—	—	—	4.22	4.19	4.18
52,360	—	—	—	4.02	3.98	3.96
55,300	3.70	3.70	3.71	3.70	—	3.63
58,440	3.71	3.70	3.69	3.73	—	3.62

[a] Pressure too high for measurement at the top of the band.
[b] Two-minute calibration curve was not reliable and values were not calculated in the regions that depended upon this calibration.

cent in the value of the extinction coefficient. The average values of $\log \epsilon$ obtained by the spectrographic measurements and the average value of $\log \epsilon$ obtained by the Beckman measurements are plotted in Fig. 2 as a function of wave number. The agreement over the region covered by the two instruments is well within the mean deviations of the separate methods and it is tentatively concluded that the accuracy of the spectrographic measurements is of the same order as their precision. No attempt has been made to carry the measurements of this compound into the discontinuous region of the hydrogen spectrum.

During the development of this method measurements were made with a 60 cm absorption tube and with longer time exposures but with fewer calibration exposures. The average values of the extinction coefficient obtained were essentially the same as those reported here but the precision of the measurements was decreased by the greater uncertainty in the calibration curves. Another series of measurements was made with nonflowing vapor. The presence of bands which increased with continued radiation gave evidence of photo-chemical reaction.

The absorption spectrum of divinyl ether is completely free of fine structure. The extinction coefficient increases from a value of 10 at 42,400 cm^{-1} to a maxi-
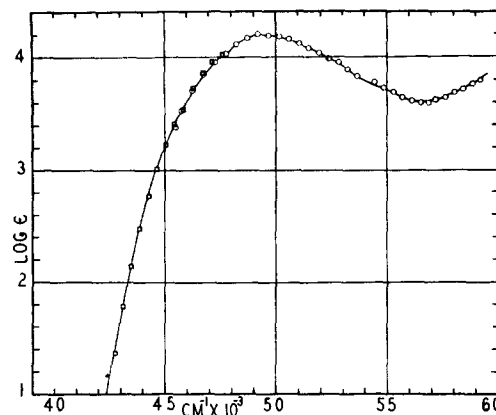

FIG. 2. Logarithm of the molar extinction coefficient vs. wave number for divinyl ether in the vapor phase. Average vacuum spectrograph measurements are shown as circles; average Beckman spectrophotometer measurements as squares.

mum of 15,900 at 49,200[3] cm^{-1} and decreases to a minimum value of 4000 at 56,700 cm^{-1} before beginning to increase again. There is a very slight step-out at 48,000 cm^{-1} which seems to be real although hardly detectable. The oscillator strength[1] of the band is 0.45.

Divinyl ether is, of course, both an oxygen containing compound and an unsaturated compound and at this time not enough compounds have been studied to permit a detailed analysis of the spectrum. A few comparisons can, however, be made. Fine structure, which is so characteristic of related compounds such as diethyl ether,[4] furan,[5] and low molecular weight unsaturated hydrocarbons,[2] does not appear. The position of the band of divinyl ether is at smaller wave numbers than the first band of either diethyl ether or non-conjugated hydrocarbons and is at larger wave numbers than the position of the first broad band of the conjugated hydrocarbons. These positions indicate some conjugation in divinyl ether. Limited conjugation has also been proposed to explain heats of hydrogenation.[6] The position of the broad band underlying the fine structure of furan is similar to that of divinyl ether but the intensity of absorption of the furan as shown by both the extinction coefficients and the oscillator strength is much less than that of the divinyl ether.

[3] The maximum in the microphotometer tracing is at 50,600 cm^{-1}. The difference between this apparent maximum and the true maximum arises from the continually decreasing intensity of the hydrogen continuum at shorter wave-lengths.
[4] G. Scheibe and Grieneisen, Zeits. f. physik. Chemie B25, 52 (1934).
[5] L. W. Pickett, J. Chem. Phys. 8, 293 (1940).
[6] G. B. Kistiakowsky and co-workers, J. Am. Chem Soc. 60, 440 (1938).