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Absorption Spectra of Some Radicals in The Visible Ragion

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Absorption Spectra of Some Radicals in The Visible Ragion

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Visible absorption spectra of the radical solutions of diphenyl, phenantrene, chrysene and α-α'dipyridyl, prepared in THF solvent by using Na, have been taken and absorption minima of the first three of the solutions were found to be located at 481, 538, 560 mμ respectively. Meantime it was found that absorption minimum of the α-α' dipyridyl is shifted to the near IR. The graphs, representing the extinction coefficients of the radical solutions as function of the radical concentrations have been drown. These curves can be used to determine the unknown concentration of the radical by the spectrophotometririal method.

INTRODUCTION

The most precise method to determine the radical concentration of a solution, is known to be the EPR spectroscopy. In this method unknown concentration of a radical solution can be calculated by comparing the unknown with that of a reference sample (1) by adding a signal integrator to the EPR spectrometer.

To avoid extensive corrections and to insure a satisfactory measurement, the reference sample should be prepared in the same solvent which was used in preparing the sample whose concentration is to be determined. Furthermore, both solutions should have nearly the same order of spin concentrations.

In the present work, the method mentioned above has been used to determine the spin concentrations through a S-band EPR spectrometer.

Immediately after the concentration determination, the nuclear relaxation time T_2 of the radical solution, has been measured by using a double-resonance, weak – field NMR spectrometer.

The relaxation time contribution of the radical in T_2 is T_2'. T_2' has been calculated by using the known T_{20} value of the pure solvent and measured T_2. The calculated T_2' values for various concentrations have been plotted against the same concentration values of the radical as measured by means of the EPR spectrometer. The resulting curve, which is observed to be linear (2) has been used to determine the unknown concentration of the solution, from the calculated T_2'.

The electronic and the nuclear interactions of some radicals prepared in the same solvent were being studed by measuring the relaxation times T_{1e} ant T_2 as functions of the spin concentratinos at room temperature (3). While doing, above, it was thought to be a useful extention, to determine the absorption of the same radicals, in the visible region, by using a Jobin-Yvon spectrophotometer. Thus the extinction coefficient values can be readily used in determining the radical concentration, without the help of an EPR spectrometer.

EXPERIMENTAL PROCEDURE

In the present work, absorption spectra of diphenyl ($C_6H_5C_6H_5$), phenantrene ($C_{14}H_{10}$), chrysene ($C_{18}H_{12}$) and dipyridyl (C_5H_4N C_5H_4N) radicals prepared in the THF solvent, have been taken.

The spectra have been taken by using the special cell shown in Fig. 1. This cell has been specially constructed in such a way

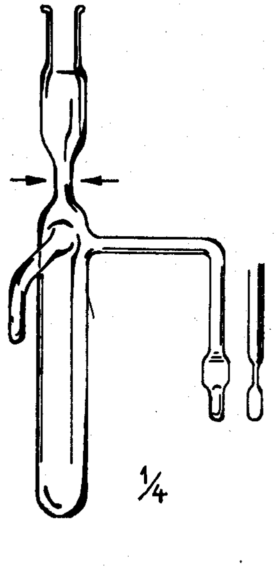


Fig. 1. Absorption cell

that the distance between parallel walls was not more than 1,5 mm. The reason being that, for a larger sample thickness, absorption measurement would be impossible due to the high optical density of the radical solutions even for very small concentrations.

The radicals have been prepared in the nitrogen atmosphere by using Na. The nitrogen and distillation of the solvent were made by means of the system shown in Fig. 2.

The nitrogen of 99,99 % purity is entered into the gas–counter (b) in order to regulate the flow. To separate O_2 and H_2O, the nitrogen then is passed through a series of traps which contain of pyrogallol and sodium hydroxide solution in water (c), concentrated H_2SO_2 (e) and $CaCI_2$ (f) respectively. As a further precaution, the gas thus cleaned is sent through the BTS contact (Badische Anilin and Soda Fabrik AG) (g) to trap any trace oxygen that may be left and the P_2O_5 column (h) to absorb the trace of water.

THF, used as a solvent for radical preparation has been boiled with pieces of Na and K for at least two days in the atmosphere of purified nitrogen as obtained above. During boiling, stopcocks <2> and <4> were closed while <1> was opened and the gas was exhaused through the trap (j).

The reservoir of the cell was calibrated for ample amount of solvent, then cleaned with the fuming sulphuric acid and dried at 300 °C for use. The amount of chemical, theoretically calculated to be sufficient to produce a concentration of about 10^{-2} molar was put into the reservoir of the cell.

Immediately after inserting a small piece of Na into the side branch, the cell was connected to the vacuum. The cell was evacuated with stopcocks <3>, <5> and <6> open, and <2> <4> closed, Then by closing <6> and opening <4> slowly and carfully, the nitrogen was introduced into the cell. This operation was repeated several times to insure the purity of nitrogen atmosphere.

By stopping the cold water flow in the C_1 column, the distillation of the solvent was obtained on the chemical. During

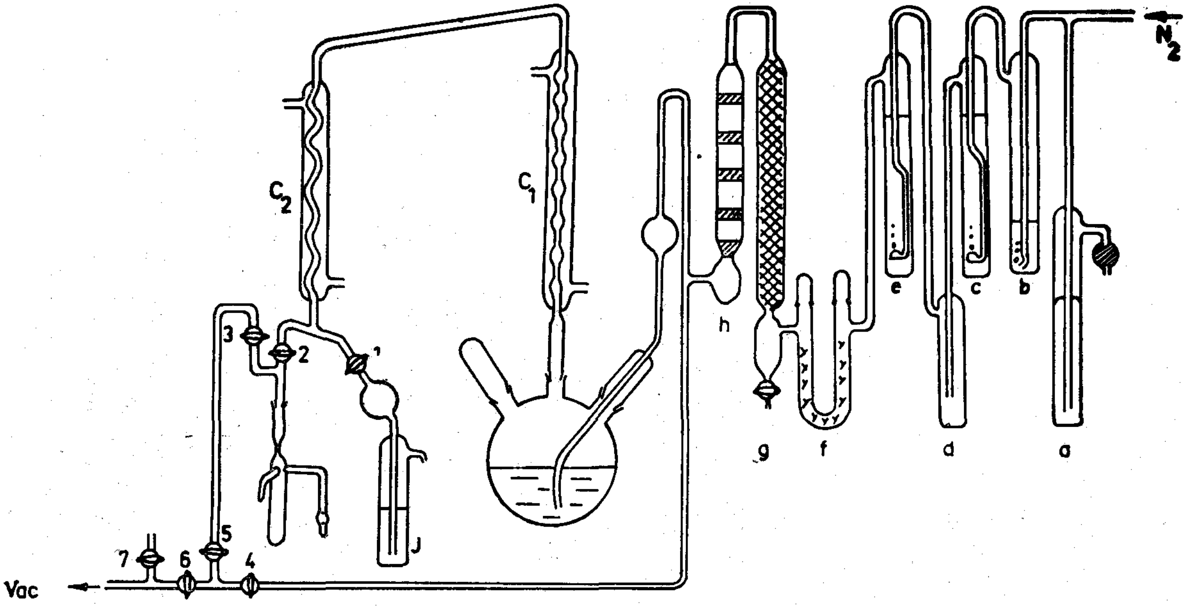


Fig. 2. System used for the preparation of the samples

the distilation process, stopcocks <1>, <4> and <7> were closed and others were opened. After distilling ample amount of solvent, stopcocks <2> and <3> were closed, and <1> was opened. The reservoir was embedded in the liquid nitrogen and the neck of the cell was sealed and cut off by a flame. Then the transparent and colourless solution in the reservoir was treated with sodium, which remained isolated in the side branch of the cell during the distillation. The formation of the radical has been controlled by the colour density of the solution. Increasing amounts of radical concentrations were obtained by shaking the Na piece proportionedly.

For each concentration, absorption spectrum of the solution was taken in the optical region appropriate to the radical, through the small cell joined to the reservoir. Immediately after taking of each spectrum, the T_2, corresponding to every radical concentration was measured.

DISCUSSION OF RESULTS

The variations of the optical densities D of diphenyl, phenantrene, chrysene are shown in Fig. 3. depending on the wave length.

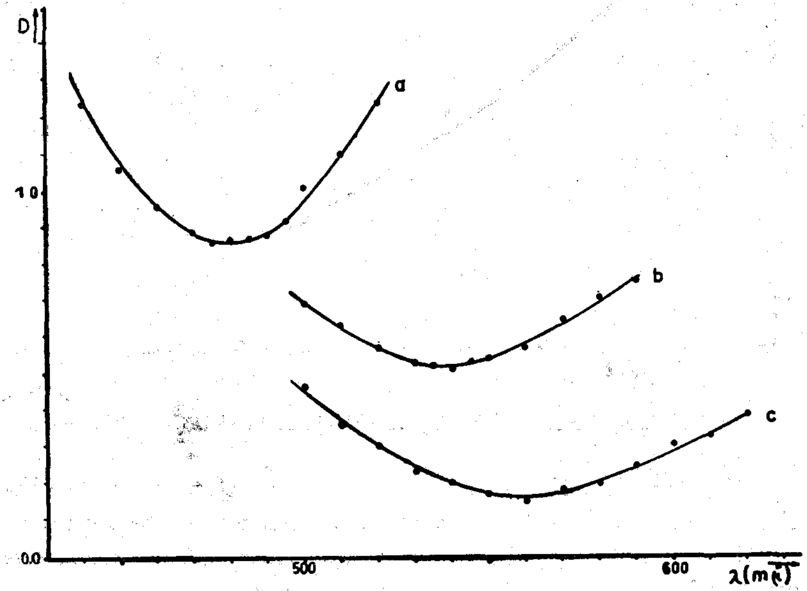
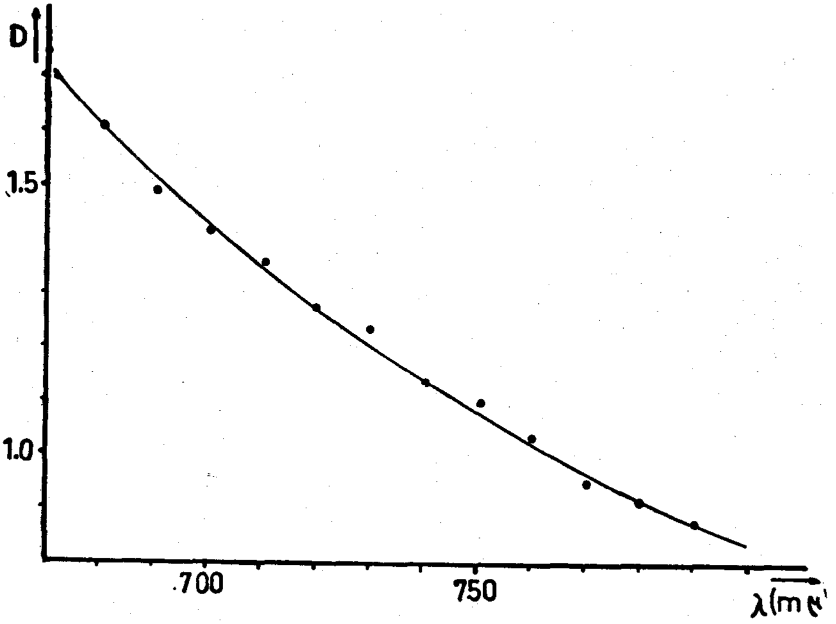


Fig. 3. Absorption minima of diphenyl (a) 1,75 10^{-3} mol.; phenantrene (b) 3,20 10^{-3} mol.; chrysene (c) 8.0 10^{-4} mol. radicals in the visible region.

Only one absorption minimum was observed in the spectra for each of these radical solutions above. Generally the number of absorption minima in the visible region are not expected to be higher, and these bands are usually rather diffused.

The absorption minima of diphenyl, phenantrene and chysene have been located at 481, 538, and 560 mμ respectively. All three of the absorption bands are symmetrical in character.

The absorption minimum of α - α'dipyridyl, on the other hand was observed as shifted to the near infrared region. The absoption curve of the last radical solution does not yield information about the location or the number of absorption minima (Fig. 4)



Fif. 4. Absorption of α - α'dipyridyl radical 4,30 10^{-3} mol. in the visible region.

For the first three radical solutions, the extinction coefficient K corresponding to the wave lengths which are represented as abscissa of the absorption minima in Fig. 3 are expressed as function of the radical concentrations in Fig. 5.

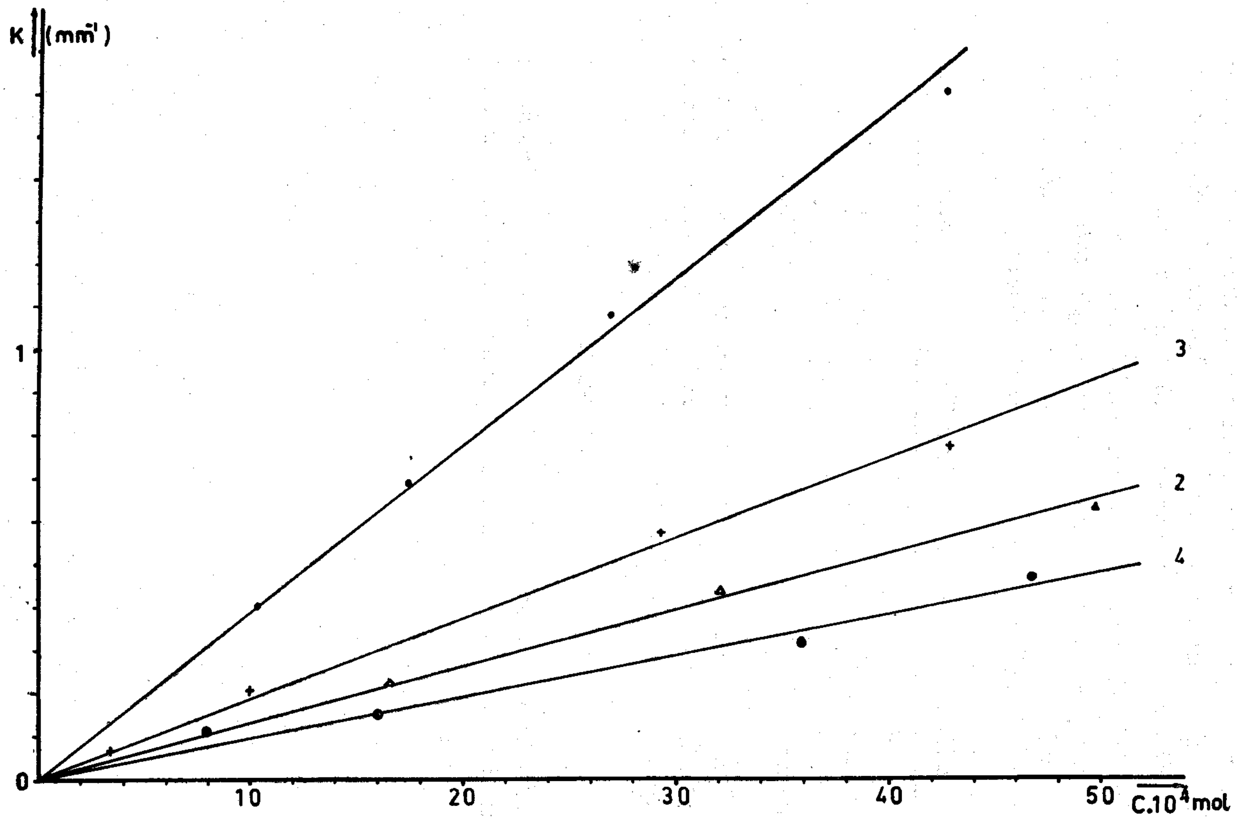


Fig. 5. Extinction coefficients of diphenyl (1), phenantrene (2), chrysene (4) and α - α' dipyridyl (3) radical as function of the concentration.

For the fourth sample, the same calculatons have been carried out for a certain wavelength $\lambda = 770$ mμ, since no ansorption minimum was observable in the visible region.

k, defined as to be K = kc, which constitute a characteristic optical constant for each radical sample corresponding to the wavelength of the absorption minima of each radical have been found and listed in the following table:

Radical	k(mol^{-1}mm^{-1})	mμ
Diphenyl	388	481
Phenantrene	126	538
Chrysene	105	560
α-α'dipyridyl	325	770

When the *extinction coefficients* are calculated by measuring the optical density, the concentration of the radicals can be easily found by using the graphs shown in Fig. 5.

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ÖZET

Difenil, fenantren, krizen ve α - α'dipiridil in THF içinde sodyum yardımile hazırlanan radikallerinin, görünür bölgede absorpsiyon spektrumları alındı ve ilk üç nümune için, sıra ile 481, 538, ve 560 mμ da absorption minimumları tesbit edildi. Dördüncü nümunenin muhtemel absorpsiyon minimumunun yakın IR 'a kaydığı görüldü.

Nümunelerin sönüm katsayılarının, radikal konsantrasyonuna bağlı eğrileri çizildi. Bu eğriler, bahiskonusu radikallerin görünür bölge spektroskopisi ile konsantrasyonlarının tayinini mümkün kılmaktadır.

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