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E.D.A. COMPLEXES OF AROMATIC HYDROCARBONS WITH RHODAN +)

W.Scholz, A.Truţia and V.Vântu
Institute of Petroleum,Gas and Geology,
Bucharest, Roumania

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Within another work on the possibility of charge-transfer phenomena between aromatic hydrocarbons and combinations containing the thiocyan group (alkyl thiocyanates or compounds of organo-metallic coordination),we were conducted to study the spectral behaviour in ultra-violet of rhodan solutions in benzene, toluene, o-, m-, p-xylene, mesitylene and m-dioctylbenzene.

Although the formation of E.D.A.complexes between aromatic hydrocarbons and halogens has been clearly pointed out relatively recently, among others, by R.M.Keefer and L.J.Andrews[1,2] and by G.Briegleb and J.Czekalla[3] and although the analogy between the behaviour of rhodan and that of halogens is known since long, the formation of such E.D.A. complexes with rhodan has not been yet pointed out.

This work should allow to establish the behaviour of the cyan groups from the standpoint of the possibility of their acceptance of electrons in the case of rhodan (or of its derivatives) as compared with the well known behaviour, from this standpoint, of the cyan group from tetracyanoethylene.

+ This work is part of the dissertation thesis sustained by W.Scholz on July 2,1964,at the Petroleum,Gas and Geology Institute of Bucharest.

1 R.M.Keefer and L.J.Andrews-J.Amer.Chem.Soc.72 4672 (1950)
2 L.J.Andrews and R.M.Keefer-J.Amer.Chem.Soc.74 4500 (1952)
3 G.Briegleb and J.Czekalla-Z.Elektrochem.63 6 (1959)

Qualitative data from literature and our preliminary quantitative experiments showed that the rate of decomposition of rhodan is varying substantially with the nature of the solvent, namely, decreases as the ionization potential of the latter decreases.

The existence of E.D.A. complexes of aromatic hydrocarbons with rhodan has been established by the study of the spectral behaviour in ultra-violet of rhodan solutions of various concentrations in aromatic hydrocarbons as compared the spectral behaviour of rhodan solutions in inert solvent (n-heptane). There has been indicated in the literature[4] the absorption spectrum of some rhodan solution in chloroform (λ_{max} = 295 mμ).

In this work we have determinated the molar extinction curve of rhodan in n-heptane[+], establishing the doubtless existence of one maximum (λ_{max} = 294 mμ, ε_{max} = 2o3). The existence of a second maximum (λ_{max} =23o-24o mμ, ε_{max} = 1o52 - 689) whose position and extinction vary, to some extent, with the concentration, appears to be less certain due to the sensibility range of the apparatus.

Then, the absorption spectrum has been determined of rhodan solutions in the above mentioned aromatic hydrocarbons within the range λ = 27o - 4oo mμ; the results obtained are indicated in Table I. From these data on may see that the maximum of rhodan at λ = 294 mμ is covered by a charge-transfer band having an extinction of another order of magnitude (1o - 25 times-greater depending on the nature of the aromatic hydrocarbon) that can be ascribed only to the formation of a complex of charge-transfer and not to an effect of the solvent.

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[4] R.G.R.Bacon and R.S.Irwin - J.Chem.Soc. 981 (1958)

[+] The spectra presented in this paper have been obtained with an electronic Jobin - Yvon spectrophotometer, by using 1 cm. cells.

TABLE I

λ_{max} and $\mathcal{E}_{max}$ of Rhodan Solutions in Various Aromatic Hydrocarbons

Hydrocarbon	Conc. $(SCN)_2$ (mol/l)	λ max (mμ)	$\mathcal{E}$ max
Benzene	$1,03.10^{-4}$	279	5280
Toluene	$2,46.10^{-4}$	286	3840
o-Xylene	$2,20.10^{-4}$	290	4480
m-Xylene	$2,20.10^{-4}$	290	3550
p-Xylene	$2,30.10^{-4}$	293	2540

The direction of the bathochrome displacement (the decrease of charge-transfer energy) of the extinction maximum when shifting from benzene to p-xylene coincides with the direction of the variation of the ionization potential of the aromatic hydrocarbon. With the exception of o-xylene, the molar extinction decreases in the same way.

Considering the instability of rhodan solutions as well as the possibility of the occurrence of some products of reaction during the spectrophotometric determinations (by photochemical initiation) the reproductibility of the obtained data has been checked. They did not exceed the error limits of the apparatus for the used concentrations. The determination of the absorption curves after a previous irradiation of rhodan in n-heptane solutions with ultraviolet light, under conditions more drastic than those in which the spectral determinations were being made,indicated an extinctions maximum characteristic for alkylthiocyanates. This maximum does not appear under normal conditions of spectra determinations.

Another problem was the possibility of the formation of polymerisation products of rhodan. But it is known that these polymers are not practically soluble in organic solvents[5]. Under conditions in which the determinations of the absorption spectra were made, no formation of precipitate was noticed. However, after a longer period of conservation of solutions or after irradiation, a polymer separated to which solid state (tablets) spectrum was determined in infra-red. The above mentioned chemical reactions and the study of the reaction products are discussed in another work now in progress.

Particular problems seem to appear where mesithylene is involved.

Since the above mentioned aromatic hydrocarbons do absorbe in used concentrations and in the range of the studied wave length, solutions of same concentrations in aromatic hydrocarbons have been used, by analogy with one of the methods descriebed in the literature[6], both for the blank sample and for the solution being investigated.

Next was checked experimentally the hypothesis of the formation of an aromatic hydrocarbon-rhodan complex in molar proportions of 1:1 by the fact that in the expresion which gives the concentration of the E.D.A. complex at equilibrium, the concentration of rhodan does not intervene directly. With this purpose determinations have also been made at various rhodan concentrations in solution.

Further, the equilibrium constants at maximum of absorption for these compounds have been determinated using the well known Benesi - Hildebrand method which holds good for complexes of 1:1 molar compositions:

$$\frac{1}{\mathcal{E}_a - \mathcal{E}_A} = \frac{1}{\mathcal{E}_C - \mathcal{E}_A} + \frac{1}{K(\mathcal{E}_C - \mathcal{E}_A)} \cdot \frac{1}{b}$$

where :

$$\mathcal{E}_a = \frac{m}{a}$$

[5] S.S.Bhatnagar, P.Kapur and B.D.Khosta - J.Indian Chem. Soc. 17 529 (194o)

[6] L.J.Andrews and R.M.Keefer-J.Amer.Chem.Soc.75 3776(1953)

m = extinction modulus or optical density of the solution
a, b = initial concentrations of the acceptor and of the donor
$\mathcal{E}_C$, $\mathcal{E}_A$ = molar extinction of the complex, respectively of the acceptor
K = equilibrium constant

The obtained results may be seen in Fig.1 and in Table II

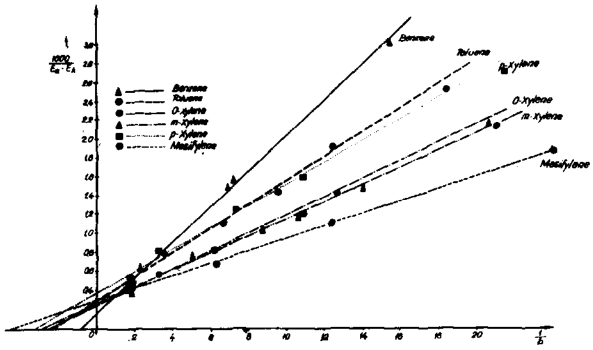

FIG. 1. The Benesi - Hildebrand method applied for E.D.A. complexes of rhodan with aromatic hydrocarbons in n-heptane, at room temperature.

T A B L E II

λ_{max}, $\mathcal{E}_{max}$ and K_x of E.D.A. Complexes between Aromatic Hydrocarbons and Rhodan in n-Heptane Solutions

Hydrocarbon	λ_{max}	$\mathcal{E}_{max}$	K_x
Benzene	279	5720	0,98
Toluene	286	3490	2,35
o-Xylene	290	4200	2,55
m-Xylene	290	3890	2,94
p-Xylene	293	2750	3,35
Mesitylene	303	3285	5,01

The values of charge-transfer energies $h\nu_{CT}$ for complexes with rhodan as acceptor depending on the ionization potential (varying between 9,2 - 8,3 eV) of the aromatic hydrocarbons being investigated which act as donor, are evidently higer than those of other known acceptors (iodine, trinitrobenzene, chloranil) versus the same hydrocarbons. Thus,the charge-transfer energies, where rhodan complexes are involved, are varying between 4,4 and 4,1 eV as compared with 4,2 and 3,7 eV in case of iodine and 3,6-3,0 eV in case of chloranil. As a whole, it is found that the molar extinctions in the case of E.D.A. complexes with rhodan are smaller as compared with those of the acceptors σ (Br_2,I_2,ClI) and are of the same magnitude as those of some acceptors π(tetracyanoethylene,SO_2,maleic anhydride). In Fig.2 is represented the absorption curve (plotted with the Benesi - Hildebrand equation on the basis of our determinations) of an E.D.A. complex of o-xylene - rhodan.

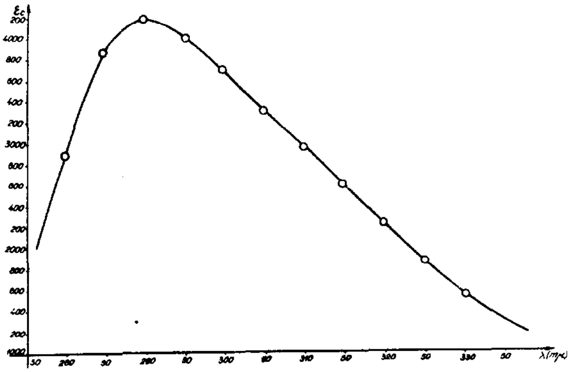

FIG. 2. Absorption curve of
o-xylene - rhodan E.D.A. complex

The values of equilibrium constants of rhodan - aromatic hydrocarbons complexes mentioned above as compared with those of the same hydrocarbons with other acceptors, determinated by other authors, are given in Table III.

T A B L E III

Equilibrium Constants K_x of Certain Acceptors with Aromatic Hydrocarbons

Hydrocarbon	Br_2 [1]	I_2 [2]	$(SCN)_2$	Maleic anhydride	Tetracyanoethylene [9]
Benzene	1,04	1,50	0,98	0,66[7]	31,1
Toluene	1,44	1,65	2,35	0,59	57,6
o-Xylene	2,29	2,80	2,55	-	108,0
m-Xylene	2,16	3,19	2,94	1,06[8]	93,2
p-Xylene	2,26	3,19	3,35	0,81[8]	119,0
Mesitylene	-	8,40	5,01	0,94[7]	269,0
Solvent	CCl_4	CCl_4	Heptane	CCl_4, $CHCl_3$	CH_2Cl_2
Temperature	25°C	25°C	room temp.	room temp.	22°C

It may be seen that the equilibrium constant values for E.D.A. complexes with rhodan are lower than in the case of complexes with tetracyanoethylene, but are higher than in the case of complexes with maleic anhydride. These values range between those found for bromine and iodine. The substantial differences between the equilibrium constant values and between the molar extinctions of rhodan complexes with the three isomers of xylene, should be mentioned. These differences are larger than in the case of other types of complexes. Lower values of equilibrium constant and higher values of molar extinction, where benzene and o-xylene are involved, may be due in this case, to a higher extent, to some nonstoechiometric complexes of charge-transfer by contact. This is in agreement with the hypothesis of L.Orgel and R.Mulliken[10], according to which, due to the electronic configuration of the component acting as an electrons acceptor,

[7] L.J.Andrews and R.M.Keefer - J.Amer.Chem.Soc. 75 3776 (1953)
[8] Authors - Work now in progress.
[9] R.E.Marriefield and W.D.Philipps - J.Amer.Chem.Soc. 80 2778 (1958)
[10] L.E.Orgel and R.S.Mulliken - J.Amer.Chem.Soc. 79 4839 (1957)
J.N.Murrel - J.Amer.Chem.Soc. 81 5037 (1959)

in excited state, effects of charge-transfer become possible at distances longer than those Van der Waals.

In the case of mesitylene, where the difference between the equilibrium constant values, for the formation reaction of rhodan complexes and those corresponding to xylenes is relatively small, as compared with the differences in the case of complexes with other acceptors, the much higher instability of rhodan solutions in mesitylene should be taken into account. This might indicate, during the irradiation, the possibility of a homolytic substitution reaction[11] in the chain, with the formation of mesityl thiocyanate or iso-thiocyanate, which do not absorbe in the measured range. That is why, in this case determinations have been made only on lower concentration solutions in mesitylene, prepared a few minutes before the measurement and only for a few points round the maximum.

The data indicated in Table IV have been obtained for various wave lengths in case of E.D.A.complex of m-dioctylbenzene (prepared, by analogy with the method described by Woods and Jucker, from m-dioctylcyclohexadiene)[12] and rhodan.

TABLE IV

ε and K_x at Various Wave Lengths for the Rhodan - m-Dioctylbenzene Complex

λ (mμ)	ε	K_x
310	778	18,57
315	790	13,90
320	620	18,00

These determinations have been made in conditions other than the previous ones, namely, at concentrations about

11 R.G.R.Bacon, R.G.Guy, R.S.Irwin and T.A.Robinson - Proc.Chem.Soc. 304 (1959)

12 G.F.Woods and J.W.Jucker - J.Amer.Chem.Soc.70 2174(1948)

ten times lower, which may lead to greater errors. Consequently, in this case, the obtained results have only an orientative character. Molar extinctions, that were found, are low (due perhaps to the great number of σ bonds in the molecule) as compared with those of the xylenes, while equilibrium constants are high. On the basis of these results, the ionization potential of m-dioctylbenzene should be lower than that of dialkylbenzenes with short chains.