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Spectroscopic Studies of Charge Transfer Complexes. IV. Benzonitrile and Iodine, Bromine, Iodine Monochloride and Iodine Monobromide

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The interactions between benzonitrile and iodine, bromine, iodine monochloride and iodine monobromide have been studied spectroscopically. It is shown that benzonitrile forms 1:1 complexes with the halogens in carbon tetrachloride solution. The following formation constants (K_c) have been obtained at 20°: 8.1 ± 0.2, 2.0 ± 0.15, 0.8 ± 0.1 and 0.2 ± 0.05 for the iodine monochloride, iodine monobromide, iodine and bromine complexes, respectively. Compared with data reported for the corresponding acetonitrile complexes, benzonitrile is a somewhat stronger donor. No charge transfer bands were observed for the present systems in the ultraviolet region above 250 mμ.

A large number of investigators have studied the charge transfer complexes between halogens and molecules with lone pair electrons.[1] Formation constants and thermodynamic functions for such systems in solution frequently have been obtained from spectroscopic data.[1] The geometrical features of many such complexes in the crystalline state have been obtained by Hassel and co-workers[2] from X-ray methods. These studies reveal that, *e.g.*, nitrogen bases like the amines are strong donors[3,4] while oxygen-containing molecules like ethers[5] or aldehydes[6] form weak complexes with iodine. Much less information is available about the donor properties of nitriles. The addition compounds of nitriles to some metal halides[7,8] have been investigated by infrared spectroscopic methods. Popov and Deskin[9] studied the complexes between acetonitrile and halogens. In this Laboratory the infrared and ultraviolet spectra have been obtained for the complexes formed between different nitriles and halogens. The visible and ultraviolet spectroscopic data for the benzonitrile-halogen complexes in carbon tetrachloride are presented here. In forthcoming papers the corresponding infrared data, with special reference to changes in hybridization of the nitrile group upon complex formation, will be reported.

Experimental Part

Chemicals.—Benzonitrile, analytical grade from Fluka AG was shaken with hydrochloric acid, washed and dried. The product was distilled in a Vigreux column, b.p. 191°, and only the middle fraction was used. Iodine, analytical grade, from Merck was sublimed with calcium oxide and resublimed under nitrogen atmosphere. Bromine, analytical grade, from Merck was used without further purification. The iodine monochloride and iodine monobromide, both from Merck, were purified by repeated fractional crystallization to constant melting points of 27.2°[10] and 42°,[11] respectively. Carbon tetrachloride, analytical grade, Merck, was shaken with a potassium hydroxide solution, washed, then treated with concentrated sulfuric acid. The solvent was washed, shaken with anhydrous calcium chloride and distilled over calcium chloride in a Vigreux column.

Stock solutions of the nitrile and the halogens were prepared every day by weighing into glass stoppered 25 ml. volumetric flasks. The mixed solutions were made in 10 ml. volumetric flasks by pipeting from the stock solutions, and the spectra were recorded immediately. Care was taken to keep the nitrile concentration in excess during preparation of the mixed solutions.

Instrumental.—The absorption spectra were obtained with the aid of a Beckman recording spectrophotometer DK-1, equipped with a thermostated cell holder. A matched pair of Beckman, stoppered silica cells of path length 1.00 cm. was used, and the temperature was kept at 20 ± 0.2°.

Results and Discussion

Benzonitrile absorbs in the near ultraviolet region with the strongest peaks at 268 and 276 mμ. At the conditions employed in this investigation, benzonitrile shows negligible absorption in the region 310–700 mμ. Iodine and bromine dissolved in carbon tetrachloride have visible absorption bands at 515 and 416 mμ, respectively. In the same solvent, iodine monochloride absorbs at 465 mμ and iodine monobromide at 492 mμ. If benzonitrile is added to a solution of any of the four halogens or interhalogens a new absorption band appears at a lower wave length. It is reasonable to assign the new band as the visible halogen band, blue shifted on complex formation. The observed absorption curves of the mixed solutions containing $4.944 \cdot 10^{-3}$ *M* iodine monochloride and different (larger) concentrations of benzonitrile are shown in Fig. 1. An isosbestic point is observed at 418 mμ and the blue shift is approximately 108 mμ. In the corresponding iodine monobromide system the complex peak is blue shifted approximately 63 mμ, and an isosbestic point is observed at 458 mμ. Iodine and bromine are expected to be weaker donors[1] than the interhalogens toward benzonitrile. Due to the strong overlap between the free and the complex peaks in the iodine and bromine solutions, the blue shifts could not be determined accurately. They are approximately 22 and 10 mμ in the iodine and bromine systems, respectively.

To determine the stoichiometry of the iodine monochloride complex, a series of absorption curves was recorded, keeping the halogen concentration at $2.325 \cdot 10^{-2}$ *M* and varying the nitrile concentration from $9.832 \cdot 10^{-3}$ *M* to $1.034 \cdot 10^{-1}$ *M*. When the absorbance at, *e.g.*, 350 and 360 mμ was plotted against the mole ratio of C_6H_5CN/ICl, breaks were observed at equimolecular concentra-

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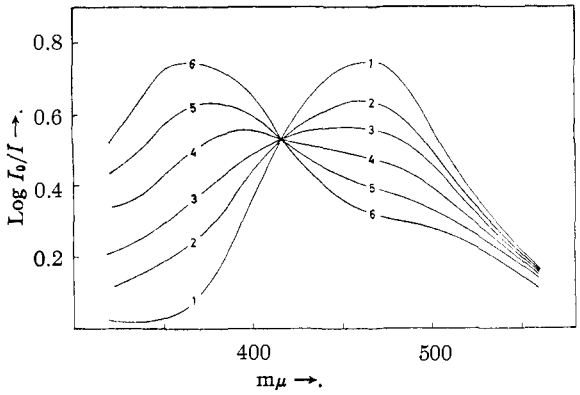

Fig. 1.—Visible absorption spectra of benzonitrile and ICl (4.9440×10^{-3} M) in CCl_4 at 20° for 1 cm. cell. The concentrations (M) of benzonitrile are: (1) zero, (2) 0.02968, (3) 0.05936, (4) 0.1187, (5) 0.2374 and (6) 0.5342.

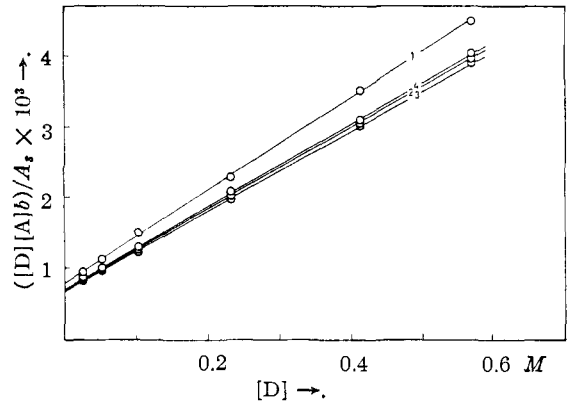

Fig. 2.—Benesi–Hildebrand–Scott plot for the C_6H_5CN–ICl complex. The curves (1), (2), (3) and (4) are obtained at 340, 350, 360 and 370 mμ, respectively.

tions. Similar results were obtained for the iodine monobromide complex. Accordingly, the interhalogen complexes are of the 1:1 type. The iodine and bromine complexes were too weak to provide any definite results by this method. However, these complexes are assumed to have 1:1 stoichiometry.

The formation constants of the benzonitrile–halogen complexes were calculated by the Benesi–Hildebrand method.[12] The Scott modification[13] of this equation was applied to the blue shifted, visible halogen absorption peaks. This equation can be written

$$\frac{[A][D]b}{A_s} = \frac{1}{K_c \cdot a_m} + \frac{[D]}{a_m}$$

[A] and [D] are the initial concentrations of the acceptor and the donor, b is the cell thickness, A_s the absorbance of the complex, K_c the formation constant expressed in M^{-1} and a_m is the molar absorptivity. If $[A][D]b/A_s$ is plotted against [D], a straight line with slope $1/a_m$ and with intercept $1/K_c a_m$ should result. However, it is a prerequisite for the equation in the present form that [D] >> [A] and that the complex absorbs at a wave length where A and D are completely

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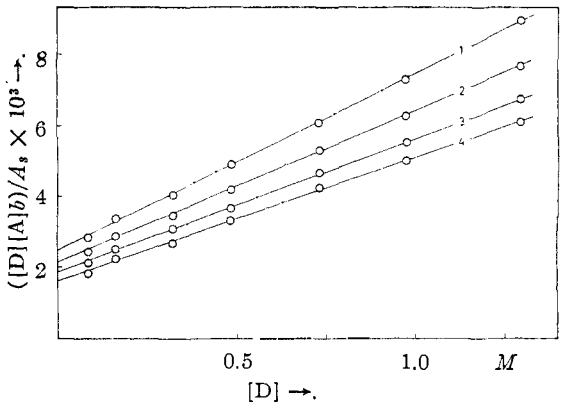

Fig. 3.—Benesi–Hildebrand–Scott plot for the C_6H_5CN–IBr complex. The curves (1), (2), (3) and (4) are obtained at 380, 390, 400 and 410 mμ, respectively.

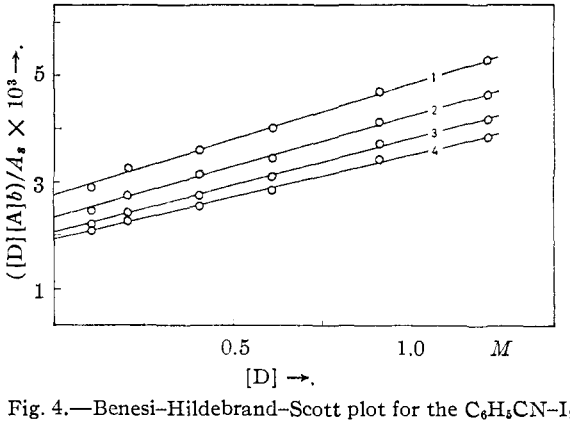

Fig. 4.—Benesi–Hildebrand–Scott plot for the C_6H_5CN–I_2 complex. The curves (1), (2), (3) and (4) are obtained at 445, 450, 455 and 460 mμ, respectively.

transparent. The second condition is not fulfilled, because in each system the free halogen band superposed the complex peak. An approximate value of K_c was assumed, and the concentration of free halogen was calculated. When the absorption due to the free halogen at the particular wave length was subtracted from the observed absorbances, the absorbance due to the complex was obtained. When these values for A_s were used in the Benesi–Hildebrand plots, a more exact value of K_c was obtained. The procedure is repeated until two successive K_c values agree within the experimental error. If the calculations are made at different wave lengths, an estimate of the error can be made. Generally, the highest precision is obtained at the wave length where the intensity ratio of the complex to the free halogen band is at a maximum.

The Benesi–Hildebrand data for the benzonitrile–iodine monochloride system obtained at four different wave lengths are given in Fig. 2. In Figs. 3, 4 and 5 the corresponding plots are given for the complexes with iodine monobromide, iodine and bromine, respectively. The values obtained for K_c from the plots are listed in Table I. It is clear that the stabilities of the benzonitrile–halogen complexes decrease in the order: iodine monochloride, iodine monobromide, iodine and bromine. Moreover, the amount of overlap between the

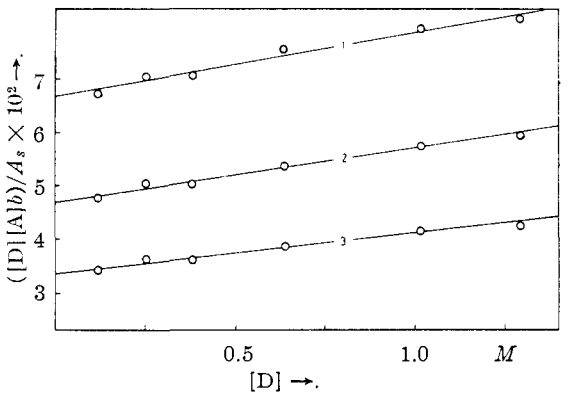

Fig. 5.—Benesi–Hildebrand–Scott plot for the C_6H_5CN–Br_2 complex. The curves (1), (2) and (3) are obtained at 345, 350 and 355 mμ, respectively.

free and the complex halogen peaks increases in the same order. The formation constants in Table I therefore have relative errors increasing considerably in the order of decreasing interactions.

TABLE I

FORMATION CONSTANTS FOR THE 1:1 COMPLEXES BETWEEN BENZONITRILE AND HALOGENS AT 20°

C_6H_5CN compl. with	Wave length, mμ	K_c, M^{-1}	Average K_c, M^{-1}
	340	8.01	
ICl	350	8.06	8.1 ± 0.2
	360	8.13	
	370	8.19	
	380	1.97	
IBr	390	1.98	2.05 ± 0.15
	400	2.03	
	410	2.11	
	445	0.75	
I_2	450	.81	0.8 ± 0.1
	455	.84	
	460	.82	
	345	.18	
Br_2	350	.22	0.2 ± 0.05
	355	.24	

The results clearly show the same progression in the relative acidities of the halogens toward benzonitrile as found in other acceptor–donor systems.[1] Furthermore increased stabilities of the complexes are accompanied by larger blue shifts. The formation constants reported for the corresponding acetonitrile complexes[9] obtained at 25° in carbon tetrachloride are 6.9 ± 0.3, 1.40 ± 0.03 and 0.57 ± 0.02 for the iodine monochloride, iodine monobromide and iodine, respectively. Even when allowing for the temperature difference between the measurements, benzonitrile appears to be a somewhat stronger donor than acetonitrile. This was expected from the lower ionization potential[14] reported for benzonitrile relative to acetonitrile $I(CH_3CN)$ = 12.39 e.v., $I(C_6H_5CN)$ = 9.95 e.v. The formation constant K_c = 153 ± 13 reported for the propionitrile–iodine monochloride complex[15] seems very high compared to the corresponding data for acetonitrile[9] and benzonitrile. The effect of conjugation on the donor properties of the nitrile group will be discussed in a forthcoming paper.

The present complexes are expected to show absorption in the near ultraviolet region if they are of the charge transfer[16] type. However, the ultraviolet absorption recorded above 250 mμ of the mixed nitrile halogen solutions appeared to be a superposition of the absorption of the components. Possible charge transfer bands may be situated below 250 mμ, outside the transparent region of carbon tetrachloride. Or they may be covered by the strong benzonitrile absorption. The use of a transparent solvent like perfluoroheptane might have revealed charge transfer bands in the present systems.

If the benzonitrile–halogen solutions were kept, spectral changes occurred in the visible and ultraviolet regions which indicated irreversible reactions. These changes were most pronounced in the iodine monochloride and iodine monobromide complexes. When the spectra were repeated after 10 minutes, 4 hr., 20 hr. and 100 hr., a new peak at 504 mμ and a broad, new absorption band at 340 mμ appeared in the iodine monochloride system. Because these changes were most pronounced at high nitrile concentration, the Benesi–Hildebrand plots were calculated for systems having [D] < 1.5 *M*. Popov and Deskin observed an increase of the electric conductance in the acetonitrile–iodine monochloride system with time and interpreted the data as a conversion from an outer complex to an inner, ionic complex. A similar explanation may be valid in the present system. However, the spectral changes may be caused by halogen substitutions in the benzonitrile or in the formation of polyhalogen ions. Considerably more work would be necessary to decide the origin of these spectral changes.

Acknowledgments.—The author is grateful to the Nansen Foundation—Norsk Hydro's Fund for a grant.

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