Spectroscopic Studies of Charge Transfer Complexes
VII. Acrylonitrile and Iodine, Iodine Monochloride and Iodine Monobromide

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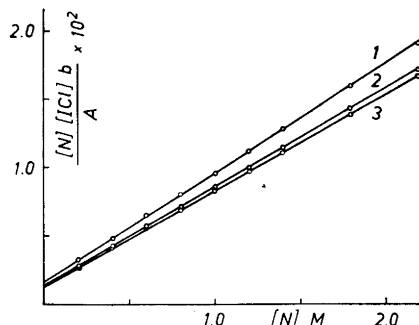*Fig. 1.* Benesi-Hildebrand-Scott plot for the $C_2H_3CN - ICl$ complex. The curves (1), (2), and (3) are obtained at 350, 360, and 370 mμ, respectively. [N] and [ICl] are the initial concentrations of nitrile and iodine monochloride, b is the cell thickness and A the absorbance of the complex.

Spectroscopic studies in the visible region have revealed that acetonitrile,[1] benzonitrile[2] and propionitrile[3] form molecular complexes in solution with the halogens and the interhalogens. The formation constants obtained for these systems in carbon tetrachloride showed that the nitriles were much weaker donors than the amines toward the halogens.

Recently the molecular complexes between 17 different nitriles and iodine monochloride were studied by infrared spectroscopic methods[4]. These data revealed that the nitriles acted as n-donors to the interhalogens. The complex bond is formed from the nitrogen to a halogen atom and is probably parallel with the C≡N bond. This geometry would also be expected from the diagonally hybridized sp lone pair orbital on the nitrogen. It was found that acrylonitrile was a weaker donor to iodine monochloride than the saturated, aliphatic nitriles and the benzonitrile derivatives. The present investigation in the visible and ultraviolet regions was carried out to check these results, to study the complex formation to the weaker donors iodine and iodine monobromide and finally to determine eventual charge transfer absorption bands.

Experimental. Acrylonitrile from Fluka AG., reagent grade, was shaken with phosphorus pentoxide and distilled from this drying agent. The product was later distilled three times in a Vigreux column, b.p. 77.3°C. The halogens and the carbon tetrachloride were purified by methods described earlier[2]. Heptane, *Uvasole,* Merck, was shaken with sulphuric acid, washed, dried, and distilled in a Vigreux column. A Beckman DK-1 spectrophotometer was used, the cell thickness was 1 cm and the temperature 20 ± 0.2°C.

Visible spectral data. When acrylonitrile was added to a solution of iodine, iodine monochloride or iodine monobromide a new absorption band appeared, partly overlapping the free halogen band. In agreement with earlier works[1-3] the new band is assigned as the visible halogen band, blue shifted on complex formation.

If the complexes are of the 1:1 type[1-4] and corrections are made for the overlapping free halogen bands, the formation constants can be calculated from the Scott modification[5] of the Benesi-Hildebrand equation[6]. A series of solutions were recorded for each system, the halogen concentration was kept constant and the nitrile concentration varied from approx. 0.1 M to 3 M. The initial concentration of acrylonitrile was kept at least 30 times larger than the initial halogen concentration. Fig. 1 shows the corrected BHS-plots for the iodine monochloride system, obtained at three different wave lengths. The formation constants (K_c) calculated from the plots and the values obtained for the blue shifts ($\Delta\lambda$) are listed in Table 1.

While the acrylonitrile-halogen complexes were surprisingly stable with time, some changes occurred when the spectra were repeated after a few hours. Therefore, no attempts were made to determine the thermodynamic functions $\Delta H°$ and $\Delta S°$ for the strongest interacting iodine monochloride system, nor could the formation constant for the reactive acrylonitrile-bromine system be determined.

Table 1. Formation constants (K_c) and blue shifts $(\Delta\lambda)$ for the 1:1 complexes between acrylonitrile and halogens in carbon tetrachloride at 20°C.

C₂H₃CN with	Wave length mμ	Calc K_c 1 M⁻¹	Aver. K_c 1 M⁻¹	$\Delta\lambda$ mμ
	350	5.2		
ICl	360	5.4	5.3 ± 0.2	95
	370	5.3		
	390	1.1		
IBr	400	1.2	1.2 ± 0.1	65
	410	1.3		
	450	0.48		
I₂	455	0.49	0.48 ± 0.06	25
	460	0.46		

The data listed in Table 1 show that acrylonitrile is a weaker donor than acetonitrile,[1] benzonitrile[2] and propionitrile[3] toward iodine and the interhalogens. Thus in the nitriles aliphatic conjugation reduced the basicity towards the halogens, while for the aldehydic carbonyl compounds,[7] conjugation seemed to increase the basicity.

Ultraviolet spectral data. No charge transfer bands characteristic of the nitrile-halogen complexes have been reported[1-3]. If the ionization potentials reported for acetonitrile and propionitrile[8] are used to predict the position of the CT-maxima for these iodine complexes applying the linear relationship of McConnel *et al.*[9], they should be situated below 210 mμ. For the benzonitrile-iodine system the CT-maximum is expected[8,9] around 260 mμ, a region where the nitrile has a very strong absorption. For acrylonitrile ($Ip = 10.75$

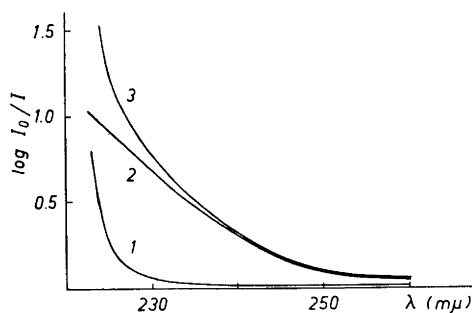*Fig. 2.* The ultraviolet absorption spectra of acrylonitrile-iodine solutions in heptane: Curves (1) 0.113 M acrylonitrile; (2) 1.97 × 10⁻⁴ M iodine and (3) 0.113 M acrylonitrile + 1.97 × 10⁻⁴ M iodine.

e.v.[8]) the CT-maximum of the iodine complex is expected around 235 mμ and for the iodine monochloride complex[10] probably at still shorter wave lengths.

Fig. 2 shows the ultraviolet absorption curves of acrylonitrile (1), iodine (2) and a mixed acrylonitrile-iodine solution (3) in heptane. Iodine absorbs strongly below 250 mμ because of contact charge transfer to heptane, while acrylonitrile has an absorption peak at 213 mμ. Above 240 mμ curve (3) showed approximately 5 % less absorption than the sum of the components. This reduction agreed quite well with the amount of iodine engaged in complex formation and thus reducing the amount engaged in contact charge transfer to the solvent. Below 235 mμ, however, curve (3) showed increasing absorption, and below 230 mμ the mixed solution absorbs more than the components. It seems reasonable to ascribe the increasing absorption of the acrylonitrile-iodine solution in this region to a charge transfer band. Because of the small formation constant, and the strong molar absorption of the components in this region the exact band maximum could not be determined. However, the position was probably around 220 mμ and undoubtly below the value predicted from the ionization potential applying the simple linear relationship[9].

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