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Spectroscopic Studies of Charge Transfer Complexes. V. Propionitrile and Iodine, Bromine, Iodine Monochloride and Iodine Monobromide

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The interactions between propionitrile and iodine, bromine, iodine monochloride and iodine monobromide have been studied spectroscopically in carbon tetrachloride solution. The following formation constants (K_c) have been obtained for the 1:1 complexes at 20°: 9.7 ± 0.2 , 2.3 ± 0.1 , 0.43 ± 0.05 and 0.09 ± 0.03 for the iodine monochloride, iodine monobromide, iodine and bromine complexes, respectively. From quantitative measurements of the intensity of the propionitrile-iodine monochloride complex band at various concentrations and temperatures, the following thermodynamic functions were calculated: $\Delta H_c^\circ = -5.2$ kcal./mole, $\Delta F_c^\circ(25^\circ) = -1.25$ kcal./mole and $\Delta S_c^\circ(25^\circ) = -13.1$ e.u. Unlike the corresponding acetonitrile complex, the propionitrile-iodine monochloride complex shows very little spectral change with time. No charge transfer bands were observed for the present systems in the ultraviolet region above 220 m μ .

The charge transfer complexes between halogens and numerous compounds with lone pair electrons have been studied.¹ However, the donor properties of nitriles have not been thoroughly investigated. The C \equiv N stretching frequency in the region around 2340 cm.⁻¹ is displaced toward higher frequencies when the nitriles are complexed to metal halides,²⁻⁶ boron trichloride⁷ or iodine monochloride,⁸ which may indicate a shortening of the C \equiv N bond upon complex formation. Moreover, time-dependent changes in the conductivity of iodine monochloride in acetonitrile were interpreted by Popov and Deskin⁹ as a slow transition from an outer to an inner complex. The data obtained for acetonitrile⁹ and benzonitrile,¹⁰ as well as other nitriles,⁸ clearly show that the nitriles are much weaker donors than the amines toward halogens.

The propionitrile-halogen complexes have been studied by visible spectroscopic methods and the data are given in the present paper. Because the propionitrile-iodine monochloride complex was quite stable with time, a determination of the thermodynamic functions ΔH_c° , ΔF_c° and ΔS_c° could be carried out.

Experimental

Chemicals.—Propionitrile from Eastman Kodak Co., White Label, was shaken with 1:5 diluted hydrochloric acid, washed and dried. The product was distilled twice over calcium chloride in a Vigreux column; b.p. 97–97.1°. The halogens and the solvent, carbon tetrachloride, were purified by methods described earlier.¹⁰

Instrumental.—The absorption spectra were recorded at 20 \pm 0.2° with the aid of a Beckman recording spectrophotometer DK-1. Moreover, the propionitrile-iodine monochloride complex was studied at 15, 20, 30, 40 and 50 \pm 0.1° with a Zeiss PMQ II spectrophotometer. Stopped silica cells of path length 1.00 cm. were used in all cases.

Results and Discussion

Propionitrile shows ultraviolet absorption bands in the region 240–265 m μ when dissolved in carbon tetrachloride. At concentrations less than 3 M, it has negligible absorption in the region 300–700 m μ . When propionitrile was added to a solution of iodine, bromine, iodine monochloride or iodine monobromide in carbon tetrachloride, a new band appeared, blue shifted relative to the visible halogen band. The new band increased in intensity with higher halogen and nitrile concentrations. In agreement with earlier work^{9,10}

it is assigned as the visible halogen band, blue shifted on complex formation. The absorption curves for the mixed solutions, containing a constant concentration of iodine monochloride and different concentrations of propionitrile, were similar to those in Fig. 1, ref. 10. An isosbestic point was observed at 417 m μ . The corresponding iodine and iodine monobromide systems had isosbestic points at 494 and 456 m μ , respectively.

The propionitrile-halogen complexes were assumed to have 1:1 stoichiometry in accordance with the results reported for other nitrile-halogen complexes.^{9,10} The formation constants of the molecular complexes were calculated by the Benesi-Hildebrand method¹¹ in the Scott modification,¹² correcting for the overlapping free halogen bands.¹⁰ Figure 1 shows the corrected B.H.S.-plots obtained at three different wave lengths for the propionitrile-iodine monochloride system. The experimental points can be fitted with straight lines in agreement with the assumption of a 1:1 complex. Similar plots were obtained for the propionitrile complexes with iodine monobromide, iodine and bromine. The formation constants K_c calculated from the plots and the values obtained for the blue shifts $\Delta\lambda$ are listed in Table I.

TABLE I
FORMATION CONSTANTS (K_c) AND BLUE SHIFTS ($\Delta\lambda$) FOR THE 1:1 COMPLEXES BETWEEN PROPIONITRILE AND HALOGENS AT 20°

| C ₂ H ₅ CN compl. with | Wave length, m μ | Calcd. K_c 1./mole | Av. K_c , 1./mole | $\Delta\lambda$, m μ |
|--|----------------------|----------------------|---------------------|---------------------------|
| ICl | 330 | 9.5 | 9.7 ± 0.2 | 98 |
| | 340 | 9.8 | | |
| | 350 | 9.7 | | |
| IBr | 385 | 2.2 | 2.3 ± 0.1 | 70 |
| | 395 | 2.2 | | |
| | 405 | 2.4 | | |
| I ₂ | 430 | 0.41 | 0.43 ± 0.05 | 34 |
| | 435 | .44 | | |
| | 440 | .44 | | |
| Br ₂ | 345 | .10 | 0.09 ± 0.03 | 12 |
| | 350 | .09 | | |
| | 355 | .08 | | |

The nitrile-halogen interaction decreases in the order iodine monochloride, iodine monobromide, iodine and bromine as expected,¹ and in agreement with the previous nitrile-halogen studies.^{9,10} The small blue shifts observed in the weaker complexes result in large relative errors in K_c for the iodine and the bromine complexes.

The propionitrile-iodine monochloride complex was studied not only at 20°, but also at other temperatures. The absorbances at 330, 335 and 340 m μ were

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TABLE II
FORMATION CONSTANTS (K_c) AND MOLAR EXTINCTION COEFFICIENTS (ϵ) OBTAINED AT THREE WAVE LENGTHS FOR THE $C_2H_5CN-ICl$ COMPLEX

| $T, ^\circ C.$ | 330 $m\mu$ | | 335 $m\mu$ | | 340 $m\mu$ | | K_c av., l./mole |
|----------------|-----------------|--------------------------|-----------------|--------------------------|-----------------|--------------------------|--------------------|
| | K_c , l./mole | ϵ , l./mole cm. | K_c , l./mole | ϵ , l./mole cm. | K_c , l./mole | ϵ , l./mole cm. | |
| 15 | 11.2 | 90.9 | 11.3 | 103.2 | 11.5 | 116.4 | 11.3 |
| 20 | 9.5 | 89.2 | 9.8 | 102.5 | 9.8 | 115.8 | 9.7 |
| 30 | 6.9 | 88.2 | 7.0 | 101.9 | 7.2 | 114.0 | 7.0 |
| 40 | 5.5 | 87.1 | 5.6 | 99.1 | 5.5 | 111.4 | 5.5 |
| 50 | 4.1 | 85.9 | 4.2 | 97.6 | 4.2 | 109.8 | 4.2 |

measured for solutions containing $7.203 \times 10^{-3} M$ iodine monochloride and nitrile concentrations ranging from 0.1562 to 1.5621 M . Separate B.H.S.-plots were calculated at each temperature from the three sets of absorption data. The concentrations were corrected for the thermal expansion of carbon tetrachloride.

In Table II are listed the values for K_c and the molar extinction coefficients ϵ obtained at different temperatures. In Fig. 2, $R \ln K_c$ is plotted vs. $1/T$, and a straight line has been fitted with a least squares method. The following thermodynamic functions have been calculated at 25° from the slope and position of the straight line: $K_c = 8.3 \pm 0.2$ l./mole, $\Delta H_c^\circ = -5.2 \pm 0.2$ kcal./mole, $\Delta F_c^\circ = -1.25 \pm 0.05$ kcal./mole and $\Delta S_c^\circ = -13.1 \pm 1.0$ e.u.

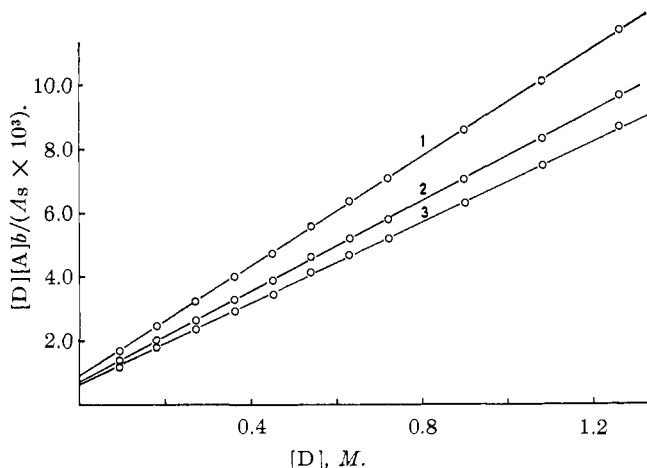


Fig. 1.—Benesi-Hildebrand-Scott plot for the $C_2H_5CN-ICl$ complex. The curves 1, 2 and 3 are obtained at 330, 340 and 350 $m\mu$, respectively.

The data show that the propionitrile-iodine monochloride complex is of intermediate stability. To the author's knowledge, no thermodynamic functions are available for any other nitrile-halogen complexes. However, the values found for the propionitrile-iodine monochloride system are probably of some significance also for other aliphatic, saturated nitriles, which show about the same formation constants with iodine monochloride⁸ at 30° . The chemical reactions taking place in the propionitrile-iodine monobromide solutions and the larger relative errors in the formation constants of the iodine and bromine complexes prevented a similar investigation of these systems.

Propionitrile has a lower ionization potential than acetonitrile [$I(CH_3CN) = 12.39$ e.v. and $I(C_2H_5CN) = 11.85$ e.v.¹³] in agreement with the stronger electron-releasing effect of an ethyl compared to a methyl group. Accordingly, propionitrile should be the stronger donor. The formation constants reported by Popov

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and Deskin for the acetonitrile complexes⁹ measured at 25° in carbon tetrachloride are 6.9, 1.40 and 0.57 for the iodine monochloride, iodine monobromide and iodine, respectively. Accordingly, propionitrile is the stronger donor toward the two interhalogens. The contradictory result for the iodine complexes may be due to the large experimental uncertainties in the determination of these small formation constants.

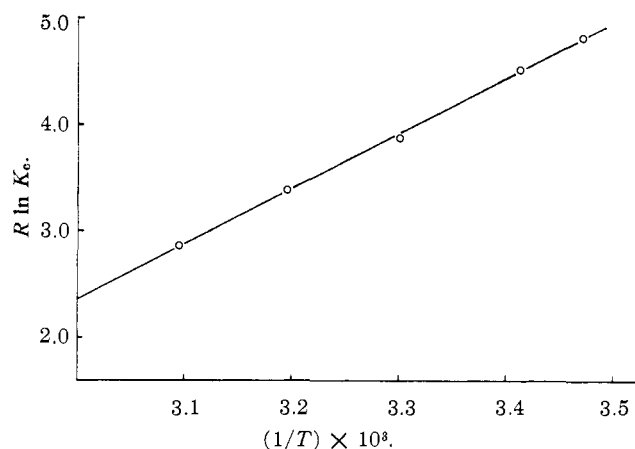


Fig. 2.—Plots of $R \ln K_c$ vs. $1/T$ for the $C_2H_5CN-ICl$ complex in carbon tetrachloride.

In agreement with the previous results reported for benzonitrile,¹⁰ no charge transfer bands were observed in the transparent region of carbon tetrachloride above 250 $m\mu$ in any of the present systems. The investigation was further extended down to 220 $m\mu$, using cyclohexane as a solvent. The absorption of the mixed nitrile halogen solutions still appeared to be a superposition of the component absorptions. Considering the high ionization potentials of these donors,¹³ the charge transfer bands may be situated at still lower wave lengths.

The absorption spectra of the bromine and iodine monobromide complexes with propionitrile changed considerably with time, probably due to substitution reactions caused by these reactive halogens. However, the iodine and iodine monochloride complexes showed negligible changes in their visible absorption spectra for several days. Therefore, a conversion from an outer to an inner complex as suggested by Popov and Deskin in the acetonitrile-iodine monochloride system⁹ seems unlikely in the present case. The present results indicate that the time-dependent changes observed in the acetonitrile⁹ and benzonitrile¹⁰-iodine monochloride solutions may be due to substitution reactions.

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