[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Infrared Absorption by the $C\equiv N$ Bond in Addition Compounds of Nitriles with Some Inorganic Halides[1]

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Addition compound formation between organic nitriles and inorganic halides results in an increase in the $C\equiv N$ stretching frequency and a marked increase in absorption by the cyanide group. The spectra reveal that in benzene solution boron trifluoride and boron trichloride addition compounds are undissociated and that nitrile–tin tetrachloride complexes dissociate to a greater extent than nitrile–titanium tetrachloride complexes.

The infrared absorption spectra of addition compounds of organic nitriles with boron trifluoride, boron trichloride, titanium tetrachloride and tin tetrachloride were investigated to ascertain the effect of nitrogen-to-metal bonding on the $C\equiv N$ stretching vibration and to determine the extent of dissociation of these addition compounds in benzene solution. Cryoscopic and dielectric constant measurements on benzene solutions of addition compounds of nitriles with titanium tetrachloride and tin tetrachloride have been reported by Nespital and co-workers.[3] These authors have concluded that in dilute solution the 2:1 complexes between the nitriles and titanium tetrachloride are dissociated into the 1:1 complexes and free nitriles, whereas free tin tetrachloride is present in the equilibrium mixture formed by dissolving a 2:1 complex of a nitrile with this acceptor molecule.

Experimental

Preparation and Purification of Compounds.—The addition compounds of boron trifluoride with nitriles were prepared by passing the gas into an ice-cooled flask containing the nitrile until the whole mass solidified. The compounds were sublimed as white solids at 20–30° and 100 mm. immediately before spectral measurements. They were analyzed for boron by alkaline hydrolysis of the sample followed by differential titration with hydrochloric acid and sodium hydroxide, using mannitol.

The addition compounds of nitriles with boron trichloride were prepared by simultaneous dropwise addition of equimolar carbon tetrachloride solutions of the nitrile and boron trichloride to 50 ml. of carbon tetrachloride in a 300-ml. flask with stirring. The white solids formed were suction filtered in a dry box. The compounds were sublimed at 50–55° and 1 mm. The sublimates were collected on a coldfinger maintained at 5–10° and analyzed for boron by differential titration and for chlorine gravimetrically.

The tin tetrachloride and titanium tetrachloride addition compounds were prepared by adding the tetrachloride to the liquid nitrile until the whole mass solidified. The reactions were carried out in a dry box and the reaction mixtures maintained at about 10°. The tin compounds were sublimed at 40–50° and 1 mm., yielding colorless crystals. The titanium compounds were sublimed at 80–90° and 1 mm., yielding yellow crystals. $(CH_3CN)_2TiCl_4$ and $(C_6H_5CN)_2TiCl_4$ are only slightly soluble in benzene. The compounds were analyzed for tin and titanium by the method of Hillebrand and Lundell,[4] and after removal of the metal were analyzed gravimetrically for chlorine. Melting points and analyses are listed in Table I.

Attempts to prepare addition compounds of nitriles with germanium tetrachloride were unsuccessful.

Trimethylamine–boron trichloride was prepared by the simultaneous addition of benzene solutions of the two components. The product was crystallized from ethanol, m.p. 246° in a sealed tube.[5] Trimethylamine–boron trifluoride was prepared by passing the two gases into dry petroleum ether with stirring and cooling. It was sublimed at 20–30° and 100 mm., m.p. 146–147°.[6]

Infrared Spectra.—Absorption measurements were obtained with a Beckman IR-2 recording spectrophotometer using a lithium fluoride monochromator in the 3–5 μ region and rock salt optics for measurements at longer wave lengths. Spectra of solutions were obtained in cells with rock salt windows. Some measurements were made in Nujol mulls and in potassium bromide disks.[7] The instrument was calibrated with carbon dioxide, taking 4.260 μ as the minimum of the absorption band in this region.

Calculations.—Absorbance–concentration curves were obtained for each of the nitriles in benzene solution. Concentrations of free nitrile in solutions containing the partially dissociated addition compounds were determined by a comparison of the absorbances of the unshifted peak with these curves. In the spectra of the addition compounds of nitriles with tin tetrachloride the absorption values of the unshifted peak were affected by the shifted peak. In evaluating the absorbances of the unshifted peaks in these complexes it was assumed that the shifted peak is symmetrical, as it is in the spectra of the addition compounds of titanium tetrachloride. The absorption data are listed in Table I. The next to last column gives the fraction of nitrile in the addition compound and the last column lists the ratio of the extinction coefficient of nitrile in the addition compound to that of the free nitrile.

Discussion

It is evident from the data of Table I that the formation of the nitrogen-to-metal bond results in an increase in the stretching frequency of the $C\equiv N$ triple bond. This increase ranges from 29 cm.$^{-1}$ in $(C_6H_5CN)_2SnCl_4$ to 111 cm.$^{-1}$ in two of the boron trifluoride addition compounds. The formation of addition compounds by benzonitrile is expected to bring about an increased contribution of the highly polar $^+C_6H_5{=}C{=}N^-$ structure, resulting in a smaller frequency increase than in the addition compounds of the aliphatic nitriles. Such an effect is evident only for the tin complexes. The increase in the $C\equiv N$ stretching frequency on coordination is in contrast to the decrease in the $C{=}N$ stretching frequency on addition compound formation[8] and on chelation,[9] and in the $C{=}O$ stretching frequency on chelation.[10]

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TABLE I

ANALYTICAL DATA AND ABSORPTION CHARACTERISTICS OF BENZENE SOLUTIONS[a]

Compound	M.p., °C.	Chlorine, %		B, Ti or Sn, %		C_2	ν_N, cm.$^{-1}$	ν_A	$\Delta\nu$	C_N	$C_A/2C_2$	ϵ_A/ϵ_N
		Calcd.	Found	Calcd.	Found							
$CH_3CN:BF_3$				9.95	10.3	0.213	2248	2359	111	0		
$C_2H_5CN:BF_3$				8.81	9.76	.450	2244	2337	93	0		6.7
$C_2H_7CN:BF_3$				7.90	8.15	.194	2244	2337	93	0		6.8
$C_6H_5CN:BF_3$				6.33	7.51	.156	2225	2336	111	0		3.5
$CH_3CN:BCl_3$	d. 180	67.22	66.4	6.84	7.04	.177		2357	109	0		
$C_2H_5CN:BCl_3$	142	61.76	61.3			.124		2339	95	0		15
$C_3H_7CN:BCl_3$	92	57.12	56.7			.190		2337	93	0		13
$C_6H_5CN:BCl_3$	167	48.18	47.6	5.00	4.98	.058		2317	92	0		5.5
$(CH_3CN)_2TiCl_4$	154–156	52.18	51.4	17.62	18.0	Nujol		2304	56			
$(C_2H_5CN)_2TiCl_4$	102–104	47.30	47.3	15.97	16.4	0.213		2285	41	0.115	0.73	11
$(C_3H_7CN)_2TiCl_4$	100–105	43.35	43.1			.217		2287	43	.160	.63	15
$(C_6H_5CN)_2TiCl_4$	160–165	35.82	35.1			Saturated		2270	45			
$(CH_3CN)_2SnCl_4$	112–114	41.40	40.9	34.65	35.7	0.155		2303	55	Trace	.95	
$(C_2H_5CN)_2SnCl_4$	69–74	38.36	38.3			.118		2278	34	0.165	.30	11
$(C_3H_7CN)_2SnCl_4$	72–74	35.57	35.6			116		2281	37	.175	.24	16
$(C_6H_5CN)_2SnCl_4$	110	30.38	30.4			101		2254	29	.155	.30	5.0

[a] The subscripts A and N refer to nitrile in the addition compound and to free nitrile, respectively.

Along with a shift in frequency, addition compound formation results in a marked increase in absorption by the C≡N functional group. Some increase was anticipated, as the formation of the nitrogen-to-metal bond increases the electronegativity of the nitrogen atom and therefore increases the polarity of the C≡N bond. An increase in polarity is usually accompanied by an increase in transition moment, but the magnitude of the increase in extinction coefficient, 16-fold for $(C_3H_7CN)_2SnCl_4$, is surprising. The frequency increase on coördination suggests that the increase in polarity of the C≡N bond in the addition compounds is not associated with greater $^+C{=}N^-$ character for the bond.

The benzonitrile addition compounds show the smallest increase in C≡N absorption. Quantitative determinations were not made of the C≡N absorption by the acetonitrile addition compounds, as their spectra are complicated by the presence of a second absorption peak at a slightly lower frequency than that assigned to the C≡N vibration. In the spectrum of the free nitrile this peak appears at 2290 cm.$^{-1}$; it has been attributed by Herzberg[11] to an overtone which has borrowed its intensity from the neighboring fundamental. This peak shifts to 2335, 2338, 2271 and 2271 cm.$^{-1}$ in the addition compounds with boron trifluoride, boron trichloride, titanium tetrachloride and tin tetrachloride, respectively.

The addition compounds of nitriles with boron trifluoride and with boron trichloride are undissociated in benzene solution. The data of Table I reveal that the addition compounds of tin tetrachloride are dissociated to a greater extent than those of titanium tetrachloride. In the solutions of the two soluble titanium complexes more than 50% of the nitriles are involved in complex formation, indicating the presence of some 2:1 complexes. In all the tin complexes except that with acetonitrile less than half of the nitrile molecules are involved in complex formation, indicating the presence of some free tin tetrachloride in the equilibrium mixtures. These data are in accord with the interpretation of the cryoscopic and dielectric constant measurements.[3]

The spectra do not give positive evidence for the presence of 1:1 complexes between nitriles and titanium and tin tetrachlorides. Investigations in this Laboratory have shown that the C≡N stretching frequency in complex cyanides, such as $K_4Fe(CN)_6$, is a function of the charge on the metal atom. This suggests that the 1:1 complex between a nitrile and a metal halide should absorb at a slightly different frequency than the 2:1 complex. Only one shifted peak was observed in the spectra of the addition compounds in solution, and the frequency of the maximum did not change with dilution.

The large moment, 7.74 debyes, obtained for the addition compound of acetonitrile with boron trichloride,[12] indicates the presence of a nitrogen-to-boron coördinate bond. Attempts were made to determine the absorption frequency associated with this bond. Peaks observed in the spectra of various nitrile–boron trifluoride compounds have a mean frequency of about 850 cm.$^{-1}$, and those for various nitrile–boron trichloride compounds have a value of about 890 cm.$^{-1}$. The spectrum of trimethylamine–boron trifluoride showed a maximum at 920 cm.$^{-1}$ and that of trimethylamine–boron trichloride at 965 cm.$^{-1}$. These peaks appeared only in the spectra of the addition compounds and did not vary by more than 5 cm.$^{-1}$ from benzene solutions to Nujol mulls to potassium bromide disks. They compare with maxima at 870 and 920 cm.$^{-1}$ observed in this Laboratory in the spectrum of bis-(N-methylsalicylaldimino)-beryllium and attributed to O–Be and N–Be stretching vibrations.

This investigation is being extended to determine the relative donor properties of nitriles and various ethers.

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