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Oxidation of the Tricyanomethanide Ion: the Tricyanocarbonium Ion

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The tricyanomethanide ion, $C(CN)_3^-$, loses two electrons when reaction occurs with strong oxidizing agents. Reaction of chlorotricyanomethane with antimony pentachloride by direct combination or in solution yields a 1:1 adduct, $ClC(CN)_3 \cdot SbCl_5$, which sublimes and is weakly ionic in dichloromethane. Conductance titrations and ^{13}C NMR spectra are in qualitative agreement with the molecular nature of the adduct and that ionic species are probably $C(CN)_3^+$ and $SbCl_6^-$. The spectroscopic properties of $C(CN)_3^-$ and $C(CN)_3^+$ are discussed.

Introduction

During an effort to obtain nitrogen donor ligands of obligate trigonal symmetry we considered the reduction of the tricyanomethanide ion, $C(CN)_3^-$, for which a convenient method of synthesis had been found by Trofimenko, Little and Mower [1]. However, our efforts at reduction using Raney nickel, lithium aluminum hydride, and sodium borohydride were unsuccessful [2]. Having a supply of potassium tricyanomethanide on hand, it was decided to further investigate the properties of the tricyanomethanide ion. Of particular interest were experiments which could lead to synthesis of the tricyanocarbonium ion, $C(CN)_3^+$. In the process, we have observed additional spectroscopic properties of $C(CN)_3^-$, have prepared the 1:1 adduct of $ClC(CN)_3$ with antimony pentachloride and have found some evidence for the formation of $C(CN)_3^+$ as a transient and/or low concentration species in solution.

Experimental

Synthesis of $KC(CN)_3$ and $ClC(CN)_3$

Potassium tricyanomethanide was prepared from commercial malononitrile, potassium cyanide, and bromine from a variety of commercial sources according to the method of Trofimenko *et al.* [1]. After recrystallization from acetonitrile, dried $KC(CN)_3$ (1.61 g, 12.5 mmol) was placed in a 100 ml flask having a vacuum stopcock and a ₸ Joint at the neck for access. After a brief period of dynamic evacuation while the $KC(CN)_3$ was heated with a hot air blower, chlorine gas (0.35 g, 5.0 mmol) was condensed into the flask with liquid nitrogen. Upon warming to room temperature, colorless, transparent needles of chlorotricyanomethane, $ClC(CN)_3$, appeared on the walls of the flask. The flask was cooled to ice temperature before the contents were briefly subjected to dynamic vacuum, after which product was removed by trap-to-trap sublimation. Except for pumping losses, the yield appeared to be quantitative although a very small amount of white deposit was left upon the glass after $ClC(CN)_3$ had been removed.

Mass Spectrum of $ClC(CN)_3$

With an AEI MS 12 spectrometer, a low-resolution mass spectrum of $ClC(CN)_3$ was obtained by insertion of a solid-charged capillary.

Potentiometric Titrations of $KC(CN)_3$

Standardized aqueous solutions of sodium hypochlorite, cerium(IV) hydrogen sulfate, and potassium permanganate were used to titrate 1.6–1.7 mmol aqueous samples of $KC(CN)_3$ under various temperature and acidity conditions. While several of the $KMnO_4$ titration end-points were observed visually, the majority of the titrations were monitored potentiometrically using platinum sensing and calomel reference electrodes with a Beckman Expandomatic pH meter.

Reaction of $ClC(CN)_3$ with $SbCl_5$

Approximately 5 mmol (0.6 g) $ClC(CN)_3$ was sublimed in vacuum to a 2 X 10 cm cylindrical vessel made from commercial 24/40 ₸ joint parts and which was fitted with a polytetrafluoroethylene stopcock. After transferring the vessel to a glove bag filled with dry nitrogen, a measured volume of liquid antimony pentachloride (Mallinkrodt Reagent) was

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added directly with a syringe-driven 1 ml graduated pipet. Immediate reaction occurred resulting in formation of a yellow-white crystalline solid. The closed vessel was returned to the vacuum line and repeatedly exposed to vacuum for several second intervals over a span of five minutes. Table II summarizes the amounts of reagents used and the residual material remaining.

Infrared and Raman Spectra

An IR spectrum of $KC(CN)_3$ as a mineral oil mull was obtained over 625–4000 cm^{-1} while its aqueous solution was used to obtain the Raman spectrum. For $ClC(CN)_3$, the spectrum of the vapor over the solid at ambient temperature was obtained in a 10 cm cell with NaCl windows. Attempts at satisfactory spectra of $SbCl_5 \cdot ClC(CN)_3$ were thwarted by its reactivity towards mulling agents, solvents, and window materials, due in large part to traces of moisture we were unable to remove. Nonetheless a partial spectrum was obtained as a mull in mineral oil obtained from a jar in which lithium metal had been stored for several years. A partial Raman spectrum of the solid was obtained from a rotating capillary. The infrared spectra were obtained with a Beckman IR-8 while the Raman spectra were observed with a Spex Industries Model 1400 using the 5145 Å line of the argon laser operated at 600 mwt.

Ultraviolet Spectra

Aqueous solutions of $KC(CN)_3$ in 1 cm silica cells were observed with a Heath/McPherson 721 spectrophotometer in the 190–360 nm region. Over the same region a spectrum of $ClC(CN)_3$ was obtained in 95% ethanol solution. The ultraviolet spectrum of $SbCl_5 \cdot ClC(CN)_3$ was not attempted for the same reasons which made it difficult to obtain an infrared spectrum.

Nuclear Magnetic Resonance

With 75% CH_2Cl_2–25% $CDCl_3$ dried over 5 Å molecular sieve as general solvent, ^{13}C NMR spectra were observed for the following solutions: (a) 0.25 *M* $ClC(CN)_3$, (b) 0.25 *M* 1:1 adduct of $SbCl_5$ to $ClC(CN)_3$ by addition of the former to solution (a) with microsyringe, (c) $SbCl_5 \cdot ClC(CN)_3$ by addition to solvent of the dry product from the synthesis above. A spectrum of $KC(CN)_3$ was obtained with the salt dissolved in hexadeuteroacetone. The instruments employed were a Brucker WH-90 and an IBM NR-80. As internal field standards, $CDCl_3$ and CH_2Cl_2 were assumed to have chemical shifts of 77.0 and 53.8 ppm from tetramethylsilane, respectively. Pulse widths ranging from 2.5 to 3.5 μsec were employed while the delay before signal acquisition varied from 83 μsec to 40 sec.

Conductivity Titration of $ClC(CN)_3$ Solution with $SbCl_5$ Solution

Methylene chloride (J. T. Baker 99.9% Photrex) was first dried with both Al_2O_3 and 5 Å molecular sieve and later with only larger amounts of molecular sieve. In a nitrogen-filled glove bag, solutions 0.1 *M* in $SbCl_5$ were prepared by direct addition with microsyringe of liquid $SbCl_5$ to 25 ml dry CH_2Cl_2; the amount transferred was observed by weight. Solutions 0.1 *M* in $ClC(CN)_3$ were prepared by addition of the weighed solid to 25 ml dry CH_2Cl_2.

A closed vessel consisting of 4.5 × 9 cm round-bottom tube and a rubber stopper with three holes was prepared. Through the holes were fitted the delivery tip of a 10 ml buret, a dipping conductivity probe (Industrial Instruments K01: 1 cm^2 platinum coated with platinum black electrodes at *ca.* 1 mm separation), and a connection for a U-tube containing 5 Å molecular sieve. A small magnetic stirring bar coated with polytetrafluoroethylene was added to the vessel.

In the glove bag, the 10 ml buret was filled with $SbCl_5$ solution by suction and the titration vessel was filled with 9.00 ml dry CH_2Cl_2 and 1.00 ml of the $ClC(CN)_3$ solution. Subsequently, the apparatus was removed from the bag and the conductance cell was connected to a General Radio 1608-A impedance bridge which allowed for measuring conductance under conditions of changing capacitance.

In order to observe conductance values typical of a strong electrolyte in CH_2Cl_2, 0.100 *M* tetra(n-butyl)ammonium iodide was prepared with the same solvent as the reagent solutions. Incremental addition to 25 ml dry CH_2Cl_2 established the relative conductance for a strong electrolyte. All conductance measurements were volume-corrected before interpretation.

Results and Discussion

Synthesis of $ClC(CN)_3$

Direct addition of a less-than-equivalent amount of gaseous chlorine to solid $KC(CN)_3$ is a convenient route for preparation of small quantities of $ClC(CN)_3$. The previously employed methods of Trofimenko *et al.* and of Kukhar' *et al.* have used chlorine and sodium hypochlorite in a variety of solvents including water [3]. Allowing the reaction between chlorine and $KC(CN)_3$ to occur directly and without solvent simplifies isolation and purification to a simple pumping-off and trap-to-trap sublimation. Spectroscopic analysis (IR, NMR, and mass spectrum) confirms the product to be $ClC(CN)_3$.

Mass Spectrum of $ClC(CN)_3$

The prepared chlorotricyanomethane displayed a mass spectrum consistent with the assumed formula.

TABLE I. Oxidation Titrations of $KC(CN)_3$.

Oxidant	Temperature	Acidity	Potentiometric End Point Sharpness	No. of Trials	Ave. Equivalents per Mol $KC(CN)_3$
$Ce(HSO_4)_4$	ambient	0.3 *M* H_2SO_4	broad	1	1.87
	2 °C	0.3 *M* H_2SO_4	broad	1	1.72
$K_2S_2O_8$	ambient	1 *M* $NaClO_4$	none observed*	1	–
$KMnO_4$	0	2 *M* H_2SO_4	colorimetric	6	2.03
	22.5	2 *M* H_2SO_4	colorimetric	6	2.04
	ambient	2 *M* H_2SO_4	sharp	1	1.96
NaClO	ambient	1 *M* HNO_3	sharp	3	2.05

*Trace of silver nitrate added as catalyst.

TABLE II. Mass Stoichiometry of $SbCl_5$–$ClC(CN)_3$ Adduct.

Trial	$SbCl_5$ mass (mmol)	$ClC(CN)_3$ mass (mmol)	Mass Residue (mass removed)	Substance Removed*
1	1.516 g (0.507)	0.639 g (0.509)	2.056 g (0.099 g)	not identified
2	1.563 (0.523)	0.681 (0.543)	2.192 (0.052)	$ClC(CN)_3$, HCl

*In Trial 1 the adduct mixture was pumped off directly to vacuum while in Trial 2 the volatile materials were collected by trap-to-trap distillation in vacuum using liquid nitrogen. Substances identified by infrared spectrum.

While the parent peaks were at 125 and 127 amu, extensive fragmentation occurred yielding fragment masses at 99, 90, and 73 amu of greater intensity than the parent peak. Also, metastable species resulted in broad peaks at 42.6 and 44.3 amu. The former are consistent with the formation of stable fragment ions $ClC(CN)_2^+$, $C(CN)_3^+$, and $(CN)_2^+$, respectively, while the metastable peaks indicate abscission of neutral $(CN)_2$ from the parent ions.

Oxidation of $KC(CN)_3$

Influenced by the ease of chlorination of $KC(CN)_3$ to $ClC(CN)_3$ and by the presence of the large $C(CN)_3^+$ peak in the mass spectrum of the latter, we attempted solution oxidation titrations of $KC(CN)_3$ to see if the tricyanocarbonium ion could be observed. A number of oxidizing agents did react with aqueous $KC(CN)_3$ but not all of the reagents yielded quantitative results. In all cases, the oxidation product(s) fairly rapidly reacted to form reddish-brown solution and solids. This tendency has been previously observed by others for both $HC(CN)_3$ and $ClC(CN)_3$ and it is likely that $C(CN)_3^+$, if formed, would behave similarly.

We observed that quantitative results could best be obtained with freshly standardized $KMnO_4$ and NaClO solutions with the titrations performed fairly rapidly. In both cases oxidation of $C(CN)_3^-$ by two electrons was indicated although $C(CN)_3^+$ was not observed as a stable species. With NaClO, $ClC(CN)_3$ is doubtless the short-term dominant oxidation product. If $C(CN)_3^+$ is formed in these aqueous reactions, it is only as a transient ion. Table I summarizes these results.

Reaction of $ClC(CN)_3$ *with* $SbCl_5$

Direct combination of chlorotricyanomethane with antimony pentachloride results in immediate formation of a product markedly different from either reactant. While these are, respectively, an easily sublimable colorless solid and a yellow liquid, the product is an off-white solid of very low vapor pressure which is also very slowly sublimable. That the product of direct combination is a 1:1 adduct is first suggested by the residual mass after brief pumping on the product or after trap-to-trap removal of the volatile material. When $ClC(CN)_3$ was in excess, it was readily identified as the predominantly removed substance by its infrared spectrum. Table II shows the results of two such combination reactions.

Infrared and Raman Results

Spectroscopic analysis of the solid product presented difficulties which we were able to surmount only partially with the facilities available to us. Although the adduct is stable in glass under vacuum and in dry inert atmosphere conditions, we were able to obtain only poor infrared and no ultraviolet spectra. Reactivity with airborne moisture, solvents, solvent moisture, mulling agents, and cell

TABLE III. Infrared and Raman Bands.

$KC(CN)_3$		$ClC(CN)_3$	$SbCl_5 \cdot ClC(CN)_3$	
IR	Raman	IR	IR[c]	Raman[d]
	139w, dep			139m, broad
	(162)[a]			143m
				183w
				191m
				298m
				345s
				367w
				381m
				508w
	660w, pol			
	678w, pol[b]			
			855s	
		862s		
				863w
		890m		
960w				
		995w		
1005w				
			1058 1064 } s	
		1075s		
		1107w		
1228 1238 } m				
1256w				
		1377m, broad		
			1560m	
1690w[b]				
			1700m	
	2168s,dep			
2170s	2222vs,pol			
			2260w	
		2265s		
				2266w
				2298 (?) vw
			2360vw	
	2487 (?) w, broad[b]			
2500w[b]				
	2925m, pol[b]			
3405w[b]				

[a] Peak observed by Long *et al.* (Ref. 4) not present in our spectrum. [b] Peaks not observed by Long *et al.* (Ref. 4). [c] Sample partially hydrolyzed as evidenced by large, broad OH band. [d] General loss of peak intensities as spectrum was recorded suggests decomposition. Polarization measurements not attempted.

windows (NaCl) was typified in that the material produced a slow darkening in even the chlorofluorocarbon grease in the ground glass joints of its container. A partial Raman spectrum was obtained with insufficient detail to provide a basis for interpretation. In Table III we present our partial infrared results along with spectra for $KC(CN)_3$ and $ClC(CN)_3$.

Our spectrum of $KC(CN)_3$ is essentially the same as that observed by Long *et al.* with the exception that we observed the higher energy combination bands at 2500 and 3405 cm^{-1} in the infrared and at 2925 cm^{-1} in the Raman spectrum [4]. In going from $KC(CN)_3$ to $ClC(CN)_3$, the asymmetric CN band moves to higher energy. This is in agreement with molecular orbital calculations which show the highest filled orbital of $C(CN)_3^-$ to have antibonding character between C and N. The C–Cl stretch presumably occurs below the range of our instrument.

TABLE IV. ^{13}C NMR Spectra.

Compound	Nitrile C Chemical Shift, ppm*	Central C Chemical Shift, ppm*	Pulse Width, μsec	Delay sec	Acquisition Time, sec	No. of Pulses
(a) $KC(CN)_3$[a,b]	121.1	4.94	3.0	83μ	1.36	41,395
(b) $ClC(CN)_3$[a,b,c]	104.4	27.6(vw)	3.5	83μ	1.36	7,048
(c)	104.5	27.5	3.0	10	0.68	6,604
(d) $SbCl_5 \cdot ClC(CN)_3$[c,d]	104.4	not observed	2.5	83μ	0.68	85,844
(e)	104.6	not observed	3.0	10	0.68	1,423
(f)	105.0	not observed	3.0	40	0.68	713

*Shift from TMS with $CDCl_3$ assigned 77.0 and CH_2Cl_2 53.8 ppm. [a]Spectrum previously observed by Zefirov *et al.* (ref. 8). [b]Solvent = acetone-d_6. [c]Solvent = 75% CH_2Cl_2, 25% $CDCl_3$. [d]First sample (d) is solid $SbCl_5 \cdot ClC(CN)_3$ dissolved in solvent while (e) and (f) were prepared *in situ*.

Upon examination of the infrared and Raman spectra of the $SbCl_5 \cdot ClC(CN)_3$ adduct, some conclusions are possible despite the quality of the observed spectra. First, the lower energy Raman bands suggest that $SbCl_5$ has gone to a moiety of C_{4v} symmetry rather than to the octahedral $SbCl_6^-$ ion [5, 6]. Although our weak Raman spectrum does not contain the low-intensity Sb–N stretch found in the 219–232 cm^{-1} region, this does not prove the absence of that linkage [7]. In the higher energy C=C and C=N region we observed bands at 1560 and 1700 cm^{-1} in the infrared. These could be associated with the adduct or with its hydrolysis product(s). That hydrolysis might have occurred was indicated by the strong, broad OH band at 2800 to 3600 cm^{-1} despite the assumed dryness of the mineral oil and efforts to exclude moisture during mull preparation.

In the C≡N region, only weak bands were observed in both the infrared and Raman spectra. The poorness of the spectra, decomposition and hydrolysis of the adduct, and/or conversion to C=C=N are rationalizations for this. In both the spectra, however, a weak band occurs near the energy of the C≡N band in $ClC(CN)_3$.

NMR Spectra

Little change is observed in going from the spectrum of $ClC(CN)_3$ to that of the 1:1 adduct (Table IV). The same spectrum was observed from addition of the prepared solid to solvent as was obtained by addition of a stoichiometric amount of liquid $SbCl_5$ to 0.25 *M* $ClC(CN)_3$ previously dissolved in the same solvent.

The greatest difference between the NMR spectra of $ClC(CN)_3$ and the 1:1 adduct is the disappearance of the signal from the central carbon. While the nitrile carbon signal remains unsplit and at virtually the same chemical shift as in $ClC(CN)_3$, the central carbon signal is unobservable under the same conditions. Allowing a 40 second delay before signal acquisition yielded no signal significantly stronger than background noise. Zefirov *et al.* added chromium(III) acetylacetonate as relaxation agent to solutions of $ClC(CN)_3$ and related compounds to obtain ^{13}C spectra [8]. This technique was not used by us out of concern that the reagent would react with $SbCl_5$ or $SbCl_5 \cdot ClC(CN)_3$.

Our interpretation of the spectrum of the 1:1 mixture is that a 1:1 molecular adduct does occur in solution and that the motion of the central carbon becomes more restricted than that of the nitrile carbons. This and the nonsplitting of the nitrile carbon signal suggests that the molecular adduct containing chlorine of $ClC(CN)_3$ bonded to antimony of $SbCl_5$ is dominant in solution. Thus the loss of signal from the central carbon atom is attributable to an increase in lattice relaxation time beyond that already observed in $ClC(CN)_3$. For $C(CN)_3^-$, Zefirov *et al.* estimate that T_1 for the central carbon exceeds 100 sec [8].

Conductivity Titrations

In an effort to obtain more information about the nature of the $SbCl_5 \cdot ClC(CN)_3$ adduct, conductance titrations were performed. One result of such a titration is shown in Fig. 1 along with part of the concentration *versus* conductance data for the strong electrolyte tetra(n-butyl)ammonium iodide.

The observed plot may be interpreted in terms of sequential reactions. First, when liquid $SbCl_5$ was added to solvent CH_2Cl_2 containing a small amount of moisture (despite drying over molecular sieves), reaction (1) occurs.

$$SbCl_5 + H_2O \rightleftharpoons SbOCl_3 + 2HCl \tag{1}$$

This adds to the $SbOCl_3$ and HCl already present as impurities in the added $SbCl_5$. Additional reactions

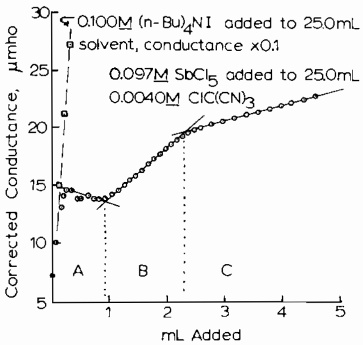

Fig. 1. Conductance measurements and titration.

(2) and (3) can occur which will increase the concentration of ionic species.

$$HCl + SbCl_5 \rightleftharpoons HSbCl_6 \tag{2}$$

$$HSbCl_6 \rightleftharpoons H^+ + SbCl_6^- \tag{3}$$

The initial sharp rise in conductance in region A of the curve is due simultaneously to the presence of these ionic species in the SbCl$_5$ solution as well as to the reaction of SbCl$_5$ with the water in the ClC(CN)$_3$ solution. At the end of region A, reaction (1) is completed. The decrease in conductance following the sharp rise may be explained by the disappearance of intermediate conductive species such as SbCl$_5$OH$^-$.

We interpret region B to be associated with the simultaneous equilibria (4) and (5):

$$SbCl_5 + ClC(CN)_3 \rightleftharpoons SbCl_5{\cdot}ClC(CN)_3,\ K \gg 1 \tag{4}$$

$$SbCl_5{\cdot}ClC(CN)_3 \rightleftharpoons SbCl_6^- + C(CN)_3^+,\ K \ll 1 \tag{5}$$

Such an interpretation is consistent with the deduction from the NMR spectra that the molecular adduct is the dominant solution species. Dissociation to ions *via* reaction (5) is consistent with the adduct's behavior as a very weak electrolyte in CH$_2$Cl$_2$,

As region C is reached, SbCl$_5$ exceeds the 1:1 ratio with ClC(CN)$_3$. That the conductance continues to increase but at a lower rate than in region B is explainable by reaction (6) which is analogous to a similar reaction for SbF$_5$ and SbF$_6^-$ [6]:

$$SbCl_5 + SbCl_6^- \rightleftharpoons Sb_2Cl_{11}^- \tag{6}$$

Thus additional SbCl$_5$ further increases the tendency of SbCl$_5$·ClC(CN)$_3$ to form ions in solution.

Approximate values for the equilibrium constants for reactions (3), (4) and (5) may be obtained from the observed conductance values from the titration of ClC(CN)$_3$ with SbCl$_5$, the conductance values from dilute tetra(n-butyl)ammonium iodide, and by use of simplifications of the exact equilibrium relationships. In terms of known concentrations C$_x$ and fractions dissociation α_y, the exact relations pertaining to region B may be written:

$$K_{ion} = \frac{[\alpha_{ion}C_{AB}(1-\alpha_{AB}) + \alpha_{HA}C_{HA}]\,[\alpha_{ion}C_{AB}(1-\alpha_{AB})]}{C_{AB}(1-\alpha_{AB})(1-\alpha_{ion})} \tag{7}$$

$$K_{AB} = \frac{1-\alpha_{AB}}{\alpha_{AB}(C_B + \alpha_{AB}C_{AB})} \tag{8}$$

Here A = SbCl$_5$, B = ClC(CN)$_3$, AB = SbCl$_5$·ClC(CN)$_3$, HA = HSbCl$_6$, K_{ion} is the equilibrium constant for reaction (5), and K_{AB} is the formation constant of reaction (4).

Interpretation of region A and comparison of the observed conductivity with that for a strong electrolyte leads to $C_{HA} = 2.16 \times 10^{-3}$ *M* (original water 1.08×10^{-3} *M*) and $\alpha_{HA} = 0.023$. Both C_{HA} and α_{HA} should remain nearly constant after completion of region A in the titration.

By assuming that K_{ion} is very small and that K_{AB} is large, it can be shown that (7) simplifies to

$$K_{ion} \approx \alpha_{HA}C_{HA}\alpha_{ion} \tag{9}$$

and that the slope S of region B should obey the relation

$$S = \frac{d[B^+]}{dC_A} \approx \alpha_{ion}(1-\alpha_{AB}), \tag{10}$$

where [B$^+$], the concentration of C(CN)$_3^+$, is equal to $\alpha_{ion}C_{AB}(1-\alpha_{AB})$ from eqn. 7.

With the above, the observed slopes, and the approximation that C_B is zero near the end of region B, one obtains approximate values $K_{AB} = 1.4 \times 10^3$ and $K_{ion} = 3.6 \times 10^{-7}$. These are in qualitative agreement with the NMR results in that 0.25 *M* SbCl$_5$·ClC(CN)$_3$ would be only 5% dissociated to SbCl$_5$ and ClC(CN)$_3$ and only 0.1% dissociated to SbCl$_6^-$ and C(CN)$_3^+$.

Ultraviolet Spectra and Electronic Structures

Although the ultraviolet spectrum of SbCl$_5$·ClC(CN)$_3$ was not obtained, we were able to obtain high quality spectra of aqueous KC(CN)$_3$ and lower quality spectra of ClC(CN)$_3$. That of KC(CN)$_3$ has been observed previously but not with sufficient variation in concentration to observe the weaker absorption bands [9, 10]. Enemark and Holm [11] have performed an extended Huckel calculation on C(CN)$_3^-$ based upon the D$_{3h}$ structure reported by Anderson and Klewe and by Bugg *et al.* [12, 13]. They assign the intense, 47,000 cm^{-1} (ϵ = 37,400) band to the $^1A_1(a_2'')^2 \rightarrow {}^1E'[(a_2'')(e')]$ transition.

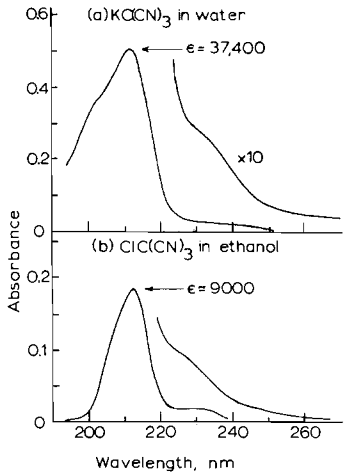

Fig. 2. Ultraviolet spectra.

For $C(CN)_3^-$ we observed two additional bands, both shoulders on the intense major absorption. At 50,000 cm^{-1} (ϵ = 18,000), there occurs a band of width comparable with that of the dominant peak. A much weaker band occurs at 42,700 cm^{-1} ($\epsilon \approx$ 1000).

In 95% ethanol, bands for $ClC(CN)_3$ were observed at 47,000 and 43,700 cm^{-1} with relative absorption coefficients of 1 and 0.108, respectively. The shape of the strong band at 47,000 cm^{-1} suggested the presence of an additional, higher energy 'hidden' shoulder centered between 48,000 and 49,000 cm^{-1}.

While the low-intensity, low-energy bands are probably associated with excitation from the σ^*, 'nonbonding', orbitals on the nitrogens into the π system, there is insufficient data here for a more complete set of assignments.

In $C(CN)_3^+$, simple Huckel treatment of the π system predicts that the C–C bonds would slightly increase in length while the C–N distance slightly decreases in comparison with $C(CN)_3^-$. Removal of two electrons from $\pi(a_2'')$ would leave the central carbon with a net positive charge near +0.4. While the total effect on the electronic spectrum is difficult to predict, it is likely that the vacancy in $\pi(a_2'')$ would result in absorption bands in the visible region. The ^{13}C NMR signal of the central carbon would be shifted downfield from its position in $C(CN)_3^-$ and beyond its position in $ClC(CN)_3$.

Summary

We have found that direct combination of chlorine and potassium tricyanomethanide without solvent is a convenient method for preparation of chlorotricyanomethane. Similarly, direct combination of the latter with antimony pentachloride results in formation of a new solid substance of low vapor pressure but which slowly sublimes. Mass stoichiometry relationships and conductance titration suggest that the solid is the 1:1 adduct $SbCl_5 \cdot ClC(CN)_3$ while solution NMR indicates that $ClC(CN)_3$ bonds to $SbCl_5$ as a Lewis base via donation from the chlorine atom. The conductance titration also suggests that this molecular adduct undergoes a small amount of ionization, possibly to $C(CN)_3^+$ and $SbCl_6^-$. Partial infrared and Raman spectra are equivocal as to whether the solid adduct features coordination via nitrogen or chlorine. That the tricyanocarbonium ion is possible is further suggested by the mass spectrum of $ClC(CN)_3$ and by the fact that $KC(CN)_3$ acts as a two-electron reducing agent with strong oxidants.

Our results suggest that the tricyanocarbonium ion could be produced chemically by reaction of species such as $XC(CN)_3$ with a Lewis acid stronger than antimony pentachloride. Also, the cation could be produced by electrolytic oxidation in an inert solvent. Spectroscopic information and molecular orbital calculations further suggest that $C(CN)_3^+$ will be colored.

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