[CONTRIBUTION FROM DEPARTMENT OF PHYSICS, UNIVERSITY OF FLORIDA]

The Infrared Spectrum of Potassium Cyanate Solutions

BY DUDLEY WILLIAMS

Penney and Sutherland[1] have collected the existing data on the vibrational frequencies of triatomic systems and have computed effective force constants by means of various approximations of the force fields involved. Triatomic systems with sixteen valence electrons are, in general, linear and the above authors have computed force constants for ClCN, BrCN, ICN and SCN^-. However, in the case of the cyanate ion OCN^-, no satisfactory data were found in the literature, and thus further experimental work on this group seemed advisable.

Pal and Sen Gupta[2] have studied the Raman spectrum of potassium cyanate solutions and report the following frequencies: 838 (1), 1229 (0), 1314 (0), and 2183 (1) $cm.^{-1}$. As the cation rarely enters into the vibrations observed for compounds in aqueous solution, the implication is that the triatomic group OCN^- ion possesses *four* vibrational frequencies, capable of producing Raman lines. This situation is rather embarrassing, since there are no harmonic relationships and the presence of a combination (such as 838 + 1314 for the observed 2183 $cm.^{-1}$) is improbable. The only previous infrared study[3] was confined to the short wave length region, the main point under consideration being a determination of the CN frequency producing a band near 4.6 μ.

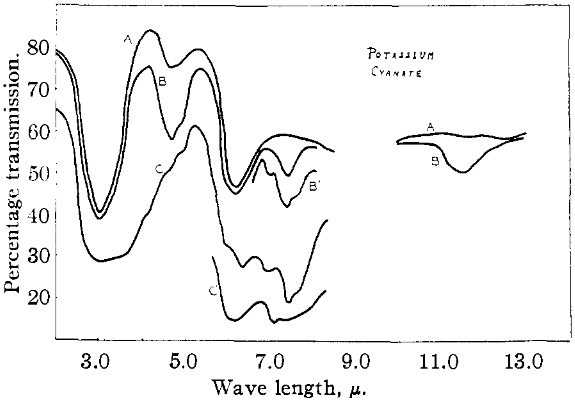

Fig. 1.—The infrared transmission of potassium cyanate solutions.

The present study covered the region 2 μ to 14 μ, a rock-salt prism spectrometer being used as a resolving instrument. Fluorite plates were used as windows for the absorption cells, cell thickness being determined by the use of 0.02-mm. mica washers. Although satisfactory for the region between 2 and 8.5 μ, the fluorite windows have intense absorption bands at longer wave lengths; therefore the galvanometer deflections even for blank comparison cells are small beyond 8.5 μ.

Several preliminary tests indicated that the spectrum of the potassium cyanate solution changed with time. Therefore it seemed advisable to study the spectrum of a solution immediately after it was prepared and then make additional studies after suitable intervals. It was found that in the spectrum of a freshly prepared solution intense bands appear at 4.6 and 11.5 μ and a weak band appears near 7.4 μ. After several days it was found that the 4.6 and 11.5 μ bands became less intense, while the absorption in the 7.4 μ region was greatly increased and additional bands appeared at 3.5 and 5.9 μ. The 7.4 μ absorption band apparently has several maxima.

In order to obtain additional information on the changes taking place in the spectrum and to attempt to identify the groups responsible for the additional bands, it was decided to measure the transmission of a saturated solution at various times for a period of ten days after preparation. The solution (in contact with excess solid) was protected as carefully as possible from the air, the container being opened only long enough for the extraction of samples each day. The results are shown in Fig. 1, the curves representing transmission of the various samples (compared with that of a fluorite blank) as a function of wave length. Curve A represents the transmission of a water cell. Curve B represents the transmission of a potassium cyanate solution immediately after preparation. (Actually forty minutes were required for a complete study of the spectral regions involved.) As one may observe, Curve B shows absorption at 4.6, 7.4 and 11.5 μ, in addition to the water bands. Curve B' shows a portion of a transmission curve obtained six hours after Curve B. The only marked variation ob-

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(1) W. G. Penney and G. B. B. M. Sutherland, *Proc. Roy. Soc.* (London), **156**, 654 (1936).

(2) Pal and Sen Gupta, *Indian J. Phys.*, **5**, 13 (1930).

(3) W. Gordy and D. Williams, *J. Chem. Phys.*, **3**, 664 (1935).

served is an increase in absorption in the region near 7 μ with additional maxima appearing near 6.9 and 7.6 μ. Although it is difficult to compare intensities in bands obtained with different cells of thicknesses of the order of 0.02 mm., it appears from a comparison with the other bands not shown in the figure that the 7 μ region of absorption is more intense than the corresponding region of Curve B. In work of this type it is difficult to duplicate cell thicknesses, but tests on water cells indicated this could be done to within 5%. After the first day the spectrum changed gradually with additional bands appearing at 3.5 and 5.9 μ and with absorption increasing in the 6.5 to 8 μ region. Curve C shows the results for the third day. After the third day the bands gradually broadened in the region beyond 3 μ and in the 6 to 8 μ region until it was impossible to separate the individual bands. Curve C′ shows the results obtained in the 7 μ region on the tenth day. The deflections obtained in the 11.5 μ region were so small that it was impossible to detect any definite changes in the band in this region. Therefore only the results for Curve B are shown, the results in the other cases not being noticeably different.

In seeking an explanation for the observed spectra, one might regard the bands in the spectrum of the freshly prepared solution at 4.6 and 11.5 μ (frequencies 2170 and 870 cm.$^{-1}$) corresponding to the observed Raman frequencies 2180 and 840 cm.$^{-1}$ as the fundamentals ν_3 and ν_1, respectively, of a linear O—C≡N$^-$ group. If this is done, one obtains the following values for the force constants

$$k_{OC} = 4.8 \times 10^5 \text{ dynes/cm. and}$$
$$k_{CN} = 16.5 \times 10^5 \text{ dynes/cm.}$$

These values are in reasonable agreement with the values for the force constants of other similar groups as given by Penney and Sutherland.[1] These values for the force constants are shown in Table I.

TABLE I

FORCE CONSTANTS OF TRIATOMIC GROUPS

Group	Frequencies, cm.$^{-1}$		Force constants, dynes/cm.	
	ν_1	ν_3	k_1	k_{CN}
ClCN	729	2201	5.1×10^5	16.7×10^5
BrCN	580	2187	4.2	16.9
ICN	470	2158	3.0	16.7
SCN$^-$	750	2066	5.4	14.4
OCN$^-$				
Raman data	840	2180	4.6	15.9
Present study	870	2180	4.8	16.5

As for the other band observed at 7.4 μ in the freshly prepared solution an assignment in terms of vibrations of an O—C≡N$^-$ group presents difficulties. Although of low intensity, this band was observed in every solution studied, and the 6.9 μ band was also usually present. An attempt to observe these bands in the spectrum of powdered potassium cyanate proved unsuccessful, but the results were not conclusive, since an entirely satisfactory sample of powder was never obtained. It is possible that the band at 7.4 μ may arise from some modification of a cyanate group present in the potassium cyanate molecule, although this seems unlikely. Another possibility is that this band may arise from cyanic acid formed by hydrolysis, as Goubeau reports a Raman frequency 1307 cm.$^{-1}$ for this acid. However, the difference between this frequency and the infrared frequency 1350 cm.$^{-1}$ seems rather large. The band at 7.6 μ (frequency 1315 cm.$^{-1}$) is in closer agreement with the Raman line reported by Goubeau.

As mentioned above, the absorption near 7 μ increases with the age of the solution and additional bands appear at 3.5 and 5.9 μ. It is possible that these bands arise from products formed in the following hydrolysis processes

$$\text{KOCN} + 3\text{H}_2\text{O} \longrightarrow \text{KHCO}_3 + \text{NH}_4\text{OH}$$
$$2\text{KOCN} + 4\text{H}_2\text{O} \longrightarrow \text{K}_2\text{CO}_3 + (\text{NH}_4)_2\text{CO}$$

The carbonate group has a very intense absorption band near 7 μ with first harmonic near 3.6 μ, while the ammonium group has bands near 3.4, 5.9 and 7 μ. Whether these groups are present as free ions or present in molecules as indicated above cannot be determined from the present data. Another indication that the cyanate ion gradually disappears from the solution lies in the disappearance of the 4.6 μ band from the spectrum of a dilute solution. There are probably intermediate steps involved in the hydrolysis reactions suggested, and the intermediate products doubtless produce further complexities in the spectrum.[4]

If the above interpretation is correct, and the frequencies of the cyanate group are ν_3 = 870 cm.$^{-1}$ and ν_1 = 2180 cm.$^{-1}$, then a third "bending" frequency should be observed in the neighborhood of 400 cm.$^{-1}$ if the angular force constant K_α is of a magnitude comparable with those of

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(4) J. W. Mellor, "Modern Inorganic Chemistry," Longmans, Green & Co., London, 1917, p. 767; V. Richter, "Organic Chemistry," Blakiston, Philadelphia, Pa., 1899, p. 417.

other similar groups. Unfortunately, this frequency has not been observed by Raman methods and, as an infrared band arising from such a vibration lies beyond the limits of rocksalt spectrometry, no data could be obtained on this point during the present study. Further study of this region seems desirable.

Summary

Measurements of the infrared transmission of potassium cyanate solutions have been made in the region 2 to 14 μ. For freshly prepared solutions intense bands were observed at 4.6 and 11.5 μ and a less intense band near 7.4 μ. In the spectra of solutions which had been allowed to stand for several days, the absorption in the 7 μ regions was found to be more intense, while additional absorption bands made their appearance near 3.5 and 5.9 μ. It is suggested that the 4.6 and 11.5 μ bands arise from vibrations of the cyanate ion, while the additional absorption is produced by ammonium and carbonate groups formed by hydrolysis.

GAINESVILLE, FLORIDA RECEIVED JUNE 24, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Contributions to the Chemistry of Indium. I. Indium Oxalate and Oxalatoindates

BY THERALD MOELLER

The formation of an insoluble oxalate of indium as a result of mixing concentrated "neutral" indium salt solutions with oxalic acid or alkali oxalate solutions has been described by Winkler,[1] and a recalculation of his analytical data for the material gives the formula $In_2(C_2O_4)_3 \cdot 6H_2O$. This precipitation also has been suggested for the microchemical detection of indium.[2]

However, it will be shown that only when oxalic acid is the precipitant do the analytical data correspond to a ratio of 1.5 oxalates to 1 indium. With sodium, potassium and ammonium oxalates this ratio becomes 2 to 1, indicating the formation of dioxalatoindates.

By analogy to aluminum, trioxalatoindates also should form. However, only compounds of unusual compositions result under conditions favorable to the formation of the trioxalato salts.

Experimental

Materials Used.—A sample of 99.98% pure indium[3] was digested with hot dilute sulfuric acid until only a small amount of the metal remained undissolved. Hydrous indium hydroxide was then precipitated from the filtered solution with ammonium hydroxide, washed, and redissolved in dilute sulfuric acid, this process being repeated three times. Finally, anhydrous indium sulfate was prepared as described by Seward.[4] Analysis proved it to be pure.

Other chemicals were of analytical reagent quality.

Analytical Procedures.—Oxalate was determined by dissolving the samples in hot 0.3 *N* sulfuric acid and titrating with standard potassium permanganate.

To eliminate the slight inhibitory effect exerted by the oxalate ion upon the precipitation of indium hydroxide, oxalate was completely destroyed by heating the weighed samples with concd. sulfuric acid until frothing ceased and sulfur trioxide fumes were evolved. The residues were then taken up in cold water, and the indium precipitated as hydroxide with ammonium hydroxide and weighed as the oxide. Addition of ammonium hydroxide to cold solutions followed by boiling the suspensions for two minutes gave precipitates which settled rapidly, filtered easily, and showed little tendency to peptize on excessive washing.

Ammonium was determined in the usual fashion by liberation of ammonia and distillation into standard acid.

Indium Oxalate Decahydrate.—To a warm solution of 1 g. of anhydrous indium sulfate in 5 ml. of water was added a solution of 0.9739 g. of oxalic acid in 10 ml. of warm water. A voluminous white precipitate formed immediately. After cooling, this precipitate was washed until sulfate-free and dried on the filter paper in a current of air at room temperature. The dry product was compact and silvery white in appearance and made up of needle-like crystals. It was somewhat soluble in cold water, more so in hot water. On ignition, indium oxide remained as residue and carbon dioxide, carbon monoxide, and water vapor were evolved.

Anal. Calcd. for $In_2(C_2O_4)_3 \cdot 10H_2O$: In, 34.07; C_2O_4, 39.19. Found: In, 34.24; C_2O_4, 39.20; C_2O_4/In, 1.493.

Dioxalatoindates.—To warm solutions of 1 g. of anhydrous indium sulfate in 5 ml. of water were added warm solutions of sodium, potassium and ammonium oxalates containing the equivalent of two oxalate ions to one indium, the volume in each case being kept as small as possible. Precipitates of white finely-divided octahedral crystals formed and were purified and dried as above. Analytical results are summarized in Table I. The presence of sodium and potassium was established by flame tests.

These compounds are but slightly soluble in cold water, more soluble in hot water, and readily soluble in hot dilute sulfuric acid.

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[1] Winkler, *J. prakt. Chem.*, **102**, 292 (1867).

[2] Huysse, *Z. anal. Chem.*, **39**, 10 (1900).

[3] From the Indium Corporation of America, Utica, New York.

[4] Seward, THIS JOURNAL, **55**, 2740 (1933).