

calculated to be 335, and the collision area of the carbon tetrachloride 22.0 sq. Å.

The conclusion is drawn that the atomic domain size of the chlorine atom is roughly the same in the gaseous molecules of carbon tetrachloride and chlorine.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE INORGANIC CHEMISTRY LABORATORY, PURDUE UNIVERSITY]

OXYCYANOGEN. II. THE FREE RADICAL

BY HERSCHEL HUNT

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Of the eight halogenoid free radicals $(\text{CN})_2$, $(\text{SCN})_2$, $(\text{SeCN})_2$, $(\text{SCSN}_3)_2$, N_3 , $(\text{TeCN})_2$, $(\text{ONC})_2$ and $(\text{OCN})_2$, the latter four have not been isolated or satisfactorily described. The author¹ has failed to check the work of Lidov. A compound of carbon, oxygen and nitrogen such as he describes was not found.

Birckenbach and Linhard² treated silver cyanate with iodine in ligroin, carbon tetrachloride, ethyl chloride, benzene and ether solutions at -20° and obtained a product which they describe as IOCN. They state that it is impossible to obtain $(\text{OCN})_x$ by this process. $(\text{SCN})_2$ and $(\text{SeCN})_2$ have been prepared in a similar manner by Söderbäck³ and Kaufmann,⁴ respectively.

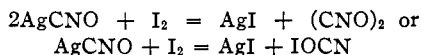
It is the purpose of this paper to describe the isolation and properties of $(\text{OCN})_x$.

Preparation

Fresh silver cyanate was prepared by precipitation from potassium cyanate and silver nitrate. The salt was carefully washed and dried. Analytical tests showed it to be free from any unchanged silver nitrate or oxidizing material. The salt was carefully dried over sulfuric acid in the dark to prevent decomposition.

The solvents which proved satisfactory for use were carbon disulfide and carbon tetrachloride. Several other common solvents, ether, alcohols and acetone, were tried but all gave difficulties of hydrolysis or side reactions. The solvents were thoroughly dried over soda lime and fractionally distilled before use.

Resublimed iodine was dissolved in the carbon tetrachloride or carbon disulfide to make a 0.05 normal solution. Greater concentrations do not react as rapidly. This solution was stirred in a mercury-sealed stirrer at room temperature for sixty days with a large excess of silver cyanate. No gas is given off but the iodine slowly disappears. This would indicate



¹ H. Hunt, *THIS JOURNAL*, **53**, 2111 (1931).

² Birckenbach and Linhard, *Ber.*, **62**, 2261 (1929); **63**, 2544 (1930); **64**, 961 (1931); **64**, 1076 (1931).

³ Söderbäck, *Ann.*, **419**, 217 (1919).

⁴ Kaufmann and Kögler, *Ber.*, **59**, 178 (1926).

When the solution became colorless, *i. e.*, when the iodine had all reacted, the stirring was stopped and the mixture examined. Since the silver cyanate was not dissolved, the silver iodide was formed only on the surface and a large percentage of the silver cyanate was left unchanged. The yellow precipitate was filtered off and treated with nitric acid. The silver cyanate decomposed leaving silver iodide corresponding to the amount of iodine consumed: g. of iodine added, 8.8, 8.0 and 6.0; g. of silver iodide found, 16.3, 14.7 and 11.1, respectively.

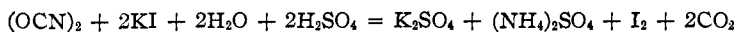
The colorless carbon disulfide solution behaves as follows. (1) On chilling to 0 to -10° a white solid separates. The white solid evaporates when the solution is left on a watch glass. While filtering off the silver iodide and silver cyanate a white solid crystallized around the top of the funnel. (2) The solution liberates iodine from potassium iodide but will not displace bromine. The liberation is faster if the solution is placed in the sunlight, indicating that we have a polymer which reacts slowly and not CNO^- . (3) The solution gives a white precipitate with Ag^+ or Ba^{++} ; the precipitate is decomposed with dilute nitric acid. (4) The solution is stable when heated in a closed tube to 100° . (5) The solution can be concentrated by distillation, the distillate being richer in oxycyanogen than the residue. If the solution is subjected to a vacuum it soon loses its oxidizing power. (6) Decomposition of the solution gave no trace of iodine, the interhalogen-halogenoid, IOCN , being thought of as one possibility. (7) The Beilstein test showed the solution to be free of any halogen. Iodine could not be displaced by stronger oxidizing agents such as chlorine or sulfuric acid.

The reaction goes faster in carbon disulfide than in carbon tetrachloride. An alcoholic solution reacts readily at room temperature but as soon as the silver iodide is filtered off the solution begins to decompose and iodine is liberated. The clear solution is a very strong oxidizer. The fresh solution probably contains IOCN .

Attempts to combine cyanogen with activated oxygen only resulted in hazardous explosions.

Analysis

The amount of $(\text{OCN})_x$ present in a given volume of solution was determined by the liberation of iodine. (See Kaufmann and Gaertner's work on thiocyanogen.)⁵



The steps of hydrolysis and reaction are presumably the same as those given for $(\text{SCN})_2$ by various authors.^{5,6}

The composition was determined by the method of Herting.⁷ $(\text{CNO})_x$ in dilute hydrochloric acid decomposes, giving ammonium chloride and carbon dioxide. The solution is then transferred to a distilling flask, made alkaline and the ammonia distilled into a standard acid. The acid is then back titrated with alkali, methyl orange being used as an indicator: grams of $(\text{CNO})_x$ present in solution as computed from iodine liberated, 0.1428, 0.1260 and 0.1470; % N_2 found, 33.30, 32.70 and 32.86; average, 32.95; % N_2 calcd., 33.33. Equal amounts of the same solution were used for the iodine liberation and the nitrogen determination. Attempts were made to

⁵ Kaufmann and Gaertner, *Ber.*, **57**, 928 (1924).

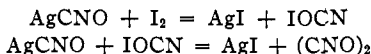
⁶ Bjerrum and Kirschner, *Kgl. Dansk. Videnskab. Selskab.* [8] I, 76 (1918); Lecher, Wittver and Speer, *Ber.*, **56**, 1104 (1923).

⁷ Herting, *Z. angew. Chem.*, **24**, 585 (1901).

determine the molecular weight but the properties of $(\text{CNO})_x$ and experimental difficulties prevent the report of a molecular weight. $(\text{CNO})_2$ is used only by analogy to $(\text{SCN})_2$.

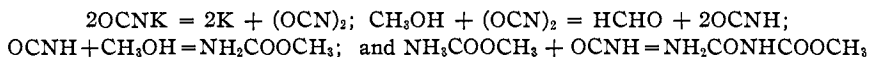
When the carbon disulfide solution of the cyanate is chilled, the white flake-like crystals which appear contain carbon disulfide. The white plates were purified by repeated fractionation. The purified crystals (plates) were found to melt at $-12 \pm 0.5^\circ$. The $(\text{OCN})_x$ decomposes quickly at room temperature when free from solvent.

Birckenbach⁸ found a secondary product in his solutions at -20° . However, he obtained mainly IOCN. Since the author could not obtain $(\text{OCN})_x$ in ether or alcoholic solutions, the two authors are now agreed. The reaction in carbon disulfide and carbon tetrachloride probably takes place in two steps



different temperatures and solvents changing the end-product of the reaction. Birckenbach did not use an excess of silver cyanate.

Birckenbach and Kellermann⁹ report that in electrolyzing an alcoholic solution of potassium cyanate they obtained an anode solution which will liberate iodine from potassium iodide and will react with copper, zinc and iron without gas evolution. They explain their results as follows



Careful repetition of this work did not yield an oxidizing solution when the alcohol was kept absolutely dry. The methyl alcohol was purified as described by Hunt and Briscoe¹⁰ for conductivity purposes. Birckenbach's apparatus was modified so as to eliminate any possibility of water being carried back with the mercury. The mercury was cleaned and dried each time before it was poured through the cathode chamber (see their description of apparatus). However, if a trace of water is added to the solution, just such a solution as they describe will be obtained. The author suggests the following explanation, which has been accepted by Birckenbach: $2\text{KOCN} = 2\text{K} (\text{amalgam}) + 2\text{OCN}^- - 2\text{E}$; $\text{CH}_3\text{OH} = \text{HCHO} + 2\text{H}^+ + 2\text{E}$; and $2\text{H}^+ + 2\text{OCN}^- = 2\text{HOCN}$, or if water is present the following: $\text{HOH} + 2\text{OCN}^- = \text{HOCN} + \text{HO}_2\text{CN} + 2\text{E}$.

Birckenbach writes that no precautions were taken to keep the solution anhydrous. Cyanic acid and formaldehyde were found in the alcoholic anode solution in large amounts. Hydrogen is not liberated at the cathode in water solution. This latter equation is in agreement with the hydrolysis of oxycyanogen. The electrolysis was then performed in an aqueous

⁸ Birckenbach, private communication.

⁹ Birckenbach and Kellermann, *Ber.*, **58**, 786 (1925).

¹⁰ H. Hunt and H. T. Briscoe, *J. Phys. Chem.*, **33**, 1495 (1929).

solution. Much larger yields of the oxidizing material were easily obtained by this method. The anode solution deposits white crystals on evaporation. A solution of the crystals shows oxidizing powers but this property is destroyed on warming the solution. The compound will oxidize methyl alcohol to formaldehyde. Further investigation is being made to determine whether the oxidizing material is a percyanic acid, HO_2CN .

Summary

1. $(\text{OCN})_x$, the free oxycyanogen radical, has been isolated and some of its properties determined.
2. An explanation is offered for the oxidizing solution obtained on the electrolysis of potassium cyanate.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 685, AND OF VASSAR COLLEGE]

THE QUINHYDRONE ELECTRODE. IV

BY OLIVE M. LAMMERT AND J. LIVINGSTON R. MORGAN

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Introduction

While a number of investigators have made determinations of the electromotive force developed between the quinhydrone and other standard half-cells in solutions other than 0.1 M hydrochloric acid, we have found no data which indicate that any extended study has been made of the effect of the composition and concentration of the solution on the reproducibility of the quinhydrone electrode itself.

Biilmann¹ tested the electrode in a number of dilute solutions ranging in P_H from 1 to 9 and compared the data with results from conductance and other measurements, with which they usually agreed to about 0.1–0.003 P_H . S. P. L. and M. Sørensen and Linderström-Lang² made a study of the inherent salt error of the quinhydrone electrode and pointed out that while the quinhydrone electrode gave the same values as the hydrogen electrode in solutions containing little or no salt it did not give the same value in solutions containing large amounts of salt or in strong acid solutions. This they explained by assuming that the electrolyte content so changed the activity ratio of quinone to hydroquinone that the potential difference measured is no longer the measure of the hydrogen-ion concentration but must be corrected by a factor other than one. Their measurements, like Kolthoff's,³ who also wrote on the reliability of the quinhydrone electrode for the measurement of hydrogen-ion concentration

¹ Biilmann, *Ann. chim.*, [9] 15, 109 (1921).

² S. P. L. Sørensen, M. Sørensen and Linderström-Lang, *ibid.*, [9] 16, 283 (1921).

³ Kolthoff, *Z. physiol. Chem.*, 144, 259 (1925).