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SMUFD d/a ltr, 8 Feb 1972

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TRANSLATION NO. 849

DATE: July 1963

DEPARTMENT OF THE ARMY
Fort Detrick
Frederick, Maryland

INORGANIC CHEMISTRY
CYANIZATION OF METALS WITH HYDROCYANIC ACID AND OXYGEN: MERCURY (*)

Note II by Member Livio Cambi and Ernestina Paglia,
presented by Member L. Cambi (**)

/Following is a translation of an article in the Italian-language periodical *Rendiconti dell'Accademia Nazionale dei Lincei (Classe di Scienze fisiche, matematiche e naturali)* (Reports of the Accademia Nazionale dei Lincei-Classes of the Physical, Mathematical and Natural Sciences), Series VIII, Vol XXVI, Fasc. 4, April 1959, pages 428-430./

The preceding Note (1) was a preliminary report on the way in which hydrocyanic acid and oxygen attack gold, with reference to their similar reaction upon mercury.

This report concerns the development of further research into this field, particularly in relation to mercury.

1. As has already been explained, this inquiry was conducted on the hypothesis that the HCN adsorbed on the surface of the metal, caused activation of the hydrogen, similar, for example, to what occurs with the organic hydrochinone compounds, the aromatic nitrogen-hydrogen derivatives, etc., which yield active hydrogen to the oxygen.

From the chemical point of view, the hypothesis can be considered as based on the formation of labile pseudo-compounds on the surface of

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(*) Research completed at the Metallurgical Chemistry Center of the National Research Council, Milan University.

(**) Read at the session of 11 April 1959

(1) L. Cambi, these Reports, 129 (1958)

the metal, considered for form's sake as having a valence of 0 (2):

$$2\,Au^{0} \leftarrow CNH + O_2 \longrightarrow 2Au^{1}CN + H_2O_2.$$

2. The process of formation of H_2O_2, to which we refer, is proof of the direct peroxidation of the hydrocyanic acid; it cannot be accounted for, as has been the general practice for gold hitherto, for example, as caused by a shift in the hydrogen brought about by the metal in the presence of CN^{-} anions (3).

The concentration of hydrocyanic ions is extremely limited in solutions of hydrocyanic acid, particularly in those acids; this fact led us to consider the possibility of an intermediate process:

$$Au^{0} \leftarrow CNH \rightleftarrows Au^{1}CN + H^{0}$$

which we shall discuss later.

3. The behavior of mercury confirms this hypothesis. We found that the metal was attacked by the HCN and by O_2, and the process precisely follows these stechiometrical patterns:

$$Hg + 2\,HCN + O_2 \longrightarrow Hg(CN)_2 + H_2O_2$$

In other words, during the initial phases, we find in solution the two products in the ratio 1 $Hg(CN)_2$: 1 H_2O_2. Thus far, we have reached concentrations of about 2 g/l of hydrogen peroxide.

The experiments were conducted in the simplest fashion. The mercury was placed in a horizontal cylinder 60 mm in diameter and 250mm in length, sealed at both ends, and equipped with tubes for gas outlet and input.

One end of the tube rested on an eccentric wooden cylinder, which imparted to it a rocking motion at six oscillations per minute, causing the metal to run back and forth. The cylinder contained about 300 g of mercury and 30cc of distilled water. The gases came from a globe containing about one litre of concentrated aqueous solution of hydrocyanic

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(2) This hypothesis leads to a consideration of compounds with coordinate values of the general type of $Me^{0}\,(CNH)_n$, in which n corresponds to the number of coordination. Obtention of such compounds, similar to those familiar to us as the carbilamines, is the object of our research.

(3) Bodlander, *Ber.* 36, 3933, (1903)

acid, with air bubbling through it to become saturated with the acid. By regulating the temperature of the hydrocyanic solution and regular renewal thereof, we maintained an almost constant concentration of HCN in the reagent tube.

The hydrocyanic acid, the hydrogen peroxide and the mercuric cyanide were measured periodically.

In two series of measurements, we worked with quantities of about 35 g/l and about 100 g/l of HCN, respectively. The speed of the process increases with the concentration of HCN, practically doubling with the rise from 35 to 100 g/l of HCN.

Thus far, we have noted no important influence of a variation in the pH of buffered solutions ranging from 4 to 9.

We show here the data on one experiment that lasted for three consecutive days, with the lower concentration of HCN at room temperature, and with pauses during the night.

1st day		2nd day		3rd day	
Hours	H_2O_2 g/l	Hours	H_2O_2 g/l	Hours	H_2O_2 g/l
1	0.170	25	0.340	46	0.490
4	0.221	28	0.442	47	0.646
9	0.340	30	0.470	50	0.986

For the process we are describing, you need a considerable excess of HCN.

4. Prolonged statis of the system, particularly at the higher concentrations of H_2O_2, leads to more or less marked regression of the content. The relative lack of HCN leads to the formation of insoluble mercury compounds, including the oxycyanides. Eventually the H_2O_2 content becomes zero.

We are also aware that, in the presence of mercury, we get the rhythmic catalytic decomposition of H_2O_2 (4), with the rhythmic formation of mercury peroxides. We observed that actually the HCN added in advance prevents or markedly reduces this decomposition effect.

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(4) Bredig & Weinmayer, "Z Phys. Ch.", 42, 601 (1903); "Antropoff. Z. Phys. Ch.", 62, 513 (1908)

This is in agreement with the relative stability of H_2O_2 which we found in strongly hydrocyanic solutions.

5. We next undertook an inquiry into the polarization of the metals we were considering under the action of HCN. We observed that gold, in the phosphoric buffer solution we used (Phosphate mono-K + phosphate bi-Na, 0.025 molar; pH = 6.88 at 20°), containing 20 to 30 g/l of HCN in an argon atmosphere, takes on a negative polarity of -0.36% -- 0.40V, with respect to the hydrogen electrode in the same buffer.

We are now conducting similar experiments with mercury. The polarization potentials, however, are markedly influenced by the pH, and are more strongly negative than was the case with gold, on the order of -0.15+ -- 0.18V.

Developments in this aspect of our research will be announced and discussed in a forthcoming Note, along with further data on the experiments of cyanidization reactions we are investigating.