UNCLASSIFIED

AD NUMBER

AD836220

NEW LIMITATION CHANGE

TO
Approved for public release, distribution unlimited

FROM
Distribution authorized to U.S. Gov’t. agencies and their contractors; Foreign Government Information; JUL 1963. Other requests shall be referred to Department of the Army Fort Detrick, Attn: Technical Release Branch [TID], Frederick, MD 21701.

AUTHORITY

SMUFD d/a ltr, 8 Feb 1972

THIS PAGE IS UNCLASSIFIED
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
dai Lincei (Classe di Scienze Fisiche, Matematische e
Naturali) (Reports of the Accademia Nazionale dei Lincei-
 Classe of the Physical, Mathematical and Natural Sciences),

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 hydrocyanine 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

(*) 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 Au⁰ ← CN⁻ + O₂ → 2Au¹CH + H₂O₂

2. The process of formation of H₂O₂, 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, by cause of a shift in the hydrogen brought about by the metal in the presence of CH⁻ anions (3).

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

Au⁰ 4 CN⁻ ←−−→ Au¹CN + P

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 O₂ and the process precisely follows these stoichiometrical patterns:

Hg + 2 HCN + O₂ → Hg(CH)₂ + H₂O₂

In other words, during the initial phases, we find in solution the two products in the ratio 1 Hg(CH)₂ : 1 H₂O₂. 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 cm in diameter and 250 cm 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 move back and forth. The cylinder contained about 300 g of mercury and 30 cc of distilled water. The gases came from a globe containing about one litre of concentrated aqueous solution of hydrocyanic acid.

(2) This hypothesis leads to a consideration of compounds with coordinate values of the general type of Me⁰ (CN)ₓ, in which x corresponds to the number of coordination. Obtention of such compounds, similar to those familiar to us as the carbamins, is the object of our research.

(3) Holmquist, Rev. 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 removal 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 6.

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.

<table>
<thead>
<tr>
<th>1st day</th>
<th>2nd day</th>
<th>3rd day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hours</td>
<td>$H_2O_2$ g/l</td>
<td>Hours</td>
</tr>
<tr>
<td>1</td>
<td>0.170</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>0.221</td>
<td>28</td>
</tr>
<tr>
<td>9</td>
<td>0.340</td>
<td>30</td>
</tr>
</tbody>
</table>

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

4. Prolonged statics of the system, particularly at the higher concentrations of $H_2O_2$, lead 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.

(4) Reddig & Weizsäcker, "Z. Phys. Ch.", 42, 601 (1933); "Antropoff, Z. Phys. Ch.", 62, 513 (1908)
This is in agreement with the relative stability of \( \text{H}_2\text{O}_2 \) 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-\( \text{K} \) + phosphate bi-\( \text{Na} \), 0.025 molar; \( \text{pH} = 6.88 \) at \( \text{25}^\circ \)), containing 20 to 30 g/l of HCN in an argon atmosphere, takes on a negative polarity of \(-0.36\% ~ - 0.40\%\) 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 \(-0.15\% ~ - 0.18\%\).

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.