**Tetrahedron Letters No.22, pp. 2501-2503, 1966. Pergamon Press Ltd. Printed in Great Britain.**

# THE ELECTROCHEMICAL REACTION OF MERCURIC CYANIDE IN THE PRESENCE OF CYCLOHEXENE[1]

Kunihisa Yoshida and Shigeru Tsutsumi
Department of Chemical Technology, Faculty of Engineering,
Osaka University, Miyakojima-ku, Osaka, Japan

**(Received 28 March 1966)**

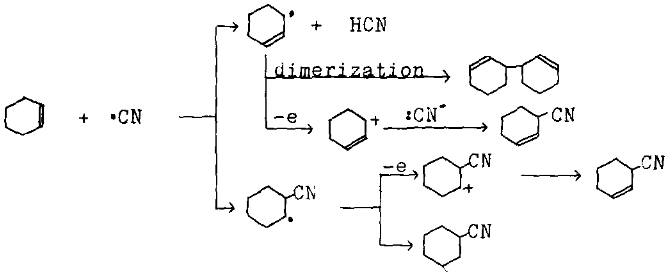
The chemistry of mercuric cyanide appears to have been little studied. In a previous paper[2] we reported the photochemical reaction of mercuric cyanide. Here we report the electrochemical behavior of mercuric cyanide.

The electrolysis was carried out by using two platinum plate electrodes (15 X 20 $mm^2$.), of which a space was 4 mm. At the beginning of the electrolysis a potential of 220 v. produced a current of 0.1 amp. In order to maintain the current (0.1 amp.), voltage was gradually shifted from 220 to 50 v. A solution of mercuric cyanide (12.6 g.) and cyclohexene (32.8 g.) in methanol (100 ml.) was electrolyzed at 10-15° for 20 hours. The electrolyzed mixture was worked up as usual to give mercury (5.7 g.), formaldehyde, hydrogen cyanide (1.1 g.), cyclohexyl cyanide (0.01 g., p-bromophenacyl cyclohexanecarboxylate, m.p. 89–90°), 3-cyanocyclohexene (0.02 g., p-bromophenacyl cyclohexene-1-carboxylate, m.p. 108–109.5°), 3,3'-bicyclohexenyl (0.07 g., tetrabromide, m.p. 157–158°), and the residues. Cyanogen and 2-cyanocyclohexene were not formed and a gas was hardly evolved.

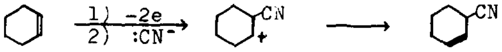
It is noteworthy in comparison with the previous observation[2] that 3-cyanocyclohexene is formed more than cyclohexyl cyanide. We posturate on the basis of the present observations that the cyanide ions, which are produced by a little dissociation of mercuric cyanide, are discharged at the anode to form cyano radicals. The following reactions of cyano radicals can then occur.

$$:CN^- \xrightarrow{-e} \cdot CN$$

$$CH_3OH + \cdot CN \longrightarrow HCN + \cdot CH_2OH$$



At the same time, cyclohexene may be oxidized in a two electron oxidation to an electrophilic intermediate which reacts with cyanide ion to form 3-cyanocyclohexene.



Further experiments concerning this subject are in progress, and the details of this reaction will be reported in a forthcoming paper.

## REFERENCES

1. A previous report from this laboratory has described that the cyano groups were introduced into aromatics by the electrochemical procedure.
K. Koyama, T. Susuki, and S. Tsutsumi, _Tetrahedron Letters_, 627 (1965).

2. K. Yoshida and S. Tsutsumi, _ibid._, 2417 (1965).