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THE PHOTOLYSIS OF ORGANOMERCURY CYANIDES

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The photolysis of diphenylmercury and related substances has been the subject of a number of investigations (1,2) in the past decade. In a recent paper (3) we reported that mercuric cyanide was photolyzed in solution to produce cyano radicals (4), but the behaviour of cyanide radicals is **uncertain.** Continuing our investigations in this field, we have studied the photolysis of organomercury cyanides.

The solution of cyclohexylmercury cyanide (15.5 g., 0.05 mole) in methanol was photolyzed at room temperature. The products consisted of mercury (5.0 g.), hydrogen cyanide (0.7 g.), bicyclohexyl (0.6 g.), cyclohexyl cyanide (0.05 g.), cyclohexylcarbinol (0.1 g.), mercuric cyanide (0.4 g.), ethylene glycol (small amount), formaldehyde (small amount), and some residue. For the purpose of comparison, the photolysis of mercuric cyanide (12.6 g., 0.05 mole) with cyclohexane (33.7 g., 0.4 mole) in methanol (150 ml.) was performed. Although the products were almost common (4.0, 0.5, 0, 0.04, and 0.1 g., respectively), it is noticeable that bicyclohexyl was not detected in the latter.

Moreover, the photolysis of phenylmercury cyanide was investigated. The results are summarized in the Table.

Table

Photolysis of organomercury cyanides in methanol

R	C_6H_{11}	C_6H_5
RHgCN (g.)	15.5	6.1
methanol (ml.)	170	170
reaction period (hr.)	24	15
hydrogen cyanide (g.)	0.7	0.3
mercuric cyanide (g.)	0.4	
RCN (g.)	0.05	trace
RR (g.)	0.6	—
RH (g.)		0.8
RCH_2OH (g.)	0.1	trace
ethylene glycol (g.)	trace	0.3
formaldehyde	trace	trace
mercury (g.)	5.0	2.3
RHgCN accounted for by mercury (g.)	8.3	3.5
RHgCN accounted for by cyano group (g.)	9.1	3.4

In neither case could we detect cyanogen.

These are consistent with the following reaction scheme:

$$RHgCN \xrightarrow{h\nu} R\cdot + \cdot HgCN$$

$$\hookrightarrow (Hg + \cdot CN)$$

$$\cdot HgCN + CH_3OH \longrightarrow HCN + Hg + \cdot CH_2OH \quad (\cdot CN + CH_3OH \longrightarrow HCN + \cdot CH_2OH)$$

$$\cdot HgCN + R\cdot \longrightarrow RCN + Hg \quad (\cdot CN + R\cdot \longrightarrow RCN)$$

$$\cdot HgCN + \cdot HgCN \longrightarrow Hg + Hg(CN)_2$$

$$R\cdot + R\cdot \longrightarrow RR$$

$$R\cdot + CH_3OH \longrightarrow RH + \cdot CH_2OH$$

$$R\cdot + \cdot CH_2OH \longrightarrow RCH_2OH$$

$$\cdot CH_2OH + \cdot CH_2OH \longrightarrow HOCH_2CH_2OH$$

$$\cdot CH_2OH \xrightarrow{-H\cdot} HCHO$$

It is probable that cyanide radicals ($\cdot$HgCN radicals) (a) dissociate to cyano radicals and mercury, (b) react with organo-radicals to form nitriles and mercury, or abstract hydrogen from methanol to form hydrogen cyanide and mercury, (c) disproportionate to mercuric cyanide and mercury, or (d) associate with organo-radicals to form organomercury cyanides.

Since the rate of photolysis of organomercury cyanides is large and in the case of the photolysis of mercuric cyanide with cyclohexane, bicyclohexyl is absent, (d) is unlikely. On the basis of Wolfrang's work (5), the formation of mercurous iodide by photolysis of organomercury iodides (2-b,c,d), and the production of mercuric cyanide* in the present work, (c) is probable. (b) is supported by Galvin's study (6), which has shown that cyanide radicals react with methyl radicals to form acetonitrile and mercury, and react with methane to form hydrogen cyanide, mercury, and methyl radicals. However, it is **impossible to** show conclusively which of the probabilities is more likely in these reactions, (a) or (b)**

(*) All mercurous salts contain the bivalent mercurous group Hg_2^{++} and changed more or less readily into mercuric salts by splitting off one atom of mercury from the molecule. Mercurous cyanide is unstable and disproportionate to mercury and mercuric cyanide.

$$Hg(NO_3)_2 + 2KCN \longrightarrow 2KNO_3 + Hg_2(CN)_2 \longrightarrow Hg + Hg(CN)_2$$

F. P. Treadwell and W. T. Hall, <u>Analytical Chemistry</u> Vol. I, p. 107. John Wiley and Sons, New York (1955).

(**) When the photolysis of cyclohexylmercury cyanide (15.5 g.) with cyclohexene (32.8 g.) in tetrahydrofuran was performed, isocyanide (3) was not detected. Therefore, (a) is less probable.

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2. The photolysis of unsymmetrical organomercury compounds appears to have been little studied:

(a) G. A. Razuvaev and G. G. Petukhov, *Zhur. Obshchei Khim.*, **21**, 646 (1951); **23**, 37 (1953).

(b) G. F. Fanta, *J. Org. Chem.*, **29**, 1610 (1964).

(c) D. H. Hey, D. A. Shingleton, and G. H. Williams, *J. Chem. Soc.*, 1958 (1963).

(d) G. E. Corbett and G. H. Williams, *ibid.*, 3437 (1964).

3. K. Yoshida and S. Tsutsumi, *Tetrahedron Letters*, 2417 (1965).

4. Although the spectroscopic and related studies of cyano radicals have been reported, very few reactions of these radicals, other than reactions in gas phase*, have been recorded.

(*) C. A. Goy, D. H. Shaw, and H. O. Pritchard, *J. Phys. Chem.*, **69**, 1504 (1965).

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