The Photochemical Reaction of Mercuric Cyanide[1]

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The reactions resulting from the photolysis of mercuric cyanide in organic media have been examined. They can be described as the addition and abstraction reactions of cyano radicals. Cyclohexene is converted to cyclohexyl cyanide, cyclohexyl isocyanide, 3-cyanocyclohexene, and 3,3′-bicyclohexenyl, and tetrahydrofuran or cyclohexane to the corresponding cyanides. It is tentatively postulated on the basis of the reactivities of substrates and the stoichiometries of the reactions that the photolysis occurs by initial fission to form cyano radical and mercurous monocyanide radical. The reactivity of cyano radical and the solvent effects are reported.

Although the spectroscopic and related studies of cyano radicals have been reported,[2] very few reactions of these radicals have been recorded.[3]

It is known that mercuric cyanide is decomposed by light, and ultraviolet irradiation of organomercury compounds produces organo radicals.[4] The absorption spectrum of mercuric cyanide[5] shows increasing absorption without a maximum in the region 210–360 mμ.

It would be expected from the above facts that the cyano radical might be produced by the irradiation of mercuric cyanide with ultraviolet light. With this in view, the reactions resulting from the photolysis of mercuric cyanide in organic media were investigated.

Results

Photolysis of Mercuric Cyanide in Simple Solvents.—The photolyses were conducted with unfiltered radiation from a high-pressure mercury lamp at temperatures between 35 and 40°. Methanol reacted slightly to form ethylene glycol, hydrogen cyanide, and formaldehyde. The gaseous fraction consisted of hydrogen, methane, and carbon dioxide. Methanol thus served as a useful solvent for investigating the reactions of more reactive compounds.

Mercuric cyanide reacted with tetrahydrofuran at approximately the same rate as it did with methanol. A mixture of 2-cyanotetrahydrofuran (I, a 15.0% yield based on the mercuric cyanide photolyzed) and 3-cyanotetrahydrofuran (1.5% yield) was obtained. The accompanying product was 2,2′-bitetrahydrofuryl (II, 51.4% yield). In no case was cyanogen formed.

Photolysis of Mercuric Cyanide in the Presence of Hydrocarbons.—A solution of cyclohexane and methanol reacted with mercuric cyanide under photolytic conditions to form mercury, hydrogen cyanide, cyclohexyl cyanide (III), cyclohexylcarbinol, and ethylene glycol.

Cyclohexene under similar conditions produced mercury, hydrogen cyanide (III, 6.8% yield), 3-cyanocyclohexene (IV, 3.5% yield), and 3,3′-bicyclohexenyl (V, 49.5% yield). The accompanying products were a small amount of methoxycyclohexane, 3-methoxycyclohexene, and cyclohexylcarbinol. The gaseous fraction consisted of hydrogen, methane, and carbon dioxide. 2- and 4-Cyanocyclohexene were not detected from the results of infrared spectroscopic and gas chromatographic measurements.

When tetrahydrofuran was used as a solvent, in addition to mercury, hydrogen cyanide, III (8.3% yield), IV (3.0% yield), and V (49.5% yield), I (4.1% yield), II (a small amount), and cyclohexyl isocyanide (1.8% yield) were produced. 3-Isocyanocyclohexene was not detected.

Solvent Effects on the Reaction of Mercuric Cyanide with Cyclohexene.—Studies were made about the solvent effects on the production of isonitrile. Because the solubility of mercuric cyanide in organic solvents is small, it is difficult to study the solvent effects systematically. When the reaction was carried out in nonhydroxylic solvents such as tetrahydrofuran and acetonitrile, the corresponding isonitrile was formed, but not in methanol or ethanol. The distribution of III–V was common to all the solvents studied.

Discussion

Since an unfiltered mercury radiation was used as a light source, it has not been determined which region of the ultraviolet spectrum is responsible for the photolysis. However, it was observed that mercuric cyanide did not undergo photolysis in solutions containing large quantities of aromatic compounds. The presence of an aromatic ring may serve as an internal filter for the photolytic radiations, particularly below 2800 A.[6] Quantitative measurements, however, are needed to verify these speculations.

We tentatively postulate on the basis of the reactivities of substrates and the stoichiometries of the reactions that the primary step in the photolysis is

$$\mathrm{Hg(CN)_2} \xrightarrow{h\nu} \cdot\mathrm{CN} + \cdot\mathrm{HgCN}$$

Mercurous monocyanide radicals, as is shown in our previous publication,[7] (a) abstract hydrogen from organic media to form hydrogen cyanide and mercury, (b) disproportionate to mercuric cyanide and mercury, (c) react with organo radicals to form nitriles and mercury, or (d) dissociate to cyano radicals and mercury. The reactions of cyano radicals seen in Scheme I can then occur.

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(1) Communicated in part: K. Yoshida and S. Tsutsumi, *Tetrahedron Letters*, 2417 (1965).

(2) N. Basco and F. M. Page, Advances in Chemical Series 36, R. F. Gould, Ed., The American Chemical Society, Washington, D. C., 1962, pp 31, 73.

(3) The reaction of cyano radicals in the gas phase has recently been recognized: C. A. Goy, D. H. Shaw, and H. O. Pritchard, *J. Phys. Chem.*, **69**, 1504 (1965).

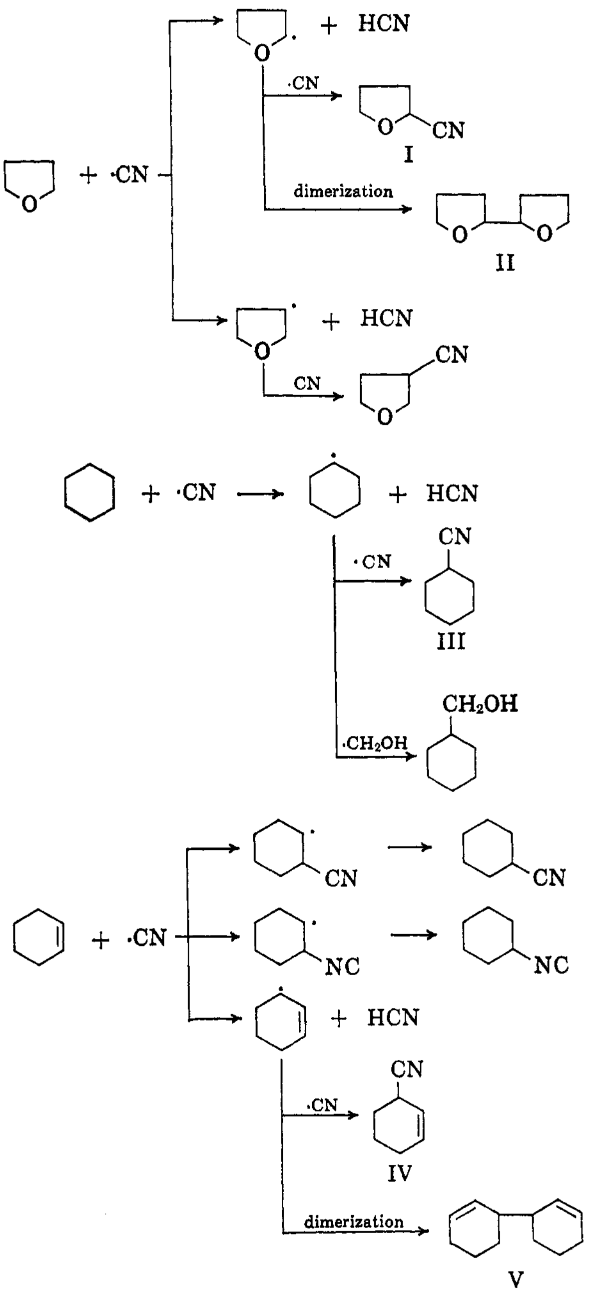
(4) (a) G. A. Razuvaev and Yu. A. Ol'dekop, *Zh. Obshch. Khim.*, **19**, 736 (1949); (b) J. M.-D. Blair, D. Bryce-Smith, and B. W. Pengilly, *J. Chem. Soc.*, 3174 (1959); (c) D. H. Hey, D. A. Shingleton, and G. H. Williams, *ibid.*, 1958 (1963); (d) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **85**, 3086 (1963); (e) G. E. Corbett and G. H. Williams, *J. Chem. Soc.*, 3437 (1964); (f) G. F. Fanta, *J. Org. Chem.*, **29**, 1610 (1964).

(5) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1454 (1955).

(6) It may involve quenching and not simply direct absorption by the aromatic compounds.

(7) K. Yoshida and S. Tsutsumi, *Tetrahedron Letters*, 281 (1966).

SCHEME I



Cyanogen has not been detected, probably because, owing to the very low stationary concentration of cyano radicals, it is formed only in very small amount. Since the cyano radical produced is surrounded with solvent, it abstracts hydrogen to form hydrogen cyanide predominantly. The product of dimerization of cyclohexyl radicals, namely, bicyclohexyl, has not been identified as well.

Cyano radicals have two reaction points based upon the following resonance forms, $\cdot C{\equiv}N| \leftrightarrow |C^{-}{\equiv}N\cdot^{+}$. Thus these radicals react with cyclohexene to form isonitrile as well as nitrile. It is not clear why the corresponding isonitrile was formed when the reaction was carried out in nonhydroxylic solvents such as tetrahydrofuran and acetonitrile but not in methanol or ethanol. Possibly the cyano radical is hydrogen bonded, making the formation of the isonitrile impossible, $\cdot C{\equiv}N|\text{---}HOR$. Though reactions are known in which radicals abstract organic groups from diorganomercury derivatives,[8] the possibility that radicals present in solution induce decomposition of mercuric cyanide is not supported by the evidence. First, this basis leads to no scheme which allows for the formation of our observed products. Secondly, the bond dissociation energy of mercuric cyanide[9] is too large (though the value in the gas phase is not always applicable for the solvated liquid phase). Chain reactions are probably unimportant, therefore except in the unlikely event that an initial photolysis is followed by a short chain reaction. Moreover, the possibility of mercury or mercuric cyanide photosensitization is unlikely as well, since in this system a high-pressure mercury lamp has been used.

The above results have shown that mercuric cyanide is available as the source of cyano radicals. They can be described as the addition and abstraction reactions of cyano radicals. Abstraction reaction is predominant. On the other hand, under suitable conditions, cyano radical is able to produce isonitrile as well as nitrile.

Experimental Section

Materials.—Mercuric cyanide was the reagent. Methanol and ethanol were refluxed in the presence of calcium oxide and were purified by fractional distillation. Tetrahydrofuran was refluxed and redistilled from lithium aluminum hydride under nitrogen. Acetonitrile was dried over anhydrous sodium sulfate and redistilled from phosphorous pentoxide. Cyclohexane was treated with mixed acid, dried, and purified by fractional distillation. Cyclohexene was refluxed and redistilled from sodium.

Photolyses.—The photolyses were conducted in 250- or 450-ml, three-necked, flat-bottom flasks. In the center neck was inserted a water-jacketed light well. A gas inlet tube and a bubble arrester were connected to the other necks. The light source was a high-pressure mercury lamp made of quartz (300 w). Mercuric cyanide was dissolved in the appropriate solvent. The material to be cyanated was then added to the mercuric cyanide solution and oxygen-free nitrogen was passed over the magnetically stirred solution for 10 min. The reaction was then photolyzed keeping the solution under an atmosphere of nitrogen pressure at 35–40° for 30 hr.

Analytical Method.—Reaction products were analyzed by gas chromatography. The columns used were Silicon DC-550 and PEG 6000. Gas chromatographic conditions were oven temperature, 180°; carrier gas, helium. Table I gives pertinent data.

Methanol.—A solution of 25.2 g of mercuric cyanide in 400 ml of methanol was irradiated. During the course of reaction, the evolution of gas was approximately 100 ml which was estimated by gas chromatography to contain hydrogen, methane, and carbon dioxide (molecular sieve and activated charcoal, 82°, helium). After removal of mercury (5.3 g) by filtration, the irradiated mixture was warmed to remove methanol. Formaldehyde in methanol was identified as 2,4-dinitrophenylhydrazone by mixture melting point measurement. The residual oil yielded 0.1 g of colorless liquid boiling at 80–90° (10 mm). It was ethylene glycol authenticated by gas chromatography and a comparison of the infrared spectrum with that of an authentic sample.

Tetrahydrofuran.—A solution of 25.2 g of mercuric cyanide in 400 ml of THF was irradiated (5.5 g of mercury was precipitated). After removal of THF by distillation, the residual oil was vacuum distilled. The vacuum distillate yielded the following fractions: (1) bp 55–68° (10 mm), 1.5 g; (2) bp 68–82° (10 mm), 1.2 g. Infrared spectrum of the early fraction showed medium absorption band at 2250 cm^{-1} (CN) and strong band at 1060 cm^{-1} (COC). It was confirmed to consist of 2-cyanotetrahydrofuran[10] (0.4 g, 15.0% yield), 3-cyanotetrahydrofuran[10] (0.04 g, 1.5% yield), and 2,2′-bitetrahydrofuryl[11] by gas chroma-

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Table I

Reaction Products and Their Physical Properties

Product	Derivative						
		Mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
Cyclohexyl cyanide	*p*-Bromophenacyl cyclohexanecarboxylate	89–90	$C_{15}H_{17}BrO_3$	55.40	5.27	55.21	5.19
3-Cyanocyclohexene	*p*-Bromophenacyl cyclohexene-1-carboxylate	108–109	$C_{15}H_{15}BrO_3$	55.74	4.68	55.64	4.80
3,3′-Bicyclohexenyl	2,2′,3,3′-Tetrabromobicyclohexyl	158–160	$C_{12}H_{18}Br_4$	29.90	3.76	29.95	3.75
Cyclohexyl isocyanide	N-cyclohexylbenzamide	147–148	$C_{13}H_{17}NO$	76.81	8.43	76.90	8.45

tographic analysis. Hydrolysis of the fraction yielded carboxylic acid, of which the infrared spectrum showed absorption bands at 1750 (C=O), 3500, and 930 cm^{-1} (OH). The methyl ester of the acid was confirmed to be methyl tetrahydrofuran-2-carboxylate by gas chromatography and a comparison of the infrared spectrum with that of an authentic sample. The latter fraction was mainly 2,2′-bitetrahydrofuryl.

Cyclohexane in Methanol.—A solution of 12.6 g of mercuric cyanide and 33.7 g of cyclohexane in 150 ml of methanol was irradiated (4.0 g of mercury was precipitated). The irradiated mixture was worked up as usual. The vacuum distillate yielded 0.3 g of colorless liquid boiling at 53–62° (10 mm). It consisted of cyclohexyl cyanide[12] (0.04 g), ethylene glycol (0.13 g), and cyclohexylcarbinol[13] (0.13 g) by gas chromatographic analysis and the infrared spectrum.

Cyclohexene in Methanol.—A solution of 12.6 g of mercuric cyanide and 32.8 g of cyclohexene in 150 ml of methanol was irradiated (6.5 g of mercury was precipitated). The gaseous fraction (approximately 100 ml) consisted of hydrogen, methane, and carbon dioxide. Distillation of the irradiated mixture gave several fractions having the following boiling point ranges: (1) bp 65–70°; (2) bp 33–55° (21 mm), 0.5 g; (3) bp 74–110° (21 mm), 1.5 g; (4) bp 110–117° (21 mm), 1.7 g; (5) bp 95–130° (0.5 mm), 2.4 g. Fraction 1 was unreacted cyclohexene with methanol as indicated by gas chromatography using a column heated to 118°, with Silicon DC-550, and helium as carrier gas. The amount of hydrogen cyanide dissolved in fraction 1 was determined gravimetrically by means of aqueous silver nitrate and found to contain 1.4 g. Fraction 2 was mainly methoxycyclohexane[14] with trace quantities of 3-methoxycyclohexene,[15] cyclohexyl cyanide, 3-cyanocyclohexene,[16] and cyclohexyl isocyanide[17] as indicated by gas chromatography and a comparison of the infrared spectrum with that of an authentic sample. Infrared spectrum of fraction 3 showed medium absorption band at 2250 cm^{-1} (CN). It was analyzed by gas chromatography, and cyclohexyl cyanide (0.48 g, 6.8% yield), 3-cyanocyclohexene (0.12 g, 3.5% yield), cyclohexylcarbinol, and 3,3′-bicyclohexenyl were confirmed (2-cyanocyclohexene[18] was not detected). Hydrolysis of 3 yielded 0.6 g of carboxylic acids, bp 125–130° (15 mm), of which the infrared spectrum showed absorption bands at 1690 (C=O), 3000, and 920 cm^{-1} (OH). 3-Cyclohexene-1-carboxylic acid[19] was not detected from infrared spectrum, for the acids were lacking in the characteristic absorption band at 650 cm^{-1}. The *p*-bromophenacyl esters of the carboxylic acids were prepared and were separated into two parts by chromatography with benzene on silica gel. One melted at 89–90° and was identified as *p*-bromophenacyl cyclohexanecarboxylate by mixture melting point measurement. The other melted at 108–109° and was identified as *p*-bromophenacyl cyclohexene-1-carboxylate[20] by mixture melting point measurement. Fraction 4 was identified as 3,3′-bicyclohexenyl by gas chromatography and the mixture melting point measurement of its tetrabromide[21] which was recrystallized from acetic acid and melted at 158–160°. Fraction 5 was a clear, viscous liquid and has not been identified. A nitrile absorption band was absent in the infrared spectrum. Similar results were obtained with ethanol.

Cyclohexene in Tetrahydrofuran.—A solution of 25.2 g of mercuric cyanide and 65.6 g of cyclohexene in 300 ml of THF was irradiated (5.0 g of mercury was precipitated). The reduced solution was worked up as usual to yield the following fractions: (1) bp 35–95° (11 mm), 3.7 g; (2) bp 93–130° (11 mm), 1.2 g. Infrared spectrum of fraction 1 showed medium absorption band at 2250 cm^{-1} (CN) and strong band at 2150 cm^{-1} (NC). Fraction 1 was analyzed by gas chromatography, and cyclohexyl cyanide (0.45 g, 8.3% yield), 3-cyanocyclohexene (0.08 g, 3.0% yield), 2-cyanotetrahydrofuran (0.1 g, 4.1% yield), cyclohexyl isocyanide (0.1 g, 1.8% yield), 2,2′-bitetrahydrofuryl (a small amount), and 3,3′-bicyclohexenyl (2.0 g, 49.5% yield) were confirmed. Fraction 1 was hydrolyzed by means of dilute hydrochloric acid to form amine, of which infrared spectrum showed absorption bands at 3500, 3350, and 1600 cm^{-1} (NH). The benzamide was prepared, recrystallized from benzene–petroleum ether (bp 40–60°), melted at 147–148°, and was identified as benzamide of cyclohexylamine by mixture melting point measurement. 3-Isocyanocyclohexene was not detected from infrared spectrum, for the amine was lacking in the several characteristic absorptions.[22] Fraction 2, of which infrared spectrum did not showed absorption of nitrile, has not been identified.

Similar results were obtained with acetonitrile, except that the wall of the light source was covered with polymeric products during the course of irradiation and the amounts of the products were decreased.

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[19] A. A. Petrov and N. P. Sopov, *Zh. Obshch. Khim.*, **17**, 2228 (1947).

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