The Thermal Decomposition of Mercuric Cyanide Vapor

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The thermal decomposition of mercuric cyanide vapor has been studied in the presence of N_2, H_2, and various hydrocarbons, and is shown to take place by two distinct mechanisms. One is a molecular reaction which leads directly to cyanogen and the other involves the production of HgCN radicals, which behave essentially as if they were CN radicals. The vapor pressure and latent heat of vaporization of mercuric cyanide have been measured. The existence of NOCN is reported.

Preliminary Qualitative Experiments. When a stream of nitrogen containing a hydrocarbon RH is passed over solid mercuric cyanide heated to 350°, chromatographic analysis of the effluent gas shows the presence of HCN, C_2N_2, and the corresponding nitrile RCN. Thus methane and ethane give methyl and ethyl cyanide, respectively, propane gives *sec*-propyl cyanide, *n*-butane gives *sec*-butyl cyanide plus some ethyl cyanide, and benzene and toluene give phenyl and benzyl cyanide, respectively; in no case is any isonitrile formed. The simplest explanation of these products is that the radical R is produced by abstraction from RH, and this R then combines with a CN radical. The existence of radicals in the system is further supported by the fact that the products also contain alkyl mercuric compounds, which can easily be recognized by their unmistakable odor. It was also noted that unchanged mercuric cyanide was deposited downstream, and it was decided to study these reactions quantitatively under controlled gas phase conditions.

When unsaturated hydrocarbons were used addition products were found, *i.e.*, ethylene gave ethyl cyanide and succindinitrile, and acetylene and butadiene gave unidentified products, which in the latter case were very high boiling. It was also found that AgCN and $Cu(CN)_2$—actually $Zn(CN)_2$ + $CuCl_2$ mixture—behaved analogously.

Vapor Pressure of Mercuric Cyanide. The vapor pressure of solid mercuric cyanide was measured over the range 237–284° by saturating a carrier gas flowing at a known rate over the heated solid, and weighing the amount of solid transported to the condensation area; no decomposition occurs in this temperature range (except for a minute trace in the presence of H_2). Variations were made in flow rate and carrier gas composition to ensure that saturation had been achieved. The vapor pressure of mercuric cyanide is about 5.7×10^{-2} mm. at 237° and about 4.7×10^{-1} mm. at 284°, giving a latent heat of vaporization of 26 ± 1 kcal./mole; no previous determination of the vapor pressure has been reported, but an estimate of the latent heat is on record.[1] The vapor pressure is given by

$$\log p \text{ (mm.)} = 9.810 - 26{,}000/2.3RT$$

In the kinetic experiments reported below, the mercuric cyanide did not always achieve its saturation vapor pressure under the conditions of carrier flow and composition used, and the amount transported in any experiment was always determined by dummy experiments carried out under the same flow conditions.

Thermal Decomposition in Pure Nitrogen. Kinetic experiments were carried out in a flow system in which the carrier gas, at about 1 cm. pressure, first flowed over solid mercuric cyanide maintained at a temperature near 250° and then into a cylindrical Pyrex reaction vessel at a higher temperature; contact times were of the order of 1 sec., and the products were analyzed mass spectrometrically. Little decomposition occurred below 410°, but at higher temperatures, surprisingly, HCN was the main product.

We had previously established that $Hg(CN)_2$ was readily hydrolyzed to HCN by water at high temperature. Consequently, water was rigorously excluded from the carrier gas by refrigeration, and in all experi-

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[1] E. Lange and W. Martin, *Z. Physik. Chem.* (Leipzig), **A180**, 233 (1937).

ments the mercuric cyanide was purified by vacuum sublimation and stored until use *in vacuo* at 150°. We had also found from mass spectrometer analyses that C_2N_2 tended to hydrolyze slowly to HCN + HOCN when trapped in recently blown sections of the system, and suitable precautions were always taken; this kind of hydrolysis, analogous to the halogens, has been recorded previously in aqueous solution.[2]

We concluded therefore that the source of the HCN was a reaction involving the traces of hydrogen (0.05–0.1%) in the nitrogen. The reaction of H_2 with C_2N_2 has been studied previously,[3] and blank experiments confirmed that only in the order of 1% of the cyanogen would be converted to HCN in our system. Hence a reaction between hydrogen and mercuric cyanide was indicated, and this was confirmed in experiments with hydrogen as carrier.

Kinetic measurements were made in nitrogen between 420 and 510°. At the lower temperatures, the HCN:C_2N_2 ratio was often as high as 3, but at the highest temperatures, the ratio was nearer 0.3. Over the same temperature range, the over-all order in $Hg(CN)_2$ rose from 1.0 to 1.5 (a similar rise in order from about 1 to about 2 was found when methane was used as carrier). We interpret this to mean that HCN is formed by a first-order reaction of $Hg(CN)_2$ with H_2, and that C_2N_2 is formed from $Hg(CN)_2$ by a second-order mechanism; this interpretation is consistent with the fact that C_2N_2 is only formed in appreciable quantities in the gas phase at 500°, but that the solid decomposes rapidly 200° lower. It will be shown conclusively later that in these reactions, the radical concentration is negligible, and cyanogen could not have been formed by any radical mechanism. Hence it is reasonable to use the rate of formation of cyanogen as a measure of the rate of the second-order reaction

$$Hg(CN)_2(g) \longrightarrow Hg(g) + C_2N_2(g) \qquad (1)$$

The Arrhenius parameters for this reaction are $E_1 = 27 \pm 3$ kcal., $\log A_1 = 12.8$ (A_1 in cc. mole^{-1} sec.$^{-1}$). Reaction 1 is thermoneutral to within experimental error,[4] *i.e.*, for $Hg(CN)_2$, $(D_1 + D_2) = D(NC\text{–}CN)$.

Thermal Decomposition in Hydrogen. When hydrogen was used as a carrier, the rate of decomposition rose so much that satisfactory rates could not be measured above 400°, and even down as low as 250° (the temperature of the solid $Hg(CN)_2$), a small but detectable decomposition occurred. At all temperatures, the product was HCN containing less than 1% C_2N_2. The kinetic results in hydrogen were very variable, and we were unable to establish the order of the reaction. We believe, however, that a chain sequence is involved in which one step is

$$H + Hg(CN)_2 \longrightarrow HCN + HgCN \qquad (2)$$

It has been previously reported that hydrogen atoms attack solid mercuric cyanide,[5] and we have found that hydrogen atoms, produced by mercury photosensitized decomposition of H_2, considerably enhance the rate of formation of HCN from H_2 and mercuric cyanide vapor at 250°; mercuric cyanide vapor itself is unaffected by irradiation in the presence of mercury. If reaction 2 is to be fast, it must be exothermic which means that $D_2 = D(Hg\text{–}CN) > 15$ kcal. if $D(NC\text{–}CN) = 145$ kcal./mole.[6]

Further support for this mechanism comes from experiments using nitrogen–hydrogen mixtures as carrier. The addition of 1% of oxygen caused the over-all rate of decomposition to be reduced, and at the same time there was a similar drop in the (small) amount of cyanogen formed. This suggests that in the low temperature region (300–400°), cyanogen is being formed by a radical mechanism which arises because of reaction 2. The most likely one is

$$HgCN + HgCN \longrightarrow 2Hg + C_2N_2 \qquad (3)$$

which is exothermic provided that $D_2 < 0.5\,D(NC\text{–}CN)$; and since D_1 must always be greater[7] than D_2, the thermoneutrality of reaction 1 ensures that this is the case (since $D_1 + D_2 = D(NC\text{–}CN)$). However, we can set a more useful limit on D_2 since, if a chain is to be maintained, the hydrogen atoms must be regenerated by

$$HgCN + H_2 \longrightarrow HCN + Hg + H \qquad (4)$$

which is exothermic provided that $D_2 < 26$ kcal. Because of the high concentration of H_2, this reaction could be sufficiently fast even if it had a small activation energy, say $E \leq 4$ kcal. which places an upper limit of about 30 kcal. on D_2. Thus $15 < D_2 < 30$ kcal., which is of comparable magnitude with $D(Hg\text{–}Cl)$ and $D(Hg\text{–}Br)$. Hence, $130 > D_1 > 115$ kcal., which means that a free-radical decomposition analogous to the mercury alkyl decompositions[8] is impossible. There appears to be no thermochemically favorable

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(2) R. Naumann, *Z. Elektrochem.*, **16**, 772 (1910).

(3) N. C. Robertson and R. N. Pease, *J. Am. Chem. Soc.*, **64**, 1880 (1942).

(4) All thermochemical data from National Bureau of Standards Circular 500 unless stated otherwise.

(5) S. Miyamato, *Chem. Abstr.*, **28**, 4319 (1934).

(6) J. Berkowitz, *J. Chem. Phys.*, **36**, 2533 (1962).

(7) H. A. Skinner, *Trans. Faraday Soc.*, **45**, 20 (1949).

(8) B. G. Gowenlock, *Quart. Rev.* (London), **14**, 133 (1960).

reaction through which CN radicals themselves could be produced.

Thermal Decomposition in Methane. Cylinder methane was freed from oxygen and then rigorously purified by repeated trap to trap distillations at temperatures in the range −218 to −204° until it was completely free from ethane; the only remaining impurities were traces of H_2 and N_2. However, in order to maintain suitable flow conditions, the methane had to be diluted with nitrogen, and the final carrier gas composition was N_2 (67%), CH_4 (33%), and H_2 (<0.1%). The over-all rate of decomposition of mercuric cyanide was unaffected by the presence of methane in the nitrogen, and above 410° the products were mainly C_2N_2 and HCN, as before, together with small amounts of ethane (1–5%) and methyl cyanide (0.1–0.2%). These new products we assume to be formed by

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (5)$$

and

$$CH_3 + HgCN \longrightarrow CH_3CN + Hg \qquad (6)$$

since we have established in separate experiments that methyl radicals do not readily attack mercuric cyanide. The methyl radicals involved in these reactions could be formed in two ways, *i.e.*

$$H + CH_4 \longrightarrow H_2 + CH_3 \qquad (7)$$

or

$$HgCN + CH_4 \longrightarrow Hg + HCN + CH_3 \qquad (8)$$

Of these, the latter is the more probable because reaction 8 is more exothermic than reaction 4, whereas reaction 7 is known to have an activation energy of the order of 10 kcal./mole. However, the radical balance shows that not all the HCN is formed by reaction 8 but that most of it comes from reaction 2 since the total HCN always exceeds the sum $[CH_3CN + 2C_2H_6]$ by a factor of from 10 to 50.

Comparison of reactions 3 and 6 shows that the ethane produced is always 10 to 50 times the amount of methyl cyanide. If we assume that reactions 3 and 6 behave as normal recombination reactions like reaction 5, we may write $R_6/R_3^{1/2}R_5^{1/2} \approx 2$, which means that the rate of formation of cyanogen by radical combination is about one-tenth to one-fiftieth that of the methyl cyanide; *i.e.*, at the highest temperatures, reaction 3 accounts for about 10^{-5} of the total cyanogen, which is our justification for assigning Arrhenius parameters to reaction 1.

It is interesting to speculate on the shape of the transition state for reactions 2, 3, 4, 6, and 8. Certainly in reaction 2 one might expect a linear configuration which could lead to the formation of HNC instead of HCN; however, infrared examination of the product hydrogen cyanide under high resolution shows it to be purely HCN. In addition, it has already been noted that when hydrocarbons are present, it is always RCN and not RNC that is produced, indicating that in all these reactions, HgCN behaves as though it were the CN radical. HNC, of course, might readily isomerize to HCN, but this would not be true of the alkyl isonitriles which are thermally quite stable. It is also interesting to note that the products obtained in the preliminary qualitative experiments would not have occurred if the nitrogen diluent used had not contained hydrogen since it is only in the presence of hydrogen that radicals appear to be formed.

Reactions in Packed Vessels. Experiments were performed with the vessel packed with Pyrex beads, increasing the surface area by a factor of 4. With nitrogen as a carrier, the rate of formation of cyanogen from $Hg(CN)_2$ rose, but the extent of the rise was obscured by the formation of paracyanogen particularly at 500°. This was the only occasion in the whole series of experiments when paracyanogen was produced. It is known that cyanogen is readily polymerized by CN radicals[9,10] and it is possible that HgCN radicals may do likewise when the cyanogen concentration is high enough. Using 20:1 nitrogen–hydrogen mixtures, however, paracyanogen is not formed, even at high temperatures; packing does not cause any change in the rate of formation of HCN at any temperature, but above 400° the rate of formation of cyanogen goes up by a factor of 8–10. Thus it seems that reaction 1 is dependent on surface. However, in the chain sequence of reactions 2 and 4, both initiation and termination are equally affected by surface; since termination is probably a wall reaction, this suggests that initiation also takes place on the walls. One might add, as in the case of the C_2N_2–H_2 reaction,[3] there is no homogeneous initiation step which is thermochemically feasible.

The Formation of NOCN. In some experiments, NO was added to the carrier gas but no NOCN was formed. However, in the photolysis of ICN with NO added, the final products did contain NOCN, identified mass spectrometrically; the amount of NOCN was about 0.2 of the C_2N_2, and could be increased by a factor of 2–3 by addition of I_2 to the reaction mixture. At the same time, the radical-catalyzed[11] decomposition of NO to N_2 and NO_2 took

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(9) D. E. Paul and F. W. Dalby, *J. Chem. Phys.*, **37**, 592 (1962).

(10) D. E. McElcheran, M. H. J. Wijnen, and E. W. R. Steacie [*Can. J. Chem.*, **36**, 321 (1958)] state that the photolysis of $CO(CN)_2$ vapor leads to copious formation of paracyanogen.

place, but no NO_2CN was formed. At the moment, our identification of NOCN rests solely on mass spectrometric analysis of the reaction products and an attempt is now being made to isolate a pure sample of NOCN from the mixture of excess NO_2 and C_2N_2. In recent flash photolysis experiments, I + NO have been shown[12] to form the transient NOI, and NO has been reported to react with CN, but the nature of the product was not known.[13]

Silver Cyanide and Cupric Cyanide. Neither of these substances is suitable for kinetic studies similar to those just described. Volatile species do exist over both substances, above about 380 and 190°, respectively. However, thermal decomposition occurs in the condensed phase at all temperatures where volatile species can be detected by flow experiments.[14]

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(11) O. P. Strausz and H. E. Gunning, *Can. J. Chem.*, **41**, 1207 (1963).

(12) G. Porter, Z. G. Szabo, and M. G. Townsend, *Proc. Roy. Soc.* (London), **A270**, 493 (1962).

(13) N. Basco, J. E. Nicholas, R. G. W. Norrish, and W. H. J. Vickers, *ibid.*, **A272**, 147 (1963).

(14) D. H. Shaw, unpublished results.