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Radiolysis of Hydrogen Cyanide in an Aqueous System.[1] II. Effects of Additives and Reaction Mechanism

Hajime OGURA

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

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The ^{60}Co γ-irradiation of dilute aqueous solutions of hydrogen cyanide (6 mM) in the absence of oxygen yielded mainly ammonia with $G=1.9$, formaldehyde with $G=1.1$, and carbon dioxide with $G=0.8$, while $G(\text{-HCN})=5.8$ molecules per 100 eV. Polymeric hydrogen cyanide was also observed with the $G(\text{-HCN(polymer)})\simeq 4$, which showed an intense broad absorption band in the UV region upon γ-irradiation. The following material balances were observed with the main products:

$$G(\text{-HCN}) \simeq G(NH_3) + G(\text{-HCN(polymer)}) \simeq G(CO_2) + G(HCHO) + G(\text{-HCN(polymer)})$$

The results can be interpreted in terms of a mechanism involving HCN^-, H_2CN, and H(OH)CN radicals. The ratio of the rate constants for the reactions of e^-_{aq} and H atoms with hydrogen cyanide to those with several scavengers have been determined as $k(e^-_{aq}+HCN)/k(e^-_{aq}+NO_3^-)=0.019$ and $k(H+HCN)/k(H+\text{2-propanol})=1.4$, all at 17°C.

In our previous papers,[1,2] studies have been made of the radiolysis of aqueous solution of hydrogen cyanide with the purpose of elucidating the nature of the reaction, the radiolytic yields of hydrogen cyanide, and the products of the radiolysis, including the HCN tetramer.

The work reported here was undertaken in order to obtain additional information about radiolytic products and a general mechanism of the radiolysis by using several scavengers.

Experimental

The general procedures have already been described,[1] but a review will be given of what was introduced in the present experiment.

Samples. A 5-m*l* portion of an air-free solution, prepared by the conventional vacuum technique with freezing-thawing recycles, was sealed in a 20 m*l* cylindrical glass cell. Nitrous oxide purified by distillation was taken in a calibrated volume until a definite pressure and temperature had been reached and then transfered to the irradiation vessel by using liquid nitrogen. The concentration of the gas in the solution was calculated from the solubility data.[3]

Irradiation. Gamma irradiation was carried out with a ^{60}Co source at a dose rate of 1.68×10^{18} eV·ml^{-1}hr^{-1} based on Fricke dosimetry, taking $G(Fe^{3+})=15.5$.

Analysis. The nitrite ion was determined spectrophotometrically at 520 mμ by using sulfanilic acid and α-naphthylamine.[4] The formaldehyde was determined by means of chromotropic acid when the solution was irradiated in an acidic medium (H_2SO_4 pH=2). However, in the neutral and basic solutions, this method could not be used because of the formation of cyanohydrin[5] from the cyanide ion and formaldehyde produced by γ-irradiation even at low concentrations. Since it has been confirmed that cyanohydrin can also be determined by the use of an acetylacetone reagent which has been generally used for the determination of

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[1] Preliminary report: H. Ogura, *J. Rad. Res.* (*Tokyo*), **8**, 93 (1967); Presented in part at the 8th and 10th Symposia on Radiation Chemistry, Tokyo, Nov. 12, 1965, and Hiroshima, Oct. 26, 1967, respectively.

[2] H. Ogura and M. Kondo, This Bulletin, **40**, 2448 (1967).

[3] Intern. Critical Tables, **3**, (1933), p. 254.

[4] F. D. Snell and C. T. Snell, "Colorimetric Method of Analysis," Vol II, 3rd ed., D. Van Norstrand, New York (1958), p. 803.

[5] N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Oxford (1937), new ed. (revised by T. W. J. Taylor and W. Baker), p. 309.

formaldehyde in a neutral medium,[6] the concentration of formaldehyde in the presence of hydrogen cyanide in a neutral medium was estimated as follows. A mixture of the irradiated solution and the acetylacetone reagent in equal volumes was kept at 58°C for 90 min; the resulting yellow coloration was determined spectrophotometrically at 412 mμ. The validity of this method under the present experimental conditions, with 6 mM HCN, was established well. The formic acid was determined as was formaldehyde after being reduced by metallic magnesium and hydrochloric acid.[7] The hydrogen peroxide was determined by the ceric sulfate method.

Results and Discussion

Yields of Products. Figure 1 presents typical results of the radiolysis of an air-free 6 mM HCN solution at a natural pH. The initial yields of products expressed as *G* (molecules per 100 eV) are summarized in Table 1. By improving the analytical procedure, it became possible to observe formaldehyde as one of major products in addition to those previously observed.[1] Besides the radiolysis products of a low molecular weight listed in Table 1, a polymeric form of hydrogen cyanide was also observed. It has been known that when a small amount of base is added to aqueous solutions of hydrogen cyanide, there appears a very strong broad absorption extending into the UV region; this formation is due to the formation of polymeric hydrogen cyanide.[8,9] In irradiated aqueous solutions of hydrogen cyanide, an absorption of nearly the same type as that chemically prepared was observed in Fig. 2, indicating the polymerization of hydrogen cyanide by γ-irradiation.[*1]

Figure 3 presents the increase in the absorbance at 230 mμ and 270 mμ against the absorbed dose. The wavelength at which the absorbance was measured was chosen for the sake of convenience in experimentation. The absorbance is seen to increase linearly with the dose, and, from the slope of the line, one can obtain the increase in absorbance per unit dose (−log *T*/dose), an increase which corresponds to the radiolytic yield of polymeric hydrogen cyanide. One can indicate

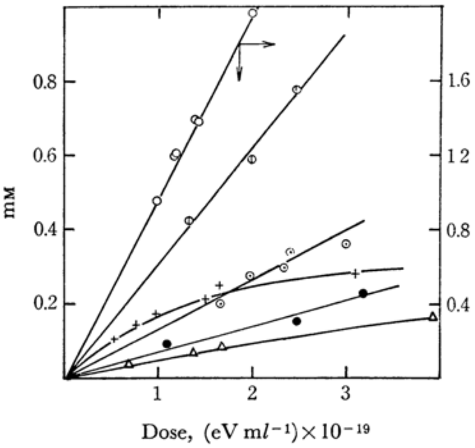

Fig. 1. Radiolysis of 6 mM HCN in air-free system.
○: HCN consumed ⦶: NH_3 produced
+: HCHO produced ⊙: CO_2 produced
●: H_2 produced △: H_2O_2 produced
Dose rate: 1.68×10^{18} eV ml^{-1} hr^{-1}

TABLE 1. PRODUCT YIELDS IN THE RADIOLYSIS OF 6 mM HCN

Product	Yield (*G*-value)
Ammonia	1.9
Formaldehyde*	1.1
Carbon dioxide	0.8
Formic acid	0.1
Nitrogen	<0.1
Hydrogen	0.42
Hydrogen peroxide	0.3
Polymeric product	$4 \simeq G(-\mathrm{HCN})$

* Presented as cyanohydrin

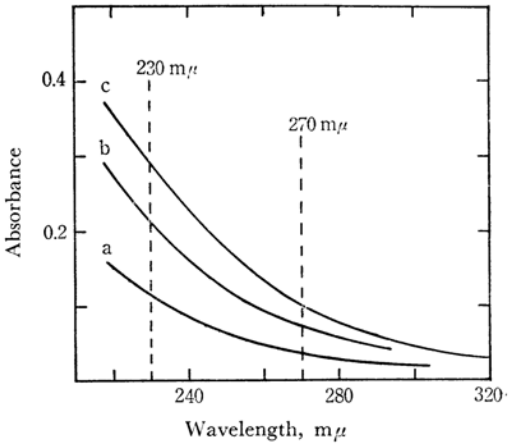

Fig. 2. UV absorption spectra of γ-irradiated 6 mM HCN in air-free system.
Dose rate: 1.68×10^{18} eV ml^{-1} hr^{-1}
a: 4 hr b: 8 hr c: 11 hr

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[6] T. Nash, *Biochem. J.*, **55**, 416 (1955).

[7] Ref. 4, p. 303.

[8] S. Fujise, N. Nagai and T. Numata, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **64**, 1889 (1961).

[9] J. Kato, I. Hayashi, I. Noda, R. Yuwanaga and T. Yoshida, *ibid.*, **65**, 92 (1962).

[*1] According to Kondo[10] and Hummel *et al.*,[14] in either pure or aqueous solutions of hydrogen cyanide at high concentrations, radiolysis with ^{60}Co γ-rays yields a massive, dark brown solid formulated as $(HCN)_n$ and quite similar in its chemical property to the azulmic acid produced from an alkaline solution of hydrogen cyanide.

[10] A. Matsumoto, T. Masuda, C. Nakazato, H. Ogura and M. Kondo, presented at the 15th Annual Meeting of Chemical Society of Japan, Kyoto, April. 1962.

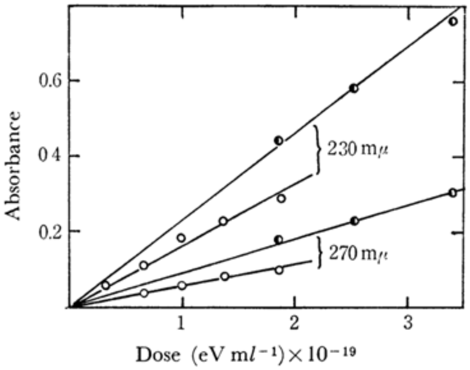

Fig. 3. Increase in absorbance at 230 mμ and 270 mμ with dose in γ-irradiated HCN solutions.
○: 6 mM HCN ◐: 23 mM HCN

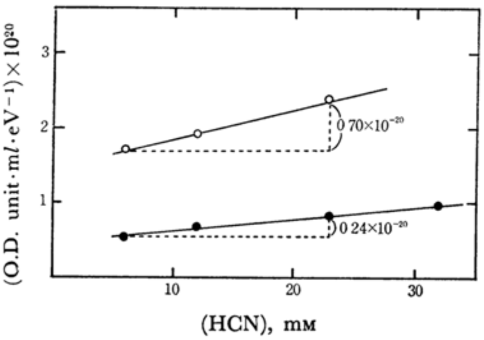

Fig. 4. Dependence of absorbance per unit dose on HCN concentration.
○: at 230 mμ ●: at 270 mμ

as examples of the calculation from Fig. 3, as written, 1.70×10^{-20} (O.D. unit ml eV^{-1}) at 230 mμ and 0.56×10^{-20} (O.D. unit ml eV^{-1}) at 270 mμ with a 6 mM HCN solution.

In Figure 4, the absorbance per unit dose is plotted against the initial concentration of hydrogen cyanide. The increase in this value with the concentration, ranging from 6 mM to 23 mM, is found to be $\Delta(-\log T/\text{dose})=0.70\times10^{-20}$ (O.D. unit ml eV^{-1}) at 230 mμ and 0.24×10^{-20} (O.D. unit ml eV^{-1}) at 270 mμ respectively. In an air-free system, G(–HCN) was determined previously to be 5.8 at 6 mM HCN and 7.5 at 23 mM HCN respectively. Assuming that this increase in the yield, $\Delta G(\text{–HCN})=1.7$, with the concentration is to be attributed to the increasing formation of a polymeric form of hydrogen cyanide*[2] which results in an increase in the optical absorption per unit dose, $\Delta(-\log T/\text{dose})$, one can find that the radiolytic yield of hydrogen cyanide leading to the polymeric form is about $G(\text{–HCN(polymer)})\simeq4$ at 6 mM HCN. The difference between the total 100 eV yield of radiolysed hydrogen cyanide and the 100 eV yield of radiolysed hydrogen cyanide leading to the polymeric form is found to be 1.8. This value may correspond to the yields of the major products which give no absorption in the UV region. These products are demonstrated to be ammonia, carbon dioxide, and formaldehyde, the 100 eV yields of which are listed in Table 1. It seems that the following material balances can be established with the major products:

$$G(-\text{HCN})\simeq G(\text{NH}_3)+G(-\text{HCN(polymer)})$$
$$\simeq G(\text{HCHO})+G(\text{CO}_2)$$
$$+G(-\text{HCN(polymer)})$$

Effect of Nitrate Ions. In a previous study,[1] it was shown that dissolved oxygen effectively reduced the radiolytic yields of hydrogen cyanide. This finding indicates the contribution of hydrated electrons to the radiolysis of hydrogen cyanide because of their high reactivity towards oxygen. To confirm this explanation, the nitrate ion, which is known as an effective scavenger[11] for the hydrated electrons, was introduced. Figure 5 illustrates the effect of these nitrate ions on the radiolysis of an air-free 6 mM HCN solution. The concentration of hydrogen cyanide was chosen at 6 mM, where an almost steady radiolytic yield, G(–HCN) $=5.8$, was observed;[1] this value is also in close agreement with the total radical yield of water. Nitrate ions are seen to reduced G(–HCN) with an increase in the concentration, leading to a steady value at 0.3 mM. Since the decrease in $G(-\text{HCN})$ at its steady value is found to be 2.9, close to the yield of hydrated electrons, $G_{\text{e}^-_{\text{aq}}}$, the effect of nitrate ions can readily be explained in terms of the scavenging action of the hydrated

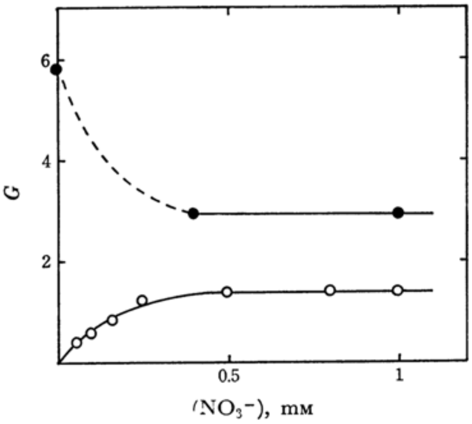

Fig. 5. Effect of nitrate ion on the radiolysis of 6 mM HCN in air-free system.
●: $G(-\text{HCN})$ ○: $G(\text{NO}_2^-)$

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*[2] Unlike the increase in the total radiolytic yield of hydrogen cyanide from 6 mM up to 23 mM HCN, the observed increases in the yields of low-molecular products listed in Table 1 are almost negligible in the same concentration region.

[11] H. A. Mahlman, *J. Phys. Chem.*, **67**, 1466 (1963).

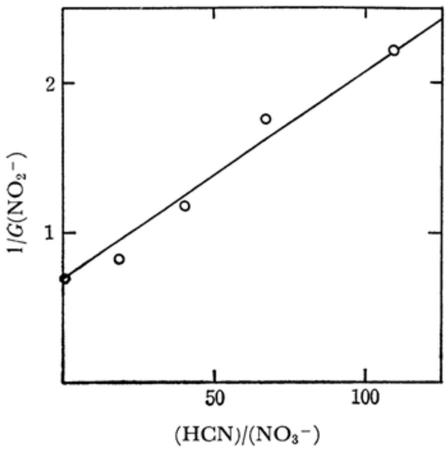

Fig. 6. Competition for hydrated electron between HCN and nitrate ion plotted according to Eq. (I).

electrons. Figure 5 also shows the yield of nitrite ions, $G(NO_2^-)$, which increases with the concentration of nitrate ions, tending to a steady value of 1.4, nearly a half of the $G_{e^-_{aq}}$ value in water radiolysis. These findings may result from the competitive reactions between hydrogen cyanide and nitrate ions for hydrated electrons:

$$e^-_{aq} + HCN \xrightarrow{k_1} P \qquad (1)$$

$$e^-_{aq} + NO_3^- \xrightarrow{k_2} NO_2 + 2OH^- \qquad (2)$$

followed by:

$$2NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \qquad (3)$$

$G(NO_2^-)$ can thus be expressed as:

$$\frac{1}{G(NO_2^-)} = \frac{2}{G_{e^-_{aq}}}\left\{1 + \frac{k_1(HCN)}{k_2(NO_3^-)}\right\} \qquad (I)$$

The plots of $1/G(NO_2^-)$ *vs.* $(HCN)/(NO_3^-)$ are presented in Fig. 6. The linear plots indicate the adequacy of the proposed mechanism given above. From the slope of the line, k_1/k_2 is obtained as 0.019. Taking the well-established rate constant of k_2 as 1.1×10^{10} M^{-1} sec^{-1},[12] the rate constant for the reaction (1) is found to be 2×10^8 M^{-1} sec^{-1}. As to what becomes of P, only two processes can be postulated. The one is an electron attachment of HCN

$$e^-_{aq} + HCN \rightarrow HCN^- \qquad (1a)$$

The presence of an anionic form of hydrogen cyanide is evidenced by the ESR spectra found in alkaline halide matrices at 77°K by Root *et al.*[13] Hummel *et al.*[14] also indicated its presence as an initiator of the radiation-induced polymerization of pure hydrogen cyanide. The other is possibly a dissociative electron capture process:

$$e^-_{aq} + HCN \rightarrow H + CN^- \qquad (1b)$$

Since the dissociation energy of H–CN is 114.9 kcal/mol,[15] and since the electron affinity of CN is 74 kcal/mol,[16] the reaction (1b) is not likely from a thermochemical point of view.

Effect of Nitrous Oxide. The effect of nitrous oxide[17] on the radiolysis of hydrogen cyanide and the formation of a gaseous product are presented in Fig. 7. The concentrations of nitrous oxide and hydrogen cyanide are about 16 mM and 5.8 mM respectively. It may be seen that nitrous oxide does not affect $G(-HCN)$ and that $G(N_2)$ is very close to $G_{e^-_{aq}}$. Since $G(N_2)$ is quite negligible (<0.1) in the absence of nitrous oxide, as is shown in Fig. 7, the nitrogen observed in this experiment can be taken as almost entirely arising from the reaction (4):

$$e^-_{aq} + N_2O \rightarrow N_2 + OH + OH^- \qquad (4)$$

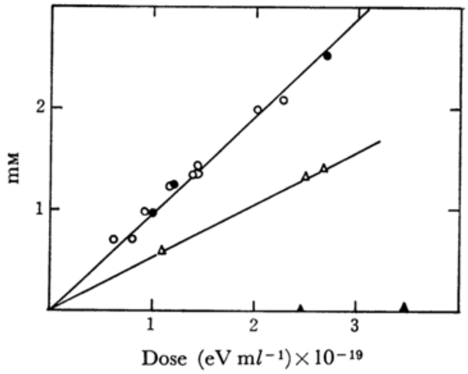

Fig. 7. Effect of nitrous oxide on the radiolysis of 6 mM HCN.
○: HCN consumed, △: N_2 produced in the presence of 16 mM N_2O, ●: HCN consumed, ▲: N_2 produced in the absence of N_2O

If one assumes that the reactivity of OH radicals towards hydrogen cyanide is nearly equal to that of hydrated electrons, the above finding can be explained well.

As for the reaction of OH radicals with hydrogen cyanide, two reactions, (5a) and (5b), can possibly be expected:

$$OH + HCN \rightarrow H(OH)CN \qquad (5a)$$

$$\searrow H_2O + CN \qquad (5b)$$

The fate of the intermediate in the reaction (5a)

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[12] J. K. Thomas, S. Gordon and E. J. Hart, *J. Phys. Chem.*, **68**, 1524 (1964).

[13] K. D. J. Root, M. C. R. Symons and B. C. Weatherly, *Mol. Phys.*, **11**, 161 (1966).

[14] D. Hummel and O. Jassen, *Z. Physik. Chem.*, **31**, 111 (1962).

[15] C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1952).

[16] J. T. Herren and V. H. Dibeler, *J. Am. Chem. Soc.*, **82**, 1555 (1960).

[17] F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc.*, (*London*), **A267**, 443 (1962).

will be described later. The dehydrogenation reaction (5b) is found not to be important on a thermochemical basis. If this occurred, most CN radicals would be expected to react with water, thus regenerating hydrogen cyanide.[18] On this basis, the reaction (5b) can be excluded.

Yield of Hydrogen. The radiolytic yield of hydrogen, $G(H_2)$, is found to be 0.42, which is independent of the concentration of hydrogen cyanide as well as of that of hydrogen ions, as is illustrated in Fig. 8; it is equal to G_{H_2}, the molecular yield of hydrogen from water.[19] One must, therefore, conclude that hydrogen is not formed from the abstraction of hydrogen atom from the HCN molecule:

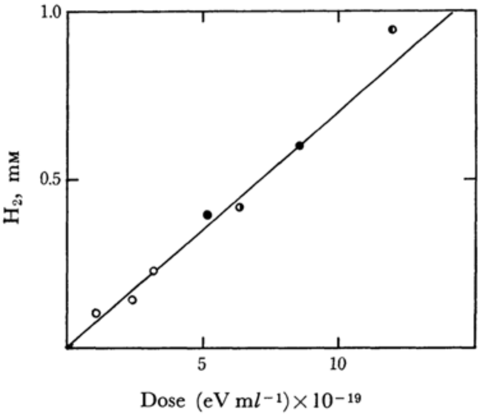

Fig. 8. Formation of hydrogen in γ-irradiated HCN solutions.
6 mM HCN; ◐: pH=1, ◑: pH=2,
○: pH=5.5
30 mM HCN; ●: pH=5.1

$$H + HCN \rightarrow H_2 + CN \qquad (6a)$$

As to the fate of the H atom produced primarily from water, an addition to hydrogen cyanide may occur, in which case the adduct will be the methyleneimino radical, H_2CN, according to the reaction (6b):

$$H + HCN \rightarrow H_2CN \qquad (6b)$$

This intermediate has been identified by Cochran *et al.*[19] by means of ESR studies at a low temperature.

Scholes *et al.*[21] have been demontrated a general method of investigating the reactivity of H atoms towards some compound which are not dehydrogenated. This includes the use of 2-propanol and nitrous oxide as scavengers of H atoms and hydrated electrons respectively, and was used in studying the reactivity of H atoms towards hydrogen cyanide in an aqueous solution. In a deaerated N_2O (16 mM)+2-propanol (5−20 mM)+HCN (6 mM) system, the following three processes are involved:

$$e^-_{aq} + N_2O \rightarrow N_2 + OH + OH^- \qquad (4)$$

$$H + HCN \rightarrow H_2CN \qquad (6b)$$

$$H + (CH_3)_2CHOH \rightarrow H_2 + (CH_3)_2COH \qquad (7)$$

In the absence of hydrogen cyanide, the yield of hydrogen, $G(H_2)$, should be equal to $G_H + G_{H_2}$, where G_H denotes the yield of H atoms. In the presence of hydrogen cyanide, $G(H_2)$ is decreased by the simple competition between the reactions (6b) and (7); therefore, the following equation is derived:

$$\frac{1}{G(H_2)-G_{H_2}} = \frac{1}{G_H}\left\{1 + \frac{k_{6b}(HCN)}{k_7(CH_3)_2CHOH}\right\} \qquad (II)$$

where k_{6b} and k_7 represent the rate constants of H atoms with hydrogen cyanide and 2-propanol respectively. The plot of the observed value of $1/[G(H_2)—G_{H_2}]$ against (HCN)/(2-propanol) shown in Fig. 9, indicates the linear relation between the two quantities. From the slope of the line, k_{6b}/k_7 is found to be 1.4; hence, $k_{6b}=3\times10^7\ M^{-1}\ sec^{-1}$, taking $k_7=2.3\times10^7\ M^{-1}\ sec^{-1}$.[22]

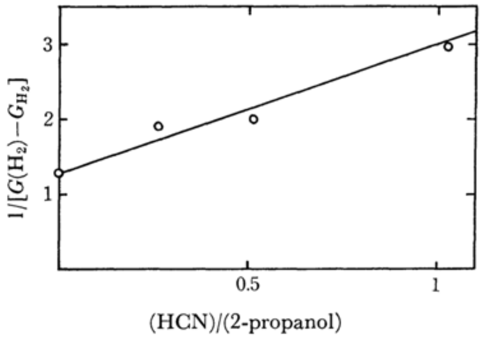

Fig. 9. Competition for H atom between HCN and 2-propanol plotted according to Eq. (II).

Reaction Mechanism. According to the findings described above and the observed yields of products, the following reaction sheme for the present study is proposed:

$$H_2O \rightsquigarrow e^-_{aq},\ H,\ OH,\ H_2,\ H_2O_2,\ H^+_{aq} \qquad (0)$$

As the reactions of the reactive species produced in reaction (0) with hydrogen cyanide, the (1a), (5a), and (6b) reaction have previously been indicated. In addition to these, the reaction (8) can be proposed:

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18) R. P. Mitra, D. V. S. Jain, A. K. Bannerjee and K. V. Raghavachari, *Nature,* **200,** 163 (1963).

19) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Norstrand, New York (1961), p. 47.

20) E. L. Cochran, F. J. Adrian and V. A. Bowers, *J. Chem. Phys.,* **36,** 1938 (1962).

21) G. Scholes and M. Simic, *J. Phys. Chem.,* **68,** 1738 (1964).

22) E. Hayon and M. Moreau, *J. Chim. Phys.,* **62,** 301 (1965).

$$\mathrm{HCN^- + H^+ \rightarrow H_2CN} \qquad (8)$$

Since $G(\mathrm{-HCN})$ is in close agreement with the total radical yield, $G_{\mathrm{e^-_{aq}}}+G_{\mathrm{H}}+G_{\mathrm{OH}}$, this finding elucidates the fact that reaction intermediates such as HCN^-, H_2CN, and H(OH)CN will not react further with HCN at low concentrations of hydrogen cyanide (6 mM). The fates of these intermediates are supposed to be as follows:

$$\begin{array}{ll} \mathrm{H_2CN + H(OH)CN} \rightarrow \mathrm{(HCN)_2 + H_2O} & (9) \\ \qquad\qquad\qquad\qquad\qquad \searrow \mathrm{H_2CNH + HCNO} & (10) \end{array}$$

Methyleneimine and cyanic acid are readily hydrolysed to yield ammonia, formaldehyde, and carbon dioxide:

$$\mathrm{H_2CNH + H_2O \rightarrow HCHO + NH_3} \qquad (11)$$

$$\mathrm{HCNO + H_2O \rightarrow CO_2 + NH_3} \qquad (12)$$

The expected mole ratio of the products, such as $NH_3 : HCHO : CO_2=2 : 1 : 1$ from the reactions (11) and (12), is almost equal to that shown in Table 1. The HCN dimer is usually considered to be iminocyanomethane, NH=CH–CN. Serre *et al.*23) and Matthews *et al.*24) have pointed out that the HCN dimer would be more stable by 20 kcal/mol in the form of amino cyanomethylene, $\mathrm{NH_2\text{–}\dot{C}\text{=}C\text{=}\dot{N}}$ (biradical), than in iminocyanomethane. Though neither isomeric form has been isolated, the HCN dimer is likely to grow into a more stable polymeric form, which is considered to be responsible for the broad absorption observed in the UV region. There was observed an increase in the UV absorption with the increase in the HCN concentration resulting from the polymeric products introduced by γ-irradiation, but it was effectively eliminated by the presence of acid or dissolved oxygen, which are effective scavengers of hydrated electrons. These results can most likely be explained in terms of the contribution of the anionic form of HCN as an initiator of the polymerization. as has been indicated by Hummel *et al*:14)

$$\mathrm{HCN^- + \mathit{n}HCN \rightarrow polymeric\ products} \qquad (13)$$

The presence of formic acid as a minor product may suggest that formamide is formed by:

$$\begin{array}{ll} \mathrm{H(OH)CN + H} \searrow & \\ \qquad\qquad\qquad \mathrm{H_2NCOH} \xrightarrow{\mathrm{H_2O}} & \\ \mathrm{H_2CN + OH} \nearrow & \\ \qquad\qquad\qquad \mathrm{HCOOH + NH_3} & (14) \end{array}$$

Formamide is usually considered to be an intermediate yielding formic acid and ammonia in the course of the hydrolysis of hydrogen cyanide in aqueous solutions.

As is illustrated in Table 1, the observed yield of hydrogen peroxide is fairly low compared with its molecular yield in water;19) however, its behavior is not clear in detail.

Although more work needs to be done to establish the detail of the system, the mechanism described above appears to be a plausible explanation of the present observation.

The author wishes to express his thanks to Professor M. Kondo of Tokyo Metropolitan University for his interest throughout this work. The author is indebted to Mr. K. Kurita for his assistances in this experimental work.

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23) J. Serre and F. Schneider, *ibid.*, **61**, 1655 (1964).

24) C. N. Matthews and R. E. Moser, *Proc. Natl. Acad. Sci.*, **56**, 1087 (1966).