Radiation-induced Formation of Tetrameric Hydrogen Cyanide in an Aqueous Solution

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(Received May 9, 1967)

It has long been well-known that the formation of polymeric hydrogen cyanide, usually called azulmic acid, is observed when a small amount of an alkaline substance is added to pure hydrogen cyanide or its highly-concentrated aqueous solution. It has also been known that the formation of azulmic acid can be observed in gamma irradiated hydrogen cyanide.[1,2] However, no work has been done on the radiation-induced polymerization of hydrogen cyanide in an aqueous solution, in which the mechanism is considered to be different from that of the pure state.

The present paper will describe a study of the radiation-induced formation of the tetrameric form of hydrogen cyanide in a dilute aqueous solution by means of UV spectroscopy and paper chromatography.

Experimental

Hydrogen cyanide was prepared by decomposing sodium cyanide of the purest grade available with 1 : 1 sulfuric acid, and it was purified by repeated distillation. Triply-distilled water was used to prepare the solution. Gamma irradiation was carried out with a ^{60}Co source at a dose rate of 2.90×10^{17} eV ml^{-1} hr^{-1}. An air-free solution of 5 ml was sealed in a cylindrical glass cell for irradiation.

The tetramer of hydrogen cyanide used as a reference was prepared according to the procedure of Webb *et al.*[3] and was recrystallized from ether until almost colorless crystals were obtained (mp 182°C).

Results and Discussion

The gamma irradiation of an air-free aqueous solution of hydrogen cyanide yields the absorption spectra shown in Fig. 1. The absorption band at 295 mμ is observed in a 0.5 M as well as in a 1 M hydrogen cyanide solution, and its intensity increases with the dose. However, the irradiation of a solution below 0.1 M yields a broad structureless absorption extending to a shorter UV region, the intensity of this absorption also increases with the dose. Webb *et al.* observed that the HCN tetramer which was extracted from azulmic acid and which was known as diaminomaleonitrile possessed an absorption maximum at 295 mμ in water.[3] Accordingly, the absorption band at 295 mμ in the present experiment may be reasonably assigned to the tetramer formed by gamma irradiation. However, its absorption curve is slightly different from that of the tetramer, this is because of the broad background absorption in

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[1] D. Hummel and O. Janssen, *Z. physik. Chem.*, **31**, 111 (1962).

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

[3] R. L. Webb, S. Frank and W. C. Schneider, *J. Am. Chem. Soc.*, **77**, 3491 (1955).

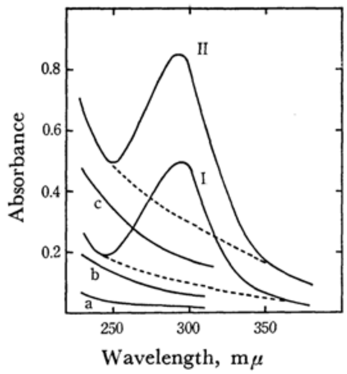

Fig. 1. UV absorption spectra of γ-irradiated aqueous HCN solutions. Dose rate$=2.90\times10^{17}$ eV ml^{-1} hr^{-1}.
0.5 M; I: 14 hr, II: 29 hr
0.1 M; a: 12 hr, b: 18 hr, c: 46 hr

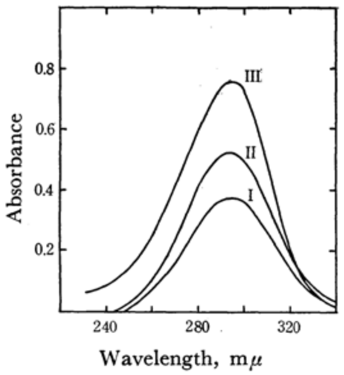

Fig. 2. Formation of HCN tetramer in γ-irradiated 0.5 M HCN solutions. Dose rate$=2.90\times10^{17}$ eV ml^{-1} hr^{-1}.
I: 14 hr, II: 29 hr, III: 6×10^{-5} M $(HCN)_4$ solution as a reference.

the UV region by some unidentified components introduced by gamma irradiation. The absorption due to the tetramer can be presented as curves I and II in Fig. 2 after the subtraction of the background absorption curve (broken line) from the total absorption in Fig. 1. The absorption curve is thus seen to be in good agreement with that of the tetramer extracted from the azulmic acid produced from pure hydrogen cyanide in the presence of a small amount of triethylamine. Taking the molar extinction coefficient of tetramer at 295 mμ as 1.40×10^4 M^{-1} cm^{-1}, the initial *G*-value of the formation of tetramer is found to be 0.43. It was found that the UV absorption at 295 mμ due to the tetramer was markedly eliminated in the presence of acid or dissolved oxygen, which is an effective scavenger of the solvated electron formed in the course of irradiation. These results most likely indicate the contribution of the solvated electron to the formation of the tetramer.

Additional confirmation of the HCN tetramer was obtained by means of paper chromatography as follows. A small amount of residue after the lyophilization of 10 m*l* of an irradiated solution was chromatographed on Toyo No. 2 filter paper, using a mixture of butanol, acetic acid and water (4 : 1 : 5) as the solvent. The HCN tetramer was identified by a comparison of its R_f value (0.82, yellow with ninhydrin reagent) with that of a pure reference compound.