bath. Carbon dioxide evolution started immediately, and in about 15 minutes a precipitate began to form. After 1 hour, the precipitate was collected, the filtrate was evaporated to dryness, and both solids were dried over P_2O_5 in high vacuum. The product, 3.3 g., was recrystallized from chloroform–hexane. On standing, the compound developed a distinct odor, reminiscent of benzaldehyde or benzonitrile. *Anal.* Calcd. for $C_{22}H_{15}N_3O_2$: C, 74.6; H, 4.3; N, 11.9; O, 9.1. Found: C, 74.6, 74.1; H, 4.5, 4.4; N, 11.64, 11.78; O, 8.6, 8.9.

Decomposition of the unknown compound at 220° gave a 20% yield of a distillate identified as crude benzonitrile, and an unidentified solid residue (nitrile trimer ?) in addition to an undetermined amount of CO_2.

[CONTRIBUTION NO. 779 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., INC., WILMINGTON 98, DEL.]

Hexacyanoethane

BY S. TROFIMENKO AND B. C. MCKUSICK

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The synthesis of hexacyanoethane, the first percyanoalkane, is described.

Percyanoalkynes[1,2] and a percyanoalkene[3] are known, but no percyanoalkane has been reported. We have now prepared hexacyanoethane, the first percyanoalkane, by treating sodium pentacyanoethanide[4] with cyanogen chloride.

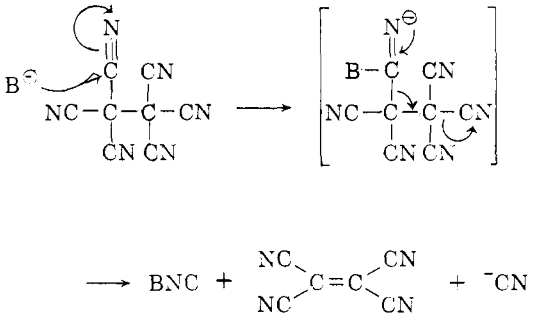
$$(NC)_3CC(CN)_2Na + ClCN \longrightarrow (NC)_3CC(CN)_3 + NaCl$$

In contrast to the usual cyanations of this type, the success of the reaction depends on the absence of a solvent for hexacyanoethane except for excess cyanogen chloride. Best results are obtained in the presence of aluminum chloride.

Careful sublimation of the crude product gave hexacyanoethane contaminated by tetracyanoethylene. The latter was removed by washing with benzene, in which hexacyanoethane is insoluble. The low yield of pure hexacyanoethane (17%) is caused by decomposition during isolation, for the infrared spectrum of the crude product is essentially that of hexacyanoethane.

Hexacyanoethane is a colorless solid that decomposes in a sealed tube above 150°. Its most striking property is its instability. It can be sublimed at 75° (2 mm.), but some decomposition to tetracyanoethylene and, presumably, cyanogen occurs during sublimation. At room temperature it soon decomposes to tetracyanoethylene and polymeric materials, but it has been stored at −80° for long periods without change. Hexacyanoethane dissolved at room temperature in ethyl acetate, tetrahydrofuran or dimethoxyethane decomposes completely overnight; this decomposition is accelerated greatly by base, moderately by acid.

On several occasions when crude hexacyanoethane was heated at reduced pressure it decomposed rather violently with the formation of tetracyanoethylene. This is reminiscent of the decomposition of isosteric hexabromoethane to the corresponding ethylene.[5] In view of the extreme sensitivity of hexacyanoethane toward base, we propose the following autocatalytic base-induced mechanism for this decomposition.



Hexacyanoethane is assigned its structure on the basis of its composition, mode of formation, decomposition to tetracyanoethylene, and infrared and mass spectra. Its infrared spectrum has only four peaks, which is consistent with a highly symmetrical structure. A single peak at 4.40 μ indicates the presence of just one kind of nitrile group, and that unconjugated. The mass spectrum shows no parent peak, but there is a large peak due to the tricyanomethyl fragment, and lesser ones corresponding to tetracyanoethylene and dicyanoacetylene.

Hexacyanoethane might be expected, like dicyanoacetylene,[6] cyanogen[6] and tetracyanoethylene,[7] to have an exceptionally high flame temperature. That this is true is indicated by a calculation like those of Kirshenbaum and von Grosse[6] based on an observed heat of combustion of about 990 kcal./mole at 25°[8]; this suggests a flame temperature in the range 4000–4600°K. Hexacyanoethane has a high endothermic heat of formation, estimated from the heat of combustion to be 240 kcal./mole at 25°; this is in fair agreement with a value of 195 kcal./mole calculated from Pauling's[9] bond energies.

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[1] C. Moureau and J. Bongrand, *Compt. rend.*, **170**, 1025 (1928).

[2] F. J. Brockman, *Can. J. Chem.*, **33**, 507 (1955).

[3] T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, Edith G. McGeer, B. C. McKusick and W. J. Middleton, *J. Am. Chem. Soc.*, **79**, 2340 (1957).

[4] O. W. Webster, W. R. Mahler and R. E. Benson, *ibid.*, **84**, 3678 (1962).

[5] M. A. Mouneyrat, *Bull. soc. chim. France*, **19**, 177 (1898); W. Taylor and A. M. Ward, *J. Chem. Soc.*, 2007 (1934).

[6] A. D. Kirshenbaum and A. Von Grosse, *J. Am. Chem. Soc.*, **78**, 2020 (1956).

[7] T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961).

[8] The experimental results are only approximate because traces of nitrogen oxides were formed during the combustion, whereas the calculations are based in the reaction of $C_8N_6 + 8O_2 \rightarrow 8CO_2 + 3N_2$.

[9] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.

Hexacyanoethane reacted readily with a number of active-hydrogen compounds to give hydrogen cyanide and tars.

Experimental

Sodium pentacyanoethanide[1] (21 g., 0.18 mole) was stirred in a dry flask with 40 ml. of cyanogen chloride. Anhydrous aluminum chloride (0.2 g.) was added, and the mixture was refluxed (wet-ice condenser) for half an hour. Cyanogen chloride was then distilled off at atmospheric pressure, and the resulting pasty solid was scraped out and air-dried (hood!) on a porous plate. The greenish crude product was divided into two portions, and each was sublimed overnight at 75° (2 mm.). The sublimates, which were mixtures of hexacyanoethane and tetracyanoethylene, were combined, crushed under benzene, and washed with benzene until the washings were no longer yellow, indicating complete removal of tetracyanoethylene. The insoluble white solid that remained was pure hexacyanoethane; weight 3.7 g. (17%). Hexacyanoethane sublimes above 150° and in a sealed capillary decomposes in the 150–300° range. Its infrared spectrum has bands at 4.40, 9.43, 9.65 and 11.55 μ.

Anal. Calcd. for C_8N_6: C, 53.3; H, 0.00; N, 46.7. Found: C, 53.4; H, 0.39; N, 47.0.

The mass spectrum of hexacyanoethane was characterized by peaks corresponding to *m/e* values of 64, 76, 90 and 128 with relative abundances 33:4.6:100:5.3 (at 145°) and 32:3.2:100:2.9 (at 155°).[10]

Partly decomposed hexacyanoethane may be purified by sublimation followed by washing with benzene.

A convenient test for hexacyanoethane in the presence of tetracyanoethylene consists of placing a drop of fresh tetrahydrofuran solution of the mixture on a filter paper strip and eluting with benzene. Tetracyanoethylene moves as a yellow band, whereas hexacyanoethane remains stationary in this system. The strip is developed with N,N-dimethylaniline. A green spot, easily distinguishable from tetracyanoethylene's blue, confirms the presence of hexacyanoethane.

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[10] The mass spectrum of tetracyanoethylene contains peaks at masses 64, 76 and 128 with relative abundances of 12, 67 and 100 and only a trace of the 90 mass ion. The spectra were obtained with a Consolidated Electrodynamics Corporation (CEC) model 21-103C mass spectrometer with a CEC heated inlet cabinet operated at 150°, a source temperature of 250°, ionizing potential of 70 v., and 10.5 μa. electron current.

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Chemistry of Tetracyanoethylene Anion Radical

BY O. W. WEBSTER, W. MAHLER AND R. E. BENSON

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Tetracyanoethylene (TCNE) reacts readily with a variety of reagents including metals, iodides and aliphatic amines to give tetracyanoethylene anion-radical (TCNE$^{\cdot-}$) derivatives. Surprisingly, TCNE also undergoes reaction with cyanide ion to give TCNE$^{\cdot-}$. Evidence that this reaction proceeds through the isolable pentacyanoethanide has been obtained through tracer studies.

Tetracyanoethylene (TCNE) is a strong π-acid, as evidenced by the large equilibrium values for its complex formation with organic π-bases.[1] In these charge-transfer complexes there is only partial electron transfer, as shown by their diamagnetic character. In addition to forming complexes of this type, TCNE also reacts with a variety of reagents to form tetracyanoethylene anion-radical (TCNE$^{\cdot-}$) derivatives, as established from electron paramagnetic resonance studies.[2] For example, TCNE reacts with potassium,[2] sodium,[2] aluminum,[3] magnesium[3] and copper[3] at room temperature to give the corresponding metal salts of TCNE$^{\cdot-}$.

The details of our earlier work are reported now together with a study of an unusual reaction of cyanide ion with TCNE to yield TCNE$^{\cdot-}$. The latter reaction was studied in some detail, since it presented a potential source of the cyano radical, which has been previously detected as a reactive species of some high-energy processes.[4] More recently, the question of the existence of the cyano radical under other conditions has been raised in reactions involving mercuric cyanide. For example, reaction of mercuric cyanide with disilicon hexachloride gave cyanotrichlorosilane, and a mechanism involving the addition of the cyano radical to the Si–Si bond was suggested.[5] In addition, reaction of mercuric cyanide with hexaphenylethane yielded cyanotriphenylmethane, but in this case it is stated that it is not certain whether the reaction involved the cyano radical or the cyanide ion.[6]

Reaction of Cyanide Ion with TCNE.—Although sodium cyanide is essentially insoluble in acetonitrile,[7] reaction with TCNE in acetonitrile solution occurs rapidly and exothermally at room temperature to give Na$^+$TCNE$^{\cdot-}$ in 70–80% yield. Efforts to demonstrate the presence of cyanogen (derived from dimerization of the potentially formed ·CN) were unsuccessful, and no appreciable quantity of hydrogen cyanide (potentially formed by abstraction of proton from the solvent by ·CN) could be detected when the reaction was conducted in the presence of ether. In addition, no polymerization occurred when TCNE was allowed to react with NaCN in the presence of either styrene or methyl acrylate, and efforts to isolate cyanosubstituted derivatives of these vinyl monomers were unsuccessful. On this basis it was concluded that ·CN was not formed as a direct product of the reaction.

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(1) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

(2) The existence of metal tetracyanoethylenides was first recognized by Prof. S. I. Weissman, Washington University, St. Louis, Mo.; see W. D. Phillips, J. C. Rowell and S. I. Weissman, *J. Chem. Phys.*, **33**, 626 (1960).

(3) O. W. Webster, W. Mahler and R. E. Benson, *J. Org. Chem.*, **25**, 1470 (1960).

(4) See, for example, J. U. White, *J. Chem. Phys.*, **8**, 79 (1940); **8**, 459 (1940).

(5) A. Kaczmarczyk and G. Urry, *J. Am. Chem. Soc.*, **81**, 4112 (1959).

(6) C. W. Schimelpfenig, *J. Org. Chem.*, **26**, 4156 (1961).

(7) We estimate the solubility of NaCN in acetonitrile to be less than 0.01%.