

High-pressure Reactions of Tetracyanoethylene

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THE hydrolysis reactions of tetracyanoethylene at atmospheric pressure have been studied by several workers. Salts of 1,1,2,3,3-pentacyanopropene were formed by reaction with water in the presence of a base such as pyridine.¹ Hydrolysis of tetracyanoethylene in neutral or acidic solutions results in the replacement of a single cyano-group by hydroxyl to form tricyanoethenol (tricyanovinyl alcohol).¹ This material was isolated as a metal or tetra-alkylammonium salt. Reaction with alcohols in the presence of catalysts such as urea or zinc acetate yielded dicyanoketen acetal.² Attempts to replace only one of the cyano-groups were not successful.

We report the reaction of tetracyanoethylene with water at high pressure and elevated temperature to give 2,3,3-tricyanoacrylamide (m.p. 175—178°). Suitable reaction conditions were found to be 75,000 to 100,000 p.s.i. and 110—150°. Although excess of water was employed, only one nitrile group could be made to react. The infrared spectrum of 2,3,3-tricyanoacrylamide clearly shows the absorption for the amide group, and the nitrile

stretching frequency is shifted to a higher wavelength of 4.58 μ . In tetracyanoethylene, the nitrile stretching frequencies are found³ at 4.42 and 4.49 μ .

Addition of methanol to tetracyanoethylene was accomplished at 130° and 75,000 p.s.i. The resulting product has been identified as *N*-methyl-2,3,3-tricyanoacrylamide (m.p. 185—187°). The infrared spectrum of this material was found to be similar to that of 2,3,3-tricyanoacrylamide except that the nitrile stretching frequency was found at 4.53 μ .

The reactions of tetracyanoethylene under high pressure have been shown to take paths completely different from those at normal pressures. Pressure apparently has facilitated the addition of alcohol and water to the nitrile group while completely suppressing the normal displacement reactions. The ease of reaction of nitriles with water under high pressure has also been demonstrated with polyacrylonitrile which was rapidly hydrolyzed to polyacrylamide.⁴

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² W. J. Middleton and V. A. Engelhardt, *J. Amer. Chem. Soc.*, 1958, **80**, 2788.

³ C. E. Looney and J. R. Downing, *J. Amer. Chem. Soc.*, 1958, **80**, 2840.

⁴ M. Prince and J. Hornyak, *J. Polymer Sci., Part A*, 1966, in the press.