

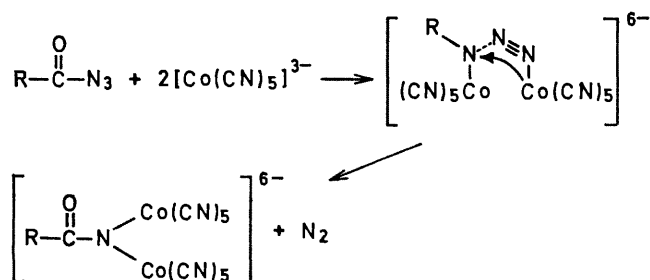
Reaction of Transition-metal Cyanides and Organic Azides

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Summary Pentacyanocobaltate(II) ion and hexacyanodinitrate(I) ion react with organic azides in water to liberate nitrogen and form metal amido-complexes, benzamidobis[pentacyanocobaltate(II)] ion.

CERTAIN transition metals, notably copper, have been reported to react with organic azides to form nitrene intermediates.¹ Iridium complexes² and iron carbonyls react with azides to form similar compounds.³ Although azides are normally inert to organic free radicals⁴ the pseudo-radical system,⁵ pentacyanocobaltate(II) ion readily liberates nitrogen from a variety of azides at 0° in aqueous solution.



When two moles of pentacyanocobaltate(II) ion at 0° in aqueous solution were added to a water-ethanol solution of

furoyl azide, one mole of nitrogen was evolved. A pale yellow solid† was isolated when the solution was added to a large volume of ethanol. In D₂O the n.m.r. spectrum of the product showed three peaks at 6.21, 5.38, and 5.23 p.p.m. with respect to Me₄Si external standard. The relative areas of the peaks were 1:1:1 and correspond to the three furan hydrogen atoms. This product can be reduced with NaBH₄ in methanol-water solution to give furamide in yields of 50%. Control experiments indicated that furamide was not formed at 0° by hydrolysis of the cobalt complex. The stoichiometry of the reaction required that two moles of pentacyanocobaltate(II) ions be used. If less than two moles were used, the quantity of nitrogen gas was reduced, and unchanged azide was isolated from the products.

The reaction of hexacyanodinitrate(I) ion with furoyl azide in aqueous methanol gave a quantitative yield of furamide; one mole of nitrogen was evolved. Nickel cyanide and yellow potassium tetracyanonickelate were isolated from the reaction mixture.

These results parallel the observations of Kauffmann and Hage with organic azides and sodium metal.⁶

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† A satisfactory elemental analysis and molecular weight was obtained for this product. Infrared data are also consistent with the assigned structure.

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