Communications TO THE EDITOR

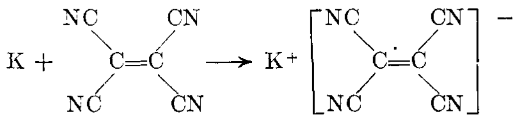
Preparation and Chemistry of Tetracyanoethylene Anion Radical

Sir:

This report describes the synthesis and preliminary study of the chemical properties of the anion radical of tetracyanoethylene (TCNE$^{\overset{\cdot}{-}}$). The physical properties of TCNE$^{\overset{\cdot}{-}}$, including spectral and electron paramagnetic resonance data, are being reported concurrently.[1]

Work in this laboratory has previously established that TCNE is an unusually strong π-acid, readily giving complexes with a variety of π-bases; *e.g.*, xylene, mesitylene, *etc.*[2] In these complexes there is only partial electron transfer, as indicated by their diamagnetic properties.

Recently, derivatives of TCNE have been synthesized in which there is complete electron transfer, as demonstrated by electron paramagnetic resonance (EPR) studies. For example, reaction of potassium with TCNE in the vapor phase has given a purple solid identified as the ion radical K$^+$TCNE$^{\overset{\cdot}{-}}$.[1] The less reactive sodium amalgam and sodium naphthalenide also convert TCNE to Na$^+$TCNE$^{\overset{\cdot}{-}}$ at room temperature. Such metals as magnesium, aluminum, zinc, and even copper are oxidized by TCNE in acetonitrile solution at room temperature to form the corresponding metal tetracyanoethylenides. In addition, nickel carbonyl undergoes oxidation and decarbonylation with TCNE to yield Ni(TCNE$^{\overset{\cdot}{-}}$)$_2$. Certain anions have also been found to convert TCNE to TCNE$^{\overset{\cdot}{-}}$ and the reaction of TCNE with potassium or sodium iodide provides a convenient laboratory synthesis of TCNE$^{\overset{\cdot}{-}}$.



$$3\mathrm{KI} + 2\mathrm{TCNE} \longrightarrow 2\mathrm{K}^+\mathrm{TCNE}^{\overset{\cdot}{-}} + \mathrm{KI}_3$$

Tetracyanoethylene (17.0 g., 0.133 mole) and potassium iodide (30.0 g., 0.181 mole) were added to 500 ml. of acetonitrile at room temperature with stirring. The potassium iodide dissolved, and 11.4 g. (51% yield) of K$^+$TCNE$^{\overset{\cdot}{-}}$ crystallized from the dark yellow solution. The bronze-colored product was purified by recrystallization from acetonitrile. *Anal.* Calcd. for C_6N_4K: C, 43.10; N, 33.51. Found: C, 43.19; N, 33.43.

K$^+$TCNE$^{\overset{\cdot}{-}}$ in the solid state is stable to usual atmospheric conditions for several weeks, and the compound can be heated at 150° in an inert atmosphere for three hours without apparent change. In solution, however, the ion radical is quite sensitive to oxygen and, to a lesser degree, to water. Reaction of K$^+$TCNE$^{\overset{\cdot}{-}}$ with water gives a 76% yield of potassium tricyanoethenolate.[3] The action of dilute hydochloric acid on K$^+$TCNE$^{\overset{\cdot}{-}}$ produces an equimolar mixture of TCNE and tetracyanoethane.[4] In addition, TCNE$^{\overset{\cdot}{-}}$ is oxidized to TCNE in 65% yield by silver trifluoroacetate.

The studies of the synthesis and properties of TCNE$^{\overset{\cdot}{-}}$ are continuing and will be reported shortly.

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[1] The existence of stable metal tetracyanoethylenides was first recognized by Prof. S. I. Weissman, Washington University, St. Louis; see W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.*, in press.

[2] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2278 (1958).

[3] W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

[4] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).