

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

Experimental

Sodium pentacyanoethanide¹ (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 min.). The sublimate, 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 C₈N₆: 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.

(10) The mass spectrum of tetracyanoethylene contains peaks at masses 61, 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 μ a. electron current.

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Chemistry of Tetracyanoethylene Anion Radical

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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⁻) derivatives. Surprisingly, TCNE also undergoes reaction with cyanide ion to give TCNE⁻. 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⁻) derivatives, as established from electron paramagnetic resonance studies.² For example, TCNE reacts with potassium,² sodium,² aluminum,³ magnesium³ and copper³ at room temperature to give the corresponding metal salts of TCNE⁻.

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⁻. 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⁻ in 70-80% yield. Efforts to demonstrate the presence of cyanogen (derived from dimerization of the potentially formed \cdot CN) were unsuccessful, and no appreciable quantity of hydrogen cyanide (potentially formed by abstraction of proton from the solvent by \cdot 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 \cdot CN was not formed as a direct product of the reaction.

(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. J. 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. Kaczmarezyk and G. Urry, *J. Am. Chem. Soc.*, **81**, 4112 (1959).

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

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

To establish that the course of the reaction was not affected by the presence of insoluble cyanide, the reaction was studied in a homogeneous system. Tetraethylammonium cyanide⁸ was synthesized for this purpose and found to be readily soluble in acetonitrile. TCNE^- was obtained in 85–95% yield from this cyanide and TCNE, regardless of the order of addition of the reagents.

However, the yield of TCNE^- was found to be markedly dependent upon the concentration of TCNE. When an excess of TCNE was used with sodium cyanide, the yield of TCNE^- fell, and a new compound having the composition $\text{NaCN}\cdot\text{TCNE}$ was isolated by diluting the acetonitrile solution with ether. With 1% excess TCNE, the yield of TCNE^- was only 10%, and the yield of $\text{NaCN}\cdot\text{TCNE}$ adduct was 33%. The adduct was obtained in 49% yield when a 10% excess of TCNE was used. This adduct was characterized as sodium pentacyanoethanide⁹ (NaPCE) on the basis of its infrared spectrum, which showed strong absorption at 4.54 and 4.65 μ attributable to a substituted malononitrile anion and the absence of absorption in the 5–6 μ region attributable to $\text{C}=\text{C}$ or $\text{C}=\text{N}$. In confirmation of the proposed structure, chlorination yielded chloropentacyanoethane, a white solid, m.p. 174–175° dec.

NaPCE was obtained as a slightly off-white solid that has moderate stability at room temperature. On heating to 140°, it is converted to TCNE^- in high yield together with cyanogen. Dissolution of NaPCE in acetonitrile at room temperature results in immediate formation of TCNE^- . The rate of this conversion is markedly lowered by the addition of 1 mole per cent. of TCNE, and this inhibitory effect is removed by the addition of CN^- .

These results suggest that NaPCE is converted to TCNE^- by CN^- and that the concentration of CN^- is appreciably lowered by the presence of TCNE. These observations are in accord with a reversible reaction involving the formation of NaPCE from TCNE and sodium cyanide as was established by studies with radioactive cyanide.

The reaction was conducted with ^{14}C -tagged KCN and a 3.2% excess of TCNE at –30° to give KPCE^* which was isolated and converted to TCNE^{-*} by heating at 140°. The latter was oxidized with 7,7,8,8-tetracyanoquinodimethan (TCNQ)¹⁰ to give TCNE^* and K^+TCNQ^- . TCNE^* was isolated by sublimation. Counting studies established that the molar activity of the isolated TCNE^* was 77.3% of the initial activity of the $^{14}\text{CN}^-$. In a separate experiment it was established that no exchange occurred between $^{14}\text{CN}^-$ and TCNE^- under the reaction conditions. Complete equilibration of $^{14}\text{CN}^-$ with TCNE to give KPCE^* would require 78.2%¹¹ of the activity

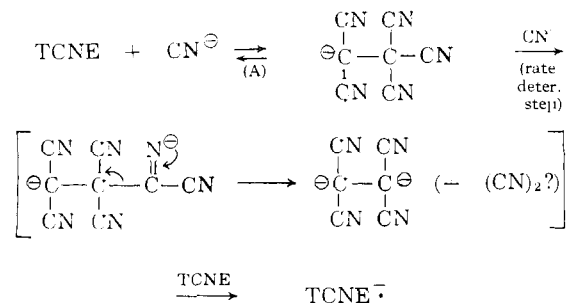
(8) Ionic cyanides that are soluble in moderately polar organic solvents are of considerable synthetic interest. The preparation of tetraethylammonium cyanide was previously described (D. S. Stromholm, *Ber.*, **31**, 2289 (1898)), but the compound was neither isolated nor characterized. See footnote 22 for synthetic details.

(9) The structure of NaPCE has been further confirmed by reaction with cyanogen chloride to give hexacyanoethane (S. Trofinenko and B. C. McKusick, to be published).

(10) D. S. Ackar, R. S. Harder, W. R. Hertler, W. Mahler, L. R. Melby, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, **82**, 6408 (1960).

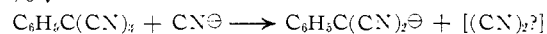
of the $^{14}\text{CN}^-$ to appear in the TCNE^{-*} (and hence in the isolated TCNE^*).

To establish that the equilibrium involved NaPCE and the reactants NaCN and TCNE, labeled TCNE was added to acetonitrile containing NaPCE . After 1.5 hours at room temperature, NaPCE^* was isolated, converted to TCNE^{-*} , and the latter oxidized to TCNE^* having molar activity corresponding to complete equilibration of the cyano groups. These results establish equilibrium A.



Furthermore, in view of the insolubility of the cyanide,⁷ it appears that the equilibrium lies far to the side of PCE^- . If CN^- is the agent responsible for the conversion of PCE^- to TCNE^- , then stabilization of solutions of PCE^- by TCNE is understood readily.

The postulated reaction of PCE^- with CN^- is unusual, since it involves not only attack of one anion on another at modest temperature but also the attack of CN^- on a nitrile group. To establish that the latter reaction could occur under these conditions, the action of CN^- on phenyltricyanomethane¹² was studied. This reaction in acetonitrile at –60° gave phenylmalononitrile anion in 60% yield



and on this basis it is believed that the attack of cyanide on PCE^- is feasible. By analogy, reaction of CN^- with NaPCE would yield disodium tetracyanoethanediide [Na_2TCNE]. In a separate experiment it was shown that Na_2TCNE , derived from tetracyanoethane and sodium hydride, reacts readily with TCNE to give TCNE^- in high yield. On this basis, the reactions in Fig. 1 are postulated for the conversion of TCNE to TCNE^- with cyanide ion.

No cyanogen, the expected by-product, was found in this study. However, it was shown that cyanogen did not survive the reaction conditions. Thus, efforts to recover added cyanogen from the TCNE – NaCN –acetonitrile reaction system were unsuccessful.

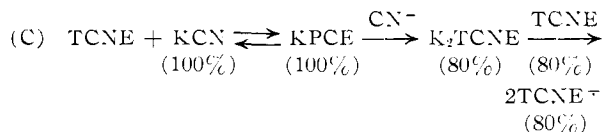
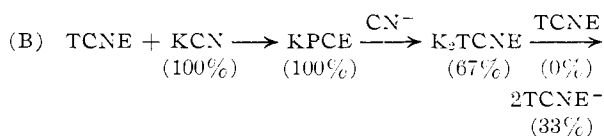
The reaction of TCNE with an equivalent of labeled potassium cyanide was examined at 25° and 40°. Under these conditions, no KPCE was isolated and K^+TCNE^- was formed directly.

If the reaction of CN^- with TCNE were considerably slower than the conversion of KPCE to K^+TCNE^- , the TCNE^- formed would be ex-

(11) Theory for complete equilibration of an equimolar amount of $^{14}\text{CN}^-$ with TCNE is 80%. However, TCNE was used in slight excess, thus accounting for the theoretical value of 78.2%.

(12) J. K. Williams, U. S. Patent 2,993,597, August 8, 1961.

pected to contain approximately 33% of the molar activity of the $CN^{\ominus*}$ (B).



However, if the reversion of KPCE to TCNE and CN^{\ominus} is much faster than the reaction of KPCE with CN^{\ominus} , the $TCNE^-$ would be expected to have molar activity approaching 80% of that of the $CN^{\ominus*}$. These values represent the extreme conditions, and, if the rates of the reactions are somewhat comparable, then molar activities for $TCNE^-$ lying between 33% and 80% are to be expected.

At 25° and 40°, 57% and 55%, respectively, of the molar activity of $CN^{\ominus*}$ appeared in $TCNE^-$, as established by counting studies on the isolated TCNE. These results suggest that under these conditions $TCNE^-$ is formed by both pathways B and C, and that the rate of reversion of KPCE to TCNE and CN^- is larger than the rate of reaction of CN^{\ominus} with KPCE.¹³

Other Syntheses of $TCNE^-$ —As reported previously,^{2,3} TCNE reacts with a variety of metals at room temperature to give metal $TCNE^-$ derivatives. For example, reaction of TCNE in acetonitrile with copper yields Cu^+TCNE^- . In addition, lead also reacts readily to give $Pb^{++}(TCNE^-)_2$. These compounds appear to have excellent stability to air in the solid state.

Iodide ion also reacts with TCNE in acetonitrile to yield $TCNE^-$. Free iodine is formed in this reaction, and excess iodide usually has been used as a scavenging agent for iodine by formation of the triiodide ion. The sodium and lithium derivatives can be prepared readily in this manner from the corresponding iodides. Alkylammonium iodides also react readily with TCNE in acetonitrile to give the corresponding ammonium $TCNE^-$ derivatives, as established from spectral analyses.

Tertiary aliphatic amines also react with TCNE in acetonitrile to give ammonium $TCNE^-$ compounds. In this respect TCNE further resembles 7,7,8,8-tetracyanoquinodimethane.¹⁰ The source of the proton has not been established, but it is presumably derived from the amine.¹⁴

Reaction of a moderately strong Lewis base with TCNE in the presence of an equimolar quantity of tetracyanoethane (H_2TCNE) yields onium $TCNE^-$ derivatives readily. For example, 1,4-diazabicyclo-[2.2.2]octane in acetonitrile with $TCNE-H_2TCNE$

(13) It is of interest that only a small temperature effect is noted. However, we do not wish to draw further conclusions from these studies because of experimental limitations. The yield of $TCNE^-$ is 65–80%, and it would be difficult to assess the effect of side reactions introducing activity into $TCNE^-$.

(14) This type of reaction is discussed at some length for the synthesis of $TCNQ^{\ominus}$ derivatives from 7,7,8,8-tetracyanoquinodimethane ($TCNQ$) and tertiary aliphatic amines (see L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Moehl, *J. Am. Chem. Soc.*, **84**, 3374 (1962)).

gives the corresponding ammonium $TCNE^-$ derivative. This salt has a volume resistivity of 1.6×10^9 ohm-cm. in compacted form.¹⁵

Presumably, a proton is removed from H_2TCNE by the base to yield $HTCNE^-$, which undergoes an electron transfer with TCNE to yield $TCNE^-$ and $HTCNE\cdot$. An acid-base reaction of the latter with the Lewis base gives $TCNE^-$ or, alternatively, disproportionation of $HTCNE\cdot$ yields TCNE and H_2TCNE . Spectroscopic evidence for formation of a variety of $TCNE^-$ derivatives by this synthetic procedure was obtained.

Chemistry of $TCNE^-$ —Metal $TCNE^-$ derivatives are relatively stable in the solid state. For example, K^+TCNE^- has been heated at 150° in an inert atmosphere for three hours with no apparent change. In addition, the compound has been exposed to atmospheric conditions for one month with no apparent change, as established from infrared absorption studies. In solution, however, metal $TCNE^-$ derivatives are quite sensitive to oxygen and, to a lesser degree, to water. For this reason solutions must be prepared in anhydrous, deaerated solvents and protected from the atmosphere. Addition of K^+TCNE^- to deaerated water has given potassium tricyanoethenolate^{16,17} in 76% yield. Furthermore, on passing oxygen through a solution of K^+TCNE^- in acetonitrile, potassium pentacyanopropenide¹⁶ and potassium tricyanoethenolate were obtained in 36% and 22% yields, respectively.

Acidification of solutions of $TCNE^-$ gives an equimolar mixture TCNE and H_2TCNE . Presumably, the anion-radical is initially protonated to yield $HTCNE\cdot$, which disproportionates to the observed products.¹⁸

$TCNE^-$ derivatives have been oxidized to TCNE by a variety of reagents. For laboratory purposes, 7,7,8,8-tetracyanoquinodimethane is a preferred reagent, since metal 7,7,8,8-tetracyanoquinodimethanides are insoluble and stable.¹⁹ Thus, the TCNE formed can be separated from the oxidant by filtration or sublimation. Silver trifluoroacetate is also an excellent oxidizing agent, giving TCNE in high yield. Bromine and chlorine also react with $TCNE^-$ to give TCNE although in lower yields.

Physical Properties of $TCNE^-$ —Characterization of $TCNE^-$ derivatives has been facilitated by spectroscopic studies. The infrared spectrum, determined in potassium bromide, is markedly simple, showing absorption at 4.53, 4.58 and 7.33 μ .

(15) The resistivities of the $TCNE^-$ derivatives are much higher than those of the corresponding derivatives of 7,7,8,8-tetracyanoquinodimethane (see reference of footnote 14).

(16) W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Ringelhardt, *J. Am. Chem. Soc.*, **80**, 2796 (1958).

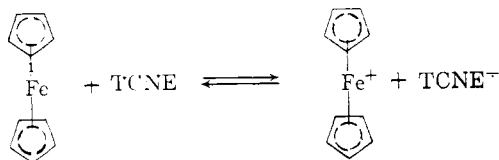
(17) C. L. Dickinson, D. W. Wiley and B. C. McKusick, *ibid.*, **82**, 6134 (1960).

(18) An alternate mechanism, proposed by D. E. Paul, D. Lipkin and S. I. Weissman (*ibid.*, **78**, 116 (1956)) for reaction of aromatic ion radicals with water, is for the $HTCNE\cdot$ to capture an electron from $TCNE^-$ giving $HTCNE^-$ and TCNE. A second protonation then completes the reaction to give H_2TCNE and TCNE.

(19) Although TCNE and 7,7,8,8-tetracyanoquinodimethane have similar reduction potentials (+0.152 and +0.127 v., respectively, referred to S.C.E. in acetonitrile), the reaction proceeds readily and essentially to completion, presumably because of the high insolubility of metal 7,7,8,8-tetracyanoquinodimethanides.

The ultraviolet absorption spectrum, determined in acetonitrile, shows broad absorption from 350 to 500 $m\mu$ with numerous vibrational maxima: 468 (ϵ 4400), 457 (ϵ 5670), 445 (ϵ 6520), 435 (ϵ 7100), 425 (ϵ 7100), 416 (ϵ 6890), 407 (ϵ 6200), 398 (ϵ 5460), 390 (ϵ 4660), 382 (ϵ 3810), 374 (ϵ 3070) and 366 $m\mu$ (ϵ 2440). In acetonitrile containing 0.1 N lithium perchlorate TCNE shows two reduction waves with $E^{1/2} +0.152$ and -0.561 v. vs. S.C.E., with nearly equal diffusion currents. On this basis it appears that TCNE is reduced to $TCNE^{\cdot-}$ and the latter to $TCNE^{2-}$. The pronounced energy difference between the formation of the ion radical and the dianion presumably accounts for the high solution stability of $TCNE^{\cdot-}$ with respect to $TCNE$ and $TCNE^{2-}$.

Ferricenium Tetracyanoethylene.—An unusual $TCNE^{\cdot-}$ derivative was formed from ferrocene. Unlike the benzenoid aromatics, which give π -complexes, ferrocene with $TCNE$ at 60° in the solid state gave the green ferricenium $TCNE^{\cdot-}$. Solutions in acetonitrile gave a strong e.p.r. signal attributable to $TCNE^{\cdot-}$, and the ultraviolet spectrum showed the presence of $TCNE^{\cdot-}$ as well as of ferrocene and $TCNE$. Addition of the product to cyclohexane brought about reversion to $TCNE$ and ferrocene, presumably because of the high solubility of ferrocene together with the low solubility of $TCNE$. These results indicate a facile equilibrium between ferrocene- $TCNE$ and ferricenium- $TCNE^{\cdot-}$.



Experimental

Acetonitrile was distilled from phosphorus pentoxide through a glass helices-packed column under nitrogen. The water content, as measured by Karl Fischer titration, was less than 6 p.p.m. Because of the sensitivity of $TCNE^{\cdot-}$ to oxygen, all reactions were conducted in a nitrogen atmosphere. To avoid exposure of solvents to the atmosphere, transfers from reagent bottles were made by a syringe.

Reagent grade potassium and sodium cyanide were dried at 100° under reduced pressure. Melting points are uncorrected.

Potassium Tetracyanoethylene.—To a solution of 5.10 g. (0.399 mole) of $TCNE$ in 500 ml. of acetonitrile cooled to about -10° was added 25.4 g. (0.390 mole) of potassium cyanide. The mixture was stirred 2 hours and then filtered. On standing overnight, 33 g. (50% yield) of $K^+TCNE^{\cdot-}$ crystallized. The product was collected by filtration, washed with acetonitrile, and dried. The e.p.r. spectrum of $TCNE^{\cdot-}$ consists of 11 lines with a spacing of 1.56 gauss.²⁰

Anal. Calcd. for C_6N_4K : C, 43.10; N, 33.51. Found: C, 42.85; N, 33.50.

Sodium Tetracyanoethylene.—A suspension of 1.76 g. (35.9 μ moles) of sodium cyanide in 50 ml. of acetonitrile was stirred at room temperature under nitrogen, and a solution of 4.60 g. (36.0 μ moles) of $TCNE$ in 50 ml. of acetonitrile was added dropwise over 4 hours. Crystalline $Na^+TCNE^{\cdot-}$ (3.17 g., 58% yield) was isolated by filtration and identified by its infrared spectrum.

Sodium Pentacyanoethanide (NaPCE).—A suspension of 10.0 g. (0.204 mole) of anhydrous sodium cyanide in 200

ml. of acetonitrile was cooled to 0° . Twenty-five grams (0.195 mole) of $TCNE$ was added to the stirred solution in one portion. The reaction mixture, which had turned dark, was stirred for 3 hours at 0° and was filtered under nitrogen. Three grams of an unidentified solid remained on the filter. The solution was diluted with 600 ml. of dry ether followed by 600 ml. of low-boiling petroleum ether. Approximately 200 ml. of a dark oil separated. This oil then was diluted with approximately 200 ml. of dry ether. Sodium pentacyanoethanide (17 g., 49% yield) crystallized, was separated by filtration, washed with two 100-ml. portions of ether, and dried. The infrared spectrum of NaPCE, determined in Nujol, shows absorption at 4.54(s), 4.65(s), 7.65(m), 8.55(w), 9.48(m) and 11.22(m) μ .

Anal. Calcd. for C_7N_5Na : C, 47.47; N, 39.55. Found: C, 48.15; N, 39.23.

Approximately 0.2 g. (1.1 μ moles) of NaPCE was heated in an oil-bath at 0.3 mm. At 140° a gas evolved vigorously and was collected in a liquid nitrogen trap. The gas evolution ceased after a few minutes. The infrared spectrum of the gas showed that it was principally cyanogen. The deep purple residue from the pyrolysis was characterized as $Na^+TCNE^{\cdot-}$ by e.p.r.

For synthesis of $TCNE^{\cdot-}$, 19.0 g. (0.1073 mole) of NaPCE was dissolved in acetonitrile at room temperature. The solution quickly turned yellow and $Na^+TCNE^{\cdot-}$ precipitated. The suspension was stirred for 1 hour and was diluted with 500 ml. of ether. Filtration gave 13.5 g. (83%) of $Na^+TCNE^{\cdot-}$ which was characterized by its infrared spectrum.

Chloropentacyanoethane.²¹—To a solution of 13.0 g. (0.102 mole) of tetracyanoethylene in 200 ml. of acetonitrile at -35° was added 4.90 g. (0.100 mole) of dried, powdered sodium cyanide. The resulting mixture was stirred for 3 hours at -40 to -25° . By this time the sodium cyanide had completely dissolved, and the dark mixture containing some crystalline platelets of sodium pentacyanoethanide was treated with 7.1 g. (0.1 mole) of gaseous chlorine for 15 minutes. The yellow mixture was filtered, and the filtrate was concentrated by distillation at room temperature and reduced pressure to give a yellow solid. Sublimation at 110° (0.1 mm.) gave 16.2 g. (85% yield) of crude chloropentacyanoethane, m.p. 172 – 174° dec. Successive rapid recrystallizations from ethylene chloride followed by sublimation afforded an analytical sample, m.p. 174 – 175° dec. The infrared spectrum shows absorption at 4.93(s), 9.10(m), 9.35(s), 9.58(sh, m), 9.96(in), 10.8(s), 11.0(m) and 12.1(s) μ . The product decomposes on standing at room temperature.

Anal. Calcd. for C_5N_5Cl : C, 44.38; N, 36.97; Cl, 18.72. Found: C, 44.57; N, 38.08; Cl, 18.39.

Reaction of $TCNE$ with Tetraethylammonium Cyanide.²²—A solution of 0.85 g. (6.64 μ moles) of $TCNE$ in 20 ml. of acetonitrile was added dropwise during 3 hours to a stirred solution of 1.03 g. (6.60 μ moles) of $Et_4N^+CN^-$ in 80 ml. of acetonitrile at room temperature. The ultraviolet spectrum of the reaction solution established that $TCNE^{\cdot-}$ was the major product. The yield of $Et_4N^+TCNE^{\cdot-}$ was 97%.

Essentially the same result was obtained when the order of addition of the reagents was reversed. A solution of 1.12 g. (7.18 μ moles) of $Et_4N^+CN^-$ in 20 ml. of acetonitrile was added dropwise over 3 hours to a stirred solution of 0.92 g. (7.19 μ moles) of $TCNE$ in 80 ml. of acetonitrile at room temperature. The ultraviolet spectrum of the reaction solution indicated that $TCNE^{\cdot-}$ was obtained in 86% yield.

(21) We are indebted to Dr. D. W. Wiley for this experiment.

(22) Although Stromholm has reported the use of an aqueous solution of tetraethylammonium cyanide,⁸ the synthesis of the compound is not described. We have found that anhydrous tetraethylammonium cyanide can be prepared by the following method: A solution of 50 g. of sodium cyanide in 1 l. of anhydrous methanol was added dropwise during 3 hours to a stirred solution of 100 g. of anhydrous tetraethylammonium chloride in 200 ml. of methanol. The entire operation was conducted under nitrogen. The reaction mixture was filtered and the filtrate evaporated to dryness under reduced pressure. The residue was extracted with 1 l. of dry acetonitrile. The resulting solution was concentrated to about 200 ml. under reduced pressure. After filtration and washing with acetonitrile there remained 47 g. of tetraethylammonium cyanide. *Anal.* Calcd. for $C_8H_{20}N_2$: C, 69.17; H, 12.90; N, 17.93. Found: C, 69.82; H, 12.96; N, 17.77. On dilution with tetrahydrofuran the filtrate yielded an additional 28 g. of the cyanide.

(20) The theoretical number of lines for four equivalent ^{14}N nuclei is nine. It has been postulated that the weak tenth and eleventh lines are due to ^{13}C satellite splittings. See footnote 2.

Reaction of TCNE with KCN-¹⁴C.—A solution of 1.501 g. (11.73 mmoles) of TCNE in 20 ml. of acetonitrile was cooled to -40° and 0.7917 g. (12.15 mmoles) of KCN-¹⁴C was added.²³ An additional 0.104 g. (0.81 mmole) of TCNE was then added and the solution was stirred at -40° to -30° for 3.5 hours. The solution was filtered cold and 250 ml. of ether was added to the filtrate. KPCE precipitated and, after cooling 30 minutes in an ice-water-bath, was collected on a filter. After drying at 56° (0.3 mm.), the KPCE weighed 1.9622 g. (84% yield). Its activity was 1.660 $\mu\text{c./mmole}$ (theor. 1.687). A portion (1.8862 g., 9.78 mmoles) was heated at $80-144^{\circ}$ (0.3 mm.) for 2 hours and gave crude K^+TCNE^- (1.652 g.). The activity was 1.156 $\mu\text{c./mmole}$. K^+TCNE^- (0.8193 g., 4.90 mmoles) was suspended in 20 ml. of tetrahydrofuran and 1.00 g. of anhydrous 7,7,8,8-tetracyanoquinodimethan was added. The mixture was stirred 2 hours, the solvent was removed under reduced pressure, and the residue was heated in a sublimator at $80-100^{\circ}$ (0.3 mm.). Slightly yellow TCNE (0.3612 g., 58% yield) was collected and then resublimed. The activity of the resublimed product was 1.335 $\mu\text{c./mmole}$. The theoretical value for complete exchange of cyano groups is 1.350 $\mu\text{c./mmoles}$.

Reaction of TCNE with KCN-¹⁴C at Room Temperature in Acetonitrile.—A mixture of 1.210 g. (9.47 mmoles) of TCNE and 0.616 g. (9.47 mmoles) of KCN-¹⁴C was stirred under nitrogen in 20 ml. of acetonitrile at 25° for 2 hours. The solvent was then removed under reduced pressure,²⁴ and 2.00 g. (9.8 mmoles) of 7,7,8,8-tetracyanoquinodimethan was added along with 20 ml. of tetrahydrofuran. The mixture was stirred 1.5 hours. The solvent was removed under reduced pressure and the residue heated in a sublimator at $80-100^{\circ}$ (0.5 mm.). Tetracyanoethylene (0.7755 g., 64% yield) sublimed. The activity of the product was 0.988 $\mu\text{c./mmole}$. The theoretical value for complete exchange of cyano groups is 1.382 $\mu\text{c./mmole}$.

Reaction of TCNE with KCN-¹⁴C at 45° .—A solution of 1.22 g. (0.95 mmole) of TCNE in 30 ml. of acetonitrile was heated to 45° , and 0.62 g. (0.95 mmole) of KCN-¹⁴C was added in one portion. The reaction mixture quickly turned brown and was stirred for 0.75 hour. The solvent was removed under reduced pressure, and the residue was heated in a sublimator at 80° (0.3 mm.) for 1 hour. No TCNE sublimed. The residue was suspended in 20 ml. of tetrahydrofuran and 2.00 g. (0.98 mmole) of 7,7,8,8-tetracyanoquinodimethan was added. After stirring 3 hours the solvent was again evaporated under reduced pressure. On heating the residue at $80-100^{\circ}$ (0.3 mm.) in a sublimator for 1 hour, 0.72 g. (59% yield) of TCNE sublimed. Its activity was 0.956 $\mu\text{c./mmole}$. The activity corresponding to complete exchange is 1.382 $\mu\text{c./mmole}$.

Exchange Study of K^+TCNE^- with KCN-¹⁴C.—A solution of 0.60 g. (3.60 mmoles) of K^+TCNE^- in 30 ml. of acetonitrile was stirred with 0.82 g. (12.6 mmoles) of KCN-¹⁴C for 12 hours. The mixture was filtered under nitrogen, the solvent was removed from the filtrate under reduced pressure, and 0.735 g. (3.61 mmoles) of anhydrous 7,7,8,8-tetracyanoquinodimethan and 20 ml. of tetrahydrofuran were added. The mixture was stirred 2 hours, the solvent was removed under reduced pressure, and the residue was heated in a sublimator at $80-100^{\circ}$ (0.8 mm.); TCNE (0.2800 g., 61% yield) sublimed. A scintillation count showed the sample to be inactive.

Exchange of Cyano Groups between Sodium Pentacyanoethane and TCNE.—A solution of TCNE-¹⁴C (0.29 g., 2.26 mmoles, 1.34 $\mu\text{c./mmole}$) in 20 ml. of acetonitrile was stirred with 0.50 g. (2.82 mmoles) of NaPCE for 1.5 hours. The deep purple solution (λ_{max} 540 m μ) was poured into 1 l. of ether and 10 ml. of petroleum ether. NaPCE (0.33 g., 66% yield) crystallized and was collected by filtration. The product was redissolved in 20 ml. of tetrahydrofuran and stirred for 2 hours at room temperature. The Na^+TCNE^- which formed was oxidized by stirring with 0.38 g. (1.86 mmoles) of 7,7,8,8-tetracyanoquinodimethan for an additional 3 hours. The solvent was removed by evaporation, and the residue was heated at $80-100^{\circ}$ (0.3 mm.) to give

TCNE (0.18 g., 76% yield). Its activity was 0.53 $\mu\text{c./mmole}$. The theoretical activity for complete equilibration is 0.52 $\mu\text{c./mmole}$.

Reaction of Phenyltricyanomethane with KCN.—A solution of 1.56 g. (9.34 mmoles) of phenyltricyanomethane¹² in 30 ml. of acetonitrile was cooled to -40° under nitrogen, and 0.65 g. (10.0 mmoles) of KCN was added in one portion. The suspension was stirred 3 hours. At the end of this time all of the potassium cyanide had dissolved and the solution was light purple. The cold solution was filtered under nitrogen into 500 ml. of dry ether. Potassium phenylmalononitrile (1.09 g., 60% yield) crystallized and was identified by comparison of its infrared spectrum with that of an authentic sample prepared from phenylmalononitrile and potassium methoxide; $\lambda_{\text{max}}^{\text{NaOH}}$ 4.57(m), 4.72(s), 6.25(m), 6.72(m), 7.70(m), 8.11(m), 8.48(w), 8.55(w), 10.3(w), 11.2(w), 13.3(m) and 14.4(m) μ .

Disodium Tetracyanoethanediide.—A suspension of 38.0 g. (0.895 mole) of sodium hydride—mineral oil dispersion (53.5% sodium hydride) in 300 ml. of glyme was cooled to -10 to -5° . A solution of 59 g. (0.46 mole) of tetracyanoethane²⁵ in 200 ml. of glyme was added dropwise to the stirred suspension over 2 hours. Hydrogen evolved profusely. The mixture was stirred an additional 6 hours at -10 to -5° . The cream-colored suspension of disodium tetracyanoethanediide was filtered under nitrogen, and the product was washed with six 100-ml. portions of glyme. After drying 8 hours at 25° (0.3 mm.) the product weighed 167.5 g. The product was solvated with glyme since a weight reduction corresponding to loss of two dimethoxyethane residues resulted on heating at 144° (0.3 mm.) for 20 hours. The infrared spectrum shows absorption at 4.45(w), 4.62(s), 4.78(s), 7.90(m) and 10.16(w) μ . Treatment of the product with acid regenerated tetracyanoethane.

Anal. Calcd. for $\text{C}_6\text{N}_4\text{Na}_2$: C, 41.39; N, 32.18. Found: C, 41.22; N, 31.70.

Reaction of Disodium Tetracyanoethanediide with TCNE.—To a solution of 1.65 g. (12.99 mmoles) of TCNE in 50 ml. of acetonitrile at 40° was added 3.67 g. (13.62 mmoles) of $\text{Na}_2\text{TCNE}\cdot 2\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$. The solution turned dark almost immediately and was warmed to room temperature over 3 hours. Crystalline Na^+TCNE^- (2.73 g.) was isolated by filtration and identified by its infrared spectrum. Dilution of the filtrate with ether caused precipitation of an additional 0.63 g. of Na^+TCNE^- . The total yield was 3.36 g. (86% yield).

Cesium Tetracyanoethylene.—To a solution of 5.80 g. (45.2 mmoles) of TCNE in 80 ml. of acetonitrile was added 11.71 g. (45.2 mmoles) of cesium iodide. The mixture was stirred 6 hours under nitrogen; Cs^+TCNE^- (5.70 g., 48% yield) was isolated by filtration. An analytical sample was prepared by recrystallization from acetonitrile. The identity of the product was confirmed by the infrared spectrum.

Anal. Calcd. for $\text{C}_6\text{N}_4\text{Cs}$: C, 27.61; N, 21.47. Found: C, 27.88; N, 21.47.

Lithium Tetracyanoethylene.—To a suspension of 5.00 g. (39.0 mmoles) of TCNE in 200 ml. of dry ether was added 4.50 g. (33.6 mmoles) of lithium iodide in 10 ml. of acetonitrile. The mixture was stirred 2 hours and filtered to give Li^+TCNE^- (1.50 g., 33% yield) identified by its infrared spectrum.

Anal. Calcd. for $\text{C}_6\text{N}_4\text{Li}$: C, 53.38; N, 41.51. Found: C, 53.88; N, 41.10.

Lead Tetracyanoethylene.—A solution of 1.50 g. (11.7 mmoles) of TCNE was stirred with 1.15 g. (5.52 mmoles) of fresh lead filings in 50 ml. of acetonitrile for 24 hours at room temperature; $\text{Pb}^{++}(\text{TCNE}^-)_2$ (2.32 g., 90% yield) was isolated by filtration. An analytical sample was dried at 80° (0.3 mm.). The infrared spectrum identified the product as $\text{Pb}^{++}(\text{TCNE}^-)_2$.

Anal. Calcd. for $\text{C}_{12}\text{N}_8\text{Pb}$: C, 31.05; N, 24.18; Pb, 44.72. Found: C, 31.19; N, 24.01; Pb, 44.60.

N-Methylquinolinium Tetracyanoethylene.²⁶—Quinoline methiodide (2.7 g., 10.0 mmoles) was dissolved in 200 ml. of boiling methylene chloride, and the solution was cooled to room temperature. Similarly, a solution of 1.28 g.

(23) The KCN-¹⁴C used in this and subsequent experiments was obtained from New England Nuclear Corp. and was in a finely powdered form prepared alkali free by precipitation from aqueous solution with ethanol. Its activity was 1.728 $\mu\text{c./mmole}$.

(24) In similar experiments, it was shown that no TCNE was present at this point.

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

(26) We are indebted to Dr. L. R. Melby for this experiment.

(10.0 mmoles) of TCNE in 100 ml. of methylene chloride was prepared. The latter was poured quickly into the methiodide solution and the flask was immersed immediately in an ice-acetone-bath. After 15 minutes, the shiny, golden brown needles were collected on a filter, washed with methylene chloride, and dried under a stream of nitrogen, then in high vacuum at room temperature. The yield of N-methylquinolinium TCNE⁻ was 0.68 g. (25%), m.p. 129–131° dec.; the volume resistivity of a compaction was 5.1×10^{10} ohm-cm.

Anal. Calcd. for C₁₆H₁₀N₅: C, 70.57; H, 3.70; N, 25.72. Found: C, 70.67; H, 3.95; N, 25.90.

Cuprous Tetracyanoethylene.—To a solution of 4.00 g. (31.2 moles) of TCNE in 15 ml. of acetonitrile was added excess copper turnings. The mixture was allowed to stand 2 days. The copper turnings, which were now coated with black Cu⁺TCNE⁻, were collected by filtration and were washed with fresh acetonitrile. The acetonitrile wash solution was diluted with 250 ml. of benzene. Black Cu⁺TCNE⁻ precipitated and was identified by its ultraviolet spectrum.

Anal. Calcd. for C₁₀N₆Cu: Cu, 33.17. Found: Cu, 33.05.

Ferricenium Tetracyanoethylene.—A mixture of 1.86 g. (10.0 mmoles) of ferrocene and 1.28 g. (10.0 mmoles) of TCNE was heated in an evacuated, sealed tube at 60° for 4 hours. Green, crystalline ferricenium TCNE⁻ formed and was purified by sublimation.

Anal. Calcd. for C₁₆H₁₀N₄Fe: C, 61.18; H, 3.22; N, 17.83; Fe, 17.79. Found: C, 60.94; H, 3.32; N, 17.76; Fe, 18.19.

A single crystal had a resistivity of 5×10^9 ohm-cm. The crystalline ferricenium TCNE⁻ exhibited no e.p.r. signal. However, solutions in acetonitrile gave a strong e.p.r. signal. The ultraviolet spectrum of ferricenium TCNE⁻ in acetonitrile clearly showed the presence of TCNE⁻ as well as TCNE and ferrocene, indicating the reversibility of the reaction. Dissolution in cyclohexane caused reversion to TCNE and ferrocene.

K⁺TCNE⁻ from TCNE, H₂TCNE and KOAc.—A solution of 11.2 g. (87.5 mmoles) of TCNE and 12.0 g. (92.4 mmoles) of H₂TCNE in 100 ml. of tetrahydrofuran was stirred with 9.00 g. (91.4 mmoles) of KOAc at room temperature. After 0.5 hour the mixture was filtered to give K⁺TCNE⁻ (7.1 g., 48% yield) identified by its characteristic e.p.r. spectrum.

Reaction of TCNE, H₂TCNE and 1,4-Diazabicyclo[2.2.2]octane.—A solution of 1.00 g. (7.81 mmoles) of TCNE and 1.00 g. (7.69 mmoles) of tetracyanoethane in 30 ml. of tetrahydrofuran was cooled to 0°, and a solution of 1.74 g. (15.5 mmoles) of dry 1,4-diazabicyclo[2.2.2]octane in 30 ml. of tetrahydrofuran was added slowly over 5 minutes. The purple solid which precipitated almost at once was collected on a filter and washed with tetrahydrofuran. After drying 4 hours at 0.2 mm., the product weighed 2.6 g. (69%). Recrystallization from acetonitrile gave 1-azonia-4-azabicyclo[2.2.2]octane tetracyanoethylene, m.p. 163° dec. The infrared spectrum was consistent with the proposed structure. The volume resistivity was 1.6×10^9 ohm-cm.

Anal. Calcd. for C₁₂H₁₃N₆: C, 59.70; H, 5.45; N, 34.80. Found: C, 59.77; H, 5.55; N, 34.42.

Quinolinium Tetracyanoethylene.²⁶—To a solution of 0.13 g. (1.02 moles) of TCNE in 25 ml. of methylene chloride at room temperature was added 0.13 g. (1.00 mmole) of H₂TCNE in 5 ml. of tetrahydrofuran; to this was added a solution of 0.26 g. (2.00 mmoles) of quinoline in 5 ml. of CH₂Cl₂, and the resulting solution was immediately cooled in ice-water. Golden-brown needles separated and after 10 minutes the solid was collected, washed with 25 ml. of CH₂Cl₂ on the funnel, and was sucked dry under nitrogen. The yield was 0.21 g. (40%). The product was identified as quinolinium tetracyanoethylene by its infrared and ultraviolet absorption spectra. The volume resistivity of a compaction was 3×10^9 ohm-cm.

Anal. Calcd. for C₁₅H₈N₅: C, 69.75; H, 3.13; N, 27.13. Found: C, 70.33; H, 3.33; N, 27.01.

2,6-Lutidinium Tetracyanoethylene.²⁶—To a solution of 0.13 g. (1.02 mmoles) of TCNE in 25 ml. of methylene chloride at room temperature was added 0.13 g. (1.00 mmole) of H₂TCNE in 5 ml. of tetrahydrofuran. To this was added a solution of 0.21 g. (2.00 mmoles) of luti-

dine in 5 ml. of methylene chloride, and the mixture was immediately cooled in ice-water. Golden brown leaves separated, and after 10 minutes, the solid was collected, washed with 25 ml. of methylene chloride on the funnel, and sucked dry under nitrogen. The yield was 0.12 g. (25%). The product was identified as 2,6-lutidinium tetracyanoethylene by its infrared and ultraviolet spectra. The volume resistivity of a compaction was 9×10^7 ohm-cm.

Anal. Calcd. for C₁₃H₁₀N₅: C, 66.08; H, 4.27; N, 29.65. Found: C, 66.26; H, 4.29; N, 29.19.

Other Tetracyanoethylenes.—Treatment of an equimolar solution of TCNE and H₂TCNE in acetonitrile with triethylamine, pyrrolidine, N,N-dimethylaniline, pyridine, butylamine or aniline produced the corresponding ammonium TCNE⁻, as evidenced by their ultraviolet spectra. The characteristic ultraviolet spectrum of TCNE was also observed on addition of either sodium sulfide, sodium thiophenylate or sodium ethylmercaptide to dilute solutions of tetracyanoethylene in acetonitrile; TCNE and tertiary aliphatic amines, such as triethylamine, produced TCNE⁻ in high yield. In addition, the characteristic ultraviolet spectrum of TCNE⁻ was observed on treatment of a dilute solution of TCNE in acetonitrile with copper, aluminum, magnesium and zinc metals and with nickel carbonyl.

Oxidation of TCNE⁻ to TCNE with 7,7,8,8-Tetracyanoquinodimethan.—A suspension of 0.83 g. (4.97 mmoles) of K⁺TCNE⁻ and 1.02 g. (5.00 mmoles) of 7,7,8,8-tetracyanoquinodimethan in 20 ml. of tetrahydrofuran was stirred 3 hours under nitrogen at room temperature. The solvent was evaporated under reduced pressure, and the residue was heated at 80–100° (0.3 mm.) for 2 hours; TCNE (0.57 g., 90% yield) sublimed and was identified by its infrared spectrum.

With Silver Trifluoroacetate.—A solution of 0.1351 g. (0.895 mmole) of Na⁺TCNE⁻ in 5 ml. of dry glyme was stirred with 0.30 g. (1.36 mmoles) of silver trifluoroacetate in 5 ml. of dry glyme for 15 minutes. The solvent was removed under reduced pressure, and the residue was heated in a sublimator at 80° (0.3 mm.). White, crystalline TCNE (0.0628 g., 55% yield) collected in the sublimation tube and was identified by its infrared spectrum.

With Chlorine.—To a suspension of 1.80 g. (10.8 mmoles) of K⁺TCNE⁻ in 30 ml. of acetonitrile, cooled to -40°, was added 130 ml. (5.8 mmoles) of gaseous chlorine. The mixture was allowed to warm to room temperature with stirring. The solvent was removed by evaporation, and the residue heated at 100° (0.3 mm.); TCNE (1.15 g., 83% yield) sublimed and was identified by its infrared spectrum.

With Nitric Acid.—K⁺TCNE⁻ (1.00 g., 5.98 mmoles) was stirred with 3 ml. of concentrated nitric acid for 1 minute. The suspension was then diluted with 15 ml. of ice-water; TCNE (0.56 g., 73% yield) was isolated by filtration and identified by its infrared spectrum.

With Sulfur Dichloride.—A suspension of 5.00 g. (29.99 mmoles) of K⁺TCNE⁻ in 30 ml. of acetonitrile at -40° was treated with 1.0 ml. (15.7 mmoles) of freshly distilled sulfur dichloride. The mixture was allowed to warm to room temperature over 3 hours and was filtered. The solvent was removed from the filtrate by evaporation under reduced pressure. There remained 3.90 g. (100% yield) of TCNE identified by its infrared spectrum.

Reaction of TCNE⁻ with Oxygen.—Dry oxygen was passed through a solution of 10 mg. of K⁺TCNE⁻ in 100 ml. of acetonitrile for 0.5 hour. Comparison of the ultraviolet and visible spectra with standard spectra for potassium tricyanoethenolate¹⁷ (λ_{\max} 297 m μ , ϵ 11,300) and potassium pentacyanopropenide¹⁶ (λ_{\max} 412 m μ , ϵ 22,100, and 283 m μ , ϵ 22,600) showed that these compounds were formed in 36 and 22% yields, respectively. In a separate experiment, the pentacyanopropenide was isolated as its tetramethylammonium salt and identified by comparison of its infrared spectrum with that of an authentic sample.

Reaction of K⁺TCNE⁻ with Water.—A solution of 10 mg. of K⁺TCNE⁻ in 100 ml. of deaerated water was allowed to stand 2 hours. The ultraviolet spectrum of the solution showed that potassium tricyanoethenolate (76%) was formed and that potassium pentacyanopropenide and K⁺TCNE⁻ were absent. In a separate experiment, the ethenolate was isolated and characterized as its tetramethylammonium salt.¹⁷

Reaction of K^+TCNE^- with Acid.— K^+TCNE^- (1.00 g., 5.98 mmoles) was added to 10 ml. of ice-cold 6 *N* hydrochloric acid. The suspension was stirred 1 minute, and the white precipitate which formed was collected on a filter and dried. The product (0.63 g., 64% yield) was shown to be a 1:1 mixture of TCNE and tetracyanoethane by comparison of its infrared spectrum with that of an equimolar mixture of authentic TCNE and tetracyanoethane.

Stability of K^+TCNE^- to Heat.—A sample of K^+TCNE^- was heated in an atmosphere of nitrogen at 150° for 3 hours. The infrared spectrum of the product showed it to be substantially unchanged. Another sample was heated at 200° for 3 hours. The infrared spectrum of this product

indicated gross decomposition. To test the stability of solid K^+TCNE^- to atmospheric oxygen and water vapor, a crystalline sample was allowed to stand in an open beaker. Periodic examination of the crystals by infrared spectroscopy showed no appreciable decomposition in 1 month.

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Aromatic Substitution XII.¹ Steric Effects in Nitronium Salt Nitrations of Alkylbenzenes and Halobenzenes

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The observed differences in isomer distributions and relative reactivities in the nitrations of alkylbenzenes and halobenzenes with a number of stable nitronium salts such as $NO_2^+BF_4^-$, $NO_2^+ClO_4^-$, $NO_2^+PF_6^-$, $NO_2^+AsF_6^-$ and $NO_2^+HS_2O_7^-$ in tetramethylene sulfone and nitromethane solution are discussed. It is suggested that these differences are due to steric effects caused by solvent participation and ion pair interactions.

Introduction

The nitronium tetrafluoroborate ($NO_2^+BF_4^-$) nitration of alkylbenzenes² and halobenzenes³ has been discussed previously. It was pointed out that solvent participation and ion pair interaction play a certain role in the isomer distributions and relative reactivities of the reactions. In the present paper this question is further discussed on the basis of extended experimental work.

Results

Competitive nitration of benzene with alkylbenzenes and with halobenzenes was carried out with different stable nitronium salts. The nitronium salts used were $NO_2^+BF_4^-$, $NO_2^+ClO_4^-$, $NO_2^+PF_6^-$, $NO_2^+AsF_6^-$ and $NO_2^+HS_2O_7^-$. The use of these stable nitronium salts in nitrations was discussed previously⁴ together with details of their preparation and handling. Two solvent systems were used for the kinetic nitrations: tetramethylene sulfone and nitromethane.

The solubility of $NO_2^+BF_4^-$ in tetramethylene sulfone at 25° is about 7%.⁴ The solubility in nitromethane is, however, very low (less than 0.2%), and nitrations with $NO_2^+BF_4^-$ in nitromethane solution could be carried out only in very high dilutions with considerable preparative difficulties. $NO_2^+PF_6^-$ and $NO_2^+AsF_6^-$ are quite soluble both in tetramethylene sulfone and nitromethane. The nitromethane solutions can reach concentrations of more than 50% (by weight). The solubilities of nitronium perchlorate and hydrogen disulfate are again negligible in nitromethane, and do not allow investigation of homogeneous nitrations. $NO_2^+SbF_6^-$ although it is quite soluble was not investigated in kinetic nitra-

tions, due to secondary reactions caused by SbF_5 with the solvents.

The method of competitive nitrations and the gas-liquid chromatographic analysis of the products was identical with that previously described.^{2,3}

The results of these competitive nitrations are summarized in Tables I and II.

Discussion of Results

The differences in nitrations of alkylbenzenes and halobenzenes with different stable nitronium salts in tetramethylene sulfone and nitromethane solutions can best be discussed treating separately the observed differences on substrate-selectivity (*e.g.*, relative rates) and positional-selectivity (*e.g.*, isomer distribution).

Effects on Substrate-selectivity. (a) Tetramethylene Sulfone as Solvent.—Only slight differences in relative reactivity over benzene were observed. These are in accordance with possible steric interference depending on the size of the anion involved. BF_4^- and ClO_4^- are isosteric and close similarities are expected. PF_6^- and AsF_6^- are larger than the fluoroborate or perchlorate ions and this may explain the observed decrease in relative rates. This is most predominant in the case of the mesitylene:benzene ratio, where the steric interference indeed should be the largest. $HS_2O_7^-$, the largest of all anions investigated, shows also the lowest relative rates. It is significant to compare the mesitylene:benzene ratio, which is given in Table III for the nitronium salts investigated.

(b) Nitromethane as Solvent.—Relative rates of competitive nitration of alkylbenzenes and benzene using nitromethane as solvent are generally lower than those observed in tetramethylene sulfone solution. Again the most predominant differences can be observed by comparing the mesitylene:benzene ratios.

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