

media, and it is not clear from the preparative procedures what solution conditions are most favorable for forming ICl_4^- .

Solutions prepared by dissolving ICl_3 in 0.5 and 1 *M* HCl are quite stable, and the λ_{max} values coincide with those of ICl_2^- . Assuming that the absorption is due to ICl_2^- alone leads to the conclusion that half of the ICl_3 is converted to ICl_2^- . The spectra and titer of these solutions remained unchanged over a period of 27 days. There was no evidence that Cl_2 could be lost from the solutions either by aging or heating.

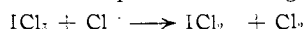
On the other hand, when ICl_3 is dissolved in 3 *M* HCl, a definite odor of chlorine can be detected. The spectrum of a freshly prepared solution is not identical to that of ICl_2^- but has a contribution from another substance (Cl_2 and/or Cl_3^-) in the region around 335 $\text{m}\mu$. As the solution ages, the spectrum approaches that of ICl_2^- , the extent of absorption indicating that all of the ICl_3 is converted to ICl_2^- .

The iodine content of these solutions was determined by reducing to iodide and then performing a potentiometric titration with AgNO_3 . This value was then compared with the oxidizing power determined by iodometric titration. These experiments showed that in 0.5 *M* HCl the iodine is present in a form or forms equivalent in oxidizing power to ICl_3 , whereas in 3 *M* HCl loss of chlorine reduces the oxidizing power to almost that equivalent to ICl .

All these facts are consistent with the following reaction occurring in 0.5 *M* HCl



In 3 *M* and higher HCl concentrations, on the other hand, the ICl_3 decomposes according to

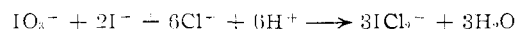


This interpretation is also consistent with the behavior of IO_3^- when added to HCl solutions. If the concentration of HCl is 3 *M* or greater, the 224 $\text{m}\mu$ peak of ICl_2^- appears within the order of minutes, along with the odor of Cl_2 . If the HCl concentration is 0.5 *M*, there is no evidence of reaction.

A study of the potentiometric titration³⁶ of IO_3^- with KI in hydrochloric acid revealed that the end-point appeared prematurely when the HCl concentration was greater than 2 *M* and that the exact position of the end-point depended on the time taken for titration. This effect can now be seen to result from the formation and loss of chlorine gas.

Fialkov and Kagan³⁷ report the use of solutions of ICl_3 for volumetric analysis. Their solutions were prepared either by dissolving solid ICl_3 in 0.2–0.4 *M* HCl or by adding KI and KIO_3 in a mole ratio of 1:2 to the acid solution. On the basis of the evidence presented so far it would appear that such solutions do not contain ICl_2 or ICl_4^- , but instead, equal amounts of ICl_2^- and IO_3^- .

As a further test of this view solutions in 0.5 *M* HCl were prepared by adding KIO_3 and KI in 4:2 and 1:2 mole ratios, keeping the amount of KI the same in both. If the only reaction that occurs is



excess IO_3^- ions will remain in the 4:2 solution, and the two solutions ought to have identical spectra in regions where IO_3^- does not absorb. On mixing the solutions a rather intense yellow-brown color developed immediately, probably due to the formation of I_3^- . Within a few minutes it was replaced by the expected light lemon-yellow color characteristic of ICl_2^- . Spectral measurements in the 270–400 $\text{m}\mu$ range showed the two solutions to be identical except for the small range 270–290 $\text{m}\mu$, where the 4:2 solution had a slightly higher absorbance. This could be ascribed to absorbance by the excess IO_3^- ions.

Thus under the conditions employed in these experiments no evidence was found for the existence of ICl_3 or ICl_4^- . Of course, other conditions, such as the presence of excess Cl_2 , may prove favorable to their existence.

(36) H. T. S. Britton, R. E. Cockaday and J. K. Foreman, *J. Chem. Soc.*, 3877 (1952).

(37) Y. A. Fialkov and F. E. Kagan, *Ukrain. Khim. Zhur.*, **19**, 55 (1952).

[CONTRIBUTION NO. 1645 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY, NEW HAVEN, CONNECTICUT

Electrolytic Conductance of Salts of Several Cyanocarbon Acids

By JOHN E. LIND, JR.,¹ AND RAYMOND M. FUOSS

RECEIVED NOVEMBER 12, 1960

The conductance at 25° of the tetraethylammonium salts of 1,1,2,3,3-pentacyanopropene and of 1,1,2,4,5,5-hexacyano-3-azapentadiene have been measured in acetonitrile and in ethylene dichloride; the penta-salt was also measured in water. The electrolytic behavior is typical for that of salts of strong acids. Association is negligible in water and in acetonitrile ($D = 36.01$); in ethylene dichloride ($D = 10.35$), association constants are 2600 and 2000 for the penta- and hexa-salts, respectively. These values, as well as the contact distances derived from them, show that the negative charge is widely distributed in both anions.

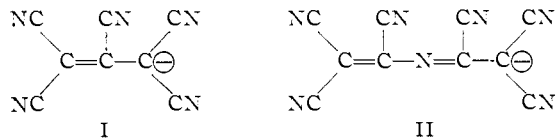
A number of cyanocarbon acids² have been prepared recently, as well as a variety of their salts. Briefly described, these acids are essentially

(1) Du Pont Postdoctoral Research Fellow, 1960–1961.

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

hydrocarbons in which all hydrogens except one or two have been replaced by nitrile groups; the resulting carbanion is so highly stabilized by resonance among a large number of canonical structures that the compounds are stable strong acids with pK_a about 2. One would therefore

expect their salts to show association to ion pairs to an extent determined solely by the size of the ions and the dielectric constant of the medium. Dr. V. A. Engelhardt of E. I. du Pont de Nemours and Company very kindly gave us samples of the tetraethylammonium salts of 1,1,2,3,3-pentacyanopropene (anion I) and of 1,1,2,4,5,5-hexacyano-3-azapentadiene (anion II). (For convenience, we shall refer to them as the "penta-salt" and the



"hexa-salt." Only one structure is shown for I and II; in I, the negative charge is distributed over the five peripheral positions and the two terminal carbons; in II, over the six peripheral positions, the two terminal carbons and the central nitrogen.)

The conductance of the penta-salt has been measured at 25° in water, acetonitrile and ethylene dichloride; the hexa-salt in acetonitrile and ethylene dichloride. (The latter was insufficiently soluble in water to permit measurement. For the penta-salt, saturation in water was about 0.0021 *N*; this low solubility required measurement to quite low concentrations, with a correspondingly large solvent correction reaching about 2% maximum.) Methods of measurement have been described in other papers from this Laboratory.³ The cells used had constants⁴ equal to 0.125052 and 0.038757. The data are summarized in Table I. As will be brought out in

TABLE I
CONDUCTANCE OF TETRAETHYLAMMONIUM 1,1,2,3,3-PENTACYANOPROPENIDE AND 1,1,2,4,5,5-HEXACYANO-3-AZAPENTADIENIDE

$10^4 c$	Λ	$10^4 c$	Λ
$\text{H}_2\text{O}-\text{Cy}_5$		$\text{CH}_3\text{CN}-\text{Cy}_5$	
19.575	64.10	14.8539	143.82
16.264	64.36	12.1250	144.89
13.149	64.62	9.2526	146.21
9.948	64.94	6.2409	147.91
7.1715	65.24	3.2496	150.17
$\text{CH}_3\text{CN}-\text{Cy}_5$		$\text{C}_2\text{H}_4\text{Cl}_2-\text{Cy}_5$	
13.2688	157.00	4.8578	42.10
10.8795	158.10	3.8542	44.05
8.7456	159.21	2.8541	46.57
5.9148	160.97	1.9791	49.55
2.9191	163.46	0.9858	54.71
$\text{C}_2\text{H}_4\text{Cl}_2-\text{Cy}_5$			
5.7818	40.61		
4.5729	42.78		
3.4857	45.32		
2.2968	49.20		
1.2648	54.48		

the subsequent discussion, normal behavior for ionophores⁵ was found in all the systems studied.

(3) H. Eisenberg and R. M. Fuoss, *J. Am. Chem. Soc.*, **75**, 2914 (1953).
(4) J. E. Lind, Jr., J. J. Zwolenik and R. M. Fuoss, *ibid.*, **81**, 1557 (1959).

(5) R. M. Fuoss, *J. Chem. Educ.*, **32**, 527 (1955).

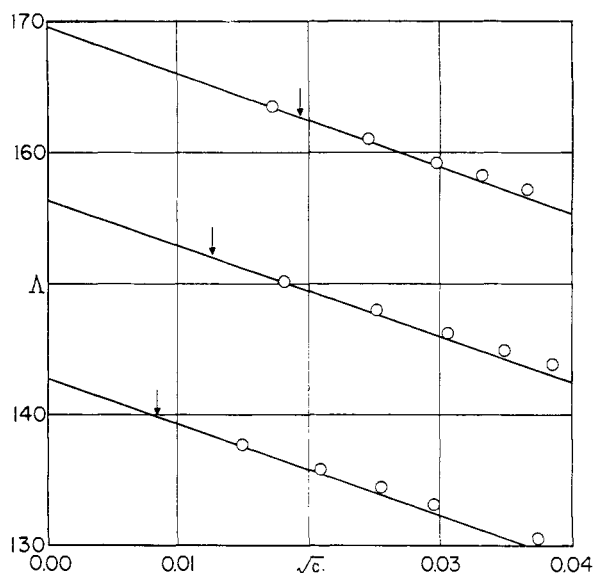


Fig. 1.—Conductance of $\text{Et}_4\text{N}\cdot\text{C}_5(\text{CN})_5$ (top curve), $\text{Et}_4\text{N}\cdot\text{C}_4\text{N}(\text{CN})_5$ (middle curve) and $\text{Et}_4\text{N}\cdot\text{BPh}_4$ (bottom curve) in acetonitrile at 25°.

The phoreograms in acetonitrile are shown in Fig. 1, where for comparison the curve for a typical unassociated salt (tetraethylammonium tetraphenylboride⁶) is shown. It will be noted that the points for all three salts lie above the corresponding limiting tangents and (except for differences in Λ_0 due to different sizes of the ions) the three curves show about the same curvature. Incidentally, these curves serve to illustrate an interesting point: straight lines *could* be drawn through the observed points, which would give values of Λ_0 about 0.5 unit too low. This behavior is due to the opposition of the linear and transcendental terms in the conductance equation⁷

$$\Lambda = \Lambda_0 - Sc^{1/2} + Jc + Ec \log c \quad (1)$$

which is valid for unassociated electrolytes. They nearly cancel in our working range of concentration; at a concentration given by⁸

$$c_0 = \exp(-J/E') \quad (2)$$

the curve will cross the limiting tangent (c_0 is shown by the arrows in Fig. 1) and then approach it *from below* in the limit of very low concentrations.

Considerable association to ion pairs is shown by both salts in ethylene dichloride, where $D = 10.35$. The values of the association constants are given in Table II; they were obtained by IBM 650 analysis⁹ of the data, using the appropriate equation for associated electrolytes.¹⁰ The value $\bar{F} = 2.0$ for the Einstein viscosity coefficient was used in the calculations. If the association constant is given by¹¹ the equation

$$K_A = 2.523 \times 10^{-3} \bar{d}^3 \text{ antilog}(243.4/\bar{d}D) \quad (3)$$

(6) D. S. Berns and R. M. Fuoss *J. Am. Chem. Soc.*, **82**, 5585 (1960).

(7) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishing Co., New York, N. Y., 1959; chapter 15.

(8) Ref. 7, equation 15.61.

(9) R. L. Kay, *J. Am. Chem. Soc.*, **82**, 2099 (1960).

(10) Ref. 7, equation 17.7, with inclusion of J_2 term, 14.104.

(11) Ref. 7, equation 16.19.

it solution for \bar{d} , using the observed K_A values, gives 6.64 and 6.99 for the penta- and hexa-salts, respectively. (The values of $K_A \approx 8$ in acetonitrile in Table II were calculated from the above \bar{d} -values, using equation 3.) As would be expected from the relative sizes of the two ions and the weaker field of the hexa-anion due to a greater spatial distribution of its single charge, the hexa-salt is noticeably less associated than the penta-salt.

TABLE II
DERIVED CONSTANTS

Salt	Solvent	Λ_0	K_A	\bar{d}_A^0	\bar{d}_K^0	\bar{d}_J
5	H ₂ O	67.19 ± 0.01	0	5.49	..	5.2
5	MeCN	169.57 ± .01	(8)	5.61	..	5.62
5	C ₂ H ₄ Cl ₂	70.81 ± .17	2570	5.50	6.64	8.7
6	MeCN	156.35 ± .01	(8)	6.10	..	6.19
6	C ₂ H ₄ Cl ₂	66.94 ± .13	2000	6.32	6.99	9.0

The hydrodynamic radii¹² calculated from the limiting conductances of the penta-salt in three quite dissimilar solvents (water, acetonitrile and ethylene dichloride) agree within a few percent., showing that no special CN-CN interaction (*e.g.*, "selective solvation") occurs in acetonitrile between solvent and anion. The hexa-salt was too low in solubility to be studied in water; the a_A values in acetonitrile and in ethylene dichloride, however, are also in good agreement with each other.

(12) R. M. Fuoss, *Proc. Natl. Acad. Sci., U. S.*, **45**, 807 (1959).

The values of a_A from Λ_0 and of a_J from J agree well for both salts in the solvents of higher dielectric constant, but $a_J > a_A$ in ethylene dichloride. This discrepancy has been noted before¹³ in solvents of low dielectric constant; its origin is suspected to lie in several of the approximations made in deriving the conductance equation¹⁴ which, while valid for large values of D , become less reliable as D decreases below about 20. The values of the contact distance, calculated by any one of the three methods, are large enough, however, to show that the charges on the polycyanions cannot possibly be localized to any one site in the ion.

The salts are colored (penta, yellow; hexa, orange) and also show strong absorptions in the near ultraviolet (molecular extinction coefficients $\epsilon = 2.2 \times 10^5$ for the penta-salt in ethylene dichloride at $\lambda = 417.5 \text{ m}\mu$; $\epsilon = 4.4 \times 10^5$ for the hexa-salt in the same solvent at $\lambda = 469.0 \text{ m}\mu$. These wave lengths correspond to the long wave length members of a double peak in the absorption spectrum). With the thought that ion pair formation might distort the anionic electron distribution, some exploratory measurements were made. The molar extinction coefficient of the penta-salt was, however, found to be unchanged over the concentration range 6.4×10^{-4} to 6.4×10^{-6} , where the fraction of paired ions varies from about 25 to 1%.

(13) E. Hirsch and R. M. Fuoss, *J. Am. Chem. Soc.*, **82**, 1018 (1960).

(14) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 868 (1957); R. M. Fuoss, unpublished calculations.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK]

The Kinetics of the Reactions of Substituted 1,10-Phenanthroline, 2,2'-Dipyridine and 2,2',2''-Tripyridine Complexes of Iron(III) with Iron(II) Ions¹

BY M. H. FORD-SMITH AND N. SUTIN

RECEIVED SEPTEMBER 29, 1960

The kinetics of the oxidation of iron(II) ions by a number of substituted 1,10-phenanthroline, 2,2'-dipyridine and 2,2',2''-tripyridine complexes of iron(III) have been investigated in both sulfuric and perchloric acid solutions using a rapid-mixing and flow technique. The logarithms of the second order rate constants were found to be linearly related to the average basicity per nitrogen atom of the ligands for oxidations by the unsubstituted and the 5-nitro-, 5-chloro-, 5-phenyl- and 5-methyl-phenanthroline complexes of iron(III). The free energies of activation for the oxidation of ferrous ions by the unsubstituted, the 5-substituted, the 5,6-dimethyl- and the 3,4,7,8-tetramethyl-phenanthroline complexes of iron(III) are linearly related to the standard free energy changes of the reactions. The absence of specific steric effects suggests that the electron-transfer between the iron(III) complex and the ferrous ion takes place in an activated complex in which the ferrous ion has penetrated the space between the phenanthroline groups.

Introduction

The kinetics of the oxidation of iron(II) ions by tris-(1,10-phenanthroline)-iron(III) ions have recently been investigated.² In a comparison of this reaction and several other iron(II) ion oxidations, it was found that the free energies of activation could be linearly related to the standard free energy changes of the reactions. We have extended this work to include the oxidation of ferrous ions by a number of substituted 1,10-phenanthroline, 2,2'-dipyridine and 2,2',2''-tri-

pyridine iron(III) complexes in both sulfuric and perchloric acid solutions. With various groups substituted in the phenanthroline nucleus, it is possible to obtain iron(II) complexes with formal oxidation potentials ranging from 0.81 to 1.25 volts.³ Substitution in the phenanthroline nucleus alters the basicity of the nitrogen atom and hence its electron-donating properties. Since an increase in the electron-donating ability of the nitrogen atom will tend to stabilize the iron(III) complex relative to the iron(II) complex, the formal oxidation potentials of the iron(II) complexes

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, **83**, 70 (1961).

(3) G. F. Smith and W. M. Banick, *Talanta*, **2**, 348 (1959).