hydroxyl groups, parallels the onset of essentially complete intractability of the polymer and occurs at approximately the decomposition temperature observed by TGA in dry nitrogen. No infrared evidence could be found to indicate any decomposition of the $OP(C_6H_5)_2O$ bridges up to temperatures of 380° at pressures of 0.01–0.02 mm. Differential thermal analysis of the polymer showed no major heat effects but only ill-defined deviations from the base line in the temperature region 335–520°. Minor exothermic effects apparently occurred at 370 and 420°. The former value corresponds closely to the thermogravimetric decomposition temperature.

TGA and DTA results for the methylphenyl and dimethyl polymer systems are complicated by the presence of acetate impurities, volatilization of which might not represent true decomposition of the polymer. Nevertheless major weight loss for the methylphenyl polymer does occur at about 365°, a value not too different from that for the diphenyl analog. Low-temperature heating results in small weight losses and a simultaneous increase in intrinsic viscosity. For the dimethylphosphinate analog only a visual examination of stability has been made, and no change was observed up to 350°.

Acknowledgments.—This investigation was supported in part by the Office of Naval Research. We are indebted to G. Mincarelli for assistance with many of the experiments and to our Analytical Department, which performed the elemental analyses and obtained the molecular weight and infrared results. We are grateful to Dr. A. Kivnick of our Process Development Department for the design of the statistical study and the analysis of the results and to W. H. Chappell for the TGA and DTA studies.

CONTRIBUTION FROM THE CENTRAL BASIC RESEARCH LABORATORY,
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Hexacarbonylbis(phenyl isocyanate) Diiron(0) and Related Compounds

BY T. A. MANUEL

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The treatment of dodecacarbonyltriiron with phenyl isocyanate yielded hexacarbonylbis(phenyl isocyanate)diiron(0), which was also obtained from the treatment of dodecacarbonyltriiron with azidobenzene. Hexacarbonylbis(butyl isocyanate)-diiron(0) was also prepared. Carbonyl(phenyl isocyanide) complexes of iron and molybdenum were formed by treatment of the metal carbonyl with phenyl isocyanate or phenyl isothiocyanate.

The reactions between organic isocyanides and metal carbonyls have been extensively investigated.[1a,b] However, organic isocyanates have not been utilized as ligands in transition metal complexes, although the multiple bonding in the functional group suggests the possibility of forming bonds to suitable atoms. This paper describes the results of treatment of certain metal carbonyls with organic isocyanates and isothiocyanates.

Experimental

General.—The phenyl isocyanate, phenyl isothiocyanate, butyl isocyanate, 4-methyl-1,3-phenylene diisocyanate, and ethylcyclohexane were Matheson Coleman and Bell products, used without further purification, as was Fisher Spectroanalyzed cyclohexane. The purity of the phenyl isocyanate was verified by mass spectrometric analysis. The azidobenzene solution was obtained from K and K Laboratories, Inc. Triiron dodecacarbonyl was prepared according to the literature.[2] Reactions and chromatography (on 3 × 50 cm. alumina columns) were carried out under nitrogen without pretreatment of solvents or substrates.

Microanalyses and molecular weight determinations (osmometric, in benzene or chloroform) were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and the Analytical Research Division of this company. The 2200–1600 and 700–400 cm.$^{-1}$ regions of the infrared spectrum were studied in cyclohexane solution on a Perkin-Elmer Model 421 instrument, with a resolution of 1 cm.$^{-1}$.[3] Nuclear magnetic resonance spectra[3] were recorded on a Varian A-60 instrument for carbon disulfide solutions with tetramethylsilane as internal standard.

The Reaction between Phenyl Isocyanate and Dodecacarbonyltriiron.—A mixture of 5.0 g. (10 mmoles) of dodecacarbonyltriiron and 3.3 g. (27 mmoles) of phenyl isocyanate in 100 ml. of cyclohexane was heated in an oil bath at 85° for 68 hr. The mixture was cooled and filtered. The filtrate was chromatographed. Elution with pentane and evaporation of the eluate yielded 200 mg. of red-brown tar, with a complex infrared spectrum in the carbonyl stretching region. This tar was sublimed at 120° (0.1 mm.) and the sublimate was crystallized (pentane) to give 15 mg. of yellow crystals, m.p. 54–56°, with carbonyl stretching bands in the infrared spectrum identical with those of the tetracarbonyl(phenyl isocyanide)iron(0) $[Fe(CO)_4(CNC_6H_5)]$[4] prepared from phenyl isothiocyanate (see below).

Subsequent elution with a 2:1 pentane:dichloromethane mixture and evaporation of the eluate yielded 500 mg. of orange crystals. Crystallization (pentane) yielded 400 mg. of red-orange needles, m.p. 129–130° dec. (yield, 6%). Higher yields (24%) were obtained with shorter reaction times and excess iron carbonyl. Recrystallization of a portion yielded an analyti-

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[1] (a) J. Chatt, *et al.*, "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, p. 483; (b) L. Malatesta, *Progr. Inorg. Chem.*, **1**, 283 (1959).

[2] R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 193 (1963).

[3] We gratefully acknowledge the help of Dr. J. J. Elliott in obtaining infrared spectra, of Mr. J. J. Waters in obtaining n.m.r. spectra, and of Dr. P. E. Butler in obtaining and interpreting mass spectrometric data.

[4] W. Hieber and D. Pigenot, *Ber.*, **89**, 193 (1956).

cal sample of hexacarbonylbis(phenyl isocyanate)diiron(0) ($[Fe(CO)_3(C_6H_5NCO)]_2$), m.p. 132–134°.

Anal. Calcd. for $C_{20}H_{10}N_2O_8Fe_2$: C, 46.37; H, 1.94; N, 5.40; mol. wt., 518. Found: C, 46.15, 46.16; H, 1.97, 2.03; N, 5.48; mol. wt., 510.

Subsequent elution with a 1:1 pentane:dichloromethane mixture and evaporation of the eluates gave 350 mg. of red-brown tar having only weak metal–carbonyl stretching bands in the infrared spectrum. From this two crystallizations (pentane–dichloromethane) gave 100 mg. of white, crystalline 1,3,5-triphenylbiuret, m.p. 147–148° (lit.[5] 150–151°). The infrared spectrum (NaCl optics, carbon disulfide solution) of this material showed carbonyl stretching bands at approximately 1730 and 1680 cm.$^{-1}$, as well as N–H and C–H stretching bands, and C–H deformation bands characteristic of phenyl rings.[6]

Anal. Calcd. for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.14; N, 12.67; mol. wt., 331. Found: C, 72.07; H, 5.14; N, 12.48; mol. wt., 330.

Reactions of Hexacarbonylbis(phenyl isocyanate)diiron(0).—A mixture of 2.0 g. (22 mmoles) of aniline and 0.14 g. (0.27 mmole) of hexacarbonylbis(phenyl isocyanate)diiron was heated at 170° for 2 hr. The cooled mixture was poured into 25 ml. of 10% hydrochloric acid. The solid which separated was washed with water and crystallized (ethanol) to give 25 mg. of white needles, identical in m.p. and m.m.p. (239°, lit.[7] 238°) with an authentic sample of *sym*-diphenylurea, prepared from phenyl isocyanate and aniline.

A mixture of 0.13 g. (0.5 mmole) of triphenylphosphine and 0.13 g. (0.25 mmole) of hexacarbonylbis(phenyl isocyanate)-diiron in 5 ml. of ethylcyclohexane was heated at 130° for 2 hr., cooled, and filtered, giving 190 mg. of large, dark red crystals, m.p. 195° dec. (77% yield). The infrared spectrum of this compound showed carbonyl stretching bands at 2001 (s), 1959 (m), 1936 (s), 1711 (vw), and 1690 (w) cm.$^{-1}$. The infrared spectrum of the 70 mg. of red solid obtained by evaporation of the filtrate showed excess triphenylphosphine, as well as the main product. An analytical sample of tetracarbonylbis(phenyl isocyanate)bis(triphenylphosphine)diiron(0) ($[Fe(CO)_2(C_6H_5NCO)P(C_6H_5)_3]_2$) was obtained by crystallization (dichloromethane–pentane) as dark red crystals, m.p. 195° dec.

Anal. Calcd. for $C_{54}H_{40}N_2O_6P_2Fe_2$: C, 65.73; H, 4.08; N, 2.84; P, 6.28; mol. wt., 987. Found: C, 64.81; H, 4.49; N, 2.97; P, 6.10; mol. wt., 930.

The Reaction between Azidobenzene and Dodecacarbonyltriiron.—A mixture of 4.0 g. (8 mmoles) of dodecacarbonyltriiron, 15 ml. of heptane containing 50 mmoles of azidobenzene, and 80 ml. of cyclohexane was heated in an oil bath at 90° for 21 hr. The cooled mixture was chromatographed. Elution with a 2:1 pentane:dichloromethane mixture caused two orange bands to develop. Evaporation of the first, orange solution left 170 mg. of red crystals. Their infrared spectrum showed only a trace of iron carbonyl complex. Two crystallizations (pentane) yielded 60 mg. of orange crystals of azobenzene, m.p. 68° (lit.[8] 68°), with an infrared spectrum showing only bands attributable to phenyl groups.

Evaporation of the second, red solution left 650 mg. of red crystals. Crystallization (pentane–dichloromethane) gave 530 mg. (9% yield) of orange crystals, m.p. 131–133°, with an infrared spectrum identical with that of hexacarbonylbis(phenyl isocyanate)diiron(0).

The Reaction between 4-Methyl-1,3-phenylene Diisocyanate and Dodecacarbonyltriiron.—A mixture of 5.0 g. (10 mmoles) of dodecacarbonyltriiron and 1.2 g. (7 mmoles) of 4-methyl-1,3-phenylene diisocyanate in 120 ml. of cyclohexane was heated in an oil bath at 90° for 22 hr. The mixture was cooled and filtered, and the filtrate was chromatographed. Elution with dichloromethane gave pale yellow solutions, which were discarded. Subsequent elution with chloroform and evaporation of the eluate gave 350 mg. of red-brown tar. Two crystallizations (pentane–dichloromethane) gave 150 mg. of a rust-colored powder, best formulated as $[Fe(CO)_3(C_9H_6N_2O_2)]_x$. The infrared spectrum (chloroform solution) of this material showed carbonyl stretching bands at 2085 (m), 2048 (vs), 2007 (vs), and 1748 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_6N_2O_5Fe$: C, 45.89; H, 1.92; N, 8.92; mol. wt., 628. Found: C, 43.42, 46.50; H, 2.98, 3.56; N, 8.68, 9.53; mol. wt., 645, 678.

The Reaction between Butyl Isocyanate and Dodecacarbonyltriiron.—A mixture of 5.0 g. (10 mmoles) of dodecacarbonyltriiron and 2.7 g. (27 mmoles) of butyl isocyanate in 80 ml. of cyclohexane was heated in an oil bath at 85° for 46 hr. The cooled mixture was chromatographed. Only traces of colored material were eluted by pentane. Subsequent elution with a 1:1 pentane:dichloromethane mixture and evaporation of the eluates gave 990 mg. of red oil. Two crystallizations (pentane) gave 180 mg. of orange crystals, hexacarbonylbis(butyl isocyanate)diiron(0) ($[Fe(CO)_3(C_4H_9NCO)]_2$), m.p. 42–43°. The infrared spectrum of the compound showed carbonyl stretching bands at 2082 (w), 2047 (vs), 2004 (vs), 1994 (vw), and 1733 (w) cm.$^{-1}$. N.m.r. spectra showed that the triplet at τ 6.73 due to the α-methylene group of butyl isocyanate was shifted upfield to τ 7.20 by complex formation.

Anal. Calcd. for $C_{16}H_{18}N_2O_8Fe_2$: C, 40.19; H, 3.79; N, 5.86; mol. wt., 478. Found: C, 40.19; H, 4.15; N, 6.16; mol. wt., 478.

The Reaction between Phenyl Isothiocyanate and Dodecacarbonyltriiron.—A mixture of 4.0 g. (8 mmoles) of dodecacarbonyltriiron and 1.2 g. (9 mmoles) of phenyl isothiocyanate in 100 ml. of cyclohexane was heated in an oil bath at 85° for 20 hr. The cooled mixture was chromatographed. Elution with pentane and evaporation of the eluates gave 900 mg. of red tar. Sublimation of this at 80° (0.1 mm.) gave 450 mg. of oily solid. Three crystallizations (pentane) of the sublimate gave 350 mg. (14% yield) of yellow solid, m.p. 55–56° (lit.[4] 60.5–61°). The infrared spectrum showed bands at 2156 (w), 2054 (m), 1997 (m), and 1970 (s) cm.$^{-1}$ [lit.[9] values for tetracarbonyl(phenyl isocyanide)iron: 2156, 2054, 1994, and 1970 cm.$^{-1}$ (chloroform solution)].

Anal. Calcd. for $C_{11}H_5NO_4Fe$: C, 48.74; H, 1.85; N, 5.16; mol. wt., 271. Found: C, 48.39; H, 1.85; N, 5.15; mol. wt., 300.

Subsequent elution with a 3:1 pentane:dichloromethane mixture and evaporation of the eluates gave 480 mg. of red tar, which could not be crystallized.

Anal. Found: C, 38.58; H, 2.23; N, 3.28; S, 9.63; mol. wt., 731.

Subsequent elution with a 1:1 pentane:dichloromethane mixture and evaporation of the eluates gave 200 mg. of brown tar, which could not be crystallized.

Anal. Found: C, 42.25; H, 2.48; N, 3.66; S, 9.91; mol. wt., 905.

The infrared spectrum of each of these oils showed at least ten carbonyl stretching bands.

The Reaction between Hexacarbonylmolybdenum and Phenyl Isocyanate.—A mixture of 2.64 g. (10 mmoles) of hexacarbonylmolybdenum and 2.2 g. (18 mmoles) of phenyl isocyanate in 50 ml. of ethylcyclohexane was heated in an oil bath at 140° for 24 hr. The cooled mixture was filtered. The infrared spectrum of the brown residue showed only traces of metal carbonyl bands. Evaporation of the filtrate left an oily brown solid with carbonyl absorptions in the infrared spectrum (sodium chloride optics) at approximately 2101, 2058, and 1961 cm.$^{-1}$. Crystallization (pentane), followed by sublimation, gave 30 mg. of a white solid, m.p. 83–86°. The infrared spectrum showed bands at 2140 (w), 2113 (vw), 2060 (w), 2012 (vw), 1987 (s), 1964 (s), 1942 (vw), and 1934 (w) cm.$^{-1}$. Comparison with the literature[10] showed the

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(5) J. W. Baker and J. B. Holsworth, *J. Chem. Soc.*, 724 (1945).

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

(7) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 287.

(8) C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," 35th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1953, p. 744.

(9) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).

mixture to be composed primarily of pentacarbonyl(phenyl isocyanide)molybdenum(0) [$Mo(CO)_5(CNC_6H_5)$] contaminated with hexacarbonylmolybdenum(0) and *cis*-tetracarbonylbis(phenyl isocyanide)molybdenum(0) [$Mo(CO)_4(CNC_6H_5)_2$].

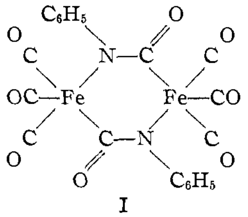
The Reaction between Hexacarbonylmolybdenum and Phenyl Isothiocyanate.—A mixture of 1.32 g. (5 mmoles) of hexacarbonylmolybdenum and 1.2 g. (9 mmoles) of phenyl isothiocyanate in 40 ml. of ethylcyclohexane was heated in an oil bath at 140° for 18 hr. The cooled mixture was filtered. The infrared spectrum of the residue showed no carbonyl bands. Evaporation of the filtrate left 570 mg. of yellow solid, with a complex infrared spectrum in the carbonyl stretching region. This was separated into several fractions by crystallization (pentane–dichloromethane). Recrystallization of the least-soluble fraction gave 100 mg. of yellow solid, m.p. 143° dec. The infrared spectrum (carbon disulfide solution) showed bands at 2128 (w), 2062 (m), 1948 (s), and 1910 (s) cm.$^{-1}$, in the pattern reported for *cis*-tricarbonyltris(phenyl isocyanide)molybdenum [$Mo(CO)_3(CNC_6H_5)_3$].[10]

Anal. Calcd. for $C_{24}H_{15}N_3O_3Mo$: C, 58.90; H, 3.08; N, 8.58; mol. wt., 489. Found: C, 57.62; H, 3.22; N, 8.02; mol. wt., 464.

The infrared spectra of the other fractions indicated that the tris(phenyl isocyanide) complex was the major product, contaminated with traces of hexacarbonylmolybdenum and the mono- and bis(phenyl isocyanide) complexes.

Results and Discussion

Treatment of dodecacarbonyltriiron with phenyl isocyanate yields volatile, air-stable hexacarbonylbis(phenyl isocyanate)diiron(0) as the main product. The infrared spectrum of this compound exhibits terminal carbonyl stretching frequencies at 2085 (m), 2048 (vs), 2006 (vs), and 1992 (vw) cm.$^{-1}$, as well as an additional band at 1751 cm.$^{-1}$, which might be due to either an organic carbonyl group or a bridging metal carbonyl group. Treatment of the complex with aniline gives *sym*-diphenylurea, showing that the isocyanate ligand exists as such in the complex. Hence, the 1751 cm.$^{-1}$ band must be caused by the carbonyl group of the isocyanate moiety. It has been shown by Fritz[11] that in the infrared spectra of hydrocarbon-substituted metal carbonyls the sum of the metal-carbon and corresponding carbon-oxygen stretching frequencies is nearly constant. The infrared spectrum of hexacarbonylbis(phenyl isocyanate)diiron shows what are apparently metal-carbon frequencies (listed with the corresponding carbonyl stretching frequencies and sums) at 539 (2085, 2624), 576 (2048, 2624), 592 (2006, 2598), and 630 (1992, 2622) cm.$^{-1}$. In addition, a band which is found at 687 cm.$^{-1}$ might correspond to the 1751 cm.$^{-1}$ mode. No sign of N-H bands is seen in either the infrared or nuclear magnetic resonance spectrum of the complex. The complicated n.m.r. pattern of free phenyl isocyanate, centered at τ 2.92, is reduced to a sharp singlet at τ 2.82 in the complex, showing that the substituent group can no longer be considered conjugated with the aromatic ring. Structure I appears to fit the available data for this compound.[12]



I

Treatment of this complex with triphenylphosphine causes loss of carbon monoxide and formation of tetracarbonylbis(phenyl isocyanate)bis(triphenylphosphine)diiron(0), without bridge splitting. This substitution produces a shift of the 1751 cm.$^{-1}$ infrared band to lower frequency, showing that the carbonyl groups responsible for this band are bonded to iron atoms.

A crystalline compound of stoichiometry and infrared spectrum similar to those of the phenyl isocyanate complex is formed from *n*-butyl isocyanate and dodecacarbonyltriiron. Treatment of 4-methyl-1,3-phenylene diisocyanate with the iron carbonyl yields a noncrystalline material, not obtained as a simple composition. The infrared spectrum of this substance has carbonyl stretching bands identical with those of hexacarbonylbis(phenyl isocyanate)diiron.

The phenyl isocyanate–iron carbonyl reaction also furnishes traces of 1,3,5-triphenylbiuret[5] and, quite surprisingly, of tetracarbonyl(phenyl isocyanide)iron(0).[4] This reduction of the isocyanate has led us to investigate the reaction between dodecacarbonyltriiron and phenyl isothiocyanate, which one might expect to lose sulfur more readily than the isocyanate loses oxygen. This reaction gives large amounts of tarry materials which still contain nitrogen, sulfur, and iron carbonyl groups, and which are apparently complicated mixtures of compounds. The expected tetracarbonyl(phenyl isocyanide)iron(0)[4] is also obtained.

The conversion of the isocyanate and isothiocyanate to isocyanide complexes has suggested that interconversion of other phenyl-nitrogen species might be possible. Treatment of azidobenzene with dodecacarbonyltriiron gives azobenzene as well as hexacarbonylbis(phenyl isocyanate)diiron(0). Since loss of nitrogen from the azide may give a highly reactive azene intermediate,[13,14] the formation of neither product is too surprising. It is possible that carbon monoxide is inserted into an azene–iron complex to give the isocyanate complex.

We have also treated the hexacarbonyls of chromium, molybdenum, and tungsten with phenyl isocyanate and phenyl isothiocyanate. Low yields of isocyanide complexes, identified by their infrared spectra,[10] are formed in these reactions as well. No sign has been observed of complexes of the unchanged initial ligands. As anticipated, hexacarbonylmolybdenum reacts more readily than its congeners, and the iso-

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[10] M. Bigorgne and L. Rassat, *Bull. soc. chim. France*, 295 (1963).

[11] H. P. Fritz and E. F. Paulus, *Z. Naturforsch.* **18B**, 435 (1963).

[12] We cannot exclude a stoichiometry [$(C_6H_5NCO)Fe(CO)_4$]$_2$, but analyses agree better with the iron tricarbonyl composition, in which each iron atom lacks two electrons of attaining the inert gas configuration, although the lone pairs remaining on the nitrogen atoms could supply the missing electrons. If these lone pairs do participate, the nitrogen atoms function as three-electron donors, as do the nitrogen atoms of nitrosyl groups. The possibility of electron delocalization around the six-membered ring is evident.

[13] P. A. S. Smith and J. H. Hall, *J. Am. Chem. Soc.*, **84**, 480 (1962).

[14] G. Smolinsky, *ibid.*, **83**, 2489 (1961).

thiocyanate reacts more readily than the isocyanate. Aryl isocyanide complexes of the group VI metal carbonyls are well known.[9,10,15,16] In all of the reactions described in this paper, material is lost in the form of highly-colored, polar materials, which cannot be removed from a chromatography column.

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[15] W. Hieber and D. Pigenot, *Ber.*, **89**, 616 (1956).

[16] W. Hieber, W. Abeck, and H. K. Platzer, *Z. anorg. allgem. Chem.*, **280**, 252 (1955).

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A Temperature-Jump Study of the Kinetics of Complex Formation between 4,5-Dihydroxybenzene-1,3-disulfonic Acid and Nickel(II), Cobalt(II), and Magnesium(II) in Aqueous Solution[1]

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The kinetics of complexation between various charged species of the ligand 4,5-dihydroxybenzene-1,3-disulfonic acid ("tiron") and the divalent metal ions of nickel, cobalt, and magnesium have been investigated by the temperature-jump method. The complex formation rate constants for the −3 species of tiron and the divalent metal ions of nickel, cobalt, and magnesium were determined at a pH of 9.00 and at 20°. The second-order rate constants for the association of the −2 tiron species and the divalent metal ions of nickel and cobalt were determined at a pH of 4.66 and at 20°. In each case the stability of the metal complex decreases by several orders of magnitude with increasing ligand protonation; however, the association rate constant changes only by an order of magnitude. The large decrease in complex stability with increasing protonation is due to a large increase in the dissociation rate constant.

Introduction

The ligand 4,5-dihydroxybenzene-1,3-disulfonic acid forms stable complexes with transition metal ions and many other metal ions. Due to the importance of its ability to complex, and hence remove, titanium and iron when these ions interfere in an analytical procedure, Schwarzenbach[2] has named this compound "tiron"—an appellation that shall be used throughout this paper.

Kinetically, tiron complexation is of interest because the large delocalized charge on this relatively small ligand results in a high charge density. By controlling the degree of protonation on tiron, it is possible to alter the charge and thereby make direct comparisons between the rates of complex formation and dissociation for the differently charged species. Likewise, comparison of the results obtained for the three different metal ions gives some indication of the role played by electronic configuration in determining the relative importance of charge on the rates of association and dissociation.

Equilibrium Constants and Relaxation Spectra

The relevant equilibrium constants necessary for a quantitative interpretation of the temperature-jump results are listed in Table I. The notation used in "Stability Constants" by Bjerrum, Schwarzenbach, and Sillén[3] will be followed, as far as possible. The symbol $[\overline{\quad}]$ represents the equilibrium concentration. Charges have been neglected in writing the constants. The symbols ti, Hti, and H_2ti represent tiron in different degrees of protonation; also, M may represent Mg, Ni, or Co. No original data are available in the case of those constants for which ref. 3 has been cited as a source; however, the values for nickel(II) and cobalt(II) have been corroborated in studies by Näsänen, *et al.*,[4] to which one should refer for experimental details.

TABLE I

STOICHIOMETRIC EQUILIBRIUM CONSTANTS[a] AT IONIC STRENGTH 0.1 M AND 20°

Equilibrium constant			Lit. ref.
K_{H_2ti}	$= [\overline{H}][\overline{Hti}]/[\overline{H_2ti}]$	$= 2.19 \times 10^{-8}$	*e*
K_{Hti}	$= [\overline{H}][\overline{ti}]/[\overline{Hti}]$	$= 2.5 \times 10^{-13}$	*e*
K_{ROH}	$= [\overline{R}][\overline{OH}]/[\overline{ROH}]$	$= 4.0 \times 10^{-5\,b}$	*f*
K_{HIn_1}	$= [\overline{H}][\overline{In_1}]/[\overline{HIn_1}]$	$= 1.1 \times 10^{-6\,c}$	*g*, *h*
K_{HIn_2}	$= [\overline{H}][\overline{In_2}]/[\overline{HIn_2}]$	$= 1.04 \times 10^{-5\,d}$	*g*, *h*
$K^{Ni}{}_1$	$= [\overline{Niti}]/[\overline{Ni}][\overline{ti}]$	$= 9.12 \times 10^{9}$	3, 4
$K^{Co}{}_1$	$= [\overline{Coti}]/[\overline{Co}][\overline{ti}]$	$= 3.09 \times 10^{9}$	3, 4
$K^{Mg}{}_1$	$= [\overline{Mgti}]/[\overline{Mg}][\overline{ti}]$	$= 7.24 \times 10^{6}$	3, 4
$K^{Ni}{}_{NiHti}$	$= [\overline{NiHti}]/[\overline{Ni}][\overline{Hti}]$	$= 1.00 \times 10^{3}$	3, 4
$K^{Co}{}_{CoHti}$	$= [\overline{CoHti}]/[\overline{Co}][\overline{Hti}]$	$= 1.20 \times 10^{3}$	3, 4
$K^{Mg}{}_{MgHti}$	$= [\overline{MgHti}]/[\overline{Mg}][\overline{Hti}]$	$= 9.55 \times 10^{1}$	3, 4

[a] In calculating the relaxation times it is often necessary to use the complex hydrolysis constant $K^{b}{}_{MHti} = [\overline{MHti}][\overline{OH}]/[\overline{Mti}] = K^{M}{}_{MHti}K_w/K^{M}{}_1K_{Hti}$, where K_w represents the ion product of water. [b] ROH is phenolphthalein. [c] HIn_1 is chlorophenol red. [d] HIn_2 is methyl red. [e] R. Näsänen, *Suomen Kemistilehti*, **30B**, 61 (1957). [f] A. Thiel and G. Coch, *Z. anorg. allgem. Chem.*, **217**, 353 (1934). [g] E. F. Chase and M. Kilpatrick, Jr., *J. Am. Chem. Soc.*, **54**, 2284 (1932). [h] I. M. Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930).

With a description of the equilibrium composition of

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[1] Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964.

[2] G. Schwarzenbach, "Complexometric Titrations," Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 40.

[3] G. Schwarzenbach and A. Willi, "Stability Constants," Part I, J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, Ed., The Chemical Society, London, 1957.

[4] *Cf.* R. Näsänen, *Suomen Kemistilehti*, **32B**, 7 (1959).