solute ions such as TiF_6^{2-} and SiF_6^{2-} rapidly exchange ^{19}F with the solvent anhydrous HF (at a rate independent of added F^- ion) *via* a low activation energy path. For the latter complexes, facile nucleophilic displacement of ^{19}F by HF is unlikely, but an HF-assisted dissociation of F^- ion seems reasonable.

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A Calorimetric Study of Prussian Blue and Turnbull's Blue Formation[1a]

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Values of ΔH° valid at zero ionic strength and 25° have been determined calorimetrically for the formation of "soluble" Prussian blue and Turnbull's blue from their constituent ions in dilute aqueous solution. The calorimetric data are shown to be consistent with literature data for the Fe^{3+}–$Fe(CN)_6^{4-}$ redox reaction. The results are discussed in terms of the energy relationships for two proposed mechanisms of complex formation.

Introduction

The "soluble" forms[2,3] of Prussian blue and Turnbull's blue have been known for many years and present interesting examples of the intense colors exhibited by species containing the same element in different oxidation states. For many years Prussian blue and Turnbull's blue were thought to be different, primarily because of the different method by which they are formed as shown by the reactions

$$Fe^{2+} + Fe(CN)_6^{3-} = \text{Turnbull's blue} \qquad (1)$$

$$Fe^{3+} + Fe(CN)_6^{4-} = \text{Prussian blue} \qquad (2)$$

Keggin and Miles[4] found the structures of the crystalline forms of Prussian blue and Turnbull's blue to be identical and to consist of one group of iron atoms surrounded by an octahedral arrangement of carbon atoms while another group of iron atoms is surrounded by an octahedral arrangement of nitrogen atoms. A theoretical treatment[5] of the electronic structure of Prussian blue based on ligand field theory considerations is consistent with the compound having the formula $KFe^{III}[Fe^{II}(CN)_6]$. Mössbauer spectra[6] of solid Prussian blue and Turnbull's blue indicate they are identical and these spectral data are in complete agreement with their formulation as a ferric ferrocyanide species. The Mössbauer spectra[6] further indicate that very weak ionic bonding exists between the nitrogen end of the bonded cyanide ion and the ferric ion. A more complete discussion of the evidence for the identity and structure of solid Prussian blue and Turnbull's blue has recently appeared.[7]

A search of the literature reveals that no thermodynamic data have been reported for the formation of soluble Prussian blue and Turnbull's blue. Such data would be useful in understanding the energy relationships involved in such formation. In this paper are presented ΔH° values for the formation of the soluble forms of Prussian blue and Turnbull's blue from their respective ions.

Experimental Section

Materials.—Reagent grade $FeSO_4 \cdot 7H_2O$ (Baker and Adamson), $K_4Fe(CN)_6$ (Mallinckrodt), $K_3Fe(CN)_6$ (Mallinckrodt), and standard iron wire (Baker and Adamson) were used in the preparation of solutions for this study. An $Fe(ClO_4)_3$ solution was prepared by dissolving a weighed amount of standard iron wire in a known volume of hot concentrated $HClO_4$ and diluting with an appropriate volume of water.

All solution preparations and manipulations were carried out under a nitrogen atmosphere to minimize oxidation of air-sensitive compounds.

Procedure.—The calorimeter and supporting equipment have been described.[8] The calorimetric procedure consisted of adding 10-ml portions of 0.1 *M* potassium ferrocyanide and potassium ferricyanide solutions to 200 ml of 10^{-3} *M* ferric and ferrous solutions, respectively. The time interval from when the solutions were mixed to when the calorimetric measurement was finished was always less than 5 min. The reagents were mixed in stoichiometric amounts in order to avoid formation of any insoluble Prussian or Turnbull's blue.[2] Corrections were made for the dilution of potassium ferricyanide and potassium ferrocyanide

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[2] G. D. Parkes, Ed., "Mellor's Modern Inorganic Chemistry," revised edition, Wiley, New York, N. Y., 1961, p 927.

[3] There appear to be two forms of Prussian blue and Turnbull's blue. One form "dissolves" in water giving a deeply colored blue "solution." This form is referred to as the "soluble" form and results when 1 equiv of Fe^{2+} is added to $Fe(CN)_6^{3-}$ or 1 equiv of Fe^{3+} is added to $Fe(CN)_6^{4-}$. The "insoluble" form results when nonstoichiometric quantities of the above salts are mixed.[2] This paper deals primarily with the "soluble" form of Prussian and Turnbull's blue which is represented as $KFeFe(CN)_6$.

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using the heat of dilution data reported for these compounds by Lange and Miederer.[9] In the 10^{-3} *M* ferric ion solutions some hydrolysis of the ferric ion had occurred. A thermal correction for this hydrolysis was made as follows. A 10-ml portion of 2 *M* $HClO_4$ was added to the ferric ion solution and the total heat of interaction was measured. The difference between this measured heat and the heat of dilution of the $HClO_4$[10] was taken to be the correction for the ferric ion hydrolysis. This correction was about −2 cal.

The time required to reach thermal equilibrium after reagents were mixed was approximately 2–3 min. The intense blue color of both Prussian and Turnbull's blue was observed to form instantly after mixing. Spectrophotometric measurements at 680 mμ showed that a reasonably constant absorbance value was reached within 2–3 min after mixing. Although kinetic parameters have not been reported for the redox reaction

$$Fe^{3+} + Fe(CN)_6^{4-} = Fe^{2+} + Fe(CN)_6^{3-} \qquad (3)$$

one would expect the second-order reverse rate constant to be of the order of magnitude of the forward rate constants reported for the Fe^{2+}–Fe^{3+} and $Fe(CN)_6^{3-}$–$Fe(CN)_6^{4-}$ redox reactions of 3.2×10^3 [11] and 1×10^5 M^{-1} sec^{-1},[12] respectively. In fact, this value could be somewhat larger since one expects that a reaction between unlike ions would occur more rapidly than that between like ions.[13] Furthermore, since the reported[14] equilibrium constant for reaction 3 is very large (1.82×10^8), the forward rate constant will be extremely large ($k_f > 10^{11}$). For these reasons it is concluded that under the conditions of the experiment chemical equilibrium was attained well within the 2–3 min required to reach thermal equilibrium.

Results

The calorimetric data for the reactions represented in (1) and (2) are given in Table I.

Values for $\Delta H°$ were calculated from the data in Table I by extrapolating a plot of ΔH *vs.* total iron concentration, [Fe_T], to [Fe_T] = 0. It was necessary to make the extrapolation against [Fe_T] rather than ionic strength because the uncertain nature of the "soluble" iron cyanide species made the calculation of the ionic strength impossible. The $\Delta H°$ values calculated in this manner for reactions 1 and 2 are −15.15 ± 0.35 and 0.72 ± 0.18 kcal/mol of Fe^{2+} and Fe^{3+}, respectively, where the uncertainties are estimated from the plots of $\Delta H°$ *vs.* [Fe_T].

Discussion

The difference between the reactants in reactions 1 and 2 is given by eq 3. The consistency of the $\Delta H°$ values reported for reactions 1 and 2 can now be checked by comparing their difference with the $\Delta H°$ value for reaction 3 since $\Delta H_2° - \Delta H_1° = \Delta H_3°$. The agreement between the $\Delta H_3°$ value calculated from reactions 1 and 2, 15.87 ± 0.35 kcal/mol, and that reported earlier,[14] 15.63 kcal/mol, is good.

The $\Delta H°$ values alone for reactions 1–3 do not provide structural or mechanistic information regarding Prussian and Turnbull's blue. However, when viewed in light of spectral results, these values lead to interesting energy relationships. For instance, the earlier Mössbauer results[6] and the observation[15] of reasonably constant values for the extinction coefficient of Turnbull's blue over a range of concentrations suggest that Turnbull's blue and Prussian blue must be identical species in solution. Assuming this to be true, the $\Delta H°$ values for reactions 1–3 are consistent with the mechansim proposed by Fluck[6] in which Prussian blue reacts by eq 2 and Turnbull's blue by eq 3 and 2 to form $Fe^{III}Fe^{II}(CN)_6^-$ in each case. Energetically this is reasonable because $\Delta H_3°$ is very small indicating that the energies of the reactants and products lie close together; *i.e.*, $Fe^{3+} + Fe(CN)_6^{4-}$ are close in energy to $Fe^{III}Fe^{II}(CN)_6^-$. In the formation of Turnbull's blue the reactants Fe^{2+} and $Fe(CN)_6^{3-}$ must be lowered about 15 kcal/mol in energy in order to form the blue

TABLE I

CALORIMETRIC DATA FOR REACTIONS 1 AND 2 AT 25°

$10^2[Fe_T]$, *M*	Q_{total},[a] cal		ΔH,[b] kcal/mol
Reaction 1:	$Fe^{2+} + Fe(CN)_6^{3-}$	=	Turnbull's blue
4.762	−17.000		−16.675
	−16.920		−16.595
	−17.045		−16.720
	−17.086		−16.761
	−17.093		−16.768
	−17.093		−16.768
		Av	−16.715 ± 0.069
3.571	−12.731		−16.600
	−12.703		−16.563
	−12.699		−16.557
	−12.842		−16.748
	−12.794		−16.684
		Av	−16.630 ± 0.083
2.381	−8.349		−16.288
	−8.334		−16.258
	−8.349		−16.28[illegible]
	−8.350		−16.288
	−8.354		−16.298
		Av	−16.284 ± 0.073
1.191	−4.091		−15.933
	−4.066		−15.839
	−4.103		−15.981
	−3.975		−15.468
		Av	−15.805 ± 0.156
Reaction 2:	$Fe^{3+} + Fe(CN)_6^{4-}$	=	Prussian blue
9.532	−3.456		0.087
	−3.492		0.069
	−3.445		0.091
		Av	0.083 ± 0.017
4.762	−2.945		0.283
	−2.971		0.256
	−2.968		0.259
		Av	0.266 ± 0.017
2.381	−1.974		0.504
	−1.962		0.528
	−1.955		0.543
		Av	0.525 ± 0.020

[a] Values for [Fe_T] × 10^2 (molarity), *Q* correction (calories), and millimoles of product, respectively, for each reaction: (1) 4.762, −0.325, 1.000; 3.571, −0.281, 0.7500; 2.381, −0.213, 0.4995; 1.191, −0.111, 0.2498; (2) 9.532, −3.626, 1.945; 4.762, −3.220, 0.9722; 2.381, −2.219, 0.4864. The *Q* correction term in each case is subtracted from Q_{total}. The *Q* correction for reaction 2 includes a correction term for the slight hydrolysis of the Fe(III) solutions. [b] Uncertainties are indicated as the standard deviation among runs.

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[15] Y. Wu, Master's Thesis, Brigham Young University, 1965, and unpublished results in this laboratory.

complex by way of reaction 2. Certainly one mechanism is not unique. It is possible to consider still another viewpoint consistent with a large negative enthalpy for reaction 1 and almost zero enthalpy for reaction 2.

In the crystal of $KFe^{III}[Fe^{II}(CN)_6]$ the two different oxidation states show preferential association[5] for the carbon ends (Fe^{II}) and nitrogen ends (Fe^{III}), respectively, of the cyanide ligands. Assuming that this behavior can be extended to the species in solution, the formation of Turnbull's blue, not Prussian blue, would cause a charge-transfer transition (−42.03 kcal/mol of electrons)[5] from Fe^{2+} to $Fe(CN)_6^{3-}$, *i.e.*, $Fe^{II}[Fe^{III}(CN)_6]^- \rightarrow Fe^{III}[Fe^{II}(CN)_6]^-$. The effect of this charge-transfer transition should be seen in the $\Delta H°$ value for reaction 1 but not in that for reaction 2. The larger $\Delta H°$ value for reaction 1 compared to that for reaction 2 is consistent with this explanation; however, the difference between the two $\Delta H°$ values (15.9 kcal/mol) is considerably less than the 42.0 kcal/mol expected from the charge-transfer transition. Nevertheless, this viewpoint is not unreasonable since other energy terms besides the charge-transfer transition are undoubtedly important in determining the magnitude of the measured $\Delta H°$ value.

Shriver, *et al.*,[16] found that the ligand field strength of the cyanide ion when bonded through nitrogen was comparable to that of H_2O. This finding is generally supported by the data presented here. In the reaction of ferric ion with ferrocyanide ion the six water molecules surrounding the ferric ion are replaced by the nitrogen ends of six cyanide ions. Since the $\Delta H°$ value for reaction 2 is very close to zero (0.72 kcal/mol), the nitrogen ends of the bonded cyanide ions appear to have essentially the same effect as the water molecules they have replaced.

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Synthesis and Reactivity of Novel Palladium(II)–Isocyanide Complexes

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Novel Pd^{II} complexes of the type $Pd(RNC)_2X_2$ (RNC = cyclohexyl and *p*-nitrophenyl isocyanide; X = Cl, I) and of the type $Pd(RNC)(L)X_2$ (RNC = phenyl, *p*-nitrophenyl, and cyclohexyl isocyanide; L = $P(C_6H_5)_3$, $As(C_6H_5)_3$; X = Cl, Br, I) have been prepared. The configuration of these compounds has been assigned, where possible, on the basis of their near- and far-infrared spectra. The reactions of the above compounds with methanol and *p*-toluidine are also reported and discussed. The products of such reactions have been formulated as carbene derivatives of Pd^{II}. The ir spectra of all complexes have been discussed with special regard to the bonding properties of the isocyanide group.

Introduction

Structural and bonding properties of isocyanide metal compounds have been discussed by many authors.[1] In general, ir studies on the stretching frequencies of CO and NC in mixed carbonyl–isocyanide derivatives have shown that isocyanides are stronger σ donors and weaker π acceptors than carbon monoxide.[2,3]

As far as isocyanide complexes of platinum group metals are concerned, only the compounds of the type $M(RNC)_2X_2$ and the Magnus salt type have been reported in the literature so far.[1] In these derivatives it has been found that the metal–isocyanide bond is particularly stable in contrast to the corresponding metal–carbonyl bond.

In the present work we report the synthesis of some novel complexes of the type $Pd(RNC)_2X_2$ and their substitution reactions of the isocyanide group with mono- and bidentate neutral ligands having N, P, and As donor atoms. The coordinated isocyanide group undergoes also addition reactions with methanol and *p*-toluidine.

An ir study is also reported in order to investigate the bonding properties of the isocyanides (RNC) in relation to the effects of the organic group R on the ν(NC) vibrations and on the corresponding Pd–X stretching frequencies, when X is in the *trans* position to the isocyanide.

Experimental Section

All isocyanides have been prepared according to the methods of Ugi and coworkers.[4,5] $Pd(CH_3CN)_2Cl_2$ has been prepared according to the standard methods of the literature. All other chemicals were reagent grade and were used without further purification.

(I) Preparation of the Complexes $Pd(RNC)_2X_2$ and $Pd(RNC)$-

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