

**Titanium(III) Reduction of the Tris(1,10-phenanthroline)cobalt(III) and Bis(2,2':6',2''-terpyridine)cobalt(III) Ions**

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The kinetics of the titanium(III) reduction of the tris(1,10-phenanthroline)cobalt(III) and bis(2,2':6',2''-terpyridine)cobalt(III) ions has been studied at 25 °C in 1 M ionic strength (NaCl) in the acidity range of 0.9 to  $2 \times 10^{-3}$  M. The titanium(III) species undergoing electron transfer is  $\text{Ti}(\text{H}_2\text{O})_5\text{OH}^{2+}$  and the kinetic data yielded the value  $K_a = 3.5 \times 10^{-3}$  M for the acid dissociation constant of hexaaquatitanium(III). The two Co(III) complexes oxidize titanium(III) with similar rates and no kinetic effect of the different spin changes in the two cobalt couples accompanying the redox process has been observed.

**Introduction**

Mechanistic interpretation of the kinetic results recently obtained for the oxidation of titanium(III) by various cobalt(III) complexes<sup>1-6</sup> and dissection of the kinetic data into appropriate specific rate constants require the knowledge of a reliable value for the acid dissociation constant of the hexaaquatitanium(III) ion. There have been inconsistencies about this value in the literature.<sup>7-9</sup>

Here we report a kinetic study of the oxidation of titanium(III) by the  $\text{Co}(\text{phen})_3^{3+}$  and  $\text{Co}(\text{terpy})_2^{3+}$  ions in aqueous chloride medium. The acidity dependence of these reactions, which are necessarily of the outer-sphere mechanism, and in which only titanium(III) undergoes a protolytic equilibrium, enabled us to obtain the value of the acid dissociation constant of hexaaquatitanium(III) at 25 °C in 1 M ionic strength (NaCl). The  $\text{Co}(\text{phen})_3^{2+}$  and  $\text{Co}(\text{terpy})_2^{2+}$  reduction products have different ground-state electron configurations and a kinetic effect of the different spin changes in the cobalt couples might have been observed in these reactions as well as effects of the unsaturated ligands on the rate when compared with the previously studied kinetics of the oxidation of titanium(III) by the  $\text{Co}(\text{NH}_3)_6^{3+}$  ion.<sup>4</sup>

**Experimental Section**

**Materials.**  $\text{Co}(\text{Cl})_2$ , 1,10-phenanthroline (phen), and 2,2':6',2''-terpyridine (terpy), all Merck analytical grade, were used without further purification.  $\text{Co}(\text{phen})_3^{2+}$  and  $\text{Co}(\text{terpy})_2^{2+}$  complex ions in solutions were prepared by mixing standard water solutions of  $\text{Co}(\text{Cl})_2$  and of phenanthroline or of terpyridine in the respective molar ratio. Oxygen was excluded from the solutions by the use of the nitrogen atmosphere. Spectra of these Co(II) complexes were found in agreement with the literature values.<sup>10,11</sup> Solutions of the  $\text{Co}(\text{phen})_3^{3+}$  and  $\text{Co}(\text{terpy})_2^{3+}$  ions at millimolar concentrations were prepared by the oxidation of the corresponding Co(II) solutions with chlorine gas.<sup>12</sup> The degree of the oxidation was checked spectrophotometrically after treatments of diluted aliquots with 1 M HCl, using the features of a very inert behavior of the Co(III) complexes and a fast dissociation of the Co(II) complexes. After the oxidation was completed the excess of chlorine was expelled from the solutions by a stream of nitrogen gas.

Titanium(III) solution in aqueous chloride medium was prepared and used as previously described.<sup>6</sup> Other materials were the same as used in the previous study.

**Kinetic Measurements.** The kinetics were followed by a Cary 17 spectrophotometer at 25 °C in the manner as previously applied.<sup>6</sup> The first-order conditions were employed and a decrease of absorbance was recorded. Kinetic runs of the reaction of  $\text{Co}(\text{phen})_3^{3+}$  were analyzed by standard plots. For the runs of  $\text{Co}(\text{terpy})_2^{3+}$  the Guggenheim method was used as a precaution. In the latter case the development of an absorption peak, slow as compared to the redox rate, was observed at 552 nm. It was found that this was due to the complexation of traces of iron(II) present in titanium(III) solution with the terpyridine ligand freed by the redox reaction. Formation of the iron(II)-terpyridine complex, a species of very high molar absorptivities,<sup>13</sup> is relatively fast in neutral solution,<sup>14</sup> but the rate is greatly reduced by acidity. A negligible absorption change at 360

Table I. Rate Constants for the Oxidation of Titanium(III) by  $\text{Co}(\text{phen})_3^{3+}$  at 25 °C and  $\mu = 1.0$  M (HCl + NaCl)<sup>a</sup>

[H <sup>+</sup> ], mM	[Ti(III)], mM	$k_{\text{obsd}} \times 10^3$ , s <sup>-1</sup>	$k_{\text{II}},^b \text{M}^{-1} \text{s}^{-1}$
875	20.8	2.72	0.130
500	4.62	1.05	0.225
200	4.62	2.70	0.59
100	3.46	4.05	1.16
64.5	2.08	3.45	1.67
48.2	2.31	5.0	2.17
19.8	1.15	4.8	4.2
10.0	0.865	7.1	8.2
5.17	0.404	5.2	12.8
3.57	1.04	17.3	16.7
2.70	1.04	18.7	18.0
2.01	0.520	9.9	19.0

<sup>a</sup>  $[\text{Co}(\text{phen})_3^{3+}] = (2.9-4.8) \times 10^{-5}$  M. <sup>b</sup>  $k_{\text{II}} = k_{\text{obsd}}/[\text{Ti(III)}]$ .

nm caused by the latter reaction and its slowness in the acidity range used made the investigation of the main redox reaction unobstructed.

The reactions were studied at 25 °C in chloride medium. Ionic strength was adjusted to 1 M by NaCl.

The completeness of the redox reaction was routinely checked by the comparisons of the spectra of the reaction solutions recorded after 6-10 half-lives with the spectra of the corresponding blank solutions.

**Results**

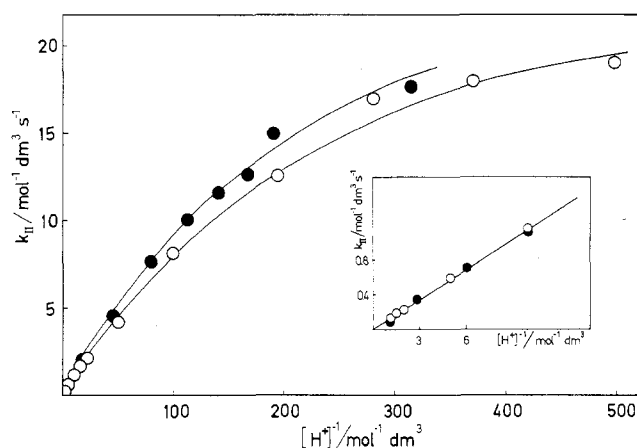
Reduction of the  $\text{Co}(\text{phen})_3^{3+}$  ion by titanium(III) was investigated at 360 or 370 nm, depending on the acidity used. The primary Co(II) product, the  $\text{Co}(\text{phen})_3^{2+}$  ion, undergoes an acid-catalyzed aquation<sup>15</sup> reaching an acid-dependent equilibrium. Qualitative blank experiments have shown that this subsequent process is fast in comparison and does not interfere with the measurements of kinetics of the electron transfer reaction. The pseudo-first-order rate constants,  $k_{\text{obsd}}$ , observed for  $\text{Co}(\text{phen})_3^{3+}$  concentrations of  $(2.9-4.8) \times 10^{-5}$  M and the second-order rate constants calculated as  $k_{\text{II}} = k_{\text{obsd}}/[\text{Ti(III)}]$  for different titanium(III) concentrations and different acidities are given in Table I.

Reduction of the  $\text{Co}(\text{terpy})_2^{3+}$  ion was followed at 360 nm. The primary  $\text{Co}(\text{terpy})_2^{2+}$  product also undergoes an acid-catalyzed aquation which proceeds to an acid-dependent equilibrium. However, blank experiments have shown that the process is slower than the one involving  $\text{Co}(\text{phen})_3^{2+}$ , with half-lives  $\leq 12$  s for  $[\text{H}^+] \geq 0.1$  M and half-lives  $\geq 7$  min for  $[\text{H}^+] \leq 10^{-2}$  M. The pseudo-first-order conditions for the redox reaction were arranged by varying titanium(III) concentrations in such a way as to avoid an interference by the subsequent  $\text{Co}(\text{terpy})_2^{2+}$  aquation. The half-lives of the electron-transfer reaction were at least nine times greater than the aquation of  $\text{Co}(\text{terpy})_2^{2+}$  in high acidities and at least six times less in low acidities. In addition, the choice of the observation wavelength at which the absorption change due to the  $\text{Co}(\text{terpy})_2^{2+}$  aquation is much smaller than the one to the redox reaction, as well as the Guggenheim method of

**Table II.** Rate Constants for the Oxidation of Titanium(III) by Co(terpy)<sub>2</sub><sup>3+</sup> at 25 °C and μ = 1.0 M (HCl + NaCl)<sup>a</sup>

[H <sup>+</sup> ], mM	[Ti(III)], mM	<i>k</i> <sub>obsd</sub> × 10 <sup>3</sup> , s <sup>-1</sup>	<i>k</i> <sub>II</sub> <sup>b</sup> , M <sup>-1</sup> s <sup>-1</sup>
825	29.5	4.0	0.135
825	4.54	0.69	0.152
650	13.6	2.6	0.190
500	29.5	6.5	0.22
350	13.6	4.7	0.34
167	5.90	4.2	0.70
100	5.67	6.7	1.17
59.4	5.40	11.3	2.10
22.2	2.85	13.9	4.50
12.5	0.98	7.5	7.7
8.85	0.98	9.9	10.1
7.05	0.79	8.8	11.6
6.00	0.67	8.4	12.6
5.30	0.59	8.8	15.0
3.18	0.36	6.3	17.5

<sup>a</sup> [Co(terpy)<sub>2</sub><sup>3+</sup>] = (5.1–15.3) × 10<sup>-6</sup> M. <sup>b</sup> *k*<sub>II</sub> = *k*<sub>obsd</sub> / [Ti(III)].

**Figure 1.** Dependence of the second-order rate constants for the oxidation of titanium(III) by Co(phen)<sub>3</sub><sup>3+</sup> (open circles) and by Co(terpy)<sub>2</sub><sup>3+</sup> (full circles) upon acidity at 25 °C in 1 M ionic strength (NaCl).

analyses of the kinetics, has helped to obtain satisfactory redox rate constants. These are presented in Table II.

Figure 1 shows the nature of the dependence of the second-order rate constants for the two reactions upon acidity. The dependence is of the inverse first order in hydrogen ion concentration at high [H<sup>+</sup>] with a trend of levelling off at low hydrogen ion concentration used. On the basis of the substitution inertness of the Co(III) reactants the redox reaction is necessarily of the outer-sphere mechanism, and since no equilibria between proton and Co(III) reactants are present, the specific hydrogen ion effect on the kinetics comes from the hydrolysis of titanium(III):



The extrapolation of the curves in Figure 1 to the zero [H<sup>+</sup>]<sup>-1</sup> value gives the zero intercept, revealing that TiOH<sup>2+</sup> is the only reacting titanium(III) species. Nevertheless, the data from Tables I and II were treated by a computer non-linear least-squares program according to eq 2:

$$k_{\text{II}} = k_{(\text{Ti}^{3+})} + k_{(\text{TiOH}^{2+})} K_a [\text{H}^+]^{-1} / (1 + K_a [\text{H}^+]^{-1}) \quad (2)$$

The trial values of the parameters were obtained by the graphical analysis of the linear plots of 1/*k*<sub>II</sub> vs. [H<sup>+</sup>]. The calculated *k*<sub>(Ti<sup>3+</sup>)</sub> formal values, in one case positive and in the other negative, are about half of their standard deviation, thus confirming that the Ti<sup>3+</sup> species does not contribute to the rate of the reactions. The other constants were then computed

**Table III.** Rate Constants for the Outer-Sphere Reduction of Some Cobalt(III) Complexes by Monohydroxopentaaquatitanium(III) at 25 °C

Complex	<i>k</i> , M <sup>-1</sup> s <sup>-1</sup>
Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	8.6 × 10 <sup>-3</sup> <sup>b</sup>
Co(NH <sub>3</sub> ) <sub>5</sub> (DMN) <sup>3+</sup> <sup>a</sup>	0.12 <sup>b</sup>
Co(bpy) <sub>3</sub> <sup>3+</sup>	13 <sup>b</sup>
Co(phen) <sub>3</sub> <sup>3+</sup>	30 <sup>c</sup>
Co(terpy) <sub>2</sub> <sup>3+</sup>	36 <sup>c</sup>

<sup>a</sup> DMN = *N,N*-dimethylnicotinamide. <sup>b</sup> Upper limit calculated from ref 4 using *K*<sub>a</sub> = 3.5 × 10<sup>-3</sup> M for Ti<sup>3+</sup>; μ = 0.5 M (LiCl).

<sup>c</sup> This work; μ = 1.0 M (NaCl).

using eq 2 by omitting the *k*<sub>(Ti<sup>3+</sup>)</sub> term and with 1/*k*<sub>II</sub><sup>2</sup> weighting. The second-order rate constants so obtained for the oxidation of TiOH<sup>2+</sup> by Co(phen)<sub>3</sub><sup>3+</sup> and Co(terpy)<sub>2</sub><sup>3+</sup> have the values *k*<sub>phen</sub> = 30.2 ± 1.8 M<sup>-1</sup> s<sup>-1</sup> and *k*<sub>terpy</sub> = 36.2 ± 2.4 M<sup>-1</sup> s<sup>-1</sup>. The hydrolysis constant of hexaaquatitanium(III) showed the value *K*<sub>a</sub> = (3.76 ± 0.28) × 10<sup>-3</sup> M obtained from the reaction with Co(phen)<sub>3</sub><sup>3+</sup> and *K*<sub>a</sub> = (3.31 ± 0.26) × 10<sup>-3</sup> M obtained from the reaction with Co(terpy)<sub>2</sub><sup>3+</sup>. The mean value between the two, *K*<sub>a</sub> = 3.54 × 10<sup>-3</sup> M, falls within their limits of confidence.

## Discussion

Kinetics of titanium(III) oxidation via the inner-sphere mechanism by some cobalt(III) complexes exhibit interesting acidity dependences.<sup>3–6</sup> It results from mechanisms by which the binuclear complex, present in a steady-state concentration, reacts in the competitive way to dissociate back to the reactants or to give the redox products. Mechanistic interpretation of such a process and dissection of the kinetic data to the specific rate constants require use of the Ti<sup>3+</sup> acid dissociation constant, *K*<sub>a</sub>. In the previous papers<sup>4–6</sup> the use of the lower *K*<sub>a</sub> literature values<sup>8,9</sup> as compared to the higher literature values<sup>3,7</sup> appears to have been justified. *K*<sub>a</sub> = 3.5 × 10<sup>-3</sup> M obtained in this work for 1 M ionic strength (NaCl) is in very good agreement with the somewhat lower values 1.6 × 10<sup>-3</sup> M in the KCl<sup>8</sup> and 2.8 × 10<sup>-3</sup> M in the KBr medium<sup>9</sup> reported for the higher ionic strength of 3 M.

The available kinetic data on the titanium(III) reduction of cobalt(III) complexes having ligands which ensure operation of the outer-sphere mechanism are collected in Table III. In all the cases the reactive titanium(III) species is TiOH<sup>2+</sup>. This is also true for the other outer-sphere oxidations of titanium(III) thus far studied, with a few exceptions. There is evidence from the acidity dependence of the rate for those cobalt(III) reductions which proceed by the competitive inner-sphere mechanism that the electron transfer occurs within the binuclear complex containing monodeprotonated titanium(III).<sup>3–6</sup> This high preference of TiOH<sup>2+</sup> over Ti<sup>3+</sup> to undergo electron transfer may be accounted for by the structural nature of the Ti(IV) product.<sup>1</sup> The primary Ti(IV) product is most likely TiOH<sup>3+</sup>. The newest kinetic data support the view that Ti(IV), when equilibrium obtains in higher acidic medium, is the TiO<sup>2+</sup> species.<sup>16</sup>

Unfavorable driving forces for the self-exchange or reduction of cobalt(III) complexes have been rationalized in part by a high-energy contribution required for the spin change within the cobalt couple to the overall energy of reorganization of coordination shells at the metal center.<sup>17</sup> The energy barrier for the spin change could arise from unfavorable thermodynamics if the cobalt(II) product of the ground *t*<sub>2g</sub><sup>5</sup>*e*<sub>g</sub><sup>2</sup> electron configuration is formed via formation of the primary cobalt(II) product in an excited low-spin *t*<sub>2g</sub><sup>6</sup>*e*<sub>g</sub><sup>1</sup> state from the ground *t*<sub>2g</sub><sup>6</sup> state of the cobalt(III) reactant or if the primary cobalt(II) product in the *t*<sub>2g</sub><sup>5</sup>*e*<sub>g</sub><sup>2</sup> state is formed from the excited *t*<sub>2g</sub><sup>5</sup>*e*<sub>g</sub><sup>1</sup> state of the cobalt(III) reactant. This consideration may hold for the cobalt complexes listed in Table III except for the

terpyridine complex, since the ground state of Co(terpy)<sub>2</sub><sup>2+</sup> is of the t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>1</sup> electron configuration.

The oxidation of Ti(H<sub>2</sub>O)<sub>5</sub>OH<sup>2+</sup> by Co(phen)<sub>3</sub><sup>3+</sup>, Co(terpy)<sub>2</sub><sup>3+</sup>, and Co(bpy)<sub>3</sub><sup>3+</sup> proceeds by similar rates (if the latter is corrected for the differences in ionic strength). It appears that the reorganization energy associated with the spin change in these cobalt couples makes a very small contribution to the activation energies and does not influence the rate of the reaction with titanium(III). This observation is not surprising. The standard redox potentials of the cobalt couples considered here have close values<sup>18,19</sup> as have rates of the self-exchange.<sup>20</sup> Similarly, not very different rates were observed for the oxidation of Co(phen)<sub>3</sub><sup>2+</sup>, Co(terpy)<sub>2</sub><sup>2+</sup>, and Co(bpy)<sub>3</sub><sup>2+</sup> by the common oxidizing agent *trans*-Co(py)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>.<sup>18</sup> The lack of a significant influence of the spin change in these cobalt couples on the reduction rate of the cobalt(III) complexes or on the oxidation rate of the cobalt(II) complexes has been rationalized by the nature of the phenanthroline, terpyridine, and bipyridine ligands. The similar kinetic behavior is most likely caused by delocalization of the cobalt electrons by the unsaturated ligands, which buries an effect of the spin change. Further evidence questioning the "multiplicity barrier" in the reduction of Co(III) has been reported recently.<sup>21</sup> The kinetic effect of the unsaturated ligands vs. saturated ligands is seen by inspection of the rates presented in Table III. The Co(phen)<sub>3</sub><sup>3+</sup>, Co(terpy)<sub>2</sub><sup>3+</sup>, and Co(bpy)<sub>3</sub><sup>3+</sup> ions oxidize Ti(H<sub>2</sub>O)<sub>5</sub>OH<sup>2+</sup> for three orders of magnitude faster than does the Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> ion. This is

consistent with a much slower rate of electron exchange between Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Co(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and with the calculation demonstrating high-energy contribution of the spin change to the activation energy of this electron-exchange reaction.<sup>17</sup>

Registry No. Co(phen)<sub>3</sub><sup>3+</sup>, 18581-79-8; Co(terpy)<sub>2</sub><sup>3+</sup>, 19137-07-6; Ti<sup>3+</sup>, 22541-75-9; hexaaquatitanium(III), 17524-20-8; Ti(H<sub>2</sub>O)<sub>5</sub>OH<sup>2+</sup>, 54630-67-0.

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## Negative Ion Chemistry of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Co(CO)<sub>2</sub> in the Gas Phase by Ion Cyclotron Resonance Spectroscopy. The $\pi$ -Acceptor Ability of PF<sub>3</sub> Compared to CO

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The gas-phase negative ion chemistry of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Co(CO)<sub>2</sub> is studied using the techniques of ion cyclotron resonance spectroscopy. Attachment of trapped electrons leads to the formation of CpCo(CO)<sub>2</sub><sup>-</sup> and CpCo(CO)<sup>-</sup>. While the molecular anion is unreactive, CpCo(CO)<sup>-</sup> reacts with the neutral precursor to yield [CpCo(CO)]<sub>2</sub><sup>-</sup>, which has been previously characterized in solution. The first observed example of a ligand displacement reaction involving an anionic transition-metal complex, in which PF<sub>3</sub> displaces CO from CpCo(CO)<sup>-</sup>, is reported and leads directly to the conclusion that PF<sub>3</sub> is a stronger  $\pi$ -acceptor ligand than CO toward CpCo<sup>-</sup> in the gas phase. Nitric oxide reacts with both CpCo(CO)<sup>-</sup> and CpCo(CO)<sub>2</sub><sup>-</sup> to yield the very stable anion CpCo(NO)<sup>-</sup>, which is isoelectronic with CpNiNO.  $\pi$  acids weaker than CO (C<sub>2</sub>F<sub>4</sub>, HCN, ethylene oxide, MeCN, NH<sub>3</sub>, NMe<sub>3</sub>, and PMe<sub>3</sub>) were not observed to react with CpCo(CO)<sup>-</sup>. The relative contribution of  $\sigma$  and  $\pi$  bonding in the metal-ligand bonds of CpCo<sup>-</sup> and CpNiB<sup>+</sup> is discussed. Reactions of the anions F<sup>-</sup> and CD<sub>3</sub>O<sup>-</sup> with CpCo(CO)<sub>2</sub> are briefly considered.

### Introduction

While the study of transition-metal complexes using the techniques of ion cyclotron resonance spectroscopy (ICR) is a rapidly expanding field of endeavor,<sup>1-7</sup> the results reported to date deal predominantly with the thermochemical properties and reactions of cationic species.<sup>1-5</sup> Only a very few reports have appeared concerning the negative ion chemistry of transition-metal complexes, and these deal almost exclusively with the photodecomposition spectra<sup>6</sup> and condensation reactions of metal carbonyls.<sup>3-7</sup> Negative ion-molecule reactions have also been observed in the high-pressure (>5 × 10<sup>-6</sup> Torr) mass spectra of chromium oxyhalides<sup>8</sup> and perchloroalkyl-mercury compounds.<sup>9</sup> Neither ligand-displacement nor condensation reactions have been observed for the nickelocene anion, Cp<sub>2</sub>Ni<sup>2-</sup>, or for Fe(CO)<sub>4</sub><sup>3-</sup>, with a variety of simple molecules. Reactions of several anionic species (F<sup>-</sup>, C<sub>2</sub>H<sub>5</sub>O<sup>-</sup>) with Fe(CO)<sub>5</sub>, which result in the formation of tetracoordinate 16-electron products, have been investigated.<sup>3</sup>

The present work describes an ICR study of the negative ion chemistry of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Co(CO)<sub>2</sub>, both alone and in mixtures with other molecules. Processes which are of particular interest include the formation of binuclear cobalt complexes which have been observed and characterized in solution.<sup>10-12</sup> The reactions of a series of  $\pi$  acids with cobalt-containing anions and of anions with neutral CpCo(CO)<sub>2</sub> are presented. Processes observed in the former instance include the first examples of ligand-displacement reactions involving transition-metal anionic complexes. These studies permit an assessment of the relative  $\pi$ -acceptor abilities of ligands in the gas phase. A previous investigation of the mass spectrometry<sup>13</sup> of CpCo(CO)<sub>2</sub> provides information useful in the interpretation of the present results.

### Experimental Section

The theory and instrumentation of ICR mass spectrometry have been previously described.<sup>14-16</sup> This work employed an instrument constructed at Caltech equipped with a 15-in. electromagnet capable