Since it was found[5] that protactinium is only poorly adsorbed from HCl–HF mixtures at high HCl concentrations, it appeared of interest to investigate whether the separation of these two elements could be improved by the use of eluants consisting of HCl–HF mixtures.

In a series of column experiments with the same batch of a strong base polystyrene–divinylbenzene resin (Dowex-1) used in the earlier work, it was found that the adsorbability of Fe(III) from 9 M HCl solutions is not appreciably affected by addition of moderate amounts of hydrofluoric acid (*i.e.*, $< 0.5\ M$ HF). Hence, excellent separation of these two elements should be possible by the use of such mixed eluants. In Fig. 2 the results of a typical experiment are given in which both Pa(V) (Pa^{233} tracer) and Fe(III) (6 mg. of Fe with Fe^{59} tracer) were adsorbed from 9 M HCl on a 5 cm. × 0.12 cm.^{2} column. The Pa(V) was eluted with 9 M HCl–0.1 M HF. Under these conditions Fe(III) remained on the column. It was removed with 0.5 M HCl. The improvement over the separation described in Fig. 1 is apparent. Although elution was carried out in the HF–HCl experiment at high flow rates (*c*, 2.5 ml./cm.^{2}/min.), "tailing" of the iron band was very small and that of the protactinium band, though considerably larger, was still moderate. In the absence of HF extensive tailing is found (compare Figs. 1 and 2. Note that Fig. 1 gives concentration on a linear scale and Fig. 2 on a logarithmic scale).

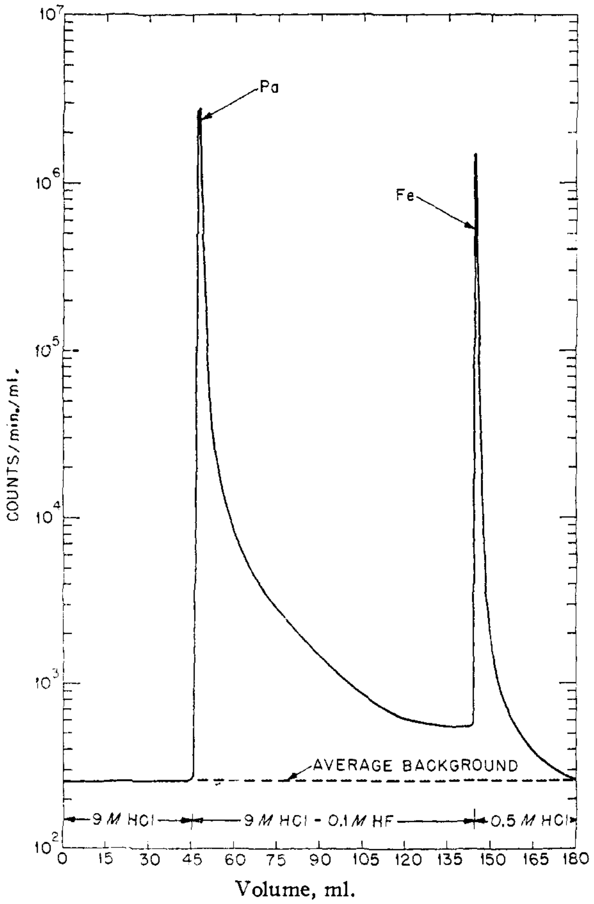

Fig. 2.—Separation of Pa(V) and Fe(III) with HCl–HF mixtures (5-cm. column, flow rate 2.5 cm./min.).

The pronounced difference in the effect of fluorides on the adsorbability of Pa and Fe indicates that protactinium forms a considerably stronger fluoride complex than iron. At considerably lower HCl concentrations where both elements are less strongly adsorbed in the absence of fluoride, fluoride complexing of iron may also become considerable, and the difference between the two elements may become less marked.

The procedure of complexing with two ligands (*e.g.*, chloride and fluoride) should be generally applicable for increasing the effectiveness of anion-exchange separations. Two elements often may show similar complexing properties with respect to one ligand, but it is less likely that they would also behave similarly with respect to two ligands. This property had earlier been taken advantage of in the separation of Nb, Ta and Pa.[5] It is now apparent that it may have general applicability and may be particularly useful in the separation of iron from other elements which show good adsorbability in chloride solutions and poor adsorption in HCl–HF mixtures such as Zr, Hf and Nb.[6]

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(5) K. A. Kraus and G. E. Moore, THIS JOURNAL, **73**, 2900 (1951).

(6) K. A. Kraus and G. E. Moore, *ibid.*, **73**, 9, 13 (1951).

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Metal-Amine Coördination Compounds. III.[1] Manganese Complexes with 2,2'-Bipyridine and 1,10-Phenanthroline

BY RONALD R. MILLER AND WARREN W. BRANDT

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The purpose of this investigation was to obtain further information concerning the nature and stability of the complexes formed by manganese(II) with 1,10-phenanthroline and 2,2'-bipyridine in solution.[2]

Experimental

Apparatus and Reagents.—Spectrophotometric curves were obtained with a Cary recording spectrophotometer. Individual absorption points were obtained with a Beckman Model B spectrophotometer. Matched 1-cm. cells were used with a distilled water blank.

The 2,2'-bipyridine and 1,10-phenanthroline were G. F. Smith Chemical Company reagent grade. The manganese(II) sulfate was obtained from Baker Chemical Company.

Spectrophotometric Study.—Neither the manganese 2,2'-bipyridine nor manganese 1,10-phenanthroline complex has an absorption maximum in the visible or near ultraviolet region of the spectrum as is shown in Fig. 1. In view of this, wave lengths of 370 and 395 mμ were arbitrarily taken to study the bipyridine and phenanthroline systems, respectively. These wave lengths were chosen for here the slope of the curve was not too great and yet the molar absorptivity was large enough so that the systems could be conveniently studied. It was found that the absorbance values of the manganese 2,2'-bipyridine and manganese

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(1) Previous paper in this series, W. W. Brandt and W. B. Howsman, Jr., THIS JOURNAL, **77**, 6319 (1955). Abstracted from a thesis submitted by Ronald R. Miller to the Graduate School of Purdue University, 1954, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Revs.*, **54**, 959 (1954).

1,10-phenanthroline complex increased with increasing *p*H; however, at *p*H 6–8 they were constant.

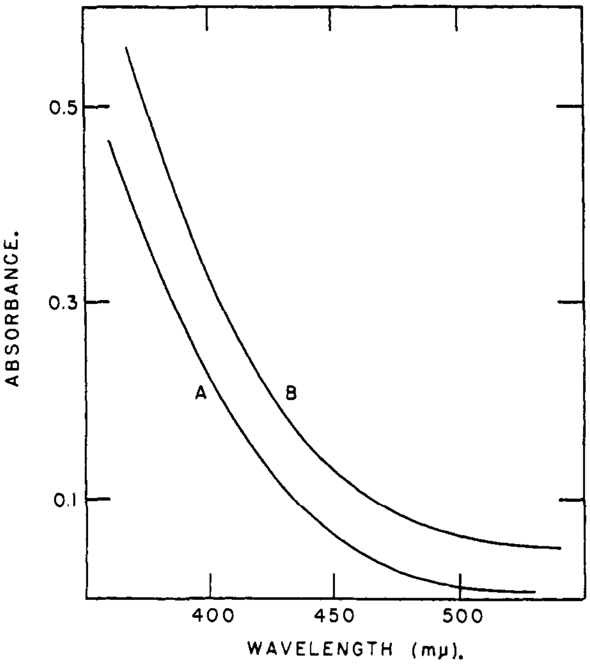

Fig. 1.—Absorption spectra for complexes of manganese(II) with 2,2′-bipyridine (A) and 1,10-phenanthroline (B).

With the manganese 2,2′-bipyridine system, a 10:1 excess of reagent was needed to give maximum color formation. At 370 mμ, the molar absorptivity was found to be 180. A 7:1 excess of reagent was necessary to realize maximum color formation of the manganese 1,10-phenanthroline complex. At 395 mμ, a molar absorptivity of 100 was obtained.

Determination of the Species.—Job's method of continuous variations[3] was used to determine the formulas of the species in solution. These studies were conducted in the *p*H range 6.2–6.4, at an ionic strength of 0.50. The solutions contained varying ratios of reagent to manganese and contained 4.0 × 10^{-4} total mole of reactants in 25 ml. of solution. Figure 2 shows the plots of absorbance *versus* mole ratio of manganese for the 2,2′-bipyridine and 1,10-phenanthroline complexes. In both cases a tris-complex is obtained.

A precipitate of the complex was obtained by salting it out from aqueous solution. The analysis of the precipitate showed it to be Mn(phen)$_2$Cl$_2$.

Anal. Calcd. for Mn(phen)$_2$Cl$_2$: Mn, 11.37; Cl, 14.60; C, 59.30; N, 11.52; H, 3.25. Found: Mn, 11.46; Cl, 14.65; C, 59.63; N, 11.69; H, 3.53.

This demonstrates that the species in solution is different from that obtained by precipitation.

Instability Constants of the Complexes.—Previous data in this study have shown that an excess of reagent is necessary for complete complex formation even above *p*H 6. It was therefore possible to measure the instability constants directly. The average value of 11 results for [Mn(phen)$_3$]$^{++}$ was 4.4 × 10^{-8} with a range of 1.2–10.9 × 10^{-8}. The average of 16 trials for the [Mn(bipy)$_3$]$^{++}$ gave a value of 5.0 × 10^{-7}. These values for the instability constants show that manganese is in its proper place below cadmium in the order of stabilities. The apparently marked deviation of the phenanthroline type systems from the regular order makes the determination of the order constants in these series of interest. The effect of ethanol upon these complexes was studied. It was found that there was no change of species in aqueous ethanol, but the manganese–reagent equilibrium was markedly altered in that increasing concentrations of ethanol required increasing amounts of reagent to reach complete color development.

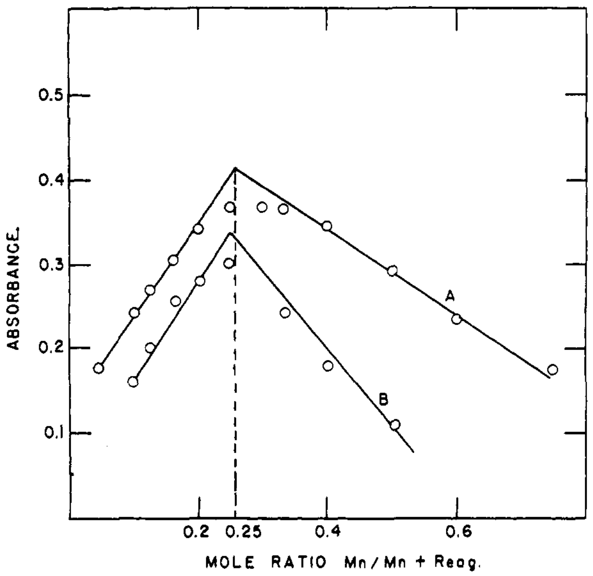

Fig. 2.—Continuous variations study of manganese(II) and 2,2′-bipyridine at 370 mμ (A) and of manganese(II) and 1,10-phenanthroline at 395 mμ. (B).

Discussion

The predominance of the Mn(phen)$_3^{++}$ and Mn(bipy)$_3^{++}$ ions in solution has been demonstrated. No evidence for a 4:1 ratio of reagent to manganese was observed under the conditions used. Calculation of the equilibrium data assuming the formation of such a species gave meaningless results. Apparently the Mn(phen)$_2^{++}$ grouping presents a more satisfactory crystalline configuration, since this species is preferentially precipitated from solutions showing primarily the Mn(phen)$_3^{++}$ ion.

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(3) P. Job, *Ann. Chim.*, [10] **9**, 113 (1928).

The Heat of Combustion of Tri-*n*-butylboron

BY STANLEY TANNENBAUM AND PAUL F. SCHAEFFER

RECEIVED SEPTEMBER 28, 1954

Certain organometallic compounds can be burned fairly completely in an atmosphere of high pressure oxygen thereby affording a good method of obtaining an estimate of their heats of combustion.[1–3] Although it is extremely difficult, if not impossible, to achieve complete combustion, one can frequently demonstrate that 99+% combustion efficiency is obtained. This method, therefore, also provides a convenient and rapid tool for the analysis of organometallic compounds.

It has been shown[3] that, under the proper conditions, a large number of alkylsilanes can be burned successfully to practical completion and it was of in-

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(1) L. H. Long and R. G. W. Norrish, *Trans. Roy. Soc.* (*London*), **A241**, 587 (1949).

(2) R. Thompson, *J. Chem. Soc.*, 1908 (1953).

(3) S. Tannenbaum, S. Kaye and G. F. Lewenz, THIS JOURNAL, **75**, 3753 (1953).