absorption spectrum taken on a Cary recording spectrophotometer. The concentration of Pa^{231} was determined by radiometric assay using 3.4×10^4 years as the α half-life.[5] Spectrographic analyses showed Pa^{231} samples prepared in this manner were free of contamination by other metals. These analyses were performed by Mr. Faris of this Laboratory. In the oxidation experiments, the neptunium(IV) and Sn(II) were added as solutions in 1 *M* HCl. The Sn(II) solutions were prereduced with hydrogen gas to remove any Sn(IV) present. All operations were performed under nitrogen.

Discussion

The absorption spectrum of Pa(IV) is reproduced in Fig. 1. It is characterized by three maxima in the ultraviolet region, at 2760, 2550 and 2237.5 Å. There is no structure in the visible region up to 8000 Å. The spectrum is remarkably similar to the spectrum of Ce(III) (configuration $4f^1$). This is of some interest, since on the basis of the actinide hypothesis[6] protactinium(IV) might be expected to have the configuration $5f^1$. Also shown in Fig. 1 is the spectrum of the Pa(V) solution obtained after air oxidation of Pa(IV) and removal of the hydrolyzed protactinium by centrifugation.

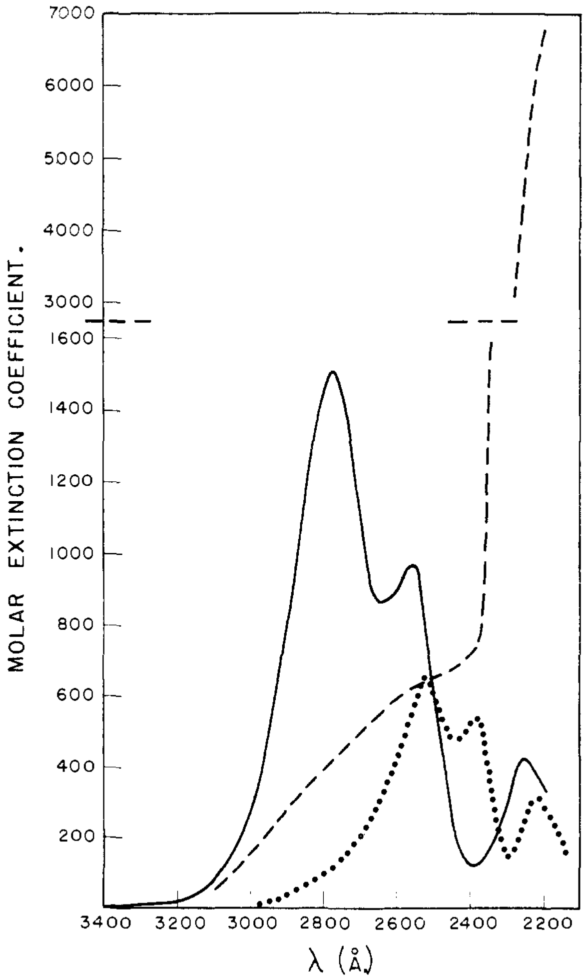

Fig. 1.—Absorption spectrum of Pa(IV) in 1 *M* HCl: ——, Pa(IV)-[Pa] = 1.1×10^{-3} *M*; – – –, Pa(V)-[Pa] = 4.2×10^{-5} *M*; · · ·, Ce(III).

The titrations of the Pa(IV) with Np(IV) were performed to (1) check the oxidation state of the protactinium and (2) to place further limits on the oxidation potential of the Pa(IV)-Pa(V) system. An excess of Np(IV) was used and the decrease in intensity of the Np(IV) band at 7230 Å. followed spectrophotometrically. There is no interference from protactinium absorption in this region. In two experiments, the calculated percentages of oxidation based on a one electron change were 95 ± 5% and 103 ± 6%, respectively. Within the experimental uncertainties, the oxidation of Pa(IV) to Pa(V) is quantitative. Since the potential of the Np(III)-Np(IV) couple is −0.14 volt,[7] the potential of the Pa(IV)-Pa(V) couple is fixed between −0.14 and +0.4 volt. This positive limit is set by the results of Haissinsky and Bouissières.[4]

Sn(II) in 1 *M* hydrochloric acid was added to give a solution containing about an eightfold excess. Apparently little or no oxidation of the Pa(IV) had occurred after a period of 24 hours since there was no evidence of precipitation of Sn^0 or Pa(V). Test of the solution indicated at least 85% of the Pa was still present as Pa(IV). Since the Pa(IV) solutions were found to oxidize slowly to Pa(V) on standing in the stoppered cells (estimated 5–10% in three days) it must be inferred that either Pa(IV) is not a strong enough reducing agent to reduce Sn(II) to Sn^0 or the rate is extremely slow. Although the slow rate of oxidation of Pa(IV) solution standing in sealed cells suggests that Pa(IV) is unstable to oxidation by H^+, further experiments are necessary before this can be considered unequivocally proved. We will tentatively estimate the potential of the Pa(IV) = Pa(V) + e^- couple to be +0.1 volt on the basis of the above observations.

One hour and 15 minutes after blowing oxygen into the absorption cell, appreciable oxidation to Pa(V) had occurred. A marked Tyndall beam was observed. On standing overnight, the oxidation was complete. These qualitative observations on the air instability of Pu(IV) are in accord with those reported by Haissinsky and Bouissières.[4]

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Formation Constants of Metal Complexes of Tropolone and its Derivatives. IV. α-Bromotropolone, Tribromotropolone and 2-Aminotropone[1]

BY BURL E. BRYANT[2] AND W. CONARD FERNELIUS

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As part of an investigation of the coördinating tendencies of various ligands containing the cyclo-

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[1] Taken in part from a thesis submitted by B. E. Bryant in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, 1952.

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heptatrienone nucleus, some experiments were run with α-bromotropolone, *sym*-tribromotropolone and 2-aminotropone.

Experimental

α-Bromotropolone, m.p. 101–103°, and tribromotropolone, m.p. 118–120°, were prepared by the methods of Cook, *et al.*,[3] who report melting points of 103–106° and 122–123°, respectively. 2-Aminotropone, m.p. 105°, was prepared by the method of Doering and Knox[4] who report m.p. 100–101°. Nozoe and co-workers report[5] m.p. 106–107° for 2-aminotropone. *Anal.* Calcd. for C_7H_7ON: N, 11.57. Found: N, 11.80.

Potentiometric titrations in 50% aqueous dioxane were conducted in the manner described previously.[6] The bromo compounds were found to be appreciably stronger acids than unsubstituted tropolone. In the solvent used, for α-bromotropolone pK_D 6.95, and for tribromotropolone pK_D 4.48. Both materials showed limited solubilities in 50% aqueous dioxane. The metal derivatives all were only indifferently soluble. The complexes of tribromotropolone were so insoluble that no formation constants could be determined.

Previously[6,7] it was observed that several of the six-coördinate divalent metals (*i.e.*, zinc) react with basic solutions of tropolone and some of its derivatives to form complex anions of the type MCh_3^-. Such behavior was not observed with α-bromotropolone. From a titration of α-bromotropolone in the presence of $Zn(NO_3)_2$, a yellow powder, m.p >300°, was isolated. *Anal.* Calcd. for $Zn(C_7H_4O_2Br)_2$: C, 36.13; H, 1.72. Found: C, 36.31; H, 1.65. From the magnitude of the formation constants as shown in Table I, it can be deduced that a third α-bromotropolonate ion would be bound very weakly, if at all, by the metal ions which sometimes exhibit a coördination number of six.

TABLE I

FORMATION CONSTANTS OF METAL COMPLEXES OF α-BROMOTROPOLONE

Metal	Be	Pb	Zn	Ni	Mg
log K_1	8.1	7.5	6.9	6.5	4.9
log K_2	7.3	5.6	5.8	5.6	3.9

A solution of 2-aminotropone alone showed no acidic behavior. In the presence of $Cu(NO_3)_2$, however, it was found that two protons were released per copper ion. This release of protons was accompanied by the precipitation of the green copper derivative described by Nozoe, *et al.*[5]

Discussion

The order of stabilities of the metal complexes of α-bromotropolone is the same as that found for other tropolones containing no fused rings. The relationship between the acid dissociation constant and formation constant of the complex with a given metal ion is the same as for the alkyltropolones.[8]

The reaction of 2-aminotropone with copper ion indicates that this material behaves as a nitrogen analog of tropolone and not as a substituted amine. Infrared spectra[9,10] indicate the presence of a hydrogen bond between the amino and carbonyl groups. From the titration data it is obvious that one of the amino hydrogens is lost upon formation of the copper derivative. Although the loss of a proton with subsequent formation of a primary metal to nitrogen bond is not unknown for bidentate ligands[11] of the diamine type, it is felt that in the present situation the nitrogen atom is not behaving as a simple amine nitrogen.

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A Spectrophotometric Study of Copper Halide Complexes

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The spectrophotometric determination of thermodynamic data for complex ion formation has always been subject to the objection that there exists no satisfactory way of either incorporating or determining activity coefficients. The usual procedure is to make measurements at constant ionic strength in the hope that the variation in the activity function is negligible. Then mass action constants for a series of solutions can be determined; and indeed heats of formation may be derived since the ratio of the mass action constants at two temperatures is then approximately equal to the ratio of the corresponding thermodynamic equilibrium constants. Free energy and entropy of dissociation calculations must be regarded as only indicative.

This note concerns a problem arising in the spectrophotometric study of copper halide complexes. Lack of agreement between Näsänen[1] and Farrington[2,3] on $CuBr^+$, and between Näsänen[4] and McConnell[5] on $CuCl^+$, together with discrepancies between their data and those of the author prompted investigation (see Table II).

It was intended to find the extent to which neglect of activity coefficients accounted for the discrepancies. The interesting result, however, is that the lack of agreement can be attributed wholly to the seemingly justifiable neglect of the dihalide complex, CuX_2. It will be shown that the usual criteria point to the existence of only the mono complex in these experiments, in spite of the presence of another complex absorbing at the same wave length. Easily attained circumstances give rise to a system containing comparable amounts of two complex species whose behavior is consistent with the assumption that only one is present. When this is considered the discordant results are reconciled.

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