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

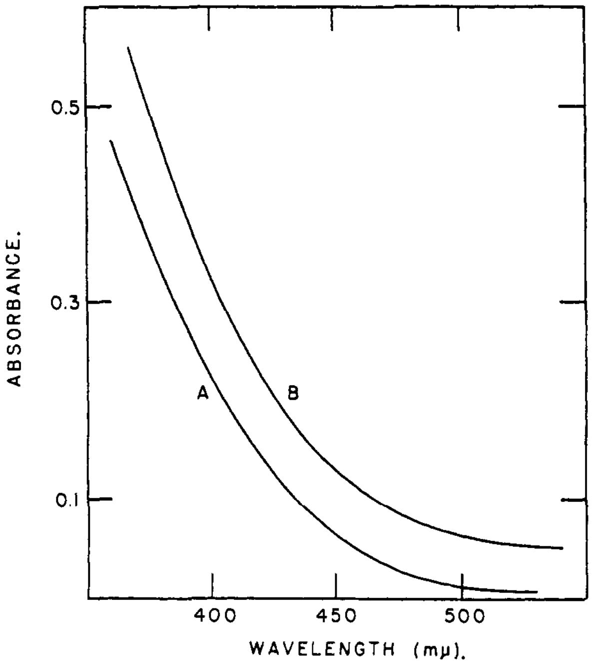

Fig. 1.—Absorption spectra for complexes of manganese(II) with 2,2′-bipyridine (A) and 1,10-phenanthroline (B).

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 $\mathrm{Mn(phen)_2Cl_2}$.

Anal. Calcd. for $\mathrm{Mn(phen)_2Cl_2}$: 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 $[\mathrm{Mn(phen)_3}]^{++}$ was 4.4×10^{-8} with a range of $1.2\text{–}10.9 \times 10^{-8}$. The average of 16 trials for the $[\mathrm{Mn(bipy)_3}]^{++}$ 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.

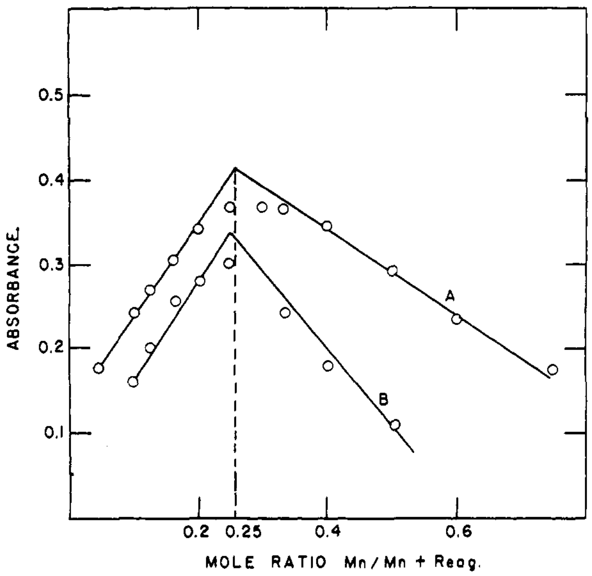

Fig. 2.—Continuous variations study of manganese(II) and 2,2′-bipyridine at 370 mμ (A) and of manganese(II) and 1,10-phenanthroline at 395 mμ. (B).

Discussion

The predominance of the $\mathrm{Mn(phen)_3^{++}}$ and $\mathrm{Mn(bipy)_3^{++}}$ 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 $\mathrm{Mn(phen)_2^{++}}$ grouping presents a more satisfactory crystalline configuration, since this species is preferentially precipitated from solutions showing primarily the $\mathrm{Mn(phen)_3^{++}}$ ion.

Acknowledgment.—The authors wish to express their appreciation for the financial support of this work by the Atomic Energy Commission.

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

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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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terest to determine whether alkylboron compounds would perform as well. Long and Norrish[1] have already investigated the combustion of trimethylboron. However, they included no evidence to substantiate the completeness of combustion other than the observation that, at the end of there action, relatively small quantities of dark material were present in the bomb.

In this research, tri-*n*-butylboron has been burned in a calorimeter and the carbon dioxide and residual boric oxide measured. The heat of combustion has been measured, and from this value the heat of formation and the B–C bond energy have been calculated.

Experimental

Tri-*n*-butylboron.—Tri-*n*-butylboron was synthesized by the method reported by Johnson, *et al.*[4] The material was carefully fractionated and the center fraction, with a boiling point of 89.5° at 9 mm. pressure, was used for this study.

Apparatus and Procedure.—A Parr Adiabatic Calorimeter with an Illium constant volume bomb[5] was used for the measurements. The bomb was calibrated using standard benzoic acid supplied by Parr Instrument Co. The details of the procedure and analysis for carbon dioxide have already been reported.[3] For this compound, 30 atmospheres proved to be a proper oxygen pressure. The boric acid present at the end of the reaction was titrated with sodium hydroxide using a mixed indicator.[6]

Results and Discussion

After several preliminary experiments, the proper conditions for good combustion were obtained and the data for the last four consecutive runs are shown in Table I.

TABLE I

Sample wt., g.	$\Delta E_{\text{comb.}}$, kcal./g.	Carbon, %	Boron, %
0.5649	11.62	78.51	5.97
.4340	11.57	78.41	5.85
.4069	11.60	78.12	5.87
.4384	11.62	[a]	5.90
Average	11.60	78.37	5.90
Theor. anal.		79.12	5.94

[a] Gas leak occurred during analysis.

In all cases, traces of dark material were found indicating that the reaction was not absolutely complete; however, the analytical data show clearly that good combustion was attained. Although only 99.1% of the expected carbon dioxide and 99.3% of the boric oxide were recovered, the heat of combustion measured might well be closer to the correct value and is considered to be within ±0.5% of this value. This is based on the fact that there are inevitable mechanical losses in the analysis and also that some heat release occurs even for the material which is not completely oxidized to B_2O_3 and CO_2. It is quite likely that the experimental value is somewhat lower than the actual value since the combustion is not absolutely complete.

The value for the heat of combustion was converted from a constant volume to a constant pressure process and in addition a correction was made for the amount of boric acid which formed.[1] No correction was made for incompleteness of combustion nor were the Washburn corrections applied.[7]

The heat of the reaction ($\Delta H_{\text{comb.}}$ 25° ref. temp.)

$$B(C_4H_9)_3(l) + 19^1/_2O_2(g) \longrightarrow 12CO_2(g) + {}^1/_2B_2O_3(s) + 13^1/_2H_2O(l)$$

then becomes -2110 ± 10 kcal./mole.

The heat of formation of $B(C_4H_9)_3(l)$ was calculated from the above reaction assuming that the heat of formation for $B_2O_3(s)$ is -306 kcal./mole,[8] for $CO_2(g)$ is -94.1 kcal./mole,[9] and for $H_2O(l)$ is -68.3 kcal./mole.[9] The value arrived at is -94 kcal./mole; by adding the heat of vaporization of 13 kcal./mole,[10] the heat of formation of $B(C_4H_9)_3(g)$ becomes -81 kcal./mole. From this value, a recent compilation of bond energies and heats of atomization,[11] and a value of 97 kcal./mole for the heat of atomization of boron,[9] the B–C bond energy was found to be 70 kcal./mole. This value is in good agreement with the value for the B–C bond energy 74 kcal./mole calculated from the heat of combustion of trimethylboron listed by the National Bureau of Standards.[9]

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Structures of Some Thorium-dye Compounds Exhibiting Selective Ion-exchange Properties

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RECEIVED OCTOBER 15, 1954

The use of the insoluble thorium–Amaranth dye compound as a selective ion exchanger in the colorimetric determination of fluoride ion[1] suggested the desirability of a study of the chemical structures and ion-exchange characteristics of other thorium–dye compounds. The chelate structure proposed[1] for the bonding of thorium ion through the hydroxy and azo groups on the Amaranth (2-hydroxy-1,1′-azonaphthalene-3,4′,6-trisulfonate ion) was not consistent with the 3:1 thorium–dye ratio subsequently found by spectrophotometric titration. This investigation was undertaken to elucidate the structures of other thorium–dye compounds which might undergo selective ion exchange.

Experimental

Spectrophotometric titrations of thorium ion with sulfonic acid dyes consisted of the reaction of a constant amount of one reactant with varying amounts of the other. The reaction mixture was filtered through a freshly precipitated and well washed barium sulfate mat in a confined spot filtration apparatus.[2] The porosity of the mat was such that it quantitatively filtered out any insoluble thorium–dye compound formed but allowed unreacted thorium ion or dye to pass through. By spectrophotometric determination of the unreacted dye in the filtrate, data were obtained from which the amount of dye which reacted with the

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