TABLE IV

INFRARED SPECTRAL DATA (CM^{-1}) (NUJOL MULLS)

$(CH_3)_4N[B_6C_2H_8Mn(CO)_3]$

2490 s, 1970 s, 1930 s, 1890 s, 1365 m, 1128 m, 1085 w, 1065 m, 948 s, 895 w, 847 w, 828 m, 773 m, 743 m, 670 s, (1992 s, 1910 s)[a]

$(CH_3)_4N[B_6C_2H_6(CH_3)_2Mn(CO)_3]$

2480 s, 1974 s, 1865 s, 1365 s, 1283 w, 1272 w, 1120 w, 970 m, 945 s, 830 m, 775 w, 723 m (2076 s, 1978 s)[a]

$(CH_3)_4N[B_6C_2H_7(C_6H_5)Mn(CO)_3]$

2503 s, 1980 s, 1875 s, 1590 m, 1380 s, 1283 w, 1180 w, 1125 w, 1102 w, 1080 m, 950 s, 913 w, 848 w, 768 s, 737 m, 702 s, 677 m, 663 m (2000 s, 1925 s)[a]

[a] In tetrahydrofuran solution.

of Abel and Wilkinson.[3] Bis(pyridine)boronium iodide was prepared as reported by Ryschkewitsch.[4] Sodium hydride was obtained from Metal Hydrides, Inc., as a dispersion in mineral oil. Manganese and rhenium carbonyls were obtained from Strem Chemicals Co. All tetrahydrofuran and diethyl ether was freshly distilled from lithium aluminum hydride and collected under nitrogen. All manganese compounds were purified in an atmosphere of nitrogen.

Preparation of Salts of $B_6C_2H_8Mn(CO)_3^-$. (a) The Reaction of $Na_2B_7C_2H_{11}$ with $Mn(CO)_5Br$.—A solution of $Mn(CO)_5Br$ (2.72 g, 9.9 mmol) in 100 ml of tetrahydrofuran was added to an ethereal suspension of $Na_2B_7C_2H_{11}$ (10 mmol). The amber reaction mixture was heated vigorously for 6 hr, cooled, and filtered. Solvent was evaporated from the filtrate *in vacuo*. An ethereal solution of a major portion of the residue was shaken with a saturated aqueous solution of tetraethylammonium chloride, pentane was added, and the resulting precipitate was filtered and dried under vacuum. The dry salt was chromatographed on silica gel, eluting with dichloromethane. Recrystallization from dichloromethane–hexane yielded 1.53 g (40.7%) of amber $(C_2H_5)_4N[B_6C_2H_8Mn(CO)_3]$. A minor portion of the crude sodium salt was chromatographed on silica gel, eluting with dichloromethane–acetone. An aqueous solution of the residue was shaken with an excess of cesium chloride and the resulting precipitate was recrystallized from aqueous acetone and from ether–hexane yielding 0.14 g (3.7%) of $Cs[B_6C_2H_8Mn(CO)_3]$. The bis(pyridine)boronium salt was similarly prepared.

(b) The Reaction of $Na_2B_7C_2H_{11}$ with $Mn_2(CO)_{10}$.—A solution of $Mn_2(CO)_{10}$ (5.17 g, 13.1 mmol) in 100 ml of tetrahydrofuran was added to an ethereal suspension of $Na_2B_7C_2H_{11}$ (13 mmol) and the mixture was stirred for 26 hr at ether reflux. The brown reaction mixture was stripped to a tar from which residual $Mn_2(CO)_{10}$ (1.4 g) was extracted with hexane. The residue from the extraction was chromatographed on a polyamide column, eluting with 5% acetone–ether. Addition of aqueous tetramethylammonium chloride to an aqueous solution of the eluted material, filtration, and recrystallization from dichloromethane–ether yielded 0.23 g (7.8% calculated from $Mn_2(CO)_{10}$ consumed) of $(CH_3)_4N[B_6C_2H_8Mn(CO)_3]$.

Preparation of Salts of $B_6C_2H_6(CH_3)_2Mn(CO)_3^-$. (a) By the Reaction of $Na_2B_7C_2H_9(CH_3)_2$ with $Mn(CO)_5Br$.—A tetrahydrofuran solution of $Mn(CO)_5Br$ (2.05 g, 7.4 mmol) was added to an ethereal suspension of $Na_2B_7C_2H_9(CH_3)_2$ (7.1 mmol) and the mixture was heated under reflux for 6.5 hr. Solvent was removed *in vacuo*. An ethereal solution of the residue was shaken with an aqueous solution of $(C_2H_5)_4NCl$, pentane was added, and the mixture was filtered. Chromatography on silica gel, eluting with dichloromethane, followed by recrystallization from dichloromethane–ether yielded orange needles of $(C_2H_5)_4N[B_6C_2H_6(CH_3)_2Mn(CO)_3]$ (0.73 g, 25.4%). The product was converted to a tetramethylammonium salt by ion exchange and reprecipitation with the appropriate cation.

(b) By the Reaction of $Na_2B_7C_2H_9(CH_3)_2$ with $Mn(CO)_5Cl$.—Three grams of $Mn(CO)_5Cl$ (15 mmol) in 100 ml of tetrahydrofuran was added to an ethereal suspension of $Na_2B_7C_2H_9(CH_3)_2$ (15 mmol). The mixture was heated at reflux for 40 hr, cooled, and filtered. The residue from the filtrate was treated with an aqueous solution of tetramethylammonium chloride. The mixture was filtered and the precipitate was chromatographed on silica gel using an upflow technique. A brown-orange band was eluted with 8% acetone–92% dichloromethane, solvent was evaporated from the eluent, and the residual orange material was recrystallized from dichloromethane–ether to give 0.12 g (2.4%) of $(CH_3)_4N[B_6C_2H_6(CH_3)_2Mn(CO)_3]$.

Preparation of $(CH_3)_4N[B_6C_2H_7(C_6H_5)Mn(CO)_3]$.—A tetrahydrofuran solution of $Mn(CO)_5Br$ (2.70 g, 9.82 mmol) was added to an ethereal suspension of $Na_2B_7C_2H_{10}(C_6H_5)$ (9.6 mmol). The resulting mixture was heated under reflux for 15 hr, cooled, and filtered. Solvent was evaporated from the filtrate and the residue was chromatographed on silica gel by an upflow technique. An amber material was eluted with dichloromethane and was converted to a tetramethylammonium salt by aqueous precipitation. Recrystallization from dichloromethane–ether–hexane yielded 1.32 g of $(CH_3)_4N[B_6C_2H_7(C_6H_5)Mn(CO)_3]$ (35.5%).

Equivalent Weight Determination.—A solution consisting of approximately 0.25 mmol of the tetramethylammonium salts of the B_6 manganese carbonyl derivatives in 50% aqueous acetone was run through an acid ion-exchange column (0.5 × 10 in. Dowex 50W-X12, 50–100 mesh). The materials were eluted with 30 ml of 50% aqueous acetone and then with distilled water. The eluents were titrated with standard sodium hydroxide solution. The titrations were typical of strong acids, with the exception of the dimethyl derivative, which appeared to decompose.

Acknowledgment.—This research was supported, in part, by the Office of Naval Research and the Army Research Office (Durham) to whom the authors express their thanks.

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Ionization Potentials of Some Sulfur Compounds

BY W. R. CULLEN, D. C. FROST, AND D. A. VROOM

Received March 3, 1969

Although there are many experimental observations which tend to support the idea that divalent sulfur atoms can act as electron acceptors when bonded to, for example, aromatic systems and carbanions[1] and that sulfur-chain compounds and radicals such as $CH_3S_x\cdot$ ($x > 1$) are stabilized by resonance interaction with adjacent sulfur atoms,[2,3] little quantitative information about the extent of delocalization of the formally non-

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(2) M. Schmidt in "Elemental Sulfur," B. Meyer, Ed., Interscience Publishers, New York, N. Y., 1965, pp 301–326.

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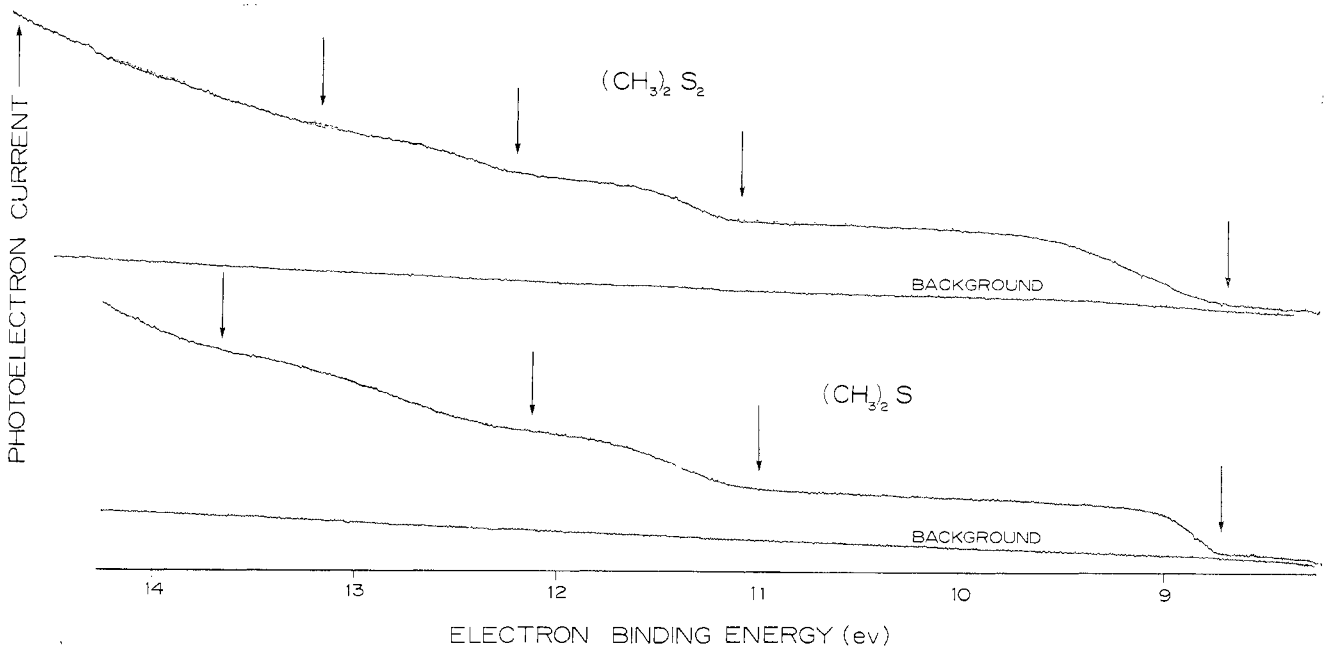

Figure 1.

bonding electron pairs is available. We wish to report values for ionization potentials (IP's) of some divalent sulfur compounds in the hope that they will be of use in checking much needed theoretical calculations of electronic energies.

Experimental Section

All compounds were prepared by methods described in the literature or were purchased from commercial sources. The IP's were determined by photoelectron spectroscopy using the apparatus and methods described by Frost, *et al.*[4] To calibrate the energy scale, a small quantity of rare gas, usually argon, was admitted simultaneously with the sample in order to produce a composite trace. The rare gas IP was known accurately, of course. The necessary correction to the energy scale rarely exceeded 0.1 eV. The IP's measured in this work are each the average of at least seven determinations, and the standard deviation of each is ~0.03 eV.

Representative photoelectron stopping curves, those of $(CH_3)_2S$ and $(CH_3)_2S_2$, are shown in Figure 1. The background trace is the collector current measured with the 584-Å source on and the sample excluded from the spectrometer. When measuring relative transition probabilities to the various electronic states, the background is subtracted out.

Results and Discussion

The adiabatic ionization potentials (IP's) as obtained from the photoelectron stopping curves are listed in Table I. There is good agreement between the first IP's determined this way and by the more conventional but less accurate electron impact method. Using this latter method, the IP's of $(CH_3)_2S$, $(CH_3)_2S_2$, and $(CH_3)_2S_3$ were found to be 8.70 ± 0.2,[5] 9.1 ± 0.2,[6] and 8.80 ± 0.15,[7] respectively. Values of 8.68 and 8.46 eV for the first IP's of $(CH_3)_2S$ and $(CH_3)_2S_2$, respectively, have been obtained by a photoionization method.[8] The spectroscopic IP of $(CH_3)_2S$ is 8.73 eV.[9]

TABLE I

ADIABATIC IONIZATION POTENTIALS OF SOME SULFUR COMPOUNDS (IN EV)

$(CH_3)_2S$	8.68	10.96	12.16	13.68	
$(CH_3)_2S_2$	8.71	11.08	12.71	13.19	14.13
$(CH_3)_2S_3$	8.73	9.14	11.08	11.59	13.61
$(CF_3)_2S$	11.11	12.58	14.45	15.30	
$(CF_3)_2S_2$	10.60	13.00	14.53	15.47	
$(CF_3)_2S_3$	10.16	12.79	13.46	14.63	15.21
$(CF_3)_2S_4$	9.75	10.99	12.57	13.68	15.12
CH_3SCF_3	9.88	12.08	13.42	14.60	
$CH_3S_2CF_3$	9.60	10.10	12.00	13.02	14.91

The model usually used for divalent sulfur compounds[2] has two σ bonds involving mainly two of the 3p orbitals on the sulfur atom leaving the 3s orbitals and the remaining 3p orbital for the four nonbonding electrons. Electron donation is believed to occur into the formally vacant 3d orbitals on the sulfur. The "free" p pair on the sulfur atom can be delocalized into any acceptor orbital such as a 3d orbital on an adjacent sulfur atom. In the case of the monosulfides the first electron is presumably lost from the "free" p pair.

The first IP of hydrogen sulfide is 10.46 eV.[10] Substitution of the hydrogen atom by the more electronegative CF_3 group results in an increased IP and substitution by the electron-releasing CH_3 group results in a decreased IP. The mixed compound CH_3SCF_3 has an intermediate value though lower than that of H_2S. The first IP's of some related molecules obtained from elec-

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[5] B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **67**, 1283 (1963).

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[10] K. Watanabe, *J. Chem. Phys.*, **26**, 543 (1957).

tron impact measurements[11] show that a chlorine atom is not as effective as a CF_3 group in increasing the IP. Thus CH_3SCl and CF_3SCl have IP's of 9.2 ± 0.1 and 10.7 ± 0.1 eV, respectively. The IP of CF_3SH by the same method is 11.35 ± 0.1 eV. The reverse trend has been reported for the first IP's of several derivatives of arsine, AsH_3.[12]

The first IP of H_2S_2 is estimated to be 10.2 eV,[13] so the series of compounds RS–SR (R = CF_3 or CH_3) shows a variation in IP similar to that of the RSR compounds. The increase in IP going from HS–SH to CF_3S–SCF_3 is less than that found for HSH and CF_3SCF_3. This is because each sulfur atom is bound to only one CF_3 group in the disulfides. The dramatic lowering of the first IP's of the compounds $(CF_3)_2S_x$ as x increases and the slow change in the series $(CH_3)_2S_x$ are noteworthy. It seems reasonable to expect that as x increases both series will converge near 9.5 eV, the value of the first IP of S_8.[14]

The inner IP's of these compounds (Table I) come from the first measurements of this kind to be made on divalent sulfur compounds.

Acknowledgments.—This work was supported by generous financial grants from the National Research Council of Canada. We thank Professor C. A. McDowell for his advice and encouragement.

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The Acid Dissociation of the Aquo(diethylenetriamine)(ethylenediamine)cobalt(III) Ion

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Received January 20, 1969

The acid dissociation constants for cobalt(III)–amine complex ions previously have been observed for only a limited number of ions. It is expected that a systematic comparison of a number of these cations will give additional insight in the nature of the cobalt(III)–amine complexes. In this study, the acidity of Co(dien)(en)H_2O^{3+} due to the reaction

$$\underset{\text{I}}{\text{Co(dien)(en)H}_2\text{O}^{3+}} + \text{H}_2\text{O} \rightleftharpoons \underset{\text{II}}{\text{Co(dien)(en)OH}^{2+}} + \text{H}_3\text{O}^+$$

is compared with the acidities of the cobalt(III)–amine complexes which have appeared in the literature. Diethylenetriamine is abbreviated to dien, while ethylenediamine is shortened to en.

The ion Co(dien)(en)H_2O^{3+} was first reported by Pearson, *et al.*,[1] in a study of the hydrolysis of Co(dien)(en)Cl^{2+}; House and Garner[2] obtained the same cation as an impurity in the synthesis of [Co(tetren)Cl]-[$ZnCl_4$].[3] The cation was found to be a product of the acid-induced decomposition of (en)(dien)CoO_2Co(dien)(en)$^{4+}$ by Beaumont.[4]

Experimental Section

Apparatus.—Potentiometric measurements were made with a Beckman Expandomatic pH meter equipped with glass and calomel electrodes. A three-necked, 250-ml, round-bottom flask was fitted with cork and rubber stoppers which held in place capillary-tipped glass tubing and the electrodes of the pH meter. One tube allowed addition of acid or base solution from a 10-ml buret; the others permitted the escape and addition of a stream of scrubbed nitrogen gas. The flask was mounted over a magnetic stirrer and was thermally shielded by asbestos pads.

Chemicals and Reagents.—Recrystallized [Co(dien)(en)Cl]Cl_2 was prepared by heating [(en)(dien)CoO_2Co(dien)(en)]$Cl_4 \cdot 6H_2O$ with 12 *M* hydrochloric acid and was used as the source of Co(dien)(en)H_2O^{3+}. Solutions of HCl and NaOH were prepared from Baker and Adamson CP reagent HCl and from carbonate-free saturated NaOH, respectively. For the latter solution, deionized, distilled, and freshly boiled water was used; the same water was used for the solution of [Co(dien)(en)Cl]Cl_2. The NaOH solution was standardized with primary standard potassium hydrogen phthalate; the HCl solution was standardized with the NaOH solution. For ionic strength variation, Fisher potassium chloride for pH determinations was used without further purification but was dried at 105° prior to being weighed. Nitrogen was obtained from a cylinder provided by Wolverine Gas Products, Inc.

The pH meter was standardized with a thymol-stabilized saturated solution of potassium hydrogen tartrate which had previously been recrystallized from deionized and distilled water (pH 3.56 at 25°).[5]

Procedure.—A 0.3–0.4-mmol sample of [Co(dien)(en)Cl]Cl_2 (0.10–0.13 g) was dissolved in a slight excess of the standard NaOH solution (0.5 mmol) and diluted to 50 ml in a volumetric flask. After a few hours, aliquots of this solution were added to 50-ml volumetric flasks containing preweighed quantities of potassium chloride. After addition of water, the contents of the latter flasks were then emptied into the titration flask which had been previously purged for several hours with a slow stream of nitrogen. For each titration, the total volume was brought to 100 ml by washing the emptied volumetric flask with water from another 50-ml volumetric flask.

Two titrations were made of each sample solution. Dilute HCl was added in the first titration until it was in excess and then dilute NaOH was added in the second until excess base was present. Plots of pH *vs.* volume of titrant gave the apparent equilibrium constants at the half-equivalence points of the titration.

Results and Discussion

The titrations yielded curves typical of those observed in the titrations of weak acids and bases. End points were determined graphically and by use of the obtained $\Delta pH/\Delta V$ data. The half-equivalence points in the titrations of Co(dien)(en)H_2O^{3+} were then calculated and the pH values were found at these points. These values are summarized in Table I.

In Figure 1, the extrapolation of half-equivalence pH values *vs.* the square root of the ionic strength gives the value of the equilibrium constant at zero ionic strength. The best line by least-squares treatment is that which

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