ment with the fact[16] that it is the bridge hydrogen atoms which are the acidic hydrogens in $B_{10}H_{14}$, although an elucidation of the exact nature of the $B_{10}H_{13}^-$ anion may show that the abstracted bridge hydrogen atom does not necessarily carry a positive charge in neutral $B_{10}H_{14}$. The calculated order of hydrogen charges is not in agreement with the fact that in B_2H_6 the bridge hydrogens are found both theoretically[17] and experimentally[18] to be more negatively charged than the terminal hydrogens.

No value of the dipole moment of $B_{10}H_{12}I_2$ has yet been published, however our calculated value of 3.85 D. for $B_{10}H_{14}$ ($K = -18.00$ e.v.) is just outside the experimental[19] range of 3.17 to 3.62 D. In each of the calculations the dipole moment of $B_{10}H_{12}I_2$ is larger than the corresponding $B_{10}H_{14}$ dipole moment. Thus we predict that the dipole moment of $B_{10}H_{12}I_2$, when it is measured, will be found to be larger than that of $B_{10}H_{14}$, possibly around 4.6 D.

The difference in magnitude between the corresponding charges and dipole moments of the two sets of results serve to warn us that the calculation of these quantities by EHT is not yet well understood and deserves further attention. It is apparent, however, that the use of the equation for the resonance integral involving K' rather than K tends to pile up negative charge on atoms which have the more negative Coulomb integrals.

In Table I we give in order the energy of excitation (which is to be regarded as strictly qualitative), the symmetry of the excited total wave function, and the polarization, if allowed, of the first four electronic transitions for each calculation. The symmetry of the excited state is the direct product of the symmetry of the energy level from which the electron is excited and the symmetry of the energy level to which the electron is excited. Both molecules have the totally symmetric A_1 ground state. In each $B_{10}H_{14}$ calculation the first two allowed transitions are polarized perpendicular to the twofold axis of the molecule and the third is polarized parallel to the twofold axis, which is in agreement with the experimental results of Haaland and Eberhardt.[20]

In $B_{10}H_{12}I_2$ the four transitions of lowest energy are from nonbonding iodine MO's to the boron framework a_1 MO. Again the first two allowed transitions are polarized perpendicular to the twofold axis of the molecule and the third is polarized parallel to the twofold axis. These theoretical polarizations are in agreement with the experimental observations of Smallwood and Eberhardt.[5]

Discussion

We also carried out the same calculations on models of $B_{10}H_{14}$ and $B_{10}H_{12}I_2$ from which all hydrogen atoms were omitted.[1] The neglect of hydrogen atoms does not materially affect the results, and in either case all of the interesting effects appear to be occurring at, or because of, the iodine–boron bond.

Finally we varied the iodine 5p Coulomb integral to see what effect this would have on the results. Making this integral more negative has the effects of increasing the molecular ionization energy, of increasing the negative charge on the iodines, at the expense of the adjacent boron atoms, of increasing the dipole moment, and of lowering the iodine energy levels rather sharply (Figure 2) and of lowering the original $B_{10}H_{14}$ energy levels somewhat less.

Acknowledgments.—We wish to thank Professor William H. Eberhardt for suggesting this problem, for his continued interest, and for his discussion of his own results. We are grateful to Professor M. F. Hawthorne for his discussion of the charge distribution in $B_{10}H_{14}$ and to Dr. Roald Hoffmann for making his extended Hückel theory program available to the Quantum Chemistry Program Exchange. We also wish to acknowledge the use of The Boeing Company's IBM 1620 and 7094 computers and the computing help of Dale Speakes, Gordon Thomas, Fran Brown, and William Cook.

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Volumes of Activation of Some Electron-Transfer Reactions

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The question of whether electron transfer proceeds through an inner or outer-sphere mechanism has constituted a central theme in recent studies of electron-transfer reactions of metal ions.[1-3] In a number of favorable cases, direct determination of the mechanism is possible, examples being the reduction of various pentaamminecobalt(III) complexes, $Co(NH_3)_5X^{2+}$ (X = Br, Cl, N_3, etc.) by Cr^{2+}(aq)[4] or by $Co(CN)_5^{3-}$,[2] which yield the substitution-inert products $Cr(H_2O)_5X^{2+}$ and $Co(CN)_5X^{3-}$, respectively, on oxidation, thereby providing proof of an inner-sphere mechanism. Frequently, however (*e.g.*, in the corresponding reactions involving Eu^{2+}, V^{2+}, or Fe^{2+} as reductants,[1,5,6] which yield substitution-labile products on oxidation), the necessary conditions of substitution inertness of reac-

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[16] See the following and the references therein for a discussion of the acidic nature of the bridge hydrogens: M. F. Hawthorne, *Advan. Inorg. Chem. Radiochem.*, **5**, 307 (1963).

[17] W. C. Hamilton, *Proc. Roy. Soc.* (London), **A235**, 395 (1956).

[18] R. A. Ogg, *J. Chem. Phys.*, **22**, 1933 (1954).

[19] R. Bottei and A. W. Laubengayer, *J. Phys. Chem.*, **66**, 1449 (1962).

[20] A. Haaland and W. H. Eberhardt, *J. Chem. Phys.*, **36**, 2386 (1962).

[1] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

[2] J. P. Candlin, J. Halpern, and S. Nakamura, *ibid.*, **85**, 2517 (1963).

[3] J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964).

[4] H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

[5] A. Haim, *ibid.*, **85**, 1016 (1963); *ibid.*, **86**, 2352 (1964).

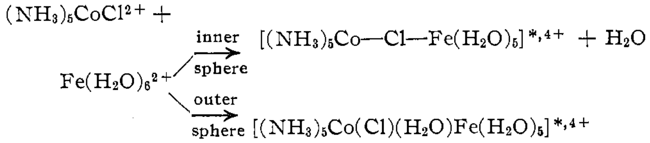
[6] J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

tants and/or products are not fulfilled and it becomes necessary to invoke indirect criteria to infer the mechanism of electron transfer. Among the criteria which have been examined from this standpoint are the entropies of activation of electron-transfer reactions[1,7] and the reactivity patterns of families of reactions involving a series of related oxidants or reductants.[1,3]

In this paper we examine still another possible such criterion for distinguishing between inner- and outer-sphere electron-transfer reactions, namely the volume of activation. Underlying this approach, as it applies to a reaction such as

$$(NH_3)_5CoCl^{2+} + Fe^{2+} + 5H^+ \longrightarrow Co^{2+}(aq) + Fe^{3+}(aq) + Cl^- + 5NH_4^+$$

is the following distinction between the inner- and outer-sphere electron-transfer paths, namely that formation of the transition state in the former case, in contrast to the latter, is accompanied by liberation of a water molecule from the coordination shell of the reductant to the solvent phase, *i.e.*



$$(NH_3)_5CoCl^{2+} + Fe(H_2O)_6^{2+} \begin{cases} \xrightarrow[\text{sphere}]{\text{inner}} [(NH_3)_5Co{-}Cl{-}Fe(H_2O)_5]^{*,4+} + H_2O \\ \xrightarrow[\text{sphere}]{\text{outer}} [(NH_3)_5Co(Cl)(H_2O)Fe(H_2O)_5]^{*,4+} \end{cases}$$

Since the effective volume of a water molecule in the liquid is almost certainly appreciably larger than that of a coordinated water molecule, a systematic difference between the ΔV^* values of inner- and outer-sphere electron-transfer reactions, in the direction of a more positive ΔV^* for the former, might be expected. This should serve as a more sensitive criterion for the distinction in question than ΔS^*, which is likely to be dominated to a greater extent by long-range electrostriction effects reflecting the over-all reactant charges.

In this paper we report the determination of ΔV^* for the reductions of a number of cobalt(III) complexes by Fe^{2+}, which were examined from this standpoint. The reactions selected were among the few of interest which could be studied by the experimental procedure used, the limitations of which precluded measurements on fast reactions ($t_{1/2} < 5$ min.) or on reactions involving relatively unstable or readily oxidized reductants such as Cr^{2+}.

Experimental

All the reactions examined here have previously been studied at atmospheric pressure.[5,6,8] The same procedures were used to prepare the materials and to follow the reactions spectrophotometrically in the present studies.

The high-pressure apparatus, designed for the study of liquid phase reactions at pressures up to 4 kbars, was essentially similar in its construction and operation to that described by Whalley, *et al.*,[9] with the following modifications: (i) the hypodermic syringe and plunger which constituted the reaction vessel were constructed of lucite and Teflon, respectively, instead of glass, an adequate seal being provided by rubber O-rings mounted on the Teflon plunger barrel; (ii) the capillary tube and valve through which samples of the reaction solution were withdrawn periodically for analysis were constructed of Hastelloy B metal; (iii) an SC air-operated oil pump (SC Hydraulic Engineering Corp., Los Angeles, Calif.) was used to generate and automatically maintain the pressure; and (iv) the reactor was charged, after assembly, through the sampling valve and capillary by injecting, from simultaneously driven syringes, separate solutions of the oxidant and reductant through a suitable mixing chamber. Using this procedure the time required to establish the desired reaction conditions and commence sampling, after initiation of the reaction, was reduced to less than 3 min.

Results and Discussion

The results of our kinetic measurements are summarized in Table I. Initial reactant concentrations were selected to give convenient rates for each reaction and were generally in the range 1×10^{-5} to 1×10^{-3} *M* oxidant and 3×10^{-4} to 1×10^{-1} *M* Fe^{2+}. Rate constants were computed assuming, in each case, a second-order rate law, $k[\text{oxidant}][Fe^{2+}]$, established in

TABLE I

RATE CONSTANTS FOR THE REDUCTION OF VARIOUS COBALT(III) COMPLEXES BY IRON(II)

Oxidant	Temp., °C.	Pressure, kbars	k, M^{-1} sec.$^{-1}$
$Co(NH_3)_5F^{2+}$ [a]	25	0.001	3.58×10^{-3}
$Co(NH_3)_5F^{2+}$ [a]	25	0.68	2.70×10^{-3}
$Co(NH_3)_5F^{2+}$ [a]	25	1.24	2.08×10^{-3}
$Co(NH_3)_5F^{2+}$ [a]	25	2.41	1.26×10^{-3}
$Co(NH_3)_5Cl^{2+}$ [a]	35	0.001	1.67×10^{-3}
$Co(NH_3)_5Cl^{2+}$ [a]	35	0.55	1.42×10^{-3}
$Co(NH_3)_5Cl^{2+}$ [a]	35	1.48	1.04×10^{-3}
$Co(NH_3)_5Cl^{2+}$ [a]	35	2.48	0.71×10^{-3}
$Co(NH_3)_5Br^{2+}$ [a]	35	0.001	1.26×10^{-3}
$Co(NH_3)_5Br^{2+}$ [a]	35	0.69	0.91×10^{-3}
$Co(NH_3)_5Br^{2+}$ [a]	35	1.03	0.92×10^{-3}
$Co(NH_3)_5Br^{2+}$ [a]	35	1.38	0.78×10^{-3}
$Co(NH_3)_5Br^{2+}$ [a]	35	2.41	0.67×10^{-3}
$Co(NH_3)_5N_3^{2+}$ [b]	25	0.001	7.28×10^{-3}
$Co(NH_3)_5N_3^{2+}$ [b]	25	0.48	5.42×10^{-3}
$Co(NH_3)_5N_3^{2+}$ [b]	25	1.10	3.79×10^{-3}
$Co(NH_3)_5N_3^{2+}$ [b]	25	1.65	2.98×10^{-3}
$Co(NH_3)_5N_3^{2+}$ [b]	25	2.02	2.22×10^{-3}
$Co(NH_3)_5N_3^{2+}$ [b]	25	2.76	1.79×10^{-3}
$Co(NH_3)_5N_3^{2+}$ [b]	25	3.52	1.45×10^{-3}
cis-$Co(NH_3)_4(N_3)_2^+$ [c]	25	0.001	1.87×10^{-1}
cis-$Co(NH_3)_4(N_3)_2^+$ [c]	25	0.52	1.33×10^{-1}
cis-$Co(NH_3)_4(N_3)_2^+$ [c]	25	0.93	1.09×10^{-1}
cis-$Co(NH_3)_4(N_3)_2^+$ [c]	25	1.42	0.77×10^{-1}
cis-$Co(NH_3)_4(N_3)_2^+$ [c]	25	2.07	0.67×10^{-1}
cis-$Co(NH_3)_4(N_3)_2^+$ [c]	25	2.59	0.42×10^{-1}
trans-$Co(NH_3)_4(N_3)_2^+$ [c]	25	0.001	0.71×10^{-1}
trans-$Co(NH_3)_4(N_3)_2^+$ [c]	25	0.72	0.64×10^{-1}
trans-$Co(NH_3)_4(N_3)_2^+$ [c]	25	1.45	0.63×10^{-1}
trans-$Co(NH_3)_4(N_3)_2^+$ [c]	25	2.49	0.57×10^{-1}
trans-$Co(NH_3)_4(N_3)_2^+$ [d]	25	0.001	0.89×10^{-1}
trans-$Co(NH_3)_4(N_3)_2^+$ [d]	25	1.35	0.76×10^{-1}
trans-$Co(NH_3)_4(N_3)_2^+$ [d]	25	2.41	0.70×10^{-1}
$Co(HY)Cl^-$ [e]	20	0.001	1.33
$Co(HY)Cl^-$ [e]	20	0.97	1.14
$Co(HY)Cl^-$ [e]	20	1.72	1.11
$Co(HY)Cl^-$ [e]	20	2.62	1.00

[a] Medium = 0.1 *M* $HClO_4$. [b] Medium = 0.1 *M* $HClO_4$, 0.9 *M* $NaClO_4$. [c] Medium = 0.001 *M* $HClO_4$, 0.2 *M* $NaClO_4$. [d] Medium = 0.02 *M* $HClO_4$, 0.2 *M* $NaClO_4$. [e] Y^{4-} = ethylenediaminetetraacetate; medium = 0.2 *M* $HClO_4$, 0.7 *M* $NaClO_4$.

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(7) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961).

(8) A. Pidcock and W. C. E. Higginson, *J. Chem. Soc.*, 2798 (1963).

(9) A. R. Osborn and E. Whalley, *Can. J. Chem.*, **39**, 1094 (1961); J. Koshikallio and E. Whalley, *Trans. Faraday Soc.*, **55**, 809 (1959).

earlier studies.[5,6,8] The values of k at atmospheric pressure were in satisfactory accord with earlier measurements when allowance was made for differences in ionic strengths. Values of ΔV^* were computed from slopes of plots of log k *vs.* pressure (which were generally linear up to at least 2 kbars) using the relation $\Delta V^* = -RT(\mathrm{d} \ln k/\mathrm{d}P)$, and are summarized in Table II.

TABLE II

VOLUMES OF ACTIVATION FOR THE REDUCTION OF COBALT(III) COMPLEXES BY IRON(II)[a]

Oxidant	ΔV^*, cm.^{3}/mole[b]
$Co(NH_3)_5F^{2+}$	+11
$Co(NH_3)_5Cl^{2+}$	+8
$Co(NH_3)_5Br^{2+}$	+8
$Co(NH_3)_5N_3^{2+}$	+14
cis-$Co(NH_3)_4(N_3)_2^+$	+14
trans-$Co(NH_3)_4(N_3)_2^+$[c]	+2.2
trans-$Co(NH_3)_4(N_3)_2^+$[d]	+2.8
$Co(HY)Cl^-$	+3

[a] Conditions are given in Table I. [b] Estimated uncertainty ±1 cm.^{3}/mole. [c] 0.001 M $HClO_4$. [d] 0.02 M $HClO_4$.

Unfortunately the mechanisms of these reactions are not known with certainty although indirect arguments for inner-sphere mechanisms have been advanced in each case.[5,6,8] The present findings of positive values of ΔV^* for all the reactions are also most readily reconciled with this interpretation, in line with the expectation noted earlier of a positive contribution to ΔV^* from the liberation of a coordinated water molecule in forming the inner-sphere bridged transition state. Positive values of ΔV^* are otherwise difficult to understand, particularly in the reactions between two cations, *e.g.*, $Fe^{2+} + Co(NH_3)_5X^{2+}$, where, in the absence of the specific effect in question, the increase in electrostriction accompanying formation of the transition state would be expected to result in a negative ΔV^*. Also in accord with this are the results of some preliminary measurements[10] which have yielded positive values of ΔV^* for several metal ion catalyzed halide solvolysis reactions whose mechanisms almost certainly involve inner-sphere halide bridged transition states, *i.e.*, $Co(NH_3)_5Cl^{2+} + Hg^{2+}$, $\Delta V^* = +2$; $Co(NH_3)_5Br^{2+} + Hg^{2+}$, $\Delta V^* = +3$; $Co(HY)Cl^- + Cu^{2+}$, $\Delta V^* = +9$; and $Co(HY)Cl^- + Cd^{2+}$, $\Delta V^* = +6$ cm.^{3}/mole.

The origin for the variation in the magnitude of the ΔV^* values in Table II is far from clear. In particular the small value of ΔV^* for *trans*-$Co(NH_3)_4(N_3)_2^+$, in contrast to $Co(NH_3)_5N_3^{2+}$ and *cis*-$Co(NH_3)_4(N_3)_2^+$, is puzzling. The reaction of *trans*-$Co(NH_3)_4(N_3)_2^+$ with Fe^{2+} is also unusual in that it exhibits an acid-catalyzed (in addition to the acid-independent) path which has been attributed to protonation of the nonbridging N_3^- ligand. Although it was not possible in the present studies to increase the H^+ concentration to the point of predominance of the acid-catalyzed path, comparison of the results for 0.001 and 0.02 M H^+ suggests that the ΔV^* values for the two paths are of the same order. One possible interpretation of this behavior is that general acid catalysis, involving binding of a water molecule to the nonbridging N_3^- ligand, and resulting in a negative contribution to ΔV^*, contributes to the H^+-independent path.

Although the conclusions reached above are necessarily tentative and subject to further verification, the results are considered as encouraging from the standpoint of pointing to the potential usefulness of ΔV^* as a criterion for distinguishing between inner- and outer-sphere electron-transfer mechanisms. It would obviously be desirable to calibrate the method by examining some reactions of known mechanism (including both inner- and outer-sphere examples) such as the Cr^{2+} [1] and $Ru(NH_3)_6^{2+}$ [3] reductions of pentaamminecobalt(III) complexes. This will require some modifications of the experimental procedures, which are presently being attempted.

Acknowledgment.—We are grateful to Dr. David L. Trimm for his contribution to the design and construction of the high-pressure apparatus and to the National Science foundation for a grant in support of this research.

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[10] J. P. Candlin and J. Halpern, unpublished results.

Correspondence

Spectral and Magnetic Properties of Hydroxo Complexes. The Position of the Hydroxide Ion in the Spectrochemical Series

Sir:

The spectrochemical series has been very valuable in the characterization of coordination compounds. However, there exist in the series several apparently anomalous arrangements. An extremely puzzling one is the arrangement of hydroxide ion below water, since hydroxide ion has both a higher charge and a greater polarizability than water. This arrangement has been rationalized on the basis of the π-bonding behavior of the two ligands.[1] In order to gain information about this conundrum we have undertaken a study of the spectral properties of compounds in which the transition metal ion is coordinated only by hydroxide groups. Jørgensen[2] in his compendium lists the spectral properties of only $Co(OH)_4^{2-}$, $Pd(OH)_4^{2-}$, and $Rh(OH)_6^{3-}$, and a search of the literature has failed to yield further

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 54.

[2] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p. 284 ff.