between a phosphorus ylide and an aldehyde. It is of interest to speculate that the proposed cycloaddition reaction precludes the formation of higher polymeric aluminum–nitrogen species from the observed elimination reaction.

Our kinetics data suggest that the major factors which influence the rate of elimination will be those which alter the equilibrium constant for adduct formation, K_a, and the second-order rate constant, k. More kinetics studies will be required to elucidate the mechanism of elimination for other Lewis acid–base systems and to distinguish the relative importance of the effects of K_a and k when identical mechanisms are involved. We are also investigating the effects of substituents and the nature of the base atom on the steric course of the proposed cycloaddition reaction.

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Registry No. $H(CH_3)_2Al$, 865-37-2; $N(C_6H_5)(CH_3)H$, 100-61-8; *cis*-$(CH_3)_2AlN(C_6H_5)(CH_3)$, 56649-31-1; *trans*-$(CH_3)_2AlN(C_6H_5)(CH_3)$, 56604-60-5.

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Kinetics of Reduction of Cobalt(III)–Ammine Complexes by Dithionite

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The kinetics of reduction of several pentaamminecobalt(III) complexes by dithionite have been studied. The observed pseudo-first-order rate constant has the general form $k = k'[S_2O_4^{2-}]^{1/2} + k''[S_2O_4^{2-}]$ which is common for dithionite reductions. The pyridine and ammonia complexes show only the k' term, and this is assigned to an outer-sphere mechanism for these as well as for the sulfato and chloro complexes. This assignment is consistent with comparisons to reductions by $Ru(NH_3)_6^{2+}$. The later comparisons also indicate that the k'' path occurs by a "bridging" mechanism for the azido, sulfato, trichloroacetato, and benzoato complexes. It is proposed that the ratio k'/k_{Ru} may be used to determine oxidant charge since the two reductants have opposite charges and respond in opposite ways to changing oxidant charge.

Introduction

Dithionite is widely used as a reducing agent, especially in in vitro biological systems under neutral or alkaline conditions. Kinetic studies on dithionite reductions[1-12] indicate that mechanism 1 is generally applicable, where Ox is the oxidizing agent.

$$S_2O_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2SO_2^- \quad K_1 = k_1/k_{-1} \tag{1a}$$

$$Ox + S_2O_4^{2-} \xrightarrow{k_2} \text{product} \tag{1b}$$

$$Ox + SO_2^- \xrightarrow{k_3} \text{product} \tag{1c}$$

The reactions considered here all involve metal-ion reduction, and three mechanistic possibilities are usually recognized. These are (i) outer-sphere electron transfer, perhaps through a porphyrin ligand if present, (ii) inner-sphere electron transfer which occurs subsequent to substitution for one ligand by the reducing agent SO_2^- or $S_2O_4^{2-}$, and (iii) a bridging mechanism in which the reducing agent forms an adduct with a coordinated ligand prior to electron transfer. The second mechanism has been eliminated in several systems[6,12] because ligand substitution was known to be much slower than electron transfer and the reduction product with the original ligand system intact could be identified.[4,12] The observations have been used to infer an outer-sphere mechanism, but, in fact, this does not eliminate a bridging mechanism, as pointed out by James and Hambright[2] and, more recently, by Eaton and Wilkins.[11]

The effect of various ligands coordinated to the metal has been explored in several cases but most extensively, with metmyoglobin as an oxidant, by Wilkins and co-workers[9,11] and by Cox and Hollaway.[10] Most systems have been studied with H_2O, OH^-, pyridine, and CN^- ligands, and the relative rates of dithionite reduction vary with the oxidant. For example, the order of rates with a manganese(III) porphyrin[2] is py > OH^- > H_2O, with a cobalt(III) porphyrin[6] $(OH_2)_2 \gg (OH_2)(OH^-) > (py)_2$, with hemin[8] $(py)_2 \gg (OH_2)_2 \gg (OH_2)(OH^-)$, and with horse heart metmyoglobin[11] py $\gg OH_2 > CN^- \gg OH^-$. These limited observations indicate that the relative rates depend on the metal ion being reduced. The results have been rationalized on the basis of relative reactant, product stability, and ligand rearrangement requirements.[6,8,12] Most recently Wilkins and co-workers[9,11] have proposed a nucleophilic attack of SO_2^- on pyridine and imidazole to explain the high reduction rates when these ligands are coordinated to horse heart metmyoglobin. This proposal was shown to be consistent with the kinetic effects of substitution on the ligand.

The systems studied thus far have the attraction of biological implication but have the concomitant property of complexity. In the hope of clarifying some of the mechanistic details of dithionite reductions this study of the reductions of pentaamminecobalt(III) complexes was undertaken. These complexes are kinetically inert and have been studied with a wide variety of reducing agents. It is hoped that there will be a sufficient basis for comparison so that something more definitive can be determined about the dithionite reductions.

Experimental Section

The pentaamminecobalt(III) complexes were prepared as the perchlorate salts by published methods and were characterized by comparison of their visible spectra to those published for the azido,[13] benzoato,[14] chloro,[15] pyridino,[16] sulfato,[17] and trichloroacetato[18] complexes. In the case of the benzoato complex the spectral parameters were not in total agreement with those of Jones and Thomas[14] and the material was purified by ion exchange to give absorption maxima at 502 and 350 nm with molar extinction coefficients of 73.0 and 59.9 M^{-1} cm^{-1}, respectively.

Stock solutions of sodium dithionite were prepared by adding solid $Na_2S_2O_4$ to a deoxygenated solution of 0.95 M $NaClO_4$ and 0.05 M Tris [tris(hydroxymethyl)aminomethane] and the pH was adjusted with 60% $HClO_4$. Appropriate quantities of this stock solution were added by syringe to a known volume of a deoxygenated solution of the oxidant in the same ionic medium in a 5- or 10-cm path length cell. Dithionite solutions were standardized periodically by reduction of ferricyanide.[6] Solutions were deoxygenated with nitrogen or argon which had been passed through two chromium(II) gas scrubbers.

The change in absorbance was monitored on a Bausch and Lomb precision spectrophotometer with a standard temperature control system.[19] The chloro complex was studied on an Aminco-Morrow stopped-flow system modified slightly in that two three-way Hamilton valves were added to the inlet system for anaerobic studies.

The data from the stopped-flow study were analyzed by an analog comparison technique. The transmittance-time curves were stored on a Tracor NS-570 signal averager and then output to a dual-trace oscilloscope for comparison to a synthetic exponential decay curve whose time constant could be changed by changing the resistance in the circuit. The system was calibrated by recording the synthetic curves on an X-Y recorder and calculating the rate constant in the usual way. Values were within 1% of those expected from the resistance setting. In practice, the accuracy is limited by the uncertainty in matching experimental and synthetic signals to ±5% for the usual signal-to-noise levels.

Results and Discussion

The overall reaction studied is the reduction of the kinetically inert cobalt(III) complex to labile cobalt(II) while dithionite is oxidized to sulfite species. However, it was found that cobalt(II)-dithionite solutions begin to form a colloidal black precipitate, possibly cobalt metal or cobalt(II) sulfide, after 3-5 min at pH 7-8. For some of the slower reactions studied here this precipitate formation prevents straightforward spectrophotometric analysis of the system. It was found that the addition of histidine to the system complexed the cobalt(II) in a form which inhibited precipitate formation.

The effect of added histidine on the reduction rate was investigated with $(H_3N)_5CoN_3^{2+}$ since the reduction was fast enough to be studied in the absence of histidine. It was found that as much as a threefold excess (the highest ratio studied) of histidine over cobalt had no effect on the reduction rate. For the azido, sulfato, and benzoato complexes it was shown that there was no reaction between the cobalt(II)-histidine complex and the cobalt(III) complex, at least not on the same time scale as the dithionite reduction.

Several other reagents were tried to prevent precipitate formation. Glycine had no effect, EDTA catalyzed the reduction somewhat, and ethylenediamine and diethylenetriamine gave strongly colored solutions, possibly due to reaction of dithionite or sulfite with the cobalt(II) complex.

The overall reaction being studied therefore is (2). The

$$(H_3N)_5CoX^{2+} + {}^1/_2S_2O_4^{2-} + 4H^+ + 7H_2O \xrightarrow{\text{slow}} Co(OH_2)_6^{2+} + 5NH_4^+ + X^- + HSO_3^- \tag{2a}$$

$$Co(OH_2)_6^{2+} + 2\text{his} \xrightarrow{\text{fast}} Co(\text{his})_2 + 2H^+ \tag{2b}$$

stoichiometry of the reduction reaction was confirmed for X^- $\equiv N_3^-$ and Cl^- by measuring the final solution absorbance of solutions initially having a cobalt(III) to dithionite ratio in the range of 0.5:1 to 2:1. The results indicate a stoichiometry of 2 ± 0.1 for both complexes.

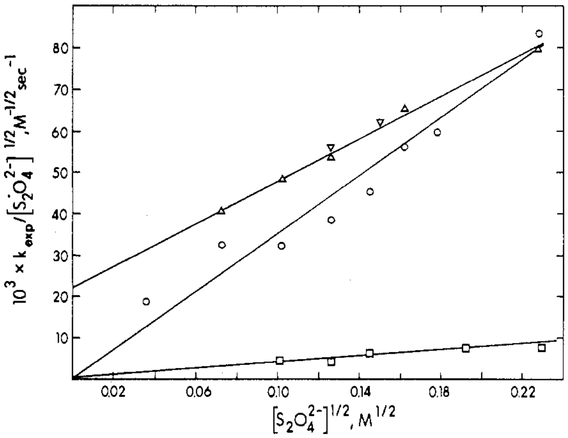

Figure 1. Variation of $k_{exptl}/[S_2O_4^{2-}]^{1/2}$ with $[S_2O_4^{2-}]^{1/2}$ for the dithionite reductions of $(H_3N)_5CoX$ complexes at 25 °C in 0.95 M $NaClO_4$ and 0.05 M Tris: (○) X ≡ $Cl_3CCO_2^-$, pH 8.7, λ 505 nm; (□) X ≡ $C_6H_5CO_2^-$, pH 8.7, λ 502 nm; (△) X ≡ SO_4^{2-}, pH 7.5, λ 517 nm; (▽) X ≡ SO_4^{2-}, pH 8.7, λ 517 nm.

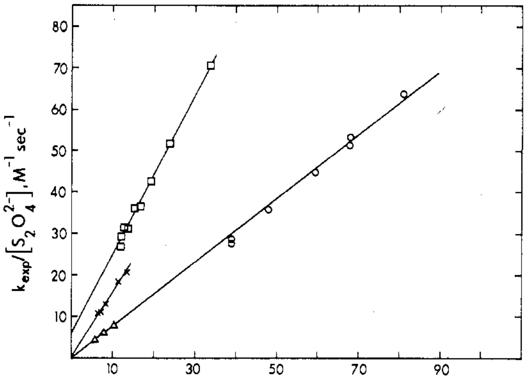

Figure 2. Variation of $k_{exptl}/[S_2O_4^{2-}]$ with $[S_2O_4^{2-}]^{-1/2}$ for the dithionite reductions of $(H_3N)CoX$ complexes at 25 °C in 0.95 M $NaClO_4$ and 0.05 M Tris: (○) X ≡ Cl^-, pH 8.0, λ 520 nm, abscissa × 10; (□) X ≡ N_3^-, pH 7.5, λ 520 nm, ordinate × 10; (×) X ≡ C_5H_5N, pH 8, λ 475 nm, ordinate × 10; (△) X ≡ NH_3, pH 8, λ 470 nm, ordinate × 10^2.

The kinetic studies were done under pseudo-first-order conditions with $[S_2O_4^{2-}] \gg [Co(III)]$ and the experimental rate law was found to be

$$-d[(H_3N)_5CoX]/dt = k_{exptl}[(H_3N)_5CoX] \tag{3}$$

where, in general

$$k_{exptl} = k'[S_2O_4^{2-}]^{1/2} + k''[S_2O_4^{2-}] \tag{4}$$

The values of k' and k'' can be determined from appropriate plots of $k_{exptl}[S_2O_4^{2-}]^{-1}$ or $k_{exptl}[S_2O_4^{2-}]^{-1/2}$ vs. $[S_2O_4^{2-}]^{-1/2}$ or $[S_2O_4^{2-}]^{1/2}$, respectively. The results are shown in Figures 1 and 2. The values of k' and k'' for the various cobalt(III) complexes are given in Table I.

Lambeth and Palmer[1] have shown that the experimental rate law (eq 4) is consistent with the mechanism in eq 1 if a steady state is assumed for SO_2^- and if

$$2k_{-1}[SO_2^-] \gg k_3[Ox] \tag{5}$$

Then

$$k' = k_3K_1^{1/2} \text{ and } k'' = k_2 \tag{6}$$

It should be noted that if K_1 represents a constantly maintained

Table I. Rate Constants for Reduction of $(H_3N)_5CoX$ by Dithionite $(k', k'')^a$ and $Ru(NH_3)_6^{2+}$ (k_{Ru})

X	k', $M^{-1/2}\ s^{-1}$	k'', $M^{-1}\ s^{-1}$	k_{Ru},^{c} $M^{-1}\ s^{-1}$
Cl^-	7.75	$(\lesssim 2)^i$	$4.7(2.6^d) \times 10^2$
N_3^-	0.20	0.55	3.37^e
SO_4^{2-}	0.022	0.255	12.9^f
$Cl_3C_2O_2^-$	$(\lesssim 8 \times 10^{-3})^i$	0.34	0.25^g
$C_6H_5CO_2^-$	$(\lesssim 2 \times 10^{-3})^i$	0.042	
C_5H_5N	0.157		0.67^g
NH_3	$7.4 \times 10^{-3\,b}$	$(\lesssim 4 \times 10^{-3})^i$	$2.4 \times 10^{-2\,g,h}$

[a] At 25 °C in 0.95 M $NaClO_4$ unless otherwise indicated. k' and k'' are defined by eq 4 in the text. [b] In 0.15 M $NaClO_4$ due to solubility limitations. [c] Values in 0.5 M Cl^- or corrected to this medium based on results with $(H_3N)_5CoN_3^{2+}$. Original values are given in parentheses. [d] H. Taube and J. F. Endicott, *J. Am. Chem. Soc.*, **86**, 1686 (1964), in ~0.2 M NaCl. [e] A. Adegite, M. Dosumu, and J. F. Ojo, *J. Chem. Soc., Dalton Trans.*, 630 (1977). [f] G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **15**, 638 (1976), quoted in ref 32, assumed to be in 0.5 M Cl^-. [g] F.-F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2674 (1974). [h] The value from footnote *d* corrected for the medium differences gives $k_{Ru} = 2 \times 10^{-2}\ M^{-1}\ s^{-1}$. [i] Upper or lower limits have been established by 95% confidence limits from a least-squares analysis.

equilibrium, then $[SO_2^-] = (K_1[S_2O_4^{2-}])^{1/2}$, and eq 5 can be rearranged to the necessary condition

$$2k_1[S_2O_4^{2-}]^{1/2}/[Ox] \gg k' \qquad (7)$$

This equation can be used conveniently to establish that the experimental conditions satisfy eq 5 since it is known that $k_1 \approx 1.7\ s^{-1}$.[1] In this study typical concentrations of $S_2O_4^{2-}$ (~5×10^{-3} M) and oxidant (~1×10^{-3} M) show that eq 7 is easily satisfied for all of the systems studied. It is noteworthy that this condition was not satisfied in the study on hemin by Cassatt et al.;[8] however, normal kinetics seem to have been observed.

The main goal of this study is to establish if the dithionite reductions can be classified as proceeding by either an outer-sphere or a bridging mechanism. Previous work on the reductions of cobalt(III) complexes indicates that two general methods can be used to establish the mechanism. First, the characteristics of a reaction which must be outer sphere can be established, and, second, the reaction rate constant should correlate with known outer-sphere rate constants with the same oxidant.[20-23] The latter method is based on the applicability of the Marcus cross-relationship.[20]

A complex which must be reduced by an outer-sphere mechanism is normally thought to be one without basic unshared electron pairs on any ligand. For metal-ion reductants the ions $(H_3N)_5Co(NC_5H_5)^{3+}$ and $Co(NH_3)_6^{3+}$ conform to this criterion. It should be noted, however, that Eaton and Wilkins[11] have recently proposed that pyridine coordinated to iron(III) in metmyoglobin undergoes nucleophilic attack by SO_2^- at the 2- or 4-positions of the pyridine ring. The reduction rate constant of $(H_3N)_5Co(NC_5H_5)^{3+}$ is larger than that of $Co(NH_3)_6^{3+}$, but the complexes show the common feature of being reduced only by SO_2^-, i.e., the k' path. If the reduction rate constants of these two complexes by SO_2^- are compared to that with the known outer-sphere reagent $Ru(NH_3)_6^{2+}$, the ratio k'/k_{Ru} is 0.23 and 0.31 for the pyridine and ammonia complexes, respectively. The larger ratio for the ammonia complex would indicate that the k' is too large, but this could be accounted for by the differences in ionic strength of the two studies. The lower ionic strength used with $Co(NH_3)_6^{3+}$ would favor reaction with the oppositely charged SO_2^- ion. In any case, the k'/k_{Ru} ratio is sufficiently constant that no special kinetic effect such as that proposed by Eaton and Wilkins[11] need be invoked in this case.

The failure of $(H_3N)_5Co(NC_5H_5)^{3+}$ to be unusually reactive with SO_2^- was unexpected in view of the observations and explanation of Eaton and Wilkins. On the basis of the pK_a values of the aquo complexes of $(H_3N)_5Co^{3+}$ and iron(III) metmyoglobin, 6.0 and 8.9, respectively, the former would be expected to cause more polarization of the pyridine ligand favoring nucleophilic attack by SO_2^-. Yet there is no evidence for unusual reactivity of $(H_3N)_5Co(NC_5H_5)^{3+}$. In studies on manganese(III) porphyrins and their pyridine complexes Hambright and co-workers[2] have explained their results on the basis of an outer-sphere mechanism.

To return to the reduction of the $(H_3N)_5CoX^{n+}$ complexes, the simplest assumption would be that k' (i.e., SO_2^- reduction) proceeds by an outer-sphere mechanism in all cases because this is the reduction path for the ammonia and pyridine complexes. If this is the case, the k'/k_{Ru} ratio should be constant, but the results derived from Table I give ratios from 3.1×10^{-1} for $Co(NH_3)_6^{3+}$ to 1.7×10^{-3} for $(H_3N)_5CoSO_4^+$. Since the two reducing agents have opposite charges, it is necessary to correct for the attendant effect. The effect of reactant charge on a rate constant, in its simplest form,[24] may be expressed as

$$k \approx k_0 \exp(-z_1 z_2) \qquad (8)$$

where k_0 is a charge-independent rate constant and z_1 and z_2 are the reactant charges. The charge compensated rate constant k_0 can be obtained by multiplying the experimental value by $\exp(z_1 z_2)$, and the results are given in Table II. The values of $(k'/k_{Ru})_0$ are constant at ~$(3.5 \pm 0.7) \times 10^{-5}$ except for the azido complex. The deviation of the latter is in the direction which could be attributed to some bridging mechanism.

A similar analysis can be applied to $(k''/k_{Ru})_0$. The ratio ranges from $<9 \times 10^{-7}$ to 4.5×10^{-4} and is clearly not constant. The implication is that $S_2O_4^{2-}$ reacts by a bridging mechanism with the azido, sulfato, trichloroacetato, and benzoato complexes. The order of reactivity of the last two complexes is opposite to that for chromium(II),[23] and the electronic effects of the substituents are consistent with $S_2O_4^{2-}$ reacting as a Lewis base in forming the bridged intermediate. This observation also may explain why the chloro complex, which is unlikely to act as a Lewis acid, does not appear to show a bridging path with $S_2O_4^{2-}$.

The mechanistic assignments that have been made here for dithionite reductions of cobalt(III) complexes can be used to analyze results from other systems. The analysis of k' indicates that reactant charge is an important feature in the ratio k'/k_{Ru}. As the oxidant charge increases from 1+ to 2+ to 3+, k'/k_{Ru} is ~2×10^{-3}, ~2×10^{-2}, and ~2×10^{-1}, respectively. For

Table II. Charge-Compensated Rate Constants for Reduction of $(H_3N)_5CoX^{a,b}$

X	k'_0	k''_0	$(k_{Ru})_0$	$10^5(k'/k_{Ru})_0$	$10^5(k''/k_{Ru})_0$
Cl^-	1.05 (−2)	<0.04 (−4)	2.5×10^4 (+4)	4.2	<0.16
N_3^-	0.027 (−2)	0.010 (−4)	184 (+4)	15	5.4
SO_4^-	8.1×10^{-3} (−1)	0.034 (−2)	95 (+2)	3.1	36
$Cl_3C_2O_2^-$		6.2×10^{-3} (−4)	13.7 (+4)		46
C_5H_5N	7.8×10^{-3} (−3)		270 (+6)	2.9	
NH_3	3.7×10^{-4} (−3)	$<1 \times 10^{-5}$ (−6)	9.7 (+6)	3.8	<0.1

[a] The reactant charge product is given in parentheses. [b] The units are $M^{-1/2}\ s^{-1}$ for $(k')_0$ and $M^{-1}\ s^{-1}$ for $(k'')_0$ and $(k_{Ru})_0$. The symbols are the charge-corrected rate constants (see eq 8) for reaction with SO_2^-, $S_2O_4^{2-}$ and $Ru(NH_3)_6^{2+}$, respectively.

high potential iron protein (HiPIP) the ratio[7,25] is $60/(3 \times 10^5) = 2 \times 10^{-4}$, consistent with ionic strength effect studies[7] indicating zero charge at the site of reduction. With horse heart cytochrome *c* the ratio is $1.5 \times 10^3/(3.8 \times 10^4) = 3.9 \times 10^{-2}$, consistent with a 2+ charge at the site of reduction. This value is in agreement with that reported by Cummins and Gray[26] from an analysis of the ionic strength dependence of $(H_3N)_5Ru(py)^{2+}$ reduction but is lower than that reported by Holwerda et al.[27] with other reducing agents.

The reduction rates of tetrakis[(*N*-methyl-4-pyridyl)porphine]cobalt(III)[6,28] give $k'/k_{Ru} = 7.7 \times 10^3/(1.2 \times 10^5) = 6.4 \times 10^{-2}$ for the diaquo complex. The ratio indicates a charge of 2+ to 3+ while the oxidant has a net charge of 5+, as a result of the four *N*-methylpyridyl substituents. This example simply illustrates the expected result that net charge on a reactant is not necessarily reflected in its reactivity. It appears that this empirical comparison of k'/k_{Ru} values could be used to determine reactant charge but applications are limited at the moment by the few k_{Ru} values available.

The mechanism assignments suggested here do not preclude the possibility that SO_2^- can react by a bridging mechanism, and in fact, this may be the case with the azido complex. Of course $S_2O_4^{2-}$ must have some outer-sphere reactivity as well. Results to date with $(H_3N)_5CoCl^{2+}$, $Co(NH_3)_6^{3+}$, spinach ferredoxin,[1] and aquometmyoglobin[12] indicate that $k''/k' \leq 0.5$ for totally outer-sphere reactions. Unfortunately, this limit on k''/k' is not useful in mechanism assignment if both paths have bridging-mechanism contributions. It has been shown, however, that the cobalt(III) complexes show a wide range of reactivity with dithionite, and future studies on such systems should be helpful in establishing the mechanisms of dithionite reductions.

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Registry No. $(H_3N)_5CoCl^{2+}$, 14970-14-0; $(H_3N)_5Co(N_3)^{2+}$, 14403-83-9; $(H_3N)_5Co(SO_4)^+$, 18661-07-9; $(H_3N)_5Co(Cl_3C_2O_2)^{2+}$, 19998-53-9; $(H_3N)_5Co(C_6H_5CO_2)^{2+}$, 30931-77-2; $(H_3N)_5Co(C_5H_5N)^{3+}$, 31011-67-3; $(H_3N)_5Co^{3+}$, 14695-95-5; $S_2O_4^{2-}$, 14844-07-6.

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Chemistry of the Boron Subhalides. Preparation, Boron Nuclear Magnetic Resonance, and Thermal Stability of Tetraboron Tetrachloride

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In radio-frequency discharges (∼10 MHz) tetraboron tetrachloride is formed from BCl_3 at rates that are significantly higher than previously reported in earlier preparations. The chemical shift of B_4Cl_4 is found to be extremely deshielded for a boron resonance. Tetraboron tetrachloride is shown to be more thermally stable than two small *closo*-carboranes of similar size, *C*,3-$(CH_3)_2$-1,2-$C_2B_3H_3$ and 1,5-$C_2B_3H_5$.

Introduction

The properties of molecules or ions containing a central core of atoms that are clustered together in a regular geometric array are of increasing interest in both main-group and transition-metal chemistry. Although many elements have been shown to form clusters, at the present time the majority of the known polyhedral species are boron containing. Rigorous MO calculations have frequently been used to explain and/or predict the structures and stabilities of boron-containing compounds,[1] but there has been a continual search for a more easily visualized approach which does not require such sophisticated methodology to yield qualitatively useful results.

The framework electron count has proven to be extraordinarily effective for the structural classification of many species that contain atoms clustered together at the core of a molecular or ionic entity. The observed geometries of many of the clusters that are formed by the main-group elements have been shown by using this simple but very powerful tool to correlate well with the number of electrons contained in the molecular orbitals that bind the framework atoms together. In particular, most of the species that are observed to occur in the closo (most compact) geometry appear to have $2n + 2$ electrons delocalized in the framework orbitals where n is the number of atoms comprising the framework.[2]

The correlation between the number of framework electrons and the structures of polyhedral compounds has also been analyzed by an algebraic graph-theoretical approach, an analysis which "provides a theoretical basis for the stability of closed deltahedral systems with n vertices and $2n + 2$ skeletal electrons".[3] For the smallest deltahedron, the tetrahedron, the conclusion from graph theory is that ten skeletal electrons are required for delocalized framework bonding,

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