density should also influence the methyl hydrogen atoms and would be expected to be greater for $B_4H_8{\cdot}PF_2OCH_3$ than for $B_4H_8{\cdot}PF_2SCH_3$. Thus, an attractive, albeit small, interaction can be envisioned as occurring between the methyl group hydrogens and the hydridic hydrogens of the $B_{2,4}$ atoms. This would create a more hindered rotation for the $B_4H_8{\cdot}PF_2OCH_3$ complex. Furthermore, this interaction would not necessarily predict a different order for the population of the two isomers at ambient temperature. If such an interaction exists in these compounds, then a repulsive interaction would probably exist between the fluorines of the CF_3 group and the hydridic hydrogens of the $B_{2,4}$ atoms in $B_4H_8{\cdot}PF_2CF_3$. This should also result in a more hindered rotation, and this complex is the only compound of those prepared in this study in which rotation is clearly slow with respect to the NMR time scale at low temperatures.

A barrier calculation for the restricted rotation about the boron–phosphorus bond for a series of these complexes would be useful. Unfortunately, programs which calculate barriers to rotation from NMR line shapes require a low-temperature spectrum in which the limiting spectrum is obtained and the rotation has been stopped. Experimentally, this could not be accomplished. X-ray structure determinations of several of these compounds are clearly desirable. Correlations between B–P bond distance, interatomic distances between the hydrogens of the $B_{2,4}$ atoms and the phosphine substituents, and determinations of the dihedral angle between the boron rings as a function of the X substituent would be of interest.

Finally, it is now clear that from the wide range of substituents in $B_4H_8{\cdot}PF_2X$ complexes which have been studied geometric isomers are usually formed. The only two compounds which have not exhibited isomers have been $B_4H_8{\cdot}PF_2H$[1] and $B_4H_8{\cdot}PF_2CF_3$ while $B_4H_8{\cdot}PF_3$[1] and $B_4H_8{\cdot}PF_2CH_3$ exist primarily as one isomer (the endo isomer). Several factors are obviously important in determining whether or not isomers are formed and what their relative populations will be. Interestingly, the PF_2H complex exhibited no hindered rotation at low temperatures while the PF_2CF_3 complex clearly exists as one rotamer at low temperatures. Also, the PF_2H complex is the only $B_4H_8{\cdot}PF_2X$ complex which exhibits long range coupling between the phosphorus atom and the ring hydrogens.[1] This implies that the electronic structure of the PF_2H complex may be different and this point deserves further study.

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Registry No. $B_4H_8{\cdot}PF_2OCH_3$, 78890-52-5; $B_4H_8{\cdot}PF_2SCH_3$, 78890-50-3; $B_4H_8{\cdot}PF_2CH_3$, 78890-51-4; $B_4H_8{\cdot}PF_2CF_3$, 78920-38-4; $B_4H_8{\cdot}PF_2C_4H_9$, 78965-40-9; B_4H_8CO, 12539-64-9.

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Reduction of Peroxomonosulfate by Oxovanadium(IV) in Acidic Solution. Role of the Sulfate Radical Anion

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The reduction of HSO_5^- by the 1-equiv reducing agent VO^{2+} cleanly obeys the rate expression $-d(HSO_5^-)/dt = k(HSO_5^-)(VO^{2+})$, although a mild inverse hydrogen ion dependence was observed over the range 0.010–1.0 M H^+. Competition studies utilizing the trapping agents HN_3 and Ce(III) strongly indicate a free-radical mechanism involving the $SO_4^-\cdot$ radical. A cursory stoichiometric study of the HSO_5^-–Cr^{2+} reaction provides additional support for this mechanistic feature. The straightforward kinetic results obtained in this study are contrasted with the complicated profiles frequently encountered in analogous reductions of hydrogen peroxide by 1-equiv species. The principal difference in the two systems is proposed to be the rare HSO_5^-–$HSO_5\cdot$ transformation in peroxomonosulfate reactions compared to the common H_2O_2–$HO_2\cdot$ involvement in hydrogen peroxide chemistry.

Introduction

Peroxomonosulfate, O_3SOOH^-, is an intermediate in the outdated electrolytic preparation of hydrogen peroxide. A convenient source of this oxidant is the commercial product OXONE, although several syntheses of reasonably pure aqueous solutions have been described.[1] A number of oxidations by peroxomonosulfate have been studied with potentially 2-equiv reducing agents.[2] The general mechanistic feature that has emerged is a nonradical reaction involving nucleophilic attack by the substrate at the peroxo moiety.[3] Oxygen transfer from the terminal peroxide position has been demonstrated in several cases.[2,4] Analogous mechanisms have been proposed for a number of peroxides including hydrogen peroxide.[3a] The principal exception is peroxodisulfate, in that radical mechanisms involving the sulfate radical anion, $SO_4^-\cdot$, predominate.[5]

Conversely, free-radical reactions may be anticipated in oxidations by peroxomonosulfate if 1-equiv reductants are used. Suprisingly, scant attention has been given to these systems, but the formation of the sulfate radical anion has been proposed in pulse radiolysis studies of the reduction of peroxomonosulfate by the hydrated electron.[6] In this communication we report the results of a study of the reaction of oxovanadium(IV), VO^{2+}, and HSO_5^- in acidic solution. Competition studies strongly indicate a free-radical mechanism

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involving the $SO_4^{-}\cdot$ radical. A similar feature is suggested for the Cr^{2+}–HSO_5^- reaction, on the basis of a brief stoichiometric investigation.

Experimental Section

Reagents. Solutions of $VO(ClO_4)_2$ in perchloric acid were prepared from commercial vanadyl sulfate by ion exchange. Solutions of HSO_5^- were prepared from OXONE, kindly supplied by Du Pont. The formula given for this material is $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. We have found that the solid is contaminated with small amounts of $K_2S_2O_8$.[7]

Lithium perchlorate was prepared from reagent grade lithium carbonate and perchloric acid and was recrystallized three times. Sodium azide was recrystallized twice according to the procedure of Browne.[8] Solutions of chromium(II) perchlorate were prepared by the reduction of hexaaquochromium(III) perchlorate with lightly amalgamated zinc under an inert atmosphere. The hexaaquochromium(III) perchlorate was synthesized as described previously[9] and recrystallized twice.

All other chemicals were of reagent grade and were used without further purification. Deionized water was distilled before use, first from acid dichromate and then from alkaline permanganate.

Analytical Procedures. Solutions of HSO_5^- were analyzed iodometrically by reaction with iodide followed by titration with thiosulfate.

Spectrophotometric assays were made for VO^{2+} (ϵ = 17.1 $M^{-1}\ cm^{-1}$ at 762.5 nm), VO_2^+ (ϵ = 389 $M^{-1}\ cm^{-1}$ at 313 nm), and Ce(IV) (ϵ = 5700 $M^{-1}\ cm^{-1}$ at 320 nm in 1.0 M H_2SO_4). When necessary, corrections were made for the absorbance due to VO^{2+} (ϵ = 11 $M^{-1}\ cm^{-1}$ at 313 nm) and VO_2^+ (ϵ = 330 $M^{-1}\ cm^{-1}$ at 320 nm).

The $Cr(H_2O)_6^{3+}$ and $(H_2O)_5CrX^{2+}$ (formed when Br^- or Cl^- was initially present) products of the reaction of excess HSO_5^- and Cr^{2+} were separated by ion exchange.[18] The chromium content of each fraction and of the spent reaction mixture was determined spectrophotometrically after oxidation to CrO_4^{2-} with alkaline hydrogen peroxide.[10]

Kinetic Procedures. The kinetics of the HSO_5^-–VO^{2+} reaction were monitored spectrophotometrically by measuring the formation of VO_2^+. A Zeiss PMQ II spectrophotometer equipped with a rapid-mixing, thermostated sample compartment was used. The kinetic experiments were usually initiated by injecting an appropriate aliquot of HSO_5^- into a stirred solution containing the other reagents at the desired temperature.

Appropriate blank experiments demonstrated that, under the present conditions, hydrazoic acid is quite unreactive toward VO^{2+} and VO_2^+, and mixtures of cerium(III) and peroxomonosulfate are stable. A previous study has shown that the reaction between hydrazoic acid and peroxomonosulfate is very slow in acidic solution.[2]

Results

Kinetics of the HSO_5^-–VO^{2+} Reaction. The ratio $(VO_2^+)_\infty/(HSO_5^-)_0$ was determined in a number of experiments with a stoichiometric excess of VO^{2+} over a range of initial reactant concentrations, acidities, temperature, and ionic strength. The average value was 1.92 ± 0.02, in close agreement with eq 1.

$$2VO^{2+} + HSO_5^- + H_2O = 2VO_2^+ + HSO_4^- + 2H^+ \tag{1}$$

The kinetics were monitored by spectrophotometric measurement of the appearance of vanadium(V) at 313 nm. The experiments were conducted under second-order conditions; plots of ln $((VO^{2+})/(HSO_5^-))$ vs. time were linear for at least 80% of total reaction. Values of the second-order rate constant, $k_{HSO_5^-}$, appropriate to eq 2, are summarized in Table I.

$$-d(HSO_5^-)/dt = k_{HSO_5^-}(VO^{2+})(HSO_5^-) \tag{2}$$

The results indicate that the rate law is obeyed regardless of whether VO^{2+} or HSO_5^- is in stoichiometric excess. The $S_2O_8^{2-}$ and HSO_4^- impurities in the peroxomonosulfate solutions do not influence the value of the rate parameter within experimental error. A small increase in the rate is observed when sulfuric acid is substituted for perchloric acid. The rate parameter increases with decreasing ionic strength, as is usual for reactions between oppositely charged ions.

Table I. Kinetic Results for the HSO_5^-–VO^{2+} Reaction

T, °C	$10^3 \times (VO^{2+})_0$, M	$10^4 \times (HSO_5^-)_0$, M	(H^+), M[a]	I, M[b]	$k_{HSO_5^-}$, $M^{-1}\ s^{-1}$
25.0	1.71	5.08	1.0	1.0	12.8
25.0[c]	2.05	4.27	1.0	1.0	12.6
20.0	2.13	6.33	1.0	1.0	8.70
15.0	2.13	6.48	1.0	1.0	5.93
15.0	1.06	12.9	1.0	1.0	5.75
15.0[d]	2.09	6.34	1.0	1.0	6.12
15.0	2.13	6.34	0.40	1.0	6.01
15.0	2.13	6.33	0.20	1.0	6.51
15.0	2.13	6.48	0.10	1.0	6.95
15.0	2.13	6.33	0.10	0.25	8.14
15.0	2.13	6.33	0.10	0.10	10.4
15.0[e]	2.09	6.34	*e*	*e*	6.95
10.0	2.13	6.33	1.0	1.0	3.81
10.0	1.16	4.08	0.10	0.10	6.24
10.0	1.16	4.08	0.040	0.10	6.72
10.0	1.16	4.08	0.020	0.10	7.17
10.0	1.16	4.08	0.010	0.10	7.57
5.0	2.13	6.33	1.0	1.0	2.63
5.0	1.06	48.4	1.0	1.0	2.44

[a] $HClO_4$ used unless otherwise indicated. [b] Maintained with $LiClO_4$. [c] 2.18×10^{-3} M added $S_2O_8^{2-}$. [d] 2.13×10^{-2} M added H_2SO_4. [e] 1.0 M H_2SO_4.

Table II. Effect of Hydrazoic Acid on the HSO_5^-–VO^{2+} Reaction[a]

$(HN_3)_0$, M	$k_{HSO_5^-}$, $M^{-1}\ s^{-1}$	$(VO_2^+)_\infty/(HSO_5^-)_0$
8.44×10^{-2}	5.85	1.35
3.19×10^{-2}	5.60	1.17
8.69×10^{-3}	6.48	1.06
3.34×10^{-3}	5.95	1.15
8.49×10^{-4}	6.08	1.41

[a] Conditions: 15.0 °C, 1.0 M $HClO_4$, $(VO^{2+})_0 = 2.13 \times 10^{-3}$ M, and $(HSO_5^-)_0 = 6.43 \times 10^{-4}$ M.

A mild inverse hydrogen ion dependence was observed, over the range of both 0.10–1.0 M H^+ at I = 1.0 M and 0.010–0.10 M H^+ at I = 0.10 M. The empirical order with respect to (H^+) was −0.072 and −0.086, respectively.

Radical-Trapping Experiments. Two series of experiments designed to intercept any radical intermediates formed during the VO^{2+}–HSO_5^- reaction were moderately successful. In the first, hydrazoic acid was used as a scavenger. The stoichiometric and kinetic results are summarized in Table II. No kinetic influence due to the presence of the hydrazoic acid was observed. However, the stoichiometric ratio $(VO_2^+)/(HSO_5^-)$ was significantly changed and was nearly 1/1 at the intermediate concentrations of HN_3 used.

Cerium(III) in sulfuric acid solution was also used as a scavenger. The stoichiometric results are summarized in Table III. The cerium(IV)–oxovanadium(IV) reaction rate is not negligible under these conditions, and thus the kinetics of this reaction were briefly studied independently. The rate expression (3) was determined at 15.0 °C, with 1.0 M H_2SO_4,

$$-d(Ce(IV))/dt = (533 \pm 1\ M^{-1}\ s^{-1})(Ce(IV))(VO^{2+}) \tag{3}$$

1.08×10^{-4} M $(VO^{2+})_0$, and $(8.11–8.77) \times 10^{-5}$ M $(Ce(IV))_0$. The results in Table III indicate that the formation of Ce(IV) is enhanced with low concentrations of VO^{2+} and high concentrations of HSO_5^-. The concentration of cerium(III) plays only a minor role provided a substantial excess is used.

Stoichiometry of the HSO_5^-–Cr^{2+} Reaction. Stoichiometric results for the extremely rapid HSO_5^-–Cr^{2+} reaction are

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Table III. Stoichiometry of the HSO_5^-–VO^{2+} Reaction in the Presence of Cerium(III)[a]

$10^4(VO^{2+})_0$, M	$10^3(HSO_5^-)_0$, M	$10^3(Ce(III))_0$, M	$10^5(Ce(IV))_\infty$, M	$(Ce(IV))_\infty/(VO^{2+})_0$	$10^5(Ce(IV))_\infty$, M (calcd[b])
0.524	13.1	9.57	4.31	0.82	4.08
0.533	6.65	9.72	3.49	0.65	3.44
1.05	13.1	9.57	7.11	0.68	6.80
1.05	11.7	9.57	6.73	0.64	6.54
1.07	6.65	9.72	5.47	0.51	5.22
1.08	2.69	9.87	3.14	0.29	2.79
1.05	13.1	2.39	6.75	0.64	6.80

[a] In 1.0 M H_2SO_4 at 15.0 °C. [b] Calculated by means of eq 10.

Table IV. Stoichiometry of the HSO_5^-–Cr^{2+} Reaction[a]

	product distribution, mol %		
scavenger	$Cr(H_2O)_6^{3+}$	$(H_2O)_5CrX^{2+}$	polymeric
	84		16
b	87		13
0.370 M Br^-	50	40	10
0.0926 M Br^-	59	39	3
0.0231 M Br^-	60	28	12
0.0926 M Cl^-	71	24	5

[a] Conditions: $(Cr^{2+})_0 = 0.0168$ M and $(HSO_5^-)_0 = 0.0137$ M (assuming no reaction occurred), 0 °C, 0.50 M $HClO_4$. Unless otherwise indicated, HSO_5^- reactant was injected into Cr^{2+}.
[b] Order of mixing reversed.

summarized in Table IV. The results are nearly independent of the mixing procedure, even though the order of addition appreciably changes the reactant concentration gradient due to the rapid reaction rate. In perchloric acid solution, the chromium(III) product is predominantly $Cr(H_2O)_6^{3+}$, although minor amounts of a dimeric or higher polymeric chromium(III) species are formed. The stoichiometry is markedly affected by the presence of Br^- in the Cr^{2+} solutions, and less so by added Cl^-. In both cases appreciable halochromium(III) is formed, largely at the expense of hexaaquochromium(III). The rate of oxidation of the added halide ion by peroxomonosulfate is negligible relative to the oxidation of the chromium(II) in these experiments.[11]

Discussion

Values of the activation parameters for the HSO_5^-–VO^{2+} reaction in 1.0 M $HClO_4$ as computed from the temperature dependence results are $\Delta H^\ddagger = 12._8$ kcal/mol and $\Delta S^\ddagger = -11$ cal/(mol deg). These values are within the range exhibited by a number of other peroxomonosulfate reactions, a feature of interest in that the other systems are presumed to involve nucleophilic attack at the peroxide moiety in a nonradical mechanism.[3] A similar attack may well occur in the present system, but if so, then HO· rather than O atom (or OH^+) transfer to the VO^{2+} results. It would be worthwhile to test this point by an oxygen-18 tracer experiment, but we have been unable to find an appropriate 1-equiv reductant. Vanadium(V) undergoes rapid oxygen exchange with solvent.[12]

The mild inverse hydrogen ion dependence noted may be ascribed to a medium effect in which the activity coefficients of the reactants or activated complex change as lithium ion is substituted for hydrogen ion at constant ionic strength. Alternatively, the effect may be due to a minor parallel path or consecutive reactions. In any case, the major reaction pathway does *not* involve the rapid preequilibrium step with the formation of the precursor complex $VO{\cdot}SO_5$. It should be noted that the p*K*a of HSO_5^- is ca. 9.3[1c,13] and that VO^{2+} undergoes little hydrolysis over the acidity range studied.[14]

The trapping experimental results are consistent with the formation of a strongly oxidizing intermediate in the HSO_5^-–VO^{2+} reaction. Hydrazoic acid is unreactive toward VO^{2+}, VO_2^+, and HSO_5^- in molar perchloric acid on the time scale of the present experiments. The absence of a kinetic effect due to added HN_3 strongly implies that the obsd. change in stoichiometry is due to an alternative reaction of the intermediate. We suggest that the intermediate is the sulfate radical anion, $SO_4^-{\cdot}$, and that it reacts with HN_3 according to reactions 4 and 5. Reaction 4 is known to be rapid,[15] and

$$SO_4^-{\cdot} + HN_3 = HSO_4^- + N_3{\cdot} \qquad (4)$$

$$2N_3{\cdot} = 3N_2 \qquad (5)$$

the formation and destruction of azide radicals are consistent with the mechanism proposed for the oxidation of HN_3 by Co(III) and Ce(IV).[16] The enhanced production of VO_2^+ at low concentrations of HN_3 is consistent with competition for the sulfate radical by VO^{2+}. However, we have no satisfactory suggestion as to why increased yields of VO_2^+ are also observed with high concentrations of HN_3.

Cerium(III) also is known to react rapidly with $SO_4^-{\cdot}$ radicals in sulfate media.[17] The reaction between VO^{2+} and Ce(IV) is rapid even in 1 M H_2SO_4, but with use of small VO^{2+} and relatively high HSO_5^- concentrations substantial production of Ce(IV) is observed. Since HSO_5^- is quite unreactive toward Ce(III), the formation of Ce(IV) strongly implies the involvement of what we take to be the sulfate radical anion. The results summarized in Table III can be adequately correlated by the reaction scheme (6)–(8).

$$HSO_5^- + VO^{2+} \overset{k_1}{=} SO_4^-{\cdot} + VO_2^+ + H^+ \qquad (6)$$

$$SO_4^-{\cdot} + Ce(III) = SO_4^{2-} + Ce(IV) \quad \text{fast} \qquad (7)$$

$$Ce(IV) + VO^{2+} + H_2O \overset{k_2}{=} Ce(III) + VO_2^+ + 2H^+ \qquad (8)$$

Elimination of time as a variable yields the rate expression 9. Integration over the entire reaction and letting (HSO_5^-)

$$d(Ce(IV))/d(VO_2^+) = (k_1(HSO_5^-) - k_2(Ce(IV)))/(k_1(HSO_5^-) + k_2(Ce(IV))) \qquad (9)$$

$= (HSO_5^-)_0$ lead to eq 10. Since values of k_1 and k_2 were

$$(VO_2^+) = (VO^{2+})_0 = -(Ce(IV))_\infty - (2k_1(HSO_5^-)_0/k_2) \ln (1 - k_2(Ce(IV))_\infty/k_1(HSO_5^-)_0) \qquad (10)$$

determined independently, the infinite cerium(IV) concentration for each experiment can be calculated by an iterative procedure that uses no adjustable parameters. The results of the calculation are summarized in the last column of Table

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III. We consider the agreement between the experimental and theoretical values to be remarkably satisfactory in view of the simplicity of the reaction scheme and the cumulative experimental uncertainties. Rather large concentrations of cerium(III) were used both to trap the $SO_4^-\cdot$ radicals efficiently and to minimize the cerium(IV)–HSO_5^- reaction.[1a] In agreement with other studies, we find no reason for invoking a HSO_5^-–$SO_4^-\cdot$ reaction.[6c,7]

The stoichiometry of the HSO_5^-–Cr^{2+} reaction was briefly examined in view of published observations on the $S_2O_8^{2-}$–Cr^{2+} reaction, for which the mechanism (11)–(14) was proposed.[18]

$$S_2O_8^{2-} + Cr^{2+} = CrSO_4^+ + SO_4^-\cdot \qquad (11)$$

$$SO_4^-\cdot + Cr^{2+} = Cr^{3+} + SO_4^{2-} \qquad (12)$$

$$SO_4^-\cdot + Br^- = SO_4^{2-} + Br\cdot \text{ (or } Br_2^-\cdot) \qquad (13)$$

$$Cr^{2+} + Br\cdot \text{ (or } Br_2^-\cdot) = CrBr^{2+} \qquad (14)$$

Our results are not as clean as those obtained by Pennington and Haim, due primarily to the formation of some polymeric chromium(III) product. However, the data in Table IV are consistent at least qualitatively with an analogous scheme for HSO_5^-, with the important difference that $SO_4^-\cdot$ *is not* transferred in the first step. Whether HO· is instead transferred is not known but is a distinct possibility. In principle, an oxygen-18 tracer experiment should settle the issue, but the lack of a suitable precipitant for Cr^{3+} has frustrated our efforts.[19]

The results obtained in this study lead us to suggest that involvement of the sulfate radical anion may be a general feature of the reduction of peroxomonosulfate by 1-equiv reductants. Suitable trapping agents are more limited than in the corresponding peroxodisulfate systems, due primarily to the greater reactivity of peroxomonosulfate toward the immediate product formed when the sulfate radical is scavenged by commonly used species such as vinyl monomers or arsenic(III). Sharply reduced yields of vanadium(V) and complicated kinetic profiles were observed when the latter scavengers were used in the present system.

The kinetic results for the HSO_5^-–VO^{2+} reaction are remarkably straightforward in view of the radical mechanism proposed. In contrast, related reductions of hydrogen peroxide by VO^{2+} or Fe^{2+}, for example, can exhibit very complicated kinetic and stoichiometric behavior.[20] The principal difference appears to be that the sulfate radical produced as a result of the rate-determining step of the HSO_5^-–VO^{2+} reaction primarily oxidizes VO^{2+}. In the hydrogen peroxide reactions, the HO· formed in the primary reaction can alternatively oxidize H_2O_2 (or VO_3^+) to varying extents depending on the experimental conditions, leading to complicated chain reactions. These features are not unexpected in view of the rate constants for reactions 15[20c] and 16[6c] and the rapid oxidation

$$HO\cdot + H_2O_2 = H_2O + HO_2\cdot \quad k = (1.2\text{–}4.5) \times 10^7 \qquad (15)$$

$$SO_4^-\cdot + HSO_5^- = SO_4^{2-} + HSO_5\cdot \text{ (or } SO_5^-\cdot) \quad k < 10^5 \qquad (16)$$

of many substrates by $SO_4^-\cdot$. As suggested previously, the HSO_5^-–$HSO_5\cdot$ transformation in peroxomonosulfate reactions may be far less common than the H_2O_2–$HO_2\cdot$ involvement in hydrogen peroxide chemistry.[7]

Registry No. HSO_5^-, 12188-01-1; VO^{2+}, 20644-97-7; Ce^{3+}, 18923-26-7; Cr^{2+}, 22541-79-3.

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^{91}Zr NMR Spectrum of $Zr(BH_4)_4$: The Zr–H Coupling Constant as a Probe for a Fast Intramolecular Process

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^{1}H, ^{11}B, and ^{91}Zr NMR spectra have been recorded for the molecule $Zr(BH_4)_4$. The ^{11}B-decoupled ^{91}Zr spectrum exhibits a 17-line spectrum with J_{obsd} = 28 Hz; $J_{^{91}Zr-^{11}B}$ was measured as 18 Hz. These data are interpreted in terms of a rapid intramolecular exchange of bridging and terminal hydrogens.

In continuation of our studies[1] on zirconium NMR spectroscopy (^{91}Zr is 11.23% abundant; $I = {}^5/_2$; $Q = -0.21 \times 10^{-28}$ m^2),[2] we chose to investigate the molecule $Zr(BH_4)_4$ in which the Zr atom is at the center of a tetrahedron of borohydride groups.[3] The initial ^{1}H NMR studies[4] showed a 1:1:1:1 quartet due to coupling to a ^{11}B nucleus ($I = {}^3/_2$) in an effectively tetrahedral environment brought about by a rapid exchange of the single terminal and three bridging protons. On cooling, the ^{1}H spectrum exhibited a broadening of the quartet lines; this was originally attributed to a slowing of the bridging H–terminal H exchange process[4] but was later shown to be more consistent with quadrupole broadening concomitant with rapid relaxation.[5]

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