

TABLE I  
INFRARED FREQUENCIES FOR  $[\text{Co}(\text{en})_2(\text{L})]\text{I}_2$

-L-			Assignment <sup>b</sup>
acac	acac-d <sub>1</sub> <sup>a</sup>	acac-d <sub>6</sub> <sup>a</sup>	
1520	1480	1520	$\nu(\text{C-O}) + \delta(\text{C-H})$
1390	1390	(?)	$\delta\text{d}(\text{CH}_3)$
1370	1370	970	$\delta\text{s}(\text{CH}_3)$
1190	925	c	$\delta(\text{C-H})$
1030 sh	1030 sh	880	$\rho_r(\text{CH}_3)$
805	665	805	$\pi(\text{C-H})$
640	640	620	$\delta(\text{C-CH}_3) + \nu(\text{MO})$

<sup>a</sup> The symbols acac-d<sub>1</sub> and acac-d<sub>6</sub> correspond to complexes enriched with deuterium at the  $\gamma$  carbon and methyl groups, respectively. <sup>b</sup> The assignments follow the notation of Nakamoto (see ref 10). <sup>c</sup> The region around 1200  $\text{cm}^{-1}$  is partially obscured by absorption due to -ND<sub>2</sub> groups; however, a shoulder is found at  $\sim 1190 \text{ cm}^{-1}$ .

to methyl vibrations are shifted while those assigned to  $\geq \text{C-H}$  vibrations are left unshifted or only slightly effected.

### Discussion

The selectivity of exchange reactions of this complex may be understood in terms of the effect of coordination upon the electronic properties of the  $\beta$ -diketonate ligand. The reactivity of the  $\gamma$  carbon of acetylacetonate ligands toward electrophilic reagents, the position of the  $\geq \text{C-H}$  stretching frequency, and other evidence have been cited to support the concept of aromaticity as applied to  $\beta$ -diketonate chelate rings.<sup>11</sup> Within this framework, the acid-catalyzed exchange reaction noted here is likely to be a special case of the more general class of electrophilic substitution reactions in this group of compounds. The general kinetic inertness of Co(III) complexes and the stability of this particular complex to acid hydrolysis conditions<sup>4</sup> suggest that the exchange takes place with the ligand coordinated.

Qualitatively, the rate of exchange of the methyl groups is strongly dependent upon the base concentration, suggesting a mechanism involving the formation of a carbanion intermediate. The stabilization of such an intermediate by delocalization of the charge into the chelate ring might be expected to favor such a reaction whether the mechanism involves a preequilibrium acid-base reaction or the rate-determining attack by base to form an active intermediate. The selectivity of this reaction and particularly the retention of the proton resonance at  $\delta = 4.53 \text{ ppm}$  during the exchange reaction strongly suggest that exchange occurs without opening of the chelate ring. Kinetic studies of both the acid- and base-catalyzed reactions have been initiated.

**Acknowledgment.**—Proton magnetic resonance spectra were obtained with a Varian A-60 nmr spectrometer purchased with matching funds from the National Science Foundation under Grant GP-3655. Thanks are due to Mr. John Martin for preparing some of the compounds used in this work and to Miss Katherine Eggers, who performed the analyses.

(11) J. P. Collman in *Advances in Chemistry Series*, No. 37, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1963, p 78.

CONTRIBUTION FROM THE EVANS AND MCPHERSON CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO

## Aluminum-Aluminum Covalent Bonds.

### I. Hexamethyltris(dimethylamino)-monoborontetraaluminum

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The treatment of aluminum trimethyl with diborane(4) tetrakisdimethylamide results in the formation of several known compounds; dimethylaminodimethylboron, trimethylboron, dimethylaminodimethylaluminum, and a nonvolatile yellow solid. The yellow solid contains aluminum in an apparent oxidation state of +1.5 and represents the first example of a compound containing Al-Al covalent bonds.

Diborane(4) tetrakisdimethylamide (*ca.* 20 mmoles) was treated with aluminum trimethyl in mole ratios,  $\text{B}_2[\text{N}(\text{CH}_3)_2]_4:\text{Al}(\text{CH}_3)_3$ , of *ca.* 1:2 to 1:5. Mole ratios of 1:3 or less yield reaction solutions which are dark red, whereas mole ratios  $>1:3$  result in solution colors varying from pale yellow to dark green. Only mole reactant ratios  $<1:3$  afford trimethylboron, the formation of which is accompanied by an increased yield of  $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$  and a decreased yield of  $(\text{CH}_3)_2\text{BN}(\text{CH}_3)_2$ . No starting material was recovered for the mole reactant ratio,  $\text{B}_2[\text{N}(\text{CH}_3)_2]_4:\text{Al}(\text{CH}_3)_3$ , of 3:8.

#### Characterization of Volatile Reaction Products

Identification of  $(\text{CH}_3)_2\text{BN}(\text{CH}_3)_2$  consisted of vapor tension data comparison with a literature value,<sup>1</sup> infrared spectrum,<sup>2</sup> H<sup>1</sup> nmr spectrum (Table I), and molecular weight determination (calcd: 84.8; found: 85.7). The H<sup>1</sup> nmr spectrum consisted of two peaks of equal area at  $-0.05$  and  $-2.32 \text{ ppm}$ , relative to tetramethylsilane (TMS). Trimethylboron was identified by its vapor tension at  $-78^\circ$ , 29 torr,<sup>3</sup> and from its known infrared spectrum.<sup>4</sup> The white crystalline solid,  $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ , was characterized by comparison of its vapor tension and melting point with the literature value,<sup>5</sup> H<sup>1</sup> nmr spectrum (Table I), and infrared spectrum (Table II). The relative molar amounts of  $(\text{CH}_3)_2\text{BN}(\text{CH}_3)_2$  and  $(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2$  produced in the reaction were estimated by volume and found to be approximately equal.

#### Characterization of Hexamethyltris(dimethylamino)-monoborontetraaluminum

Treatment of  $\text{B}_2[\text{N}(\text{CH}_3)_2]_4$  with  $[\text{Al}(\text{CH}_3)_3]_2$  results in the formation of the volatile species:  $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2]_2$ ,  $(\text{CH}_3)_2\text{BN}(\text{CH}_3)_2$ , and  $(\text{CH}_3)_3\text{B}$ . After re-

(1) G. E. Coates, *J. Chem. Soc.*, 3481 (1950).

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(4) W. J. Lehmann, C. O. Wilson, and I. Shapiro, *J. Chem. Phys.*, **23**, 777 (1958).

(5) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

TABLE I  
SUMMARY OF  $H^1$  NMR DATA FOR VARIOUS AMINO AND  
ALKYL COMPOUNDS OF BORON AND ALUMINUM

Compd	Ppm (relative to TMS)	Intensity ratios proceeding to higher field
$R_2AlNR_2NR_2^a$	-1.68 NR, +0.88, AIR <sup>b</sup>	4:3
$R_3AlNR_2CH_2NR_2$	-1.95 NR, +1.30 AIR <sup>b</sup>	4:3
$[Al(NR_2)_3]_2$	-1.62 terminal, -1.42 bridge <sup>c</sup>	2:1
$R_2BNR_2$	-2.32 NR, -0.05 <sup>d</sup>	1:1
$[R_2AlNR_2]_2$	-1.82 NR, +1.00 AIR <sup>d</sup>	1:1
$BR_3$	-1.23 <sup>e</sup>	...
$B_2(NR_2)_4$	-2.42 <sup>d</sup>	...
$[AlR_3]_2$	-0.47 bridge, +0.67 terminal <sup>f</sup>	1:2 <sup>g</sup>
$Al_4B(NR_2)_3R_6$	-2.72 BR, -2.40 NR <sup>d</sup> -0.23 BR, +0.77 AIR	1:6:1:4

<sup>a</sup> R = methyl. <sup>b</sup> N. R. Fetter, B. Bartocha, F. E. Brinckmann, Jr., and D. W. Moore, *Can. J. Chem.*, **41**, 1359 (1963). <sup>c</sup> J. K. Ruff, *Inorg. Chem.*, **1**, 612 (1962). <sup>d</sup> This work. <sup>e</sup> T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 4138 (1961). <sup>f</sup> N. Muller and D. E. Pritchard, *ibid.*, **82**, 248 (1960). <sup>g</sup> At  $-78^\circ$ .

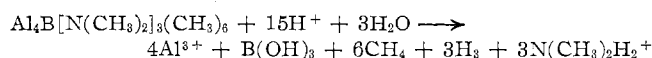
TABLE II  
INFRARED SPECTRAL DATA FOR  $[(CH_3)_2AlN(CH_3)_2]_2^a$

Frequency, $cm^{-1}$ , $\pm 20$	Intens	Frequency, $cm^{-1}$ , $\pm 20$	Intens
2935	s	1122	s
2810	m	902	vs
1460	s	776	w
1231	m	690 b	s
1202	vs		

<sup>a</sup> b, broad; vs, very strong; s, strong; m, medium; w, weak.

removal of these materials by vaporization *in vacuo*, there remains a nonvolatile yellow solid which is soluble in carbon tetrachloride, cyclopentane, and benzene. Each of these solutions is red in color. Purification was effected by filtration and subsequent removal of the solvent, cyclopentane, under vacuum. Repeated solution formation and solvent vaporization resulted in the complete vaporization of  $[(CH_3)_2AlN(CH_3)_2]_2$  (vapor tension  $< 1$  torr at  $20^\circ$ ), small amounts of which are physically trapped in the yellow solid.

Hydrolysis of the yellow solid (435.0 mg) was effected in 48 hr at  $80^\circ$  with 50% aqueous HCl in a sealed glass ampoule. The ampoule was opened to a vacuum system and the generated  $H_2$  and  $CH_4$  were collected and measured. The hydrolysis residue was analyzed for boron, aluminum, and nitrogen; the results are presented in Table III. The empirical formula of the yellow solid, based on the analytical data, is  $Al_{3.9}B_{1.0}[N(CH_3)_2]_{3.1}(CH_3)_{5.8}$ . The assumption that N is present as  $N(CH_3)_2$  results in 99.6% mass balance. The acid hydrolysis of  $Al_4B[N(CH_3)_2]_3(CN_3)_6$  may be described by



The molecular weight was determined isopiesticly by allowing 241.9 mmoles of cyclopentane to equilibrate between 0.314 mmole of azobenzene and 116.7 mg of the yellow solid for 2 weeks at  $25^\circ$ . Calcd for  $Al_4B[N(CH_3)_2]_3(CH_3)_6$ : 340.8. Found: 342.

TABLE III  
HYDROLYSIS ANALYSIS DATA,  $Al_4B[N(CH_3)_2]_3(CH_3)_6$

	Wt %	
	Calcd	Found
Al	31.7	30.8
N	12.3	12.7
B	3.2	3.3
$CH_4$ (hydrolyzable)	26.4	25.6
$CH_4:H_2$	2.0	1.95
Equiv wt, mg/mmmole of $H_2$	115.3	114.2

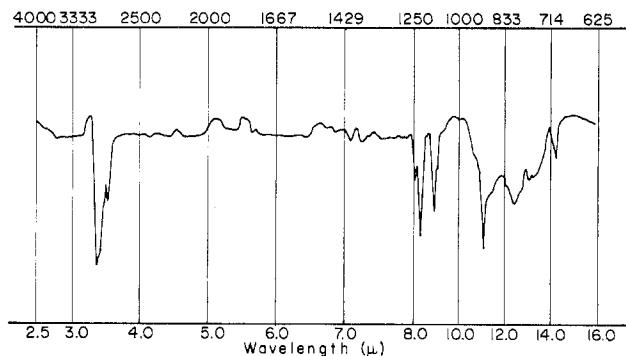


Figure 1.—Infrared spectrum of  $Al_4B[N(CH_3)_2]_3(CH_3)_6$ .

The infrared spectrum of  $Al_4B[N(CH_3)_2]_3(CH_3)_6$  appears in Figure 1 and is summarized in Table IV. The lack of infrared absorption bands in the range  $2630$  to  $1430\text{ cm}^{-1}$  precludes the possibility of  $AlH$ ,  $AlHA$ ,  $BH$ , and  $BHB$  bonds;<sup>6-8</sup> the referenced bond types occur in alkyl and aminoalkyl hydrides of boron and aluminum. The most likely sources of  $H_2$ , produced during hydrolysis, are  $B-H$ ,  $Al-H$ ,  $B-B$ ,  $Al-B$ , and  $Al-Al$  bonds. In view of the infrared data, two remaining possibilities are  $Al-B$  and  $Al-Al$  bonds.

TABLE IV  
INFRARED SPECTRAL DATA FOR  
HEXAMETHYLTRIS(DIMETHYLAMINO)MONOBORONTETRAALUMINUM

Frequency, $cm^{-1}$ , $\pm 20$	Intens	Frequency, $cm^{-1}$ , $\pm 20$	Intens
2922	s	1121	s
2798	m	1110	w
1405	vw	901	s
1380	vw	800	m
1235	m	757	w
1198	s	704	w

The  $B^{11}$  nmr spectrum of  $Al_4B[N(CH_3)_2]_3(CH_3)_6$  consists of one broad absorption at  $-44.6$  ppm from boron trifluoride diethyl etherate. For comparison, the  $B^{11}$  nmr spectra of several covalent boron compounds are listed in Table V. The  $B^{11}$  nmr absorption of  $Al_4B[N(CH_3)_2]_3(CH_3)_6$  is found at the same frequency as that of  $(CH_3)_2BN(CH_3)_2$ , one of the reaction products. It is not possible that this resonance is due to  $(CH_3)_2-BN(CH_3)_2$  physically trapped in the yellow solid, but rather it is most likely due to boron in  $(CH_3)_2BN(CH_3)_2$  which is in turn bonded to the aluminum species. A suggested structure for  $Al_4B[N(CH_3)_2]_3(CH_3)_6$  appears

(6) R. C. Lord and E. Nielsen, *J. Chem. Phys.*, **19**, 1 (1951).

(7) G. Schomburg and E. G. Hoffman, *Z. Elektrochem.*, **61**, 1110 (1957).

(8) J. K. Ruff, *Inorg. Chem.*, **2**, 515 (1963).

TABLE V  
SUMMARY OF B<sup>11</sup> NMR DATA FOR  
VARIOUS AMINO AND ALKYL BORON COMPOUNDS

Compd	Ppm (relative to F <sub>3</sub> BO(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> )	Ref
BR <sub>3</sub> <sup>a</sup>	-86.3	b
R <sub>2</sub> BNR <sub>2</sub>	-44.6	c
B <sub>2</sub> (NR <sub>2</sub> ) <sub>4</sub>	-35.1	d
Al <sub>4</sub> B(NR <sub>2</sub> ) <sub>3</sub> R <sub>6</sub>	-44.6	c

<sup>a</sup> R = CH<sub>3</sub>. <sup>b</sup> W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959). <sup>c</sup> This work. <sup>d</sup> S. C. Malhotra, *Inorg. Chem.*, **3**, 862 (1964).

in Figure 2. This structure incorporates three Al-Al bonds, which is consistent with the apparent oxidation state of aluminum, and involves the attachment of (CH<sub>3</sub>)<sub>2</sub>BN(CH<sub>3</sub>)<sub>2</sub>, through the nitrogen atom to aluminum atom no. 4 via a σ bond.

The H<sup>1</sup> nmr spectrum of Al<sub>4</sub>B[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(CH<sub>3</sub>)<sub>6</sub> (-40°) consists of four absorptions with intensity ratios of ca. 1:6:1:4 at -2.72, -2.40, -0.23, and +0.77 ppm, respectively, relative to TMS, Figure 3. The breadth of the peaks at -2.40 and +0.77 ppm is ca. 0.7 ppm near the base line. At 30 and 60° the H<sup>1</sup> nmr spectrum contains two additional side peaks both -2.5 cps from the -2.40 and +0.77 ppm absorptions. The relative areas of these peaks are ca. 2 (-2.36 ppm):1 (+0.73 ppm). The development of the side peaks in the H<sup>1</sup> nmr spectrum at -2.40 and +0.77 ppm may be the result of five-coordinate-lower coordination equilibrium for the aluminum atom labeled no. 1, Figure 1, with nitrogen atoms no. 5 and 6. The ratio of intensities for the side peaks is the expected 2:1, N(CH<sub>3</sub>)<sub>2</sub>:AlCH<sub>3</sub>. The implied nonequivalence of the N(CH<sub>3</sub>)<sub>2</sub> groups as well as the AlCH<sub>3</sub> groups, in the suggested structure, would be obscured by the breadth of the H<sup>1</sup> nmr signals, ca. 0.7 ppm. To explain the nonequivalence of the two B-CH<sub>3</sub> groups, methyl bridging involving both boron and aluminum is invoked. The presence of B-C bonds is suggested by the H<sup>1</sup> nmr absorption at -0.23 ppm (relative to TMS); the infrared spectrum, Figure 1, which includes an absorption centered at 1121 cm<sup>-1</sup> exhibiting a shoulder at 1110 cm<sup>-1</sup>, may be due to a boron-carbon stretching vibration<sup>2</sup> and the position of B<sup>11</sup> resonance which is identical with that of (CH<sub>3</sub>)<sub>2</sub>BN(CH<sub>3</sub>)<sub>2</sub>. Boron-carbon bonds are not usually susceptible to acid hydrolysis at 80°; however, the presence of metal ions, e.g., Cu<sup>2+</sup>, Ag<sup>+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, or Hg<sup>2+</sup>, is known to facilitate aryl-boron bond cleavage.<sup>9</sup> Likewise, it is suggested that acid hydrolysis of boron-alkyl bonds in Al<sub>4</sub>B[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(CH<sub>3</sub>)<sub>6</sub> is facilitated by the presence of aluminum ions in unknown oxidation states.

Electron spin resonance investigation of a benzene solution containing Al<sub>4</sub>B[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(CH<sub>3</sub>)<sub>6</sub>, 10<sup>-6</sup> mmole, over the temperature range -196 to 30°, indicates a diamagnetic species. A signal to noise ratio of 100 was found for 10<sup>-6</sup> mmole of diphenylpicrylhydrazyl.

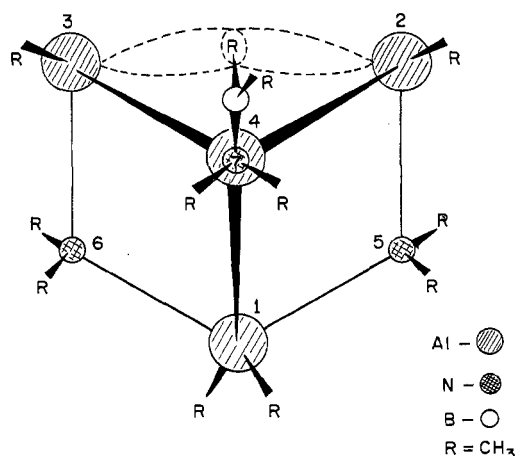


Figure 2.—Possible structure for Al<sub>4</sub>B[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(CH<sub>3</sub>)<sub>6</sub>.

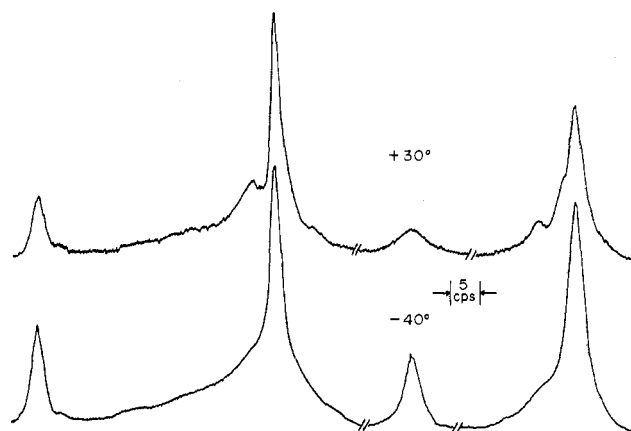


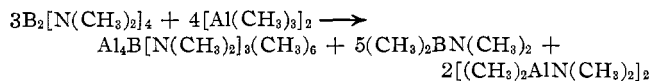
Figure 3.—H<sup>1</sup> nmr spectra of Al<sub>4</sub>B[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(CH<sub>3</sub>)<sub>6</sub>.

#### Physical Properties of Al<sub>4</sub>B[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(CH<sub>3</sub>)<sub>6</sub>

The pure material, Al<sub>4</sub>B[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(CH<sub>3</sub>)<sub>6</sub>, is a yellow solid which has a fiberlike appearance. On heating to ca. 70° it is converted to a viscous red liquid from which pale yellow crystals grow over a period of several months at room temperature. The red liquid is thermally stable to ca. 120°. Slow thermal decomposition takes place above this temperature to yield yellow material of decreased solubility in cyclopentane and a sublimable white solid. At 250°, a 235-mg sample afforded 2.34 mmoles of H<sub>2</sub>, 1.53 mmoles of CH<sub>4</sub>, 0.2 mmole of C<sub>2</sub>H<sub>4</sub>, plus two additional unidentified gaseous species found by gas chromatography, ca. 0.02 mmole total. A nonvolatile shiny black solid remained in the pyrolysis bulb.

#### Summary

The reaction of diborane(4) tetrakisdimethylamide with aluminum trimethyl may be described by



The new species hexamethyltris(dimethylamino)monoborontetraaluminum, Al<sub>4</sub>B[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(CH<sub>3</sub>)<sub>6</sub>, was characterized by elemental analyses, equivalent and molecular weight determinations, and infrared, H<sup>1</sup> nmr, and

$B^{11}$  nmr spectral correlations. Infrared studies indicate the absence of both boron and aluminum hydrides. Analytical and molecular weight data demonstrated the presence of only one boron atom per molecule of  $Al_4B[N(CH_3)_2]_3(CH_3)_6$ ; hence, the absence of boron-boron bonds is assured. Hydrolysis of  $Al_4B[N(CH_3)_2]_3(CH_3)_6$  affords 3 moles of  $H_2$  per mole of  $Al_4B[N(CH_3)_2]_3(CH_3)_6$ , indicating an apparent oxidation state of aluminum of +1.5, or the presence of three aluminum-aluminum covalent bonds. A structure has been suggested which incorporates three Al-Al bonds and contains the correct number of  $CH_3$  and  $(CH_3)_2N$  groups in environments which are consistent with the  $H^1$  nmr spectrum.

The chemistry of  $Al_4B[N(CH_3)_2]_3(CH_3)_6$  is being investigated. Reduction of other periodic group III alkyls as well as group IV alkyls with diborane(4) compounds is in progress, and the results of these investigations will be reported at a later date.

#### Experimental Section

All chemical reactions were carried out in a vacuum line equipped with mercury-float valves. Analyses for boron, aluminum, and nitrogen were by the standard mannitol titration, 8-hydroxyquinoline precipitation, and the Kjeldahl method, respectively. Methane and hydrogen were collected and measured by means of a calibrated volume Toepler pump assembly and characterized by combustion over  $CuO$  to afford  $CO_2$  and  $H_2O$ . The molecular weight of nonvolatile materials was determined by the isopiestic technique; the vapor density method was used for volatile species. Infrared spectra were recorded with a Perkin-Elmer 337 grating spectrometer. Volatile materials were contained in a 10-cm gas cell, whereas nonvolatile compounds were dissolved in benzene (0.1-cm cell path). The cells were equipped with sodium chloride optics.  $H^1$  and  $B^{11}$  nmr spectra were obtained with Varian Associates instruments A-60 (60 Mc) and HR-60 (19.3 Mc), respectively. The solvents employed were benzene and cyclopentane. Electron spin resonance studies were performed with a low-field, <500 gauss, esr spectrometer constructed by Professor R. Gerkin, The Ohio State University.

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## Two-Electron Oxidation of Vanadium(II) by Thallium(III)<sup>1</sup>

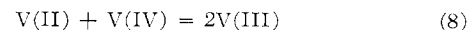
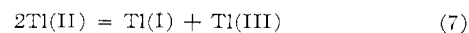
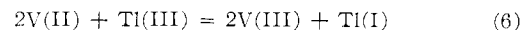
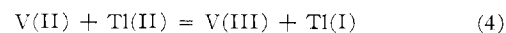
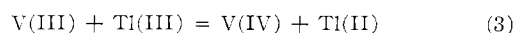
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In the reduction of two-equivalent oxidizing agents such as  $Tl(III)$ , an important question is whether the reduction occurs in a single two-electron step, in

successive one-electron steps, or by a termolecular mechanism.<sup>3</sup> The ions of  $V(II)$  and  $V(III)$  are particularly interesting in this connection since they can act either as one- or two-electron reducing agents in aqueous acid solutions. It has been shown that the oxidation of  $V(II)$  by molecular oxygen proceeds predominantly by a two-electron change to  $V(IV)$  and that  $H_2O_2$  produces significant amounts of  $V(IV)$ .<sup>4</sup> Conversely, although it is thermodynamically possible for the  $V(III)$ - $Tl(III)$  reaction to occur by a two-electron change, this is not the case.<sup>5</sup> The  $V(II)$ - $Tl(III)$  reaction has now been investigated and we find that the vanadium product is predominantly  $V(IV)$  and that the rate of reaction is significantly less than for  $V(III)$ . The results presented here indicate that the reaction proceeds predominantly by a two-electron change.

The most plausible set of reactions to be considered is



#### Experimental Section

The stock solutions of  $V(II)$ ,  $V(III)$ , and  $Tl(III)$  were prepared and analyzed as previously described.<sup>5</sup> The  $Tl(III)$  solutions were analyzed by adding excess standardized  $V(II)$  followed by excess standard  $Ce(IV)$  and back titration with standard  $Fe(II)$ . This method gave results about 2% lower than the previous method, which was based on the slow reaction with excess  $Fe(II)$ . This small discrepancy may be due to difficulties in handling  $V(II)$  or to a component in the  $Tl(III)$  which is reduced by  $Fe(II)$  but not by  $V(II)$ . The analysis based on  $V(II)$  is favored because of its dependence on the reaction of interest.

Induction experiments were performed by injecting a fine jet of  $V(II)$  or  $V(III)$  solution into rapidly stirred, slowly reacting solutions of  $Fe(II)$  and  $Tl(III)$  or of  $U(IV)$  and  $Tl(III)$ . Unreacted excess reducing agent was determined by quenching with  $Ce(IV)$  and back titrating with  $Fe(II)$ . The jet orifice size ranged from 0.1 to 0.3 mm, stirring was by a small glass propeller as close as possible to the orifice, and rotation was usually about 1000 rpm but ranged as high as 2100 rpm. Spectrophotometric measurements were made using a Cary Model 14 spectrophotometer equipped with thermostated, stirred, 10-cm cells. The wavelength was 760  $m\mu$ , where the extinction coefficients of  $V(II)$ ,  $V(III)$ ,  $V(IV)$ , and  $Tl(III)$  were determined to be 2.0, 0.7, 17.8, and 0  $M^{-1} cm^{-1}$  at 0° in 1  $M HClO_4$ . In the kinetic experiments, the final reactant was injected into the cell with a hypodermic syringe with a Teflon needle. All solutions were swept with argon and protected from air oxidation.

#### Results

**Induction Experiments.**—In agreement with the earlier report<sup>5</sup> it was found that  $V(III)$  is capable of inducing the normally slow reaction between  $Fe(II)$  and  $Tl(III)$ . However, under our experimental conditions

(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) Student summer employee.

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