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-mm 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)[1]

By F. B. Baker, W. D. Brewer,[2] and T. W. Newton

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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.[3] 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).[4] 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.[5] 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

$$\mathrm{V(II) + Tl(III) = V(IV) + Tl(I)} \tag{1}$$

$$\mathrm{V(II) + Tl(III) = V(III) + Tl(II)} \tag{2}$$

$$\mathrm{V(III) + Tl(III) = V(IV) + Tl(II)} \tag{3}$$

$$\mathrm{V(II) + Tl(II) = V(III) + Tl(I)} \tag{4}$$

$$\mathrm{V(III) + Tl(II) = V(IV) + Tl(I)} \tag{5}$$

$$\mathrm{2V(II) + Tl(III) = 2V(III) + Tl(I)} \tag{6}$$

$$\mathrm{2Tl(II) = Tl(I) + Tl(III)} \tag{7}$$

$$\mathrm{V(II) + V(IV) = 2V(III)} \tag{8}$$

Experimental Section

The stock solutions of V(II), V(III), and Tl(III) were prepared and analyzed as previously described.[5] 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 mμ, 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[5] 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

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] Student summer employee.

[3] (a) J. Halpern and L. E. Orgel, *Discussions Faraday Soc.*, **29**, 7 (1960); (b) W. C. E. Higginson, *et al.*, *ibid.*, **29**, 49 (1960).

[4] J. H. Swinehart, *Inorg. Chem.*, **4**, 1069 (1965).

[5] N. A. Daugherty, *J. Am. Chem. Soc.*, **87**, 5026 (1965).

the induction factors (moles of Fe(II) oxidized per mole of V(III) added) were about 50% greater than previously reported. In a typical experiment at 0° in 1 *M* $HClO_4$ the reactant concentrations were 0.013 *M* Tl(III), 0.007 *M* Fe(II), and 0.005 *M* V(III), the stirring rate was 1170 rpm, and the induction factor was found to be 0.93. In other experiments the initial [Fe(II)]/[V(III)] ratios were varied from 1.02 to 2.38, the stirring rates ranged from 400 to 2180 rpm, and the induction factors ranged from 0.89 to 0.99. Similar experiments were done in which V(III) was added to U(IV)–Tl(III) mixtures. In this system the observed induction factors (moles of U(IV) oxidized per mole of V(III) added) were much more dependent on experimental conditions than in the previous system. Observed factors ranged from about 0.2 to 0.5; the highest values occurring at the highest stirring rates and the highest initial [U(IV)]/[V(III)] ratios. As before, the temperature was 0°, the solutions were 1 *M* in $HClO_4$, and Tl(III) was in large excess. These experiments show that the reaction between V(III) and Tl(III) produces an intermediate, presumably Tl(II), which can react either with Fe(II) or with U(IV). The difference in observed induction factors in the two systems suggests that the intermediate reacts significantly faster with Fe(II) than with U(IV).

The same apparatus and conditions were then used to investigate the induction of the U(IV)–Tl(III) reaction by V(II). Experiments were done in 1.2 *M* $HClO_4$ at 0° with stirring rates as high as 2300 rpm and initial [U(IV)]/[V(II)] ratios as high as 2.3. Under these conditions the induction factor was close to zero, -0.01 ± 0.01 for eight experiments. This result suggests that Tl(II) reacts very much faster with V(II) than it does with V(III) or that no Tl(II) is produced in the oxidation of V(II) by Tl(III).

Kinetic Experiments.—Rates of the reaction between V(II) and Tl(III) were determined from changes in absorbance at 760 mμ where V(IV) is the principal absorbing species. Apparent second-order rate constants were determined from plots of the usual expression written in terms of A_0, A, and A_∞, the absorbance values at time $t = 0$, t, and ∞

$$\log\,[1 + (c_1/c_2 - 1)(A_\infty - A_0)/(A_\infty - A)] = \log\,[c_1/c_2] + (c_1 - c_2)k't/2.303 \quad (9)$$

where k' is the second-order rate constant and c_1 and c_2 are the initial concentrations of the excess and limiting reactants, respectively. The plots showed distinct curvature indicating an increase in the apparent second-order rate constant as the reaction proceeded. V(III) was found to catalyze the reaction; so it is reasonable to attribute the curvature to a small buildup of V(III). The results are summarized in Table I.

TABLE I

INITIAL APPARENT SECOND-ORDER RATE CONSTANTS

(0°, 1 *M* $HClO_4$)

Initial concentrations, $M \times 10^3$			Initial rate constant
V(II)	V(III)	Tl(III)	k', M^{-1} sec^{-1}
2.32	0.00	1.85	72
2.32	0.00	1.96	73
2.32	0.00	2.47	62
2.32	0.00	2.61	58
2.84	0.00	2.61	67, 63, 66, 63
4.21	0.00	2.61	68, 75
4.21	0.00	3.24	68
1.83	0.09	1.80	102
1.83	0.45	1.80	122
1.83	0.90	1.80	128

Stoichiometric Experiments.—Absorbance changes were determined when Tl(III) was injected into an excess of V(II) and in parallel determinations when Tl(III) was in excess. Under the latter conditions V(II) is oxidized completely to V(IV); the reaction between V(III) and Tl(III) is relatively rapid[5] and that to produce V(V) is quite slow[2b] under the experimental conditions. Observed absorbance changes were divided by those required for the net change given by reaction 1 to give the quantity called *R*. Stoichiometric ratios, V(IV) produced/Tl(III) added, were calculated from *R* using the following expression based on the Beer–Lambert law

$$\text{stoichiometric ratio} = \frac{R + 2(\epsilon_{V(II)} - \epsilon_{V(III)})/(\epsilon_{V(IV)} - \epsilon_{V(II)})}{1 + 2(\epsilon_{V(II)} - \epsilon_{V(III)})/(\epsilon_{V(IV)} - \epsilon_{V(II)})} \quad (10)$$

where the ϵ values are the indicated extinction coefficients. The results are summarized in Table II.

Discussion and Interpretation

The data in Table I show an insignificant [V(II)] dependence; so it has been concluded that reaction 6 is unimportant compared with reaction 1 or 2. Reaction 7 is probably unimportant with respect to reaction 4 or 5 since Tl(II) is a very reactive intermediate which occurs only at very low concentrations. Reaction 8 is quite slow and therefore unimportant with respect to the other reactions in the scheme; interpolation of published data[6] gives a rate constant of about 0.13 M^{-1} sec^{-1} at 0° in 1 *M* $HClO_4$. These three reactions were thus excluded from further consideration and calculations were made to determine the adequacy and relative importance of the remaining reactions (1–5). The usual steady-state approximation in Tl(II) leads to

$$-\mathrm{d}[\mathrm{V(II)}]/\mathrm{d}t = (k_1 + k_2)[\mathrm{V(II)}][\mathrm{Tl(III)}] + Q \quad (11)$$

$$-\mathrm{d}[\mathrm{V(III)}]/\mathrm{d}t = (k_3[\mathrm{V(III)}] - k_2[\mathrm{V(II)}])[\mathrm{Tl(III)}] - (1 - (k_5/k_4)[\mathrm{V(III)}]/[\mathrm{V(II)}])Q \quad (12)$$

$$\mathrm{d}[\mathrm{V(IV)}]/\mathrm{d}t = (k_1[\mathrm{V(II)}] + k_3[\mathrm{V(III)}])[\mathrm{Tl(III)}] + ((k_5/k_4)[\mathrm{V(III)}]/[\mathrm{V(II)}])Q \quad (13)$$

where

$$Q = (k_2[\mathrm{V(II)}] + k_3[\mathrm{V(III)}])[\mathrm{Tl(III)}]/(1 + (k_5/k_4)[\mathrm{V(III)}]/[\mathrm{V(II)}]) \quad (14)$$

Any two of the three differential equations are linearly independent and particular solutions were obtained numerically. A program based on the Runge–Kutta method[7] was written in Fortran IV which allowed the

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[6] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **68**, 228 (1964).

[7] (a) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p 469; (b) H. R. Siewert, P. N. Tenney, and T. Vermeulen, University of California Radiation Laboratory Report, UCRL-10575, 1962.

TABLE II

STOICHIOMETRIC RESULTS (0°, 1 M $HClO_4$)

	Init concn, $M \times 10^3$		ΔA[a]			Stoichiometric ratio	
	V(II)	Tl(III)	Obsd	Calcd[b]	R[c]	Obsd[d]	Calcd[e]
1	2.29	2.95	0.358, 0.361	0.359	0.99_7, 1.00_6		
2	2.29	3.65	0.357	0.359	0.99_4		
3	2.72	2.95	0.425, 0.428	0.427	0.99_5, 1.00_2		
4	3.51	2.95	0.454	0.463	0.98_1	0.98	0.979
5	4.09	2.95	0.454, 0.452	0.463	0.98_1, 0.97_6	0.98, 0.98	0.978
6	7.02	2.95	0.456	0.463	0.98_5	0.99	0.976
7	10.5	2.95	0.451	0.463	0.97_4	0.98	0.975
8	14.0	2.95	0.448	0.463	0.96_8	0.97	0.975
9	14.0	1.48	0.221, 0.224	0.231	0.95_7, 0.97_0	0.96, 0.97	0.975
10[g]	4.09	2.95	0.455, 0.456	0.463	0.98_3, 0.98_5	0.99, 0.99	0.996
11[g]	4.09	2.95	0.460	0.463	0.99_4	0.99	0.998
12	4.47	2.96	0.226[f]	0.464	0.48_7	0.56	
13[g]	2.98	2.96	0.236[f]	0.464	0.50_9	0.58	

[a] Absorbance change in 10 cm when Tl(III) injected into V(II) solution, corrected for increase in volume. [b] Calculated assuming [V(IV)] formed equals the initial concentration of limiting reactant, based on average of first three lines where V(II) was limiting. [c] $R = \Delta A(\text{obsd})/\Delta A(\text{calcd})$. [d] Calculated from eq 10 using $(\epsilon_{V(II)} - \epsilon_{V(III)})/(\epsilon_{V(IV)} - \epsilon_{V(II)}) = 0.088$. [e] Calculated assuming $k_1/(k_1 + 2k_2) = 0.95$ and $k_4/k_3 = 10^{-6}$. [f] Chloride present, solution was 0.02 M HCl and 0.98 M $HClO_4$. [g] Initial concentration of V(III) is zero, except in expt 10 (2.68×10^{-3} M), 11 (6.71×10^{-3} M), and 13 (4.50×10^{-3} M).

calculation of the concentrations of reactants and products as a function of time for various initial concentrations and values of k_1, k_2, k_3, and k_5/k_4. The calculations were taken to essentially complete reaction and the ratio $[V(IV)]_{formed}/[Tl(III)]_{added}$ was calculated for comparison with the experimental stoichiometric ratios. The rate constant $(k_1 + 2k_2)$ was taken as 70 M^{-1} sec^{-1} in accord with Table I, while k_3 was taken as 310 M^{-1} sec^{-1}, obtained by interpolating published data.[5] Two sets of initial concentrations were chosen to correspond to line 8 and line 11 in Table II. The results of these calculations are summarized in Table III.

TABLE III

$[V(IV)]_{formed}/[Tl(III)]_{added}$ FOR VARIOUS VALUES OF k_5/k_4 AND $k_1/(k_1 + 2k_2)$[a]

	$k_1/(k_1 + 2k_2)$				
k_5/k_4	0.0	0.4	0.8	0.95	1.00
0	0.529[b]	0.711	0.901	0.975	1.000
	0.960[c]	0.976	0.992	0.998	1.000
0.02	0.531	0.711	0.901	0.975	1.000
	1.015	1.027	1.041	1.047	1.049
0.1	0.540	0.715	0.902	0.975	1.000
	1.149	1.159	1.168	1.172	1.173
0.5	0.581	0.732	0.904	0.975	1.000
	1.405	1.407	1.409	1.410	1.410
2	0.671	0.776	0.911	0.976	1.000
	1.637	1.629	1.622	1.619	1.618
8	0.794	0.849	0.929	0.979	1.000
	1.788	1.769	1.752	1.746	1.744
10^3	0.981	0.984	0.991	0.997	1.000
	1.883	1.851	1.824	1.815	1.812

[a] For all calculations $k_1 + 2k_2 = 70$ M^{-1} sec^{-1} and $k_3 = 310$ M^{-1} sec^{-1}. [b] Upper figures apply to $[V(II)]_0 = 14 \times 10^{-3}$ M, $[V(III)]_0 = 0$, and $[Tl(III)] = 3.03 \times 10^{-3}$ M. [c] Lower figures apply to $[V(II)]_0 = 4.09 \times 10^{-3}$ M, $[V(III)]_0 = 6.71 \times 10^{-3}$ M, and $[Tl(III)] = 3.03 \times 10^{-3}$ M.

The results in the first column of the table show that a scheme consisting of reactions 2, 3, 4, and 5 is not consistent with both sets of data. However, if the two-electron oxidation, reaction 1, is considered to be important, much better agreement is obtained in the region of high values of $k_1/(k_1 + 2k_2)$ and low values of k_5/k_4. The rest of the data are also in agreement with the conclusion that the reaction is predominantly a two-electron oxidation of V(II) by Tl(III). The last column in Table II gives stoichiometric ratios calculated assuming $k_1/(k_1 + 2k_2) = 0.95$ and $k_5/k_4 = 10^{-6}$.

The effect of low concentrations of chloride is quite striking. Daugherty reported that chloride strongly inhibits the V(III)–Tl(III) reaction.[5] In agreement, we find an initial apparent second-order rate constant of 0.1 M^{-1} sec^{-1} in 0.02 M HCl–0.98 M $HClO_4$ solutions. In similar solutions V(II)–Tl(III) mixtures produce only about half as much V(IV) at about the same rate as in the absence of chloride. The stoichiometric ratios shown in lines 11 and 12 of Table II are consistent with the idea that although reaction 3 is strongly inhibited by chloride, reaction 2 is more strongly catalyzed than is reaction 1.

CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH AND DEVELOPMENT CENTER, SCHENECTADY, NEW YORK

The Synthesis of Copper Disulfide

BY RONALD A. MUNSON

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Over the years there have been a number of reported syntheses of copper polysulfides.[1] Gattow and Rosenberg,[2] who investigated these claims roentgenographically, conclude that all hitherto reported compounds of composition $CuS_{>1}$ were mixtures of CuS and sulfur and not distinct compounds of copper. In no case was synthesis attempted at both elevated

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(1) "Gmelins Handbuch der Anorganischen Chemie," Verlag Chemie, Weinheim/Bergstrasse, 1958, pp 483, 484.

(2) G. Gattow and O. Rosenberg, *Naturwissenschaften*, **51**, 213 (1964).