Table I. ^1H Chemical Shifts, Coupling Constants, and Colors for Trimethylsilyl Metal Compounds

Compound	Color	δ,[a] ppm	*J*, Hz	
			$^{199}Hg-^1H$	$^{29}Si-^1H$
$Hg(SiMe_3)_2$	Yellow	1.30[d]	40.8[d]	6.7[d]
$LiHg(SiMe_3)_3(DME)_3$[b]	Red	1.36[c,e]	25.8[c,e]	5.2[c,e]
$Li_2Hg(SiMe_3)_4(DME)_4$[b]	Yellow	1.56[c,e]	18.1[c,e]	4.8[c,e]
$Li_2Hg(SiMe_3)_4$	White			
$Na_2Hg(SiMe_3)_4$	Light violet			
$K_2Hg(SiMe_3)_4$	Blue-gray			
$LiSiMe_3$	Yellow	1.73[c]/1.33[d]		2.8[c]/3.5[d]

[a] All relative to cyclopentane and at higher field. [b] DME = dimethoxyethane. [c] In dimethoxyethane. [d] In cyclopentane. [e] At low temperature (~−40 to −55°).

Fermi contact is the dominant term in this coupling, the decrease is consistent with the hybridization being sp in $Hg(SiMe_3)_2$, sp^2 in $LiHg(SiMe_3)_3$, and sp^3 in $Li_2Hg(SiMe_3)_4$. It should be noted, however, that $LiHg(SiMe_3)_3(DME)_3$ contains more DME (dimethoxyethane) than would be required to satisfy all the acceptor sites on the lithium and may involve coordination of the ether to the mercury.

The proton nmr of $LiHg(SiMe_3)_3$ in DME solution gives a single broadened peak at 40°. The broadening is due to exchange of trimethylsilyl groups between different mercury sites and partial collapse of the ^{199}Hg satellites. At −40° the central peak and the satellites are sharp. From the consistency of the chemical shift for 40 to −40°, it appears that there is no significant dissociation of the anion in this range. If the $LiHg(SiMe_3)_3$ contains even very small amounts of $Hg(SiMe_3)_2$, a single sharp peak with no ^{199}Hg satellites results even at −60°. The $^{29}Si-^1H$ coupling is still observed indicating that exchange of methyl groups between silicon atoms is slow. The complete collapse of the ^{199}Hg satellites is due to the very rapid transfer of a trimethylsilyl group (and associated lithium) between $Hg(SiMe_3)_2$ and $LiHg(SiMe_3)_3$. A dissociation mechanism would appear to be unlikely because of the relatively slow self-exchange of $LiHg(SiMe_3)_3$. The exchange of trimethylsilyl groups on $Hg(SiMe_3)_2$ is slow as shown by the sharpness of the central peak and satellites at room temperature.

Seitz and Hall's proposal that a very small amount of $LiHgMe_3$ would cause broadening of the ^{199}Hg satellites of dimethylmercury by rapid exchange of methyl groups (and associated lithium) seems quite reasonable in light of the very fast exchange between $Hg(SiMe_3)_2$ and $LiHg(SiMe_3)_3$. The concentration of $LiHgMe_3$ would not have to be large although the rate of exchange would have to be considerably faster than the reaction

$$HgMe_2 + LiMe \rightleftharpoons LiHgMe_3$$

or the LiMe resonance would also be broadened.

DME solutions containing $Li_2Hg(SiMe_3)_4$ undergo rapid self-exchange, exchange with $LiHg(SiMe_3)_3$, or exchange with $LiSiMe_3$. This is due to the rapid equilibrium reaction in etheral solutions.

$$LiSiMe_3 + LiHg(SiMe_3)_3 \rightleftharpoons Li_2Hg(SiMe_3)_4$$

This equilibrium lies far to the left at room temperature, imparting a red color to the solutions. At low temperature the equilibrium lies to the right, the solutions are green, and all three species can be observed in the proton nmr spectrum. The form of the equilibrium constants is not known, since the association of the various species have not been determined, but ΔH is negative for the reaction as written. $Na_2Hg(SiMe_3)_4$ undergoes a similar equilibrium, but it appears to be much less dissociated under similar conditions.

The analyses of the solid complexes were performed as follows. A weighed sample of a complex was placed in an nmr tube. A measured amount of benzene and sufficient water to hydrolyze the sample was added by distillation from the vacuum line and the tube sealed off. The amount of $HSiMe_3$, $Hg(SiMe_3)_2$, and DME produced by hydrolysis was determined by careful integration against the benzene standard. The tube was broken open and hydroxide produced was titrated against standard HCl. The determination satisfactorily accounted for the total weight of the sample.

All the compounds are air and water sensitive except $Hg(SiMe_3)_2$ which is stable to water. The alkali metal compounds should be considered pyrophoric. All manipulations were performed under high vacuum or a nitrogen atmosphere dried by sodium–potassium alloy. $LiSiMe_3$ was prepared by the reaction

$$2Li + Hg(SiMe_3)_2 \longrightarrow 2LiSiMe_3 + Hg$$

in benzene or ether.[4,5] If made in benzene $LiSiMe_3$ can be sublimed under high vacuum and 60°. $LiSiMe_3$ is much less reactive to DME than *t*-butyllithium. $Hg(SiMe_3)_2$ was made by the method of Eaborn[6] and sublimed before use. Nmr spectra were obtained on a Varian Associates A-60A spectrometer. Chemical shifts were obtained on dilute solutions and calibrated *vs.* cyclopentane as internal standard.

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The Metal Ion Dependence of the Tin(II)–Vanadium(V) Reaction in Perchloric Acid

Sir:

In perchloric acid solutions both the stoichiometry and the rate of the Sn(II)–V(V) reaction differ markedly from those observed in hydrochloric acid solutions.[1]

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(1) D. J. Drye, W. C. E. Higginson, and P. Knowles, *J. Chem. Soc.*, 1137 (1962).

Determination of the stoichiometry in hydrochloric acid showed V(III) to be the predominant vanadium product of the reaction of V(V) with excess Sn(II). We have used titrimetric and spectrophotometric techniques to study the stoichiometry in perchloric acid. When the initial $[\mathrm{Sn(II)}]_0/[\mathrm{V(V)}]_0$ is as high as 35:1, less than 5% of the V(V) is reduced to V(III) and at ratios of 10:1 or less, no V(III) is detected among the products. Therefore, under the conditions employed in the present study, the stoichiometry of the reaction is given by

$$\mathrm{Sn(II)} + 2\mathrm{V(V)} \longrightarrow \mathrm{Sn(IV)} + 2\mathrm{V(IV)} \qquad (1)$$

Higginson found that in hydrochloric acid the rate of the reaction was too fast to measure. In perchloric acid solutions the reaction is not rapid and we have used conventional spectrophotometric techniques[2] to measure the rate over a wide range of initial reactant concentrations. A computer program which utilizes the differential form of the rate law[3] was used to calculate apparent rate constants from the absorbance *vs.* time data.

A rate law which is consistent with all of the data is shown in eq 2. Rate laws which contain only a second-

$$-\frac{d[\mathrm{V(V)}]}{dt} = k_2[\mathrm{Sn(II)}][\mathrm{V(V)}] + k_3[\mathrm{Sn(II)}][\mathrm{V(V)}]^2 \qquad (2)$$

or only a third-order term do not fit all of the data. Table I compares rate constants calculated for second-order, third-order, and a mixed second- plus third-order rate law.

Table I. Apparent Rate Constants at Different Initial Reactant Concentrations. Conditions: 20°, 1.0 *M* $HClO_4$, $\mu = 2.0$ ($LiClO_4$)

Initial [V(V)], $M \times 10^3$	Initial [Sn(II)], $M \times 10^3$	k_2, M^{-1} sec^{-1}	$k_3 \times 10^{-3}$, M^{-2} sec^{-1} *a*	*b*
5.59	1.08	13.5	3.19	3.09
5.59	0.868	14.6	3.17	3.07
5.59	0.434	16.0	3.13	3.05
2.80	0.434	7.40	3.09	2.90
2.80	0.217	7.94	3.06	2.88
2.80	0.108	8.02	3.05	2.88
1.32	0.514	3.14	3.47	2.96
1.32	0.257	3.74	3.44	3.03
0.992	0.770	2.06	3.58	2.89
0.661	0.514	1.64	4.11	2.98
0.272	0.634	0.96	6.04	3.18
0.106	1.28	0.60	11.9	2.87
0.079	1.03	0.60	14.6	3.42
0.079	0.513	0.60	12.6	3.08
0.079	0.513	0.46[c]		

[a] No correction made for second-order term. [b] Two-term rate law, with k_2 fixed at 0.46 M^{-1} sec^{-1}. [c] Two-term rate law, with k_3 fixed at 3000 M^{-2} sec^{-1}.

Runs in which the reaction products, Sn(IV) and V(V), were present initially at concentrations two to ten times higher than the initial concentration of the limiting reagent indicate that the products have no effect on the rate. Rate constants obtained for runs in which V(IV) appearance was followed were in excellent agreement with those obtained for runs in which V(V) disappearance was monitored.

Although rate laws give information regarding the composition of the most important activated complexes formed in the reaction, rate laws usually give very little information regarding the details of the mechanism. However, the mechanistic implications of the data in Table I and the form of eq 2 are of interest.

A plausible mechanism involving the formation of V(III) as a reactive intermediate is shown below.

$$\mathrm{Sn(II)} + \mathrm{V(V)} \underset{k_{-1}}{\overset{k}{\rightleftharpoons}} \mathrm{V(III)} + \mathrm{Sn(IV)}$$

$$\mathrm{V(III)} + \mathrm{V(V)} \xrightarrow{k_2} 2\mathrm{V(IV)}$$

Assuming steady-state behavior for V(III) leads to the rate law shown in eq 3.

$$-\frac{d[\mathrm{V(V)}]}{dt} = \frac{2k_1k_2[\mathrm{Sn(II)}][\mathrm{V(V)}]^2}{k_{-1}[\mathrm{Sn(IV)}] + k_2[\mathrm{V(V)}]} \qquad (3)$$

Equation 3 predicts that Sn(IV) should inhibit the rate and that at high V(V) concentrations second-order behavior should be observed. The products have no effect on the rate, and at high V(V) concentrations nearly clean third-order behavior is observed. Therefore, the mechanism shown cannot be correct. Similar arguments can be brought to bear against a one-electron mechanism in which Sn(III) is a reactive intermediate.

The rate law observed for the reaction indicates that two important activated complexes of different compositions are formed by parallel paths. The net activation processes[4] leading to the formation of the two activated complexes are shown in eq 4 and 5.

$$\mathrm{Sn^{II}} + \mathrm{V^{V}} \longrightarrow [\mathrm{V^{V}\text{-}Sn^{II}}]^{*\,5} \qquad (4)$$

$$\mathrm{Sn^{II}} + 2\mathrm{V^{V}} \longrightarrow [(\mathrm{V^{V}})_2\mathrm{Sn^{II}}]^{*} \qquad (5)$$

The activated complex $[(\mathrm{V^V})_2\mathrm{Sn^{II}}]^*$ could be formed by reaction of $\mathrm{V^V}$ "dimer" with Sn(II) or by reaction of V(V) with a $\mathrm{V^V\text{-}Sn^{II}}$ species formed in a rapid previous step. Unfortunately kinetic data alone do not allow one to determine which, if either, of these mechanisms for the formation of $[(\mathrm{V^V})_2\mathrm{Sn^{II}}]^*$ is correct.

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[3] We are indebted to Drs. T. W. Newton and R. H. Moore of the Los Alamos Scientific Laboratory for making this program available.

[4] T. W. Newton and S. W. Robideau, *J. Phys. Chem.*, **63**, 365 (1959).

[5] The formulas give compositions but imply nothing about the structures of the activated complexes.

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Acid-Catalyzed Hydrolysis and Isotope Exchange in $LiBH_3CN$[1]

Sir:

The following observations on the hydrolysis of $LiBH_3CN$ are difficult to reconcile with suggested mechanisms of hydrolysis of boron hydrides.[2,3] They are also important to the synthetic utility of the sub-

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[1] This work was supported by the National Science Foundation through GP-7915.

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