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-

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

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 $\mathrm{HClO_4}$, $\mu = 2.0$ ($\mathrm{LiClO_4}$)

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.

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

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.

Acknowledgment. This work was supported by National Science Foundation Grant GP-6846.

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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.

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(5) The formulas give compositions but imply nothing about the structures of the activated complexes.

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Received March 26, 1969

Acid-Catalyzed Hydrolysis and Isotope Exchange in $\mathrm{LiBH_3CN}$[1]

Sir:

The following observations on the hydrolysis of $\mathrm{LiBH_3CN}$ 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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stance, which depends on its resistance to acid hydrolysis.[4]

Hydrolysis rates were determined by following the loss of reducing power iodometrically.[5] The reaction consumes acid, and the pH was maintained with a Radiometer pH-Stat. Exchange rates were determined by following the disappearance of the proton nmr signal of BH_3CN^-, as well as the loss of reducing power. When the hydrolysis rate alone was being measured, the $LiBH_3CN$ concentration was about 10^{-2} *M*. When the nmr signal was also being monitored, the $LiBH_3CN$ concentration was about 2.5 *M*. All the $LiBH_3CN$ used in these experiments was the monodioxanate, prepared by digesting one part of "$LiBH_3CN$" (Alfa Inorganics, Inc.) with 50 parts of ether, filtering off the undissolved material, and precipitating the dioxanate with 10 parts of dioxane.

In all of the determinations pseudo-first-order kinetics were observed,[6] within the accuracy of the measurements, even though, in the exchange reactions, the substrate was changing by the incorporation of deuterium during the course of the observations. The pseudo-first-order rate constant, k_1^{hydr}, was shown to be proportional to (H^+) in 10 *M* H_2O in methanol, and the pseudo-first-order rate constant for exchange, k_1^{exch}, was shown to be proportional to (D^+) in 2.5 *M* electrolyte–2.5 *M* dioxane, in D_2O. (In the last case the electrolyte was initially $LiBH_3CN$ and changed to lithium borate during the course of the hydrolysis.) In water, when (H^+) was ~ 0.1 *M*, the increase in k_1^{hydr} was somewhat less than the increase in (H^+), and this is tentatively attributed to unproductive protonation on nitrogen. Second-order rate constants, k_2^{hydr}, given in Table I, or k_2^{exch}, are average values of $k_1^{hydr}/(H^+)$, $k_1^{hydr}/(D^+)$, or $k_1^{exch}/(D^+)$ except for the aqueous solutions in which case k_2^{hydr} is based on the more dilute acid values only. The acid concentration was determined electrometrically with a properly calibrated glass electrode.[7]

Table I. Second-Order Rate Constants for Hydrolysis

Medium	$10^2 k_2^{hydr}$, M^{-1} sec^{-1}
H_2O	1.7
10.0 *M* H_2O in MeOH	2.7
1.95 *M* H_2O in MeOH	21[a]
13.9 *M* H_2O in THF	2.5
D_2O	2.3[a]
2.5 *M* electrolyte– 2.5 *M* dioxane in D_2O	1.6

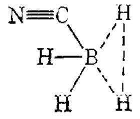
[a] Based on one acid concentration, only.

In 2.5 *M* $LiBH_3CN$–2.5 *M* dioxane, with D_2O as solvent, k_2^{exch} is 2.2×10^{-1} M^{-1} sec^{-1}, about 15 times the hydrolysis rate.

Qualitatively similar results for amine–boranes have been interpreted[4] in terms of rate-determining protonation on nitrogen and/or rate-determining B–N cleavage. An analogous mechanism, involving protonation of the cyano group, is structurally possible for BH_3CN^- also, but should permit this ion to hydrolyze *faster* than BH_4^- rather than 10^8 *slower*, as observed. Thus this mechanism cannot apply to BH_3CN^- hydrolysis.

Rate-determining proton transfer accompanied by evolution of molecular hydrogen has been suggested for hydrolysis of BH_4^-.[2] It is difficult to reconcile $k_H/k_D < 1$ with such a mechanism. Further, in both of the foregoing mechanisms exchange must be attributed to an unrelated side reaction, which is unattractive.

Our observations, and much earlier work on hydrolysis of BH_4^- and related substances, are consistent with a mechanism in which BH_3CN^- is reversibly protonated to give I as an *intermediate*.[8]



I

It has been previously suggested that a structure like I corresponds to a transition state.[2] Such a postulate fails to circumvent the difficulties of a one-step mechanism, but as an intermediate I reconciles all the available evidence. Loss of H_2 gives product. In the case that the incoming H^+ is replaced with D^+, the initial product would be mostly HD as observed in BH_4^- hydrolysis.[9] Reversion to starting material leads to exchange. Since, in the case of BH_3CN^-, reversion is 15 times faster than H_2 evolution, the hydrolysis mechanism can be described as A-1, and $k_H^{hydr}/k_D^{hydr} < 1$ is expected.[10] The experimental k_H^{hydr}/k_D^{hydr} is ~ 0.7. On the other hand, for BH_4^- hydrolysis formation of the intermediate is rate determining so $k_H^{hydr}/k_D^{hydr} > 1$ is expected and found.[11] Such a mechanism also explains the small isotope effect observed when BD_4^- is substituted for BH_4^-,[2,11] since, for these ions, the B–H bonds are not being broken in the rate-determining step.

In the transition state for hydrolysis an electron pair is being entirely removed from the molecule, while the transition state for exchange only involves protonation of that electron pair so, although both rates should be reduced by the electron-withdrawing CN group,[12] the hydrolysis is expected to be more sensitive than exchange. Under conditions where water must be the base to remove H^+ or D^+ from the intermediate, exchange is barely detectable for BH_4^-,[13] while it is 15 times as fast as hydrolysis for BH_3CN^-.

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Received March 22, 1969

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