steps nor the details of the side reaction which is responsible for the observed values of R being over 3.00 are elucidated by these kinetic data.

The observed mild dependence of the empirical second-order rate coefficient upon Γ is consistent with the complete rate law; at $p\text{H} \cong 5.6$, the empirical second-order rate coefficient is approximately equal to k_1 which corresponds to ΔZ^2_{act} of +2, while at $p\text{H} \cong 4$, the empirical second-order rate coefficient is approximately equal to k_2 which corresponds to ΔZ^2_{act} of −2. (The use of this latter value is subject to some uncertainty since the salt effect upon the buffer equilibrium must be taken into account; if one writes for the formation of the transition state the reaction $HSO_3^- + HAc + BrO_3^- = \{H_2SO_3{\cdot}BrO_3^-\}^{\ddagger} + Ac^-$, the value of ΔZ^2_{act} is zero.)

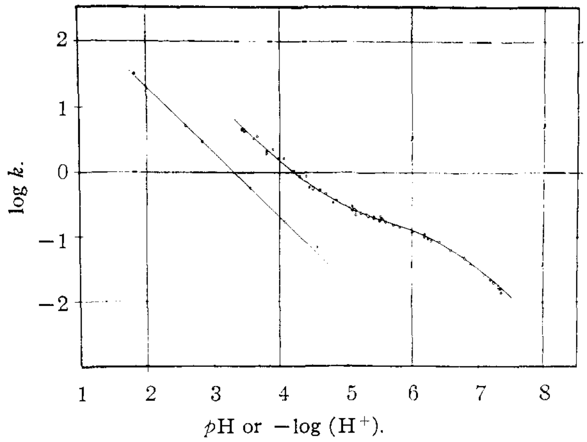

Fig. 1.—Log k (defined by equation 5) *versus* pH (measured) (for 25° data, upper line) or $-\log (\text{H}^+)_{\text{calculated}}$ (for 0° data, lower line). The solid lines are calculated using the parameters given in the text.

Taking cognizance of the uncertainty in the relationship between (H^+) and the measured pH value, a quantity h, defined $\log h = -p\text{H}$, will be used in the rate equation; equation 4 becomes

$$-\frac{\mathrm{d}(\text{S}^{\text{IV}})}{\mathrm{d}t} = (\text{BrO}_3^-)(\text{S}^{\text{IV}}) \left\{\frac{k'_1 + k'_2h}{h/K'_1 + 1 + K'_2/h}\right\} \quad (4')$$

where $k'_1 = k_1$, $k'_2 = k_2\,(\text{H}^+)/h$, $K'_1 = K_1h/(\text{H}^+)$ and $K'_2 = K_2h/(\text{H}^+)$. At the lowest acidity studied at 25°, $h/K_1 < 1$; therefore values of only the three parameters k'_1, k'_2 and K'_2 are obtained from the data at 25.0°. The values calculated by the method of averages are $k'_1 = 0.173$ l mole^{-1} sec.$^{-1}$, $k'_2 = 1.29 \times 10^4$ l^2 mole^{-2} sec.$^{-1}$ and $K'_2 = 4.45 \times 10^{-7}$. Figure 1 shows both the experimental points and the curve calculated using these parameters; the average difference between the experimental values of k (defined by equation 5) and the values calculated using the parameters of equation 4′ is 6.0%.

The values of k obtained at 0° are also presented in Fig. 1. Except for the point at the lowest acidity studied, the values of the second-order rate coefficient are consistent with the equation $k/(\text{H}^+) = 2.0_3 \times 10^3$ l. mole^{-1} sec.$^{-1}$; this is the value of k_2 at 0°. At the lowest hydrogen ion concentration studied, $(\text{H}^+) \cong 2.8 \times 10^{-5}$, the k_1 term is, presumably, contributing significantly to the rate, accounting for this point falling above the line. At the highest hydrogen ion concentration studied, $(\text{H}^+) \cong 1.5 \times 10^{-2}$, approximately one-third of sulfur(IV) is present as SO_2 plus H_2SO_3, and one would expect a change in the slope of the log k *versus* log (H^+) plot. Such is not observed. This could be due to the fortuitous equality $[(SO_2) + (H_2SO_3)]/(HSO_3^-) = (SO_2{\cdot}BrO_3{\cdot}H)^{\ddagger}/(SO_2{\cdot}BrO_3^-)^{\ddagger}$, or more likely to the fact that there are simply insufficient data in the region $(\text{H}^+) \gtrsim K_1$ to lead to any definite statement regarding the activated complex $\{SO_2{\cdot}BrO_3{\cdot}H + pH_2O\}^{\ddagger}$.

Acknowledgment.—The authors wish to thank Professor C. H. Sorum for his assistance in this work. They are indebted for the financial support already cited.[2]

MADISON, WISCONSIN

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

The Reaction of Sodium Hydride with Methyl Borate in Solvents. Convenient New Procedures for the Synthesis of Sodium Borohydride[1,2]

BY HERBERT C. BROWN, EDWARD J. MEAD[3] AND PAUL A. TIERNEY[4]

RECEIVED APRIL 22, 1957

The product obtained by the reaction of methyl borate with sodium hydride in the absence of a solvent has been established to be essentially sodium trimethoxyborohydride. This product is soluble in diglyme. The dissolution is followed by a rapid disproportionation into soluble sodium borohydride and insoluble sodium tetramethoxyborohydride. Sodium trimethoxyborohydride also undergoes rapid disproportionation in tetrahydrofuran. In this solvent sodium borohydride is insoluble and sodium tetramethoxyborohydride is highly soluble. However, in this solvent the sodium borohydride formed as a result of the disproportionation fails to precipitate completely as a result of its solubility in sodium tetramethoxyborohydride–tetrahydrofuran solutions. The passage of diborane through a solution of sodium tetramethoxyborohydride in tetrahydrofuran results in the quantitative conversion of the salt into sodium borohydride.

Sodium trimethoxyborohydride originally was prepared through the reaction of sodium hydride with methyl borate in excess methyl borate under reflux.[5] The sodium hydride available at that time

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(1) Addition Compounds of the Alkali Metal Hydrides. VIII.

(2) Based upon theses submitted by E. J. Mead and P. A. Tierney in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Research assistant on a grant from the National Science Foundation, 1953–1954.

(4) Standard Oil Research Foundation Fellow, 1955–1956. Parke, Davis and Company Fellow, 1956–1957.

(5) H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, THIS JOURNAL, **75**, 192 (1953).

was a reactive material which participated readily in the reaction. When an attempt was made to repeat this synthesis several years ago with the sodium hydride which was then available commercially, it was observed that the reaction was much more sluggish and required extended reaction periods for completion.[6]

In attempting to overcome this difficulty, it was observed that tetrahydrofuran greatly increased the rate of reaction of the methyl borate with the sodium hydride. Accordingly, an attempt was made to carry the synthesis out in this solvent as the reaction medium.[6]

In the course of these preparations, certain unexpected phenomena were encountered. Methyl borate readily reacted with sodium hydride, but the analysis of the tetrahydrofuran solution revealed that the sodium/hydrogen ratio decreased from the 1:1 value expected for the trimethoxyborohydride to much lower ratios. At the same time, a white precipitate was observed.[7]

It was considered that the reaction proceeded through the formation of sodium trimethoxyborohydride, followed by a disproportionation of this material to sodium tetramethoxyborohydride and materials richer in hydride ion than the original compound. A careful study of this phenomenon appeared desirable.

Results

The following procedure was developed to study the reaction of methyl borate with sodium hydride. Methyl borate in slight excess was added to a suspension of sodium hydride in a measured quantity of refluxing tetrahydrofuran under nitrogen. The reaction mixture was maintained under gentle reflux. At appropriate intervals of time, filtered aliquots of the solution were removed and analyzed for sodium (as sodium hydroxide), boron (as boric acid) and hydride (as hydrogen gas).

Had the reaction proceeded simply to produce the soluble sodium trimethoxyborohydride

$$\mathrm{NaH(insol.)} + \mathrm{B(OCH_3)_3(soln.)} \longrightarrow \mathrm{NaBH(OCH_3)_3(soln.)}$$

the boron content of the solution should have remained constant and the sodium and hydride content should have increased from their initial zero value to a value equivalent to the sodium hydride originally present. The broken horizontal lines in Fig. 1 indicate the values anticipated on this basis for a typical experiment.

These predicted values were not observed. Within a few minutes after the addition of the methyl borate, a white finely divided precipitate appeared. The boron content of the solution exhibited a decrease from the calculated value. Similarly, sodium and hydrogen did not increase to their predicted values, but reached a relatively constant value somewhat lower than the calculated values, the discrepancy being considerably larger for hydrogen than for sodium. Data for two typical experiments are summarized in Table I. Calculation revealed that the losses of sodium, boron and hydrogen were in the atomic ratios of approximately 1:1:4. These results are represented graphically in Fig. 1.

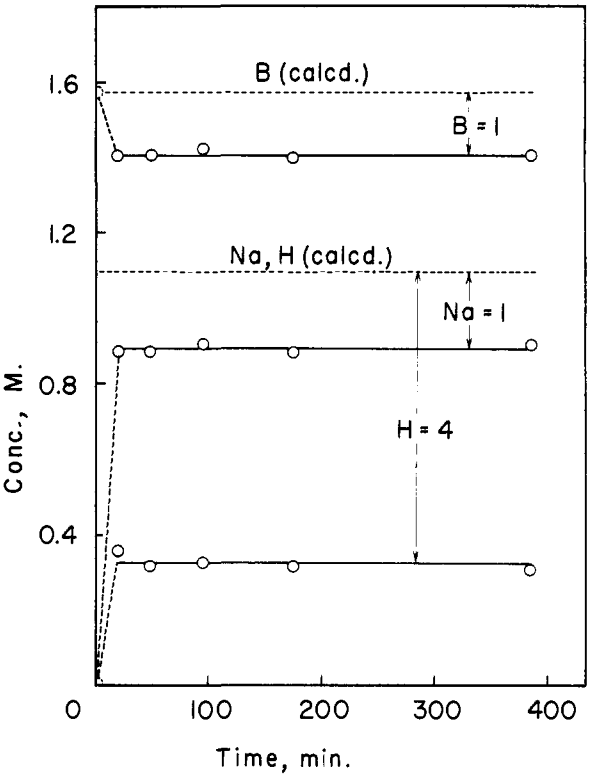

Fig. 1.—Reaction of sodium hydride with methyl borate in tetrahydrofuran.

The data clearly indicate that sodium borohydride is being formed, presumably through the disproportionation of the initially formed trimethoxyborohydride, and is precipitating from the solution. Sodium borohydride is insoluble in tetrahydrofuran. On this basis it is puzzling that the reaction fails to proceed to completion.

TABLE I

COMPOSITION OF THE SOLVENT PHASE IN THE REACTION OF SODIUM HYDRIDE WITH METHYL BORATE IN TETRAHYDROFURAN AT 65°

Methyl borate, mmoles	Sodium hydride, mmoles	Tetrahydrofuran, ml.	Time, min.	Boron, *M*	Sodium, *M*	Hydride, *M*
94.4	65.8	50.0	0	1.573	0.000	0.000
			20	1.404	.884	.358
			48	1.403	.885	.311
			95	1 421	901	.328
			175	1.400	.880	.310
			385	1.405	.903	.308
				(1.573)[a]	(1.096)[a]	(1.096)[a]
90.3	63.1	100	0	0.821	0.000	0.000
			20	.771	.494	.338
			53	.772	.487	.300
			110	.760	.485	.250
			179	.740	.467	.234
			390	.748	.474	.226
				(0.821)[a]	(0.574)[a]	(0.574)[a]

[a] Calculated for formation of a soluble product.

One explanation is that the reaction proceeds to completion, but that sodium borohydride possesses a limited solubility in tetrahydrofuran solutions of sodium tetramethoxyborohydride. Accordingly, a study was undertaken of this possibility.

Excess sodium borohydride was shaken with tetrahydrofuran containing known concentrations

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(6) H. C. Brown and E. J. Mead, THIS JOURNAL, **75**, 6263 (1953).

(7) H. C. Brown, E. J. Mead and C. J. Shoaf, *ibid.*, **78**, 3616 (1956).

of sodium tetramethoxyborohydride. Aliquots of the clear supernatant solution were removed and analyzed for total boron and total hydride ion. It was observed that such solutions exhibited an increase in boron and hydride content in the atomic ratio of 1:4. The increase was attributed to sodium borohydride and its solubility in these solutions estimated on this basis.

At constant temperature, an increase in the concentration of sodium tetramethoxyborohydride results in an increase in the concentration of dissolved sodium borohydride. With the concentration of sodium tetramethoxyborohydride maintained constant, the amount of sodium borohydride in solution increases with decreasing temperature. At 0° limiting ratios of 1.00 $NaBH_4$/1.00 $NaB(OCH_3)_4$ are observed. The data are summarized in Table II.

The data obtained at 65° agree closely with the composition of the solutions obtained in the reaction of sodium hydride with methyl borate in the same solvent.

TABLE II

SOLUBILITY OF SODIUM BOROHYDRIDE IN SODIUM TETRAMETHOXYBOROHYDRIDE–TETRAHYDROFURAN SOLUTIONS

$NaB(OCH_3)_4$, M	$NaBH_4$, M	Time	Temp., °C.	Molar ratio $NaBH_4$/$NaB(OCH_3)_4$
0.0756	0.0550	1 week	25	0.74[a]
.1550	.1550	1 week	0	1.00[a]
.1550	.0850	1 week	25	0.57[a]
.3422	.0872	1 week	25	0.25
.067	.064	24 hr.	0	1.04
.089	.088	36 hr.	0	0.99
.193	.189	48 hr.	0	.98
.0496	.0124	18 hr.	65	.25[b]
.445	.0598	18 hr.	65	.13[b]
.568	.0463	18 hr.	65	.08[b]
1.057	.0758	18 hr.	65	.07[b]

[a] Duplicate values were obtained with a time of 2 weeks.
[b] Similar values were obtained using methyl borate and sodium hydride.

The ready disproportionation in tetrahydrofuran raised a question as to whether the product obtained by the reaction of sodium hydride with methyl borate in the absence of solvents was sodium trimethoxyborohydride as we had believed,[5] or was an equivalent mixture of sodium borohydride and sodium tetramethoxyborohydride.

Sodium borohydride is readily soluble in diglyme.[8] However, sodium tetramethoxyborohydride is essentially insoluble in this solvent. Consequently, this solvent offered a possible test of the homogeneity of the product (sodium trimethoxyborohydride?) obtained from the reaction of methyl borate and sodium hydride in the absence of solvents.

Freshly prepared material of this kind dissolves in diglyme to form clear solutions. Immediate analysis of these solutions (approximately 0.1 *M*) yielded a ratio of sodium, boron and hydridic hydrogen of roughly 1:1:1. After a few minutes the solution became cloudy and a white precipitate formed. Analysis revealed that sodium and boron were disappearing from solution in an equivalent ratio, while the concentration of active hydrogen remained unchanged. Upon completion of this reaction, the clear solution yielded an analysis for sodium, boron and hydride of 1:1:4. The sodium and boron concentrations had decreased to one-fourth of their original value and the hydride content had remained essentially constant.

These observations are clearly in accord with a disproportionation of sodium trimethoxyborohydride originally dissolved in the solvent.

$$4NaBH(OCH_3)_3(soln.) \longrightarrow NaBH_4(soln.) + 3NaB(OCH_3)_4\downarrow$$

Typical results are summarized in Table III.

TABLE III

THE DISPROPORTIONATION OF SODIUM TRIMETHOXYBOROHYDRIDE IN DIGLYME AT 25°

Time, min.	Sodium, M	Boron, M	Hydride, M	Atomic ratios B/Na	H/Na
2	0.082	0.079	0.071	0.96	0.87
10	.184	.217	.276	1.18	1.50
60	.162	.164	.276	1.01	1.70
2	.090	.092	.104	1.02	1.15
10	.076	.075	.126	0.99	1.65
55	.058	.055	.102	0.95	1.76
1440	.0232	.0240	.094	1.03	4.05

It was shown previously that sodium tetramethoxyborohydride reacts with diborane in the absence of a solvent to produce sodium borohydride and methyl borate.[9] The high solubility of sodium tetramethoxyborohydride in tetrahydrofuran suggested that this reaction would be advantageously carried out in this solvent. Accordingly a slight excess of diborane was passed into a solution of sodium tetramethoxyborohydride in tetrahydrofuran and sodium borohydride was obtained in quantitative yield as a white, finely divided solid.

$$3NaB(OCH_3)_4 + B_2H_6 \longrightarrow 3NaBH_4 + 4B(OCH_3)_3$$

On the other hand, when diborane was passed into a solution containing an excess of the tetramethoxy salt, no precipitate was obtained, even though the solution contained all of the active hydrogen introduced into the reaction vessel. In this case, in accordance with the previous discussion, the sodium borohydride formed is believed to be retained in solution by the excess sodium tetramethoxyborohydride.

Discussion

The results support the conclusion that in the absence of solvents sodium hydride and methyl borate react to form a product which is essentially sodium trimethoxyborohydride. This material undergoes rapid disproportionation in solvents such as tetrahydrofuran (THF) and diglyme (DG) to form sodium borohydride and sodium tetramethoxyborohydride

$$NaH + B(OCH_3)_3 \longrightarrow NaBH(OCH_3)_3$$

$$4NaBH(OCH_3)_3(soln.) \xrightarrow{DG} NaBH_4(soln.) + 3NaB(OCH_3)_4\downarrow$$

$$4NaBH(OCH_3)_3(soln.) \xrightarrow{THF} NaBH_4\downarrow + 3NaB(OCH_3)_4(soln.)$$

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[8] H. C. Brown, E. J. Mead and B. C. Subba Rao, THIS JOURNAL, **77**, 6209 (1955).

[9] H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *ibid.*, **75**, 199 (1953).

The failure of sodium borohydride to precipitate completely from the tetrahydrofuran reaction mixture can be interpreted in two ways. On the one hand, the incomplete precipitation can be attributed to a solubility of sodium borohydride in tetrahydrofuran solutions of sodium tetramethoxyborohydride. Alternatively, the result might be interpreted in terms of a series of mobile equilibria involving sodium borohydride, tetramethoxyborohydride and the various intermediate derivatives.

In terms of the latter interpretation the solution of sodium borohydride in tetrahydrofuran solution of sodium tetramethoxyborohydride would be attributed to a series of rapid reactions establishing an equilibrium distribution among the possible products.

$$NaBH_4 + NaB(OCH_3)_4 \rightleftarrows NaBH_3OCH_3 + NaBH(OCH_3)_3$$

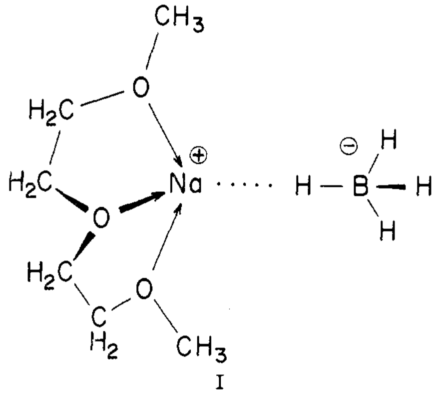
$$NaBH_3OCH_3 + NaB(OCH_3)_4 \rightleftarrows NaBH_2(OCH_3)_2 + NaBH(OCH_3)_3$$

On this basis the failure of sodium borohydride to precipitate completely in the reaction of sodium hydride with methyl borate in tetrahydrofuran would be attributed to the effect of increasing concentration of tetramethoxyborohydride in favoring the formation of the intermediate soluble derivatives.

The observation that at 0° solutions of sodium tetramethoxyborohydride of varying concentrations dissolve an equimolar amount of sodium borohydride (Table II) argues against this interpretation. This result is in much better accord with the formation of a definite 1:1 compound between the two salts which is relatively stable at 0° and is partially dissociated at higher temperatures.

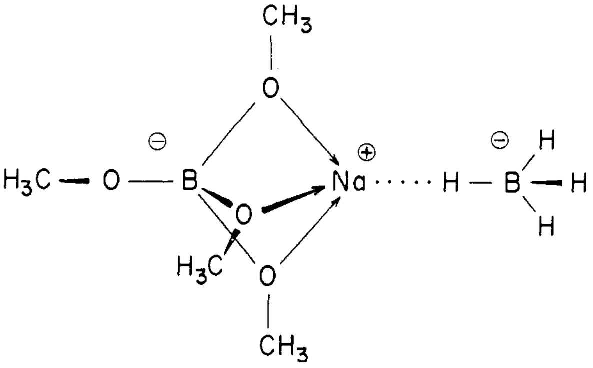
$$(THF)_xNa^+B(OCH_3)_4^- + Na^+BH_4^- \rightleftarrows (THF)_xNa^+B(OCH_3)_4^-\cdot Na^+BH_4^-$$

Sodium borohydride is easily soluble in diglyme and crystallizes from this solvent as a 1:1 solvate.[8] The unusual stability of this solvate is presumably related to the ability of diglyme to serve as a tridentate chelate in coördinating with the sodium ion (I).



I

The tetramethoxyborohydride ion likewise possesses three oxygen atoms in a suitable geometrical configuration to serve as a tridentate chelate. Conceivably, the tetramethoxyborohydride ion in tetrahydrofuran solution is able to play a similar role to that attributed to diglyme in chelating the sodium ion of sodium borohydride (II), resulting in a measurable solubility of this salt.



II

The diglyme solvate is stable at 25–40°, but is unstable at higher temperatures. A similar stability for the tetramethoxyborohydride would account for the increased solubility of sodium borohydride at lower temperatures, increasing to a maximum at 0° of one sodium borohydride molecule per molecule of sodium tetramethoxyborohydride in solution.

Experimental Part

Materials.—Sodium hydride was a commercial sample obtained from Metal Hydrides. Analysis indicated it to be 92% sodium hydride. The sodium borohydride was recrystallized from diglyme.[8] Analysis indicated a purity of 99.8%. Sodium tetramethoxyborohydride was prepared as described earlier.[10] Sodium trimethoxyborohydride was both synthesized from sodium hydride and methyl borate[5] and used in the form of a commercial sample from Metal Hydrides. Methyl borate was supplied by Metal Hydrides. The material was purified by fractionation through a helix-packed column rated at 52 theoretical plates. Diborane was prepared by the addition of sodium borohydride in diglyme to boron trifluoride–ethyl etherate in diglyme.

Diglyme was obtained from the Ansul Chemical Co. The solvent was twice distilled from lithium aluminum hydride under reduced pressure; b.p. 64° at 16 mm., $n^{20}D$ 1.4087. Tetrahydrofuran (du Pont) was purified by allowing the material to stand over sodium hydroxide pellets for two hours and then distilling twice from lithium aluminum hydride under dry nitrogen[11]: b.p. 65° at 742 mm.

Analyses.—The analyses were carried out by procedures similar to those described in earlier related studies. Samples were hydrolyzed. Sodium was determined as sodium hydroxide by titration with standard acid using methyl red as indicator; boron was then determined by adding mannitol and back-titrating with standard carbonate-free base using phenolphthalein as indicator. Hydride content was determined both as hydrogen gas upon hydrolysis, or by iodate titration.[12]

Reaction of Methyl Borate with Sodium Hydride in Tetrahydrofuran.—The apparatus and procedures utilized were similar to those described in previous studies.[7] Typical experimental data are summarized in Table I.

Solubility of Sodium Borohydride in Tetrahydrofuran Solutions of Sodium Tetramethoxyborohydride.—Sodium tetramethoxyborohydride was dissolved in tetrahydrofuran to form solutions of known molarity. These solutions were maintained at constant temperature and shaken with excess sodium borohydride for lengths of time sufficient to give equilibration. Aliquots of the clear supernatant solution were removed and analyzed for total boron and total hydride ion. The sodium borohydride present was estimated from these data. The solutions were quite viscous at 0° and it was possible to work only with relatively dilute solutions at this temperature. The data are summarized in Table II.

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[10] H. C. Brown and E. J. Mead, THIS JOURNAL, **78**, 3614 (1956).

[11] T. Higuchi, *Anal. Chem.*, **22**, 534 (1950); *ibid.*, **73**, 2676 (1951).

[12] D. A. Lyttle, E. H. Jensen and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

Disproportionation of Sodium Trimethoxyborohydride in Diglyme.—Both commercial sodium trimethoxyborohydride and freshly synthesized samples were utilized with no significant difference in the results. The apparatus was thoroughly dried. All operations were carried out under nitrogen and the utmost precautions were taken to protect the materials from any contact with oxygen, carbon dioxide or water. Only by careful attention to detail was it possible to realize material balances of 90–95% of the hydride originally introduced.

The samples of sodium trimethoxyborohydride were dissolved rapidly in the samples of diglyme. At appropriate intervals of time a filtered aliquot was removed, and analyzed for sodium, boron and hydride. Typical results are presented in Table III.

Reaction of Diborane with Sodium Tetramethoxyborohydride in Tetrahydrofuran.—In the reaction vessel was placed 2.73 g. (17.3 mmoles) of sodium tetramethoxyborohydride and 30 ml. of tetrahydrofuran. The vessel was flushed out with nitrogen. Over a period of one hour 12 mmoles of diborane was introduced. When slightly more than one-half the diborane had been introduced, the solution became cloudy. At the end of the reaction there was a finely divided white solid suspended in the tetrahydrofuran. Filtration of the solid offered difficulties. Accordingly, the tetrahydrofuran was distilled off. From the weight of the flask, the product weighed 0.605 g. This material was easily soluble in diglyme. An aliquot of the solution was analyzed for boron and hydride. The ratio, B/H of 3.98, confirmed the formation of $NaBH_4$.

In another experiment, 36.6 g. (220 mmoles) of sodium tetramethoxyborohydride was dissolved in 100 ml. of tetrahydrofuran. Into this concentrated solution, 2.2 *M*, was passed 5.8 mmoles of diborane. No precipitate was observed. Treatment of the clear solution with acid liberated the hydrogen quantitatively.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Prediction of Solubility Product Constants[1]

BY A. F. CLIFFORD

RECEIVED APRIL 25, 1957

It is shown that for a large class of species having largely covalent bonds, the degree to which the species separates in aqueous solution into its ions, $A_xB_{y(c)} \rightleftarrows xA^{+y}{}_{(aq)} + yB^{-x}{}_{(aq)}$, is as a first approximation a function of the difference in electronegativity, Δx, between A and B, when Δx is not large. $pK = a - b\Delta x$. This relationship is followed very closely by the solubility product constants of most of the insoluble sulfides, selenides, tellurides and hydroxides, as well as by insoluble halides, etc. On the other hand, typically ionic species, such as insoluble sulfates, fluorides, etc., or species for which hydration and electrostatic crystal energies are especially large and might be expected to predominate over covalency factors—*e.g.*, $Be(OH)_2$—do not obey this relationship. The relationship can be used to predict constants not yet determined or constants for unstable substances, which may appear as reaction intermediates. A thermodynamic explanation is offered, based on the relationship due to Hannay and Smyth between the amount of ionic character of the bond and the difference in electronegativity between the bonded atoms.

The regular trend of the solubilities of the heavy metal sulfides as one crosses the periodic table is one of the striking features of sulfide chemistry. When the trends are examined more closely, however, irregularities are observed which appear to follow closely the irregularities in the trend of electronegativities as can be seen in Table I.

TABLE I

	MnS	FeS	CoS	NiS	CuS	ZnS	CdS	PtS	HgS
pKsp	13.1	16.4	21.3	22.0	35.4	20.0	26.2	72	50
x^a	1.4	1.65	1.7	1.7	1.8	1.5	1.5	2.1	1.9

[a] Haïssinsky's electronegativity.[3]

Thus Cu^{++}, which is more electronegative than either of its neighbors, Ni^{++} and Zn^{++}, produces a sulfide which is more insoluble than either NiS or ZnS. This observation suggests that a relationship may exist between the solubility and the difference in electronegativity between the two elements involved.

The Insoluble Sulfides.—Examination of the pK_{sp}'s of the 1:1 sulfides[2] *versus* Δx (taken from Haïssinsky's[3] values) revealed a striking degree of correlation. Furthermore the available data for the selenides and tellurides likewise fell into line if the electronegativity of tellurium were taken as 2.3 rather than 2.1 as listed by Haïssinsky. The correlation is shown in Fig. 1.

It will be noted that the correlation is good with the exception of the compounds of Fe, Co and Ni. Several reasons for the lack of agreement for these compounds are possible. The first, that the K_{sp}'s are inaccurate, may be dismissed by noting that all four compounds disagree by the same amount. The second, that the difference is due to the crystal structure (all four compounds have NiAs structure, which is different from those of all the other compounds considered) cannot be dismissed so easily, although it may be noted that among the compounds in good agreement several different structures are represented. The third is that due to the difficulties of determining electronegativities in this part of the periodic table, the values for Fe^{+2}, Co^{+2} and Ni^{+2} are off by a constant amount. That this is probably so is strongly indicated by the fact that FeS and FeSe are off by the same amount. Revision of the electronegativities of these three elements downward by 0.2 unit brings them into harmony with the others. Likewise, if their neighboring element Cu has its electronegativity revised downward by 0.1 both CuS and CuSe fall into line. The revised electronegativities are thus: Fe^{+2} 1.45, Co^{+2} 1.5, Ni^{+2} 1.5, Cu^{+2} 1.7. Further justification for this will be offered below. A least squares analysis of these data yields the relationship

$$pK_{sp} = 102.5 - 80.6\Delta x \qquad (1)$$

Correlation of the pK_{sp} *vs.* Δx relationship for Ag_2S, Cu_2S, Tl_2S and Tl_2Te (Tl_2Se was omitted as

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[1] Presented before the Division of Analytical Chemistry, 131st National A.C.S. meeting, Miami, Florida, April 10, 1957.

[2] Taken for the most part from W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, New York, N. Y., 1952.

[3] M. Haïssinsky, *J. Phys.*, **7**, 7 (1946).