[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.]

Absolute Isotopic Abundance Ratio and the Atomic Weight of Silver[1a]

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An absolute value for the isotopic abundance ratio of natural silver is obtained by the use of isotopic standards prepared from nearly pure separated silver isotopes. Mass spectrometric data result in a value for the ratio, $Ag^{107}/Ag^{109} = 1.0754_7 \pm 0.0013$. Within the stated limits, no variation in natural abundance is found among six samples of native silver and commercial silver nitrate. A seventh native silver sample, obtained from Cobalt, Ontario, shows a statistically significant deviation. The calculated physical and chemical atomic weights of silver are 107.9028 ± 0.0013 ($O^{16} = 16$) and 107.8731 ± 0.0020 ($O = 16$), respectively. On the recently proposed unified physical and chemical atomic weight scale ($C^{12} = 12$), the atomic weight is 107.8685 ± 0.0013. The indicated uncertainties are over-all limits of error based on 95% confidence limits for the mean and on allowances for effects of known sources of possible systematic error.

Introduction

The present generally accepted value for the isotopic abundance ratio of silver ($Ag^{107}/Ag^{109} = 1.005 \pm 0.003$)[1b] is that originally reported by White and Cameron[2] and adopted in 1950 by Bainbridge and Nier[3] after careful consideration of measurements reported up to that time. Recently Hess, Marshall and Urey,[4] in a comparison of the isotopic abundance of silver from terrestrial and meteoritic sources, reported a Ag^{107}/Ag^{109} ratio 2.5% greater than the accepted value or nearly an order of magnitude greater than the stated uncertainty in the measurements of White and Cameron. However they were in agreement with an earlier determination of $Ag^{107}/Ag^{109} = 1.080 \pm 0.006$ by Paul.[5] Hess, *et al.*, were primarily interested in relative measurements. They were limited in size of sample and experienced much difficulty in obtaining steady emission of Ag^+ ions without the addition of boric acid to the material deposited on the sample filament. Consequently, they were inclined to ascribe the discrepancy between their results and those of White and Cameron to discrimination in the surface emission instrument.[6]

The present measurements were undertaken in an attempt to resolve the above discrepancies and more specifically to establish the absolute isotopic abundance ratio of silver used in an accurate electrochemical determination of the Faraday. Any possible discrimination or bias in the mass spectrometric measurements is evaluated by the use of calibration samples of known isotopic composition prepared by weighing and mixing portions of nearly pure isotopes of silver. In addition, a number of native silver samples collected from widely scattered localities were examined to determine whether any detectable variation occurred in natural silver.

While the present work was in progress, Crouch, *et al.*,[7] reported a surface ionization study of silver, resulting in the ratio $Ag^{107}/Ag^{109} = 1.0849 \pm 0.0007$, in support of the results of Hess, *et al.*, and of Paul. Crouch, *et al.*, concluded that in their measurements the effect of mass discrimination was negligible in the initial vaporization of the sample. This was based on discriminatory effects observed when 90% of the sample was vaporized. Unfortunately, such an observation is not conclusive evidence for the absence of instrumental bias.

Experimental

Instrumentation.—Details of the mass spectrometer used to compare the isotope abundance ratios of the natural silver samples with the known mixtures of the separated isotopes will be published elsewhere. Briefly, however, it is a 12-inch radius-of-curvature, 60° deflection, single focusing instrument. The triple-filament source[8] used all rhenium ribbons, 1 × 30 mils. The usual techniques for preparing sample filaments for surface emission were followed. Silver was deposited on the sample filaments as silver nitrate from solutions containing about 15 mg./ml. of solution. The deposited material was dried cautiously by passing a suitable electric current through the filament. The filament was then enclosed in a hydrogen atmosphere and the current was increased slowly until the silver nitrate melted. The filament was maintained at that temperature until conversion to silver was complete (usually one or two minutes). A sample size of the order of 100 μg. was sufficient to give hours of useful Ag^+ ion emission. No extraneous material was ever required to produce a steady emission.

Ion currents were measured by means of a vibrating reed electrometer. Filament temperatures were adjusted to give a nominal current output of about 1×10^{-11} amp. The usual tests were applied to establish the degree of linearity of the detecting and recording system and the accuracy of attenuation factors. Spectra were obtained by varying the magnetic field by means of a reversible electric motor drive on the control helipot. All samples were run in random order over a 6-months period.

Preparation of Calibration Samples.—Separated silver isotopes, in the form of metal powder, were obtained[9] from the Oak Ridge National Laboratory of the Union Carbide Nuclear Company (UCNC). Details of preparation accompanying the samples[10] indicated a high degree of homogeneity and chemical purity, although the latter was based only on spectrographic analysis. A subsequent analysis with higher sensitivity by M. M. Darr of the Spectrochemistry Section at NBS indicated total impurities detectable by this means at less than 0.01%. In the absence of other undetected impurities this amount has a

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(1) (a) This work was supported in part by the U. S. Atomic Energy Commission. (b) Uncertainties reported for the results of other workers are stated (and qualified) exactly as given in the literature references cited.

(2) J. R. White and A. E. Cameron, *Phys. Rev.*, **74**, 991 (1948).

(3) K. T. Bainbridge and A. O. Nier, "Relative Isotopic Abundance of the Elements," Preliminary Report No. 9, National Research Council, Washington, D. C.

(4) D. C. Hess, R. R. Marshall and H. C. Urey, *Science*, **126**, 1291 (1957).

(5) W. Paul, *Z. Physik*, **124**, 244 (1947–1948).

(6) Although White and Cameron took many precautions to reduce the probability of systematic errors in the measurement of Ag^+ ions from AgCl vapor by electron impact, there was no unequivocal means of establishing the degree of discrimination in the two very similar instruments used in their work.

(7) E. A. C. Crouch, E. R. Preece, I. G. Swainbank and A. H. Turnbull, *Nature*, **184**, No. 4683 (Suppl.), 358 (1959).

(8) M. G. Inghram and W. A. Chupka, *Rev. Sci. Instr.*, **24**, 518 (1953).

(9) The isotopes were obtained through the courtesy of W. J. Hamer, Chief, Electrochemistry Section, NBS.

(10) Private communication from Dr. P. S. Baker.

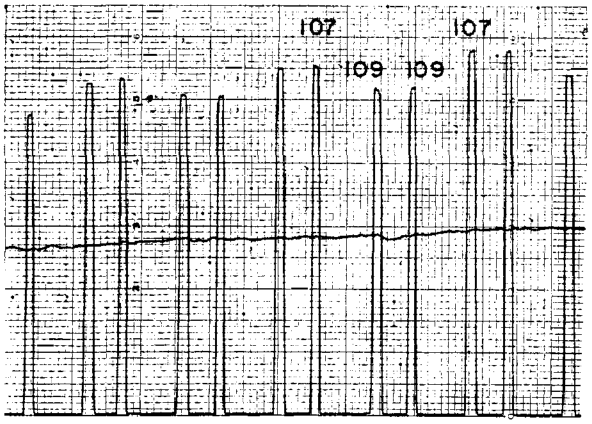

Fig. 1.—A portion of a mass spectrometer record showing the repetitious sweep of the Ag-107 and Ag-109 peaks for a commercial silver nitrate. The slowly varying trace indicates a known fraction of the sum of the isotopic ion currents as measured by a grid collector. It is used only to monitor experimental conditions.

negligible effect on the present results. Accordingly, a preliminary set of calibration samples (S-1 to S-3) was prepared by mixing weighed portions of the isotopes without further chemical purification. These samples were dissolved at room temperature in dilute nitric acid, evaporated to dryness and redissolved in distilled water, using great care to prevent contamination or discrimination. The dissolved separated isotopes and the mixtures showed very faint, flocculent precipitates and small amounts of a dark insoluble material. These impurities were estimated to be distributed equally in the isotopic material and of negligible proportions in the weighed mixtures. Nevertheless, two additional calibration samples (S-4 and S-5) were prepared from purified "Ag-107" and "Ag-109" isotopes. In purifying these isotopes, approximately 2.5 g. of each isotope was dissolved in dilute nitric acid, and each solution was then evaporated to dryness and redissolved in 30 ml. of distilled water. These solutions, containing traces of insoluble material, were filtered through fine sintered-glass frits. The filtrates were clear and remained so when diluted to 50 ml. with distilled water. Two cathodes were prepared by fusing a small quantity of each isotope in cleaned Vycor capillary tubes. About 0.5 ml. of concentrated HNO_3 was added to each isotope solution and in separate runs about 80% of the silver was deposited electrolytically on the appropriate cathode using a current density of approximately 10 ma./cm.^{2} and a gold anode. The anode solution was 2% HNO_3 containing an excess of oxalic acid. Anode and cathode solutions were connected by three syphons and two intermediate vessels containing 2% HNO_3. During the electrolysis, small reference electrodes, identical with the cathodes, were introduced into the cathode solution to measure the potential at which silver was deposited on the cathode. Potential differences between cathode and reference electrode never exceeded 0.04 volt. The deposited silver was removed easily from the cathodes, leached in 10% HF solution with subsequent repeated leaching with distilled water. Each silver sample was fused in vacuum in a small quartz tube that had previously been leached with hot concentrated nitric acid, carefully rinsed with distilled water and dried. The resulting silver buttons were removed from the tubes and again leached in hydrofluoric acid, washed with distilled water and dried. Small pieces were cut from each button, some of which were used for spectroscopic analysis, for isotopic analysis and to make the calibration mixtures. The chemical and isotopic compositions of the purified isotopes obtained in this Laboratory are given in Table I. Our measurements of the isotopic compositions of the unpurified isotopes as received from UCNC were indistinguishable from the values given in Table I.

Other Silver Samples.—A commercial silver nitrate, lot No. 90138, was used without purification as a working standard. Seven samples of native silver from Arizona, Michigan, Montana, Canada, Honduras, Mexico and Norway were kindly provided by P. E. Desautels, National Museum, Washington, D. C. Small pieces of each elemental silver sample were cut from the mass and dissolved as described previously for the calibration samples.

Results and Discussion

A typical set of spectra obtained for a commercial silver nitrate is shown in Fig. 1. Measurements of nearly pure Ag^{107} indicate an abundance sensitivity at $m/e = 108$ better than 10^{-4}; *i.e.*, the contribution of Ag^{107} ions to the 108 mass position is less than 10^{-4} of the Ag^{107} abundance. It is further estimated that the contribution is at least one order of magnitude less at $m/e = 109$. This is supported by measurements of nearly pure U^{233} wherein the abundance sensitivity at $m/e = 235$ is better than 10^{-5}. In only a few instances were any corrections necessary for extraneous ions. Occasionally, small peaks were observed at $m/e = 106$, 108 and 110 and attributed to ZrO^+ ions. Generally the required correction at $m/e = 107$ for $Zr^{91}O^{16}$ was less than the reading error on the recorder strip chart.

Table I

Chemical and Isotopic Composition of Purified Materials Used in Calibration Samples

Material[a]	Chemical impurities (p.p.m.)	Isotopic composition (atom %)[b]
Ag-107P	Total <1	$Ag^{107} = 98.79_8 \pm 0.02$
	Cu, 0.05; Fe, 0.2;	
	Mg, 0.02; Sn, 0.1;	
	no others detected	$Ag^{109} = 1.20_2 \pm .02$
Ag-109P	Total <1	$Ag^{107} = 0.91_0 \pm .02$
	Cu, 0.05; Fe, 0.2;	
	Mg, 0.02; Sn, 0.5;	
	no others detected	$Ag^{109} = 99.09_0 \pm .02$

[a] Portion of original materials purified by electrodeposition. Original designations: "Ag-107," Series HO, Sample 936 (a) and "Ag-109," Series HO, Sample 937 (b). The isotopic composition, in atom per cent., was reported by UCNC (10) as: "$Ag^{107} = 98.81 \pm 0.02$, $Ag^{109} = 1.19 \pm 0.02$; and $Ag^{107} = 0.94 \pm 0.02$, $Ag^{109} = 99.06 \pm 0.02$," respectively. The indicated uncertainty was stated to be "an expression of the precision of this measurement only."
[b] Composition corrected for instrumental bias. See text and Table II.

Table II summarizes the calculated and observed Ag^{107}/Ag^{109} ratios for the three calibration mixtures (S-1, S-2, S-3) prepared from the separated isotopes as obtained from UCNC and for the two mixtures (S-4, S-5) prepared from the silver isotopes purified by electrodeposition. A comparison of ratios for all mixtures confirms the original assumption of chemical purity and homogeneity of the separated isotopes as adequate for these measurements and also indicates a consistent bias of approximately +0.5% for the observed Ag^{107}/Ag^{109} ratio compared with the calculated ratio. Although this instrumental bias may have several origins, it is of the order of magnitude expected for separation of the isotopes according to the square-root of the ratio of the nuclidic masses. Bias that is directly dependent on mass differences is independent of the ratio measured and, consequently, is the same for nearly pure, separated isotopes and for mixtures prepared from them. Thus the isotopic compositions summarized in Table I and used in the calculations of Table II,

TABLE II

CALCULATED AND OBSERVED ISOTOPIC RATIOS OF SILVER IN CALIBRATION MIXTURES

Mixture number	Isotopic materials	Isotopic ratio, Ag^{107}/Ag^{109} Calcd.[a]	Isotopic ratio, Ag^{107}/Ag^{109} Obsd.[b]	Bias (calcd./obsd.)
S-1	Original	1.07970 ± 0.0008	1.08628 ± 0.0014 (8)	0.99394
S-2	Original	1.06848 ± .0008	1.07462 ± .0014 (8)	.99429
S-3	Original	1.07663 ± .0008	1.08118 ± .0014 (8)	.99579
S-4	Purified	1.07040 ± .0008	1.07599 ± .0016 (6)	.99480
S-5	Purified	1.07810 ± .0008	1.08555 ± .0016 (6)	.99314
				Weighted average = 0.99444 ± 0.00062[b]

[a] Limit of error assuming a 2% limit of error of bias on the minor isotope in the analysis of the separated isotopes. [b] 95% confidence limits; numbers in parentheses indicate number of analyses (18 determinations per analysis).

column 3, are corrected for the observed degree of bias.

Table III summarizes the Ag^{107}/Ag^{109} ratio for a number of silver samples. Within the 95% confidence limit, the abundance ratios of six of the native silver samples are indistinguishable from commercial silver nitrate, and it is estimated that any variation in natural abundance among these samples is less than 0.2% of the ratio.[11] This is in agreement with the observations reported by Hess, *et al.*, and by Crouch, *et al.* Thus, the observed isotopic abundance ratio for the commercial silver nitrate (1.08148 ± 0.00108) is taken as the value for the uncorrected abundance ratio of natural silver. However, this ratio must be corrected for the average instrumental bias determined from Table II. Thus the corrected ratio is $Ag^{107}/Ag^{109} = (1.08148)(0.99444) = 1.07547 \pm 0.0013$.[12]

TABLE III

ISOTOPIC ABUNDANCE RATIOS OF SILVER FROM VARIOUS SOURCES

Sample no.[a]	Description	Analyses[b]	Obsd. ratio,[c] Ag^{107}/Ag^{109}
...	Commercial silver nitrate, Lot 90138	24	1.08148 ± 0.00108
65154	Silver King Mine, Pinal Co., Arizona	4	1.0794 ± 0.0025
5791	Ontonagon, Lake Superior District, Michigan	4	1.0826 ± .0025
81784	Gagnon Mine, Butte, Montana	4	1.0804 ± .0025
112858	Montana El Mochito Mine, Honduras	4	1.0806 ± .0025
C-162	Chihuahua, Mexico	4	1.0815 ± .0025
62845	Kongsberg, Norway	4	1.0804 ± .0025
C-140	Cobalt, Ontario, Canada	8	1.0843 ± .0015

[a] National Museum Catalog Numbers. [b] 18 determinations per analysis. [c] 95% confidence limits based on pooled estimate of variance.

Although not yet published, accurate mass spectrometric doublet measurements of the masses of the stable silver isotopes have been obtained by Dr. Walter H. Johnson, Jr., in Professor Nier's laboratory at the University of Minnesota.[12a] Using the "peak matching" technique for doublet determination, Johnson[13] obtained the values $Ag^{107} = 106.93899 \pm 0.00010$ and $Ag^{109} = 108.93928 \pm 0.00010$ ($O^{16} = 16$). These are in good agreement with two recent tabulations of nuclidic masses of silver based on nuclear disintegration energies. Duckworth[14] reports $Ag^{107} = 106.93881 \pm 0.00035$ and $Ag^{109} = 108.93923 \pm 0.00035$ as calculated from Pd^{108} and Cd^{108}. Also, Johnson, Quisenberry and Nier[15] give the values $Ag^{107} = 106.93882 \pm 0.00030$ and $Ag^{109} = 108.93924 \pm 0.00030$. The latter values are based on Halsted's[16] combination of mass spectroscopic and nuclear reaction data. In all cases, $O^{16} = 16$.[12a]

TABLE IV

SUMMARY CALCULATION OF PHYSICAL AND CHEMICAL ATOMIC WEIGHTS OF SILVER

Corrected isotopic ratio	$Ag^{107}/Ag^{109} = 1.07547 \pm 0.0013$[b]
Corrected isotopic composition, atom %	$Ag^{107} = 51.818 \pm 0.052$[c] $Ag^{109} = 48.182 \pm 0.052$[c]
Nuclidic masses[a] ($O^{16} = 16$)	$Ag^{107} = 106.93899 \pm 0.00010$ $Ag^{109} = 108.93928 \pm 0.00010$
Uncertainty components:	
Ratio determination	±0.00059 (random error)[b]
Composition of separated isotopes	±0.00040 (LE of bias)
Nuclidic masses	±0.00030 (LE of bias)
Total	±0.00129
Physical atomic weight ($O^{16} = 16$)	107.9028 ± 0.0013[c]
Conversion factor (phys. to chem. scale) uncertainty	1.000275 ± 0.000007[d]
Chemical atomic weight (O = 16)	107.8731 ± 0.0020[c]
Conversion factor (phys. $O^{16} = 16$ to phys. $C^{12} = 12$ scale)	1.000317917[e]
Precision	17 parts in 10^9
Proposed unified atomic weight ($C^{12} = 12$)	107.8685 ± 0.0013[c]

[a] See ref. 13. [b] 95% confidence limits. [c] Over-all limit of error based on 95% confidence limits for the mean and allowances for effects of known sources of possible systematic error. [d] As suggested by A. O. Nier, private communication. [e] See ref. 17.

Combining the mass spectrometric data for the abundance ratio and for the nuclidic masses results in an atomic weight of silver on the physical scale

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(11) The abundance ratio for silver from Cobalt, Ontario, is significantly different. Additional samples from this region have been obtained and are now under study.

(12) Applying the correction for bias introduces a small additional uncertainty in the ratio.

(12a) NOTE ADDED IN PROOF.—Prof. J. Mattauch and co-workers have obtained recently (to be published in *Nuclear Physics*) a least squares adjusted value for the nuclidic masses of silver for which data quoted here were part of the input. The final results differ from the present values by a few parts in 10^7 and have negligible effect on the quoted atomic weight.

(13) By private communications from Dr. W. H. Johnson, Jr., and Prof. A. O. Nier. The uncertainty is considered to be the standard error of the reported value.

(14) H. E. Duckworth, "Progress in Nuclear Physics," Vol. VI, Pergamon Press, New York, N. Y., 1957, p. 155.

(15) W. H. Johnson, Jr., K. S. Quisenberry and A. O. Nier, "Handbook of Physics," McGraw-Hill Book Co., New York, N. Y., 1958, 9–55.

(16) R. E. Halsted, *Phys. Rev.*, **88**, 666 (1952).

($O^{16} = 16$) of 107.9028 ± 0.0013, where the indicated uncertainty is an over-all estimate of limit of error based on 95% confidence limits for the mean and including allowances for effects of known sources of possible systematic error. If, in conformity with the International Commission on Atomic Weights, the factor 1.000275 is used to convert to the chemical scale, we obtain 107.8731 ± 0.0020 for the chemical atomic weight (O = 16). Furthermore, using the factor 1.000317917 ± 17×10^{-9}[17] to convert from the physical scale to the recently proposed[18] unified physical and chemical scale ($C^{12} = 12$), we obtain an atomic weight of 107.8685 ± 0.0013. In this case, an entirely negligible increase in uncertainty results from the scale conversion. These data with the identified uncertainty components are summarized in Table IV. The chemical scale (O = 16) value differs significantly from the 1957 international value of 107.880.[19] However, the uncertainty in the present physical determination of this atomic weight is nearly an order of magnitude less than that previously reported.[20]

Summary and Conclusions.—A determination of the absolute isotopic abundance ratio of silver results in a new value for the chemical atomic weight of this element, which is one of the key elements in chemical determinations of atomic weights. Also of great importance are the atomic weights of chlorine and bromine through which the atomic weights of many elements are determined with respect to silver. Absolute isotopic abundance measurements of these halogens together with the present absolute abundance measurement of silver would be of inestimable value in establishing the chemical atomic weights of many isotopic elements.

Acknowledgments.—The authors are indebted to Ernest Garner for many of the careful mass spectrometric measurements included in this study, to W. J. Hamer for supplying the separated isotopes, to P. E. Desautels for supplying the native silver samples, to Mrs. M. M. Darr for spectroscopic analyses of the separated isotopes, to J. M. Cameron for statistical analysis and to W. H. Johnson, Jr., and A. O. Nier for communicating data on the nuclidic masses of silver. We also gratefully acknowledge helpful and encouraging discussions with F. L. Mohler and many other colleagues.

[17] "Atomic Masses of Nuclides, $A \leq 70$," F. Everling, L. A. König, J. H. E. Mattauch and A. H. Wapstra, submitted for publication (by private communication with Professor Mattauch).

[18] J. Mattauch, THIS JOURNAL, **80**, 4125 (1958); *Z. Naturforsch.*, **13a**, 572 (1958); T. P. Kohman, J. H. E. Mattauch and A. H. Wapstra, *Science*, **127**, 1431 (1958); *Physics Today*, **12**, 30 (1959); E. Wichers, *ibid.*, **12**, 28 (1959).

[19] E. Wichers, Report on the 1957 meeting of the International Committee on Atomic Weights, THIS JOURNAL, **80**, 4121 (1958).

[20] A. O. Nier, *Science*, **121**, 737 (1955).

[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, ST. LOUIS RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY, ST. LOUIS, MISSOURI]

Hexaalkyl Phosphorous Triamide Borines

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Methods of preparation and properties of hexaalkyl phosphorous triamide borines are discussed. It was found that $P[N(CH_3)_2]_3$ is a stronger base than $N(CH_3)_3$, the order of coördination thus being P > N with respect to BH_3 as the reference acid. Accordingly, the reactivity of the hexaalkyl phosphorous triamide borines is lower than that of trimethylamine borine. The structure of the new compounds was established as being $(R_2N)_3PBH_3$.

G. Kodama[1] recently described the reaction of phosphorous trifluoride borine and ammonia. This reaction proceeds by direct substitution of the fluorine atoms with NH_2 groups without rupture of the phosphorus–boron bond, according to the equation

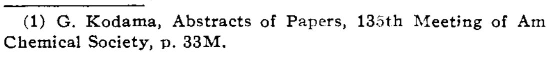
$$F_3PBH_3 + 6NH_3 \longrightarrow (NH_2)_3PBH_3 + 3NH_4F$$

Prior to this report we had prepared the hexamethyl phosphorous triamide borine, $[(CH_3)_2N]_3PBH_3$, by methods entirely different from that of Kodama. Our methods may be illustrated by the equations

$$(CH_3)_3NBH_3 + P[N(CH_3)_2]_3 \longrightarrow [(CH_3)_2N]_3PBH_3 + N(CH_3)_3 \quad \text{I}$$

$$NaBH_4 + P[N(CH_3)_2]_3 + CO_2 \longrightarrow HCOONa + [(CH_3)_2N]_3PBH_3 \quad \text{II}$$

$$NaBH_4 + P[N(CH_3)_2]_3 + CH_3COOH \longrightarrow CH_3COONa + [(CH_3)_2N]_3PBH_3 + H_2 \quad \text{III}$$



$$NaBH_4 + P[N(CH_3)_2]_3 + CH_3\underset{\underset{\displaystyle O}{\|}}{C}CH_3 + H_2O \longrightarrow [(CH_3)_2N]_3PBH_3 + NaOH + C_3H_7OH \quad \text{IV}$$

$$NaBH_4 + P[N(CH_3)_2]_3 + HCl \longrightarrow [(CH_3)_2N]_3PBH_3 + NaCl + H_2 \quad \text{V}$$

$$B_2H_6 + 2P[N(CH_3)_2]_3 \longrightarrow 2[(CH_3)_2N]_3PBH_3 \quad \text{VI}$$

High yields were obtained in all cases except III, where the yield was relatively poor due to competing reactions. Sodium borohydride alone does not react with $P[N(CH_3)_2]_3$. Apparently a conversion of $NaBH_4$ into a more reactive intermediate is required to enable $P[N(CH_3)_2]_3$ to react. The course of reaction II appears to be

$$NaBH_4 + CO_2 \longrightarrow Na[BH_3OOCH] \quad \text{VII}$$

$$Na[BH_3OOCH] + P[N(CH_3)_2]_3 \longrightarrow NaOOCH + [(CH_3)_2N]_3PBH_3 \quad \text{VIII}$$

Similarly, reaction III possibly proceeds through an intermediate of the same type

$$NaBH_4 + HOOCCH_3 \longrightarrow Na[BH_3OOCCH_3] + H_2 \quad \text{IX}$$

$$Na[BH_3OOCH_3] + P[N(CH_3)_2]_3 \longrightarrow NaOOCCH_3 + [(CH_3)_2N]_3PBH_3 \quad \text{X}$$

In these reactions possible intermediates are sodium formato borohydride (VII) and sodium acetato borohydride (IX).

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[1] G. Kodama, Abstracts of Papers, 135th Meeting of American Chemical Society, p. 33M.