distinct possibility. Our data give no basis for choice. Paper II[13] describes experiments involving the blocking of various preequilibria involving protons by substituting ethyl groups to form $(EtO)_3P$:, $(EtO)_2P({=}O)H$, and $(EtO)_2P({=}O)Et$, and studying their oxidation by $HCrO_4^-$.

(13) G. P. Haight, Jr., F. Smentowski, M. Rose, and C. Heller, *J. Am. Chem. Soc.*, in press.

Dissociation Energies of Bismuth–Antimony Molecules[1a]

Fred J. Kohl[1b] and K. Douglas Carlson

Contribution from the Department of Chemistry, Case Western Reserve University, University Circle, Cleveland, Ohio 44106. *Received March 20, 1968*

Abstract: This article describes measurements of the dissociation energies of heteronuclear diatomic and tetratomic molecules in the equilibrium vapor of liquid solutions of bismuth and antimony. The experiments are based on the molecular beam sampling method using mass spectrometric detection. The following energies have been determined for dissociation of molecules to atoms at 0°K: $BiSb_3$ (8.27 ± 0.11 eV), Bi_2Sb_2 (7.52 ± 0.08 eV), Bi_3Sb (6.82 ± 0.06 eV), and BiSb (2.58 ± 0.04 eV). These values are shown to have quantitatively systematic trends in relation to the known homonuclear molecules Sb_4, Bi_4, Sb_2, and Bi_2 and others in the same family group. Some discussion of single bond energies of the group Va elements is given.

Recent experiments have shown that a large number of stable heteronuclear diatomic and tetratomic molecules are formed by intercombinations of atoms of the nitrogen family elements.[2a] These molecules are expected to be analogs of the well-known homonuclear species of these elements and, consequently, should have systematically related properties as members of the same group.[2b] This article describes measurements of dissociation energies which establish this systematic relationship for the homonuclear and heteronuclear molecules of Bi and Sb.

Experimental Methods

The experiments reported here involve the molecular beam sampling by mass spectrometric detection of vapors in equilibrium with liquid solutions of Bi–Sb over a temperature range of 225° in the region of 625°. The mass spectrometer, Knudsen cell, and other experimental equipment and devices used are well described elsewhere.[3,4] In general, the experimental methods were similar to those used previously for a study of the bismuth system.[3]

Measurements of the ion intensities of the gaseous Bi–Sb species at various temperatures were carried out with liquid solutions of composition 11, 21, 40, and 60 atom % Sb. Because these metals form a continuous series of solutions with no eutectic,[5] the measurements were straightforward, and in all cases the change in composition with vaporization was less than 1% over the duration of the experiments. Measurements of ion intensities of Bi_2^+ from pure Bi(l) and Sb_4^+ from pure Sb(s) were made under identical conditions following each set of experiments on the binary system to obtain scaling factors which convert ion intensities to absolute partial pressures.

Parent Molecules and Fragmentation Contributions

Appearance potentials of the ion species from the vapor of a 40 atom % Sb solution at 625° and the relative intensities of these species at electron-impact energies of 20 eV are given in Table I of ref 1. It is shown that all possible homonuclear and heteronuclear monatomic, diatomic, triatomic, and tetratomic ions are formed by 20-eV electrons with intensities ordered in agreement with the relative volatilities of the two pure metals. The appearance potentials confirm, however, that there are only nine parent molecules in detectable concentrations: Sb_4, $BiSb_3$, Bi_2Sb_2, Bi_3Sb, Bi_4; Sb_2, BiSb, Bi_2; and Bi. All other ions are formed by electron-impact fragmentation of these molecules.

Fragmentation also enhances the ion currents of the parent monatomic and diatomic ions, and this complicates the measurements of the heats of reaction. The table shows that Sb_4 and $BiSb_3$ to a smaller extent contribute the major current of Sb_2^+ while $BiSb_3$, Bi_2Sb_2, and Bi_3Sb contribute heavily to the current of $BiSb^+$. Furthermore, the ion current of Bi_2^+ is enhanced by fragmentation of Bi_2Sb_2 and Bi_3Sb. According to a detailed analysis of a similar problem discussed elsewhere,[3] the parent ion current may be obtained from expressions of the form

$$I(Bi_2^+) = I_t(Bi_2^+) - (\sigma_f/\sigma_d)I(Bi_2Sb_2^+) - (\sigma_f'/\sigma_d')I(Bi_3Sb^+) \quad (1)$$

which is applicable in this example to the Bi_2^+ ion current. The term $I(Bi_2^+)$ represents the unknown parent ion current, $I_t(Bi_2^+)$ represents the measured total current, and σ_f/σ_d and σ_f'/σ_d' represent the ratios of the fragmentation cross sections for the production of Bi_2^+ from parent Bi_2Sb_2 and Bi_3Sb to the direct ionization cross sections for the formation of $Bi_2Sb_2^+$ and Bi_3Sb^+. From a practical standpoint, these ratios also include the sensitivity and other instrument constants.

On the basis of the relative intensities of Sb_4^+ and Sb_2^+ from pure Sb vapor measured with 20-eV electrons and a knowledge of the concentrations of the

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[1] (a) Research sponsored by the U. S. Army Research Office—Durham, Department of the Army, Contract No. DA-31-124-ARO-D-304. (b) National Aeronautics and Space Administration Predoctoral Fellow.

[2] (a) F. J. Kohl, J. E. Prusaczyk, and K. D. Carlson, *J. Am. Chem. Soc.*, **89**, 5501 (1967); (b) K. D. Carlson, F. J. Kohl, and O. M. Uy, "Inorganic Applications of Mass Spectrometry," Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.

[3] F. J. Kohl, O. M. Uy, and K. D. Carlson, *J. Chem. Phys.*, **47**, 2667 (1967).

[4] O. M. Uy, F. J. Kohl, and K. D. Carlson, *J. Phys. Chem.*, **72**, 1611 (1968).

[5] M. Hansen and K. Anderko, "Constitution of Binary Alloys," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1958, p 333.

neutral molecules, the cross-section ratio σ_f/σ_d for the fragmentation of Sb_4 to Sb_2^+ was found empirically to be approximately $^1/_3$. It was then assumed that this same ratio multiplied by a statistical factor would be applicable to the heteronuclear tetratomic species fragmenting to diatomic ions. In the case of Bi_2Sb_2, for example, it was assumed that fragmentation has about equal probability of forming Bi_2^+ or Sb_2^+ or any one of four $BiSb^+$ ion combinations, giving $^1/_6$ as the statistical probability for the production of Bi_2^+ and $^1/_{18}$ as the fragmentation cross-section ratio.

Explicit expressions were obtained by this prescription for the corrected ion currents of $BiSb^+$ and Bi_2^+, eq 2 and 3, respectively. Similar expressions for the

$$I(BiSb^+) \simeq I_t(BiSb^+) - \frac{1}{6}I(BiSb_3^+) - \frac{2}{9}I(Bi_2Sb_2^+) - \frac{1}{6}I(Bi_3Sb^+) \quad (2)$$

$$I(Bi_2^+) \simeq I_t(Bi_2^+) - \frac{1}{18}I(Bi_2Sb_2^+) - \frac{1}{6}I(Bi_3Sb^+) \quad (3)$$

corrected ion currents of Sb_2^+ and Bi^+ were not required for the thermodynamic measurements.

According to these expressions, 70% or more of the measured ion current of $BiSb^+$ at 20 eV for the 40% composition at 625° is due to fragment ions. These fragment contributions were found to remain constant at higher electron-impact energies but to decrease to zero in the region of 11 eV. Fragment contributions to the ion current of Bi_2^+, however, are less than 4% of the measured total intensity at electron energies of 20 eV.

Dissociation Energies

Ion intensities of all the parent species as a function of temperature were measured with 20-eV electrons. Lower impact energies would have reduced the fragmentation contributions to the currents of the diatomic ions but also would have reduced the intensities of the heteronuclear tetratomic molecules to intolerably low values. Except for reactions involving BiSb, however, fragmentation problems with 20-eV electrons were circumvented by considering only the following gas-phase equilibria.

$$4BiSb_3 = 2Bi_2 + 3Sb_4 \quad (4)$$

$$2Bi_2Sb_2 = 2Bi_2 + Sb_4 \quad (5)$$

$$4Bi_3Sb = 6Bi_2 + Sb_4 \quad (6)$$

The BiSb equilibria were studied differently, and the others involving reactions among the homonuclear molecules Sb_4, Sb_2 and Bi_4, Bi_2, Bi have been well established by other experiments on the vaporization of the pure elements.[3,6]

Heats of these reactions for all four compositions of the liquid phase were obtained by the usual second-law treatment of the temperature and ion-intensity data. These heats were found to be entirely independent of the composition of the liquid phase, as required. Averaged values at a common temperature of 850°K, which is near the mean temperature of all the measurements, are reported in Table I of this article.

One gas-phase equilibrium reaction involving the BiSb molecule is the only other reaction required to determine the vapor-phase composition. In this case, the reaction

$$4BiSb = 2Bi_2 + Sb_4 \quad (7)$$

was determined for the liquid of 40 atom % Sb with ionizing electrons of 11 eV to avoid fragmentation contributions completely. The heat of this reaction at 850°K is given in Table I along with the other measured heats.

Table I. Heats of Reaction Involving the Heteronuclear Molecules of Bi and Sb (kcal)

Reaction	$\Delta H°_{850}$	$\Delta H°_0$
$4BiSb_3 = 2Bi_2 + 3Sb_4$	41.48 ± 0.60	42.74 ± 0.84
$2Bi_2Sb_2 = 2Bi_2 + Sb_4$	42.06 ± 0.39	43.30 ± 0.48
$4Bi_3Sb = 6Bi_2 + Sb_4$	131.88 ± 1.08	136.00 ± 1.28
$4BiSb = 2Bi_2 + Sb_4$	−64.32 ± 1.32	−65.43 ± 1.64

These heats may be converted to the values at 0°K also given in Table I with the use of enthalpy functions based on estimated molecular parameters. First, it was assumed on the basis of the known tetrahedral structures of P_4 and As_4[7] that the tetratomic Bi–Sb molecules have $^1A_1$ electronic ground states with T_d symmetries for Sb_4 and Bi_4, related C_{3v} symmetries for $BiSb_3$ and Bi_3Sb, and C_{2v} symmetry for Bi_2Sb_2. The BiSb molecule is known to have a $^1\Sigma_g^+$ ground state.[8] Then, internuclear separations were estimated from the nearest neighbor distances in the solid elements.[9] Vibrational frequencies for Sb_4 and Bi_4 were estimated from the frequencies of the diatomic molecules Sb_2 and Bi_2[8] using the ratios of known frequencies for the P_4 and P_2 molecules.[8,10] Vibrational frequencies for the heteronuclear species were estimated from the frequencies for Sb_4 and Bi_4 using group theory to decide the splitting of the degenerate modes of T_d.

These estimated parameters and the thermodynamic functions derived from them are given in Table II. The enthalpy functions given here and those for Bi_2 given elsewhere[11] were combined with the high-temperature heats of reaction and the known atomization energies of Bi_2 and Sb_4 to obtain the dissociation energies of the new heteronuclear Bi–Sb molecules reported in Table III. Dissociation energies of Sb_2, Bi_2, Sb_4, and Bi_4 are included in this table for comparison. These energies show very systematic trends which will be discussed later.

Pressures and Third-Law Estimates

Scaling factors k_i/σ_i relating ion currents I_i to partial pressure p_i were determined directly for Bi_2 and Sb_4 from their known pressures[3,6] and measurements of the intensities of Bi_2^+ and Sb_4^+ in the vapors over the pure condensed elements, as described in the second section of this article. On the basis of similarities in the molecules and other evidence,[3] the factors $k(Bi_2)/\sigma(Bi_2)$ and $k(Sb_4)/\sigma(Sb_4)$ were then adopted as the scaling factors for all the diatomic and tetratomic species, respectively. The ion currents were corrected for fragmentation and then converted to partial pressures with the use of these scaling factors according

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(6) A. J. H. Boerboom, H. W. Reyn, H. F. Vugts, and J. Kistemaker, *Physica*, **30**, 2137 (1964).

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(8) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, Inc., Princeton, N. J., 1950.

(9) C. S. Barrett, "Structure of Metals," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1952, p 646.

(10) H. S. Gutowsky and C. J. Hoffman, *J. Am. Chem. Soc.*, 72, 5751 (1950).

(11) D. R. Stull and G. C. Sinke, Advances in Chemistry Series, No. 18, American Chemical Society, Washington, D. C., 1956.

Table II. Estimated Molecular Parameters and Thermodynamic Functions for Bismuth–Antimony Molecules

Internuclear separations, Å		r(Bi–Bi)		r(Bi–Sb)		r(Sb–Sb)
Tetratomic		3.11		3.00		2.90
Diatomic				2.54		
Molecule[a]	$\mathrm{Bi_4}$ ($\mathrm{T_d}$)	$\mathrm{Bi_3Sb}$ ($\mathrm{C_{3v}}$)	$\mathrm{BiSb_3}$ ($\mathrm{C_{2v}}$)	$\mathrm{BiSb_3}$ ($\mathrm{C_{3v}}$)	$\mathrm{Sb_4}$ ($\mathrm{T_d}$)	BiSb
Frequencies, cm^{-1}						
ν_1	134 ($\mathrm{A_1}$)	150 ($\mathrm{A_1}$)	160 ($\mathrm{A_1}$)	180 ($\mathrm{A_1}$)	210 ($\mathrm{A_1}$)	220 ($\mathrm{A_1}$)[b]
ν_2	80 (E)	110 ($\mathrm{A_1}$)	145 ($\mathrm{A_1}$)	150 ($\mathrm{A_1}$)	126 (E)	
ν_3	103 ($\mathrm{T_2}$)	110 (E)	110 ($\mathrm{A_1}$)	150 (E)	160 ($\mathrm{T_2}$)	
ν_4		90 (E)	110 ($\mathrm{A_2}$)	120 (E)		
ν_5			140 ($\mathrm{B_1}$)			
ν_6			140 ($\mathrm{B_2}$)			
$H_T - H°_0$, cal mole^{-1} [c]						
298.15	5,130	5,070	4,900	4,820	4,750	2410
800	15,060	14,990	14,800	14,710	14,610	6860
900	17,040	16,970	16,780	16,690	16,590	7750
$S°_T$, eu[d]						
298.15	96.2	97.2	94.7	92.4	87.4	64.6
800	115.8	116.7	114.1	111.8	106.8	73.3
900	120.2	119.1	116.5	114.1	109.2	74.3

[a] $^1\mathrm{A_1}$ ground states for tetratomic molecules; $^1\Sigma^+$ for BiSb. [b] Experimental value, ref 8. [c] Estimated uncertainties of ±230 cal mole^{-1} [d] Estimated uncertainties of ±0.2 eu for BiSb and ±2.2–3.6 eu for the others.

Table III. Dissociation Energies of Bismuth–Antimony Molecules

Molecule[a]	$D°_0$, eV[b]
$\mathrm{Sb_2}$	3.06 ± 0.06
BiSb	2.58 ± 0.04
$\mathrm{Bi_2}$	2.06 ± 0.03
$\mathrm{Sb_4}$	9.04 ± 0.15
$\mathrm{BiSb_3}$	8.27 ± 0.11
$\mathrm{Bi_2Sb_2}$	7.52 ± 0.08
$\mathrm{Bi_3Sb}$	6.82 ± 0.06
$\mathrm{Bi_4}$	6.03 ± 0.08

[a] Value for $\mathrm{Sb_2}$ taken from G. DeMaria, J. Drowart, and M. G. Inghram, *J. Chem. Phys.*, **31**, 1076 (1959); $\mathrm{Sb_4}$ from ref 6; $\mathrm{Bi_2}$ and $\mathrm{Bi_4}$ from ref 3. [b] Refers to dissociation to atoms in every case.

Table IV. Least-Squares Parameters for the Partial Pressures of Bismuth–Antimony Molecules[a]

Molecule[b]	Liq atom % Sb	A[c]	B
$\mathrm{Sb_4}$	11	6472 ± 103	0.328 ± 0.117
	21	5872 ± 95	0.729 ± 0.110
	40	6665 ± 80	2.332 ± 0.096
	60	7307 ± 264	3.803 ± 0.320
$\mathrm{BiSb_3}$	11	7496 ± 98	1.479 ± 0.112
	21	7030 ± 108	1.757 ± 0.125
	40	7571 ± 85	2.774 ± 0.101
	60	7669 ± 123	3.310 ± 0.148
$\mathrm{Bi_2Sb_2}$	11	8573 ± 130	2.072 ± 0.148
	21	7878 ± 146	1.821 ± 0,169
	40	8533 ± 72	2.697 ± 0.086
	60	7979 ± 73	2.185 ± 0.088
$\mathrm{Bi_3Sb}$	11	9539 ± 99	3.081 ± 0.113
	21	8422 ± 102	2.106 ± 0.119
	40	9149 ± 100	2.697 ± 0.119
$\mathrm{Bi_2}$	11	9988 ± 69	5.246 ± 0.078
	21	9446 ± 98	4.720 ± 0.133
	40	9873 ± 76	4.881 ± 0.091
	60	8880 ± 195	3.639 ± 0.237
BiSb	11	10882 ± 91	5.308 ± 0.104
	21	9835 ± 98	4.558 ± 0.114
	40	10451 ± 86	5.070 ± 0.103
	60	9252 ± 146	4.142 ± 0.177

[a] Log p (atm) $= -A/T + B$; temperature range 750–975°K. [b] Partial pressures of $\mathrm{Bi_4}$, Bi, and $\mathrm{Sb_2}$ can be determined from these values and the equilibrium data given in ref 3 and 6. [c] Uncertainties are standard deviations.

to the well-known relationship

$$P_i = (k_i/\sigma_i)I_iT \qquad (8)$$

Logarithms of these pressures were adjusted by least-squares to equations of the usual linear form, and parameters for these equations are reported in Table IV for all molecules except $\mathrm{Bi_4}$, Bi, and $\mathrm{Sb_2}$. Partial pressures for these three species can be calculated from equilibrium constants for the pure Bi and Sb systems[3,6] combined with the pressures reported here. Total vapor pressures of the Bi–Sb alloys were calculated from these equations to obtain an estimate of the liquid–vapor-phase diagram illustrated in Figure 1. This diagram is similar to that for the Na–Bi system.[12] Various partial molar properties of these alloys also may be deduced from these equations, and they show reasonable trends. Uncertainties in these quantities, however, are necessarily large because of uncertainties in the scaling factors, fragmentation corrections, and other unavoidable errors.

The gas-phase equilibria are the principal concern, and the absolute partial pressures are intended to confirm the reliability of the second-law heats through a comparison of entropies. Second-law entropies for reactions 4, 5, 6, and 7 were found to be 24.3 ± 0.4, 30.4 ± 0.2, 92.9 ± 0.5, and −36.8 ± 0.3 eu, respectively, in good agreement with third-law values of 21 ± 14, 27 ± 6, 85 ± 13, and −38 ± 2 eu based on the estimated molecular parameters. Additional support for the reliability of these measurements is given by the results of earlier studies on the pure Bi system obtained by comparable methods.[3]

Discussion

We now consider trends in the dissociation energies. First of all, there is a systematic decrease in these from $\mathrm{Sb_2}$ to $\mathrm{Bi_2}$ or $\mathrm{Sb_4}$ to $\mathrm{Bi_4}$ as the atoms of the first homonuclear molecule are successively replaced by atoms of the second. A similar decrease occurs in the threshold ionization potentials. Furthermore, these trends are quantitative in the framework of bond-energy arguments. The diatomic species may be considered to have triple bonds with heteronuclear bond energies equal to the average of homonuclear bond energies. Thus, the average of the dissociation energies of $\mathrm{Sb_2}$ and $\mathrm{Bi_2}$ is 2.56 eV, in excellent agreement with the experimental value, 2.58 eV, for BiSb. In an equivalent

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(12) A. K. Fischer, S. A. Johnson, and S. E. Wood, *J. Phys. Chem.*, 71, 1465 (1967).

sense, the tetratomic molecules might be considered to have six single bonds with heteronuclear bond energies equal to the average of homonuclear single-bond energies. Thus, three-fourths the atomization energy of Sb_4 plus one-fourth the atomization energy of Bi_4 give 8.29 eV, in excellent agreement with the experimental value, 8.27 eV, for $BiSb_3$.

Although these comparisons must be viewed entirely as empirical correlations rather than fundamental relationships, as we shall point out, they tend to confirm the assumption of structural similarities for the group of Bi–Sb molecules. Together with the trends in binding energies for all other known molecules of this family,[2b] they tend also to confirm that this group is only one part of a complete class of related molecules composed of all combinations of the group Va atoms. Only a few of these possible combinations have been observed to date,[2a] but their dissociation energies should be predictable on the basis of empirical bond energies. Conspicuously absent among the known tetratomic molecules is N_4, but its dissociation energy cannot be predicted directly from available bond energies.

The usual tabulation of single-bond energies for the nitrogen family molecules shows an anomalously low value of 1.67 eV for the N–N single bond based on data for hydrazine and similar molecules.[13] A P–P bond energy of 2.07 eV taken as one-sixth of the atomization energy of P_4 is considerably larger, and others down the family systematically decrease. Recent theoretical calculations[14] on the electronic structure of P_4, however, have shown that the bonding in this molecule and presumably others in the same family does not involve localized two-centered bonds but instead involves delocalized electrons in an unsaturated structure. The so-called anomaly is, therefore, a result of an irrelevant comparison between localized N–N bonding in hydrazine and delocalized bonding in the tetrahedral molecules. It is not unreasonable to presume that a stable tetrahedral N_4 molecule does exist as a member of the same class of group Va molecules with a dissociation energy considerably larger than that of P_4.

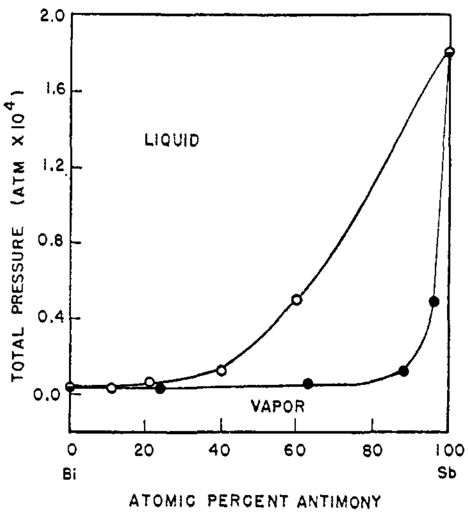

Figure 1. Pressure–composition phase diagram for the Bi–Sb system at 625°.

Acknowledgments. The authors thank Mr. Kenneth R. Thompson for helpful discussions concerning the estimation of the molecular parameters and Mr. C. Larry Sullivan for assistance in carrying out the experiments.

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A Mass Spectrometric Investigation of the Low-Pressure Pyrolysis of Triphosphine-5

T. P. Fehlner

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. Received March 1, 1968

Abstract: Triphosphine-5, an intermediate in the pyrolysis of diphosphine-4, thermally decomposes in a Pyrex reactor over the pressure range 0.2–10 mtorr into phosphine and diphosphine-2 by a reaction which is first order in triphosphine-5, and into diphosphine-4 and diphosphine-2 by a reaction which is zero order in triphosphine-5. The first-order reaction is autocatalytic in diphosphine-2, and the zero-order reaction is similar to the thermal decomposition of diphosphine-4. Both reactions appear to be heterogeneous. The products diphosphine-4 and diphosphine-2 decompose further to yield phosphine and tetraatomic phosphorus. These results are discussed from the viewpoint of the stability of higher phosphorus hydrides.

The apparent instability of the phosphorus hydrides poses the intriguing question of whether these compounds contain inherently weak bonds or whether they possess some type of excessive reactivity under ordinary conditions. To explore this problem, we are carrying out a number of studies which entail the intimate examination of reacting systems containing phosphorus hydrides. In a preceding paper[1] we reported that the low-pressure pyrolysis of diphosphine-4 in a Pyrex vessel proceeds *via* a surface reaction and results in the formation of diphosphine-2 and phosphine. The unstable intermediate, diphosphine-2, de-

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[1] T. P. Fehlner, *J. Amer. Chem. Soc.*, **89**, 6477 (1967).