actions because the charge-transfer crystal orients the potential reactants with respect to one another. The first-order kinetics indicate that the subsequent reaction operates at the molecular level. No acceleration with time occurs; no "critical temperature" is observed. Instead the kinetics are first order to high per cent reaction, and a linear plot of log k vs. $1/T$ is obtained. At the lower temperatures, the product of the reaction is a pure isomer, with no trace of the other isomer or monobrominated product detectable via vapor phase chromatographic analyses.

Such observation of a unique product from a solid-state reaction is often evoked as proof that the crystal matrix controls the reaction. Schmidt clearly shows cinnamic acid dimer structure is correlated with monomer crystal structure.[25] Prelog, et al.,[26] recently observed that the decomposition of cyclodecyl tosylate in the solid state leads exclusively to cis-cyclodecene, while the reaction in the liquid phase yields 20% cis and 80% of the trans isomer. However, in our own studies, as well as in general, it is not usually possible to conduct a given reaction under the same conditions of temperature and concentration in both the solid and fluid (or solution) phases. It should be remembered that some of these effects may be rate or equilibrium controlled rather than crystal controlled. This is possibly the explanation for the observation that 3,10-dibromoperylene forms in detectable concentrations at $-9°$, but not at lower temperatures.

The reaction under consideration is unusually fast for a solid-state reaction.[1] One interpretation of this is that the probability factor for collisions having the proper orientation for reaction is high in this solid matrix. The large negative entropy of activation implies that the transition state for this reaction is considerably more ordered than the ground state, but this entropy factor is not known reliably.

One of the most important problems in the field of electrophilic aromatic substitution in homogeneous solution is to decide the nature of the intermediate which, for example, Melander's work on isotope effects in aromatic substitution requires.[27] The view is that a typical substitution reaction occurs in two steps, with an intermediate forming which can, in principle, be isolated. It was one of our purposes to be able to comment on the nature of this intermediate. Although the perylene–bromine complex isolated in this work appears to be, from infrared data, a σ-type complex, we can neither definitely establish this nor be assured that the solid-state reactive species is identical with the reactive intermediate in solution.

The extent to which the solid matrix can be used to control the course of substitution reactions is currently being explored for a wide variety of aromatic derivatives entering into charge-transfer interactions and will be described in future publications.

(25) G. M. J. Schmidt, *J. Chem. Soc.*, 2014 (1964).
(26) V. Prelog, W. Kung, and T. Tomljenovic, *Helv. Chim. Acta*, **45**, 1352 (1962).

(27) L. Melander, *Arkiv Kemi*, **2**, 211 (1951); "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960.

Comparative Stabilities of Gaseous Alane, Gallane, and Indane

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A technique is described for the mass spectrometric study of gaseous hydrides formed by atom reactions in a fast flow system. The relative abundances of alane, gallane, and indane formed in these reactions are used to classify the order of stability of these hydrides. The gases GaH_3 and InH_3 were found to be far less stable than AlH_3 despite the use of a wide range of reaction parameters. The implications of these results are discussed along with bond energetics in connection with the conflicting literature on the III-B metal hydrides. The present results support recent experimental observations concerning the instability and difficulty of preparation of liquid Ga_2H_6 and polymeric $(GaH_3)_x$ in contrast to earlier reports of high stability and ready preparation.

Introduction

Wiberg and co-workers[1-3] have described the synthesis of a liquid Ga_2H_6 and the solid hydrides $(GaH_3)_x$ and $(InH_3)_x$. However, several recent studies[4,5] have repudiated the validity of these syntheses, and the hydrides were shown to be far less stable than had been asserted. Since the present writers[6] had been able to study mass spectrometrically the conditions governing the formation of gaseous AlH_3 and Al_2H_6 in a fast flow system of aluminum vapor and partially dissociated hydrogen, it was thought that an extension of this technique to the study of the analogous gaseous hydrides of the heavier III-B metals, Ga and In, would delineate the relative stabilities of the gaseous trihydrides of these metals and perhaps eliminate any lingering doubt about the claims of ref. 1-3. Al-

(1) E. Wiberg and T. Johannsen, *Naturwiss.*, **29**, 320 (1941).
(2) E. Wiberg and M. Schmidt, *Z. Naturforsch.*, **7b**, 577 (1952).
(3) E. Wiberg, O. Dittmann, and M. Schmidt, *ibid.*, **12b**, 57 (1957).
(4) D. F. Shriver, R. W. Parry, N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Inorg. Chem.*, **2**, 867 (1963).
(5) N. N. Greenwood and M. G. H. Wallbridge, *J. Chem. Soc.*, 3912 (1963).
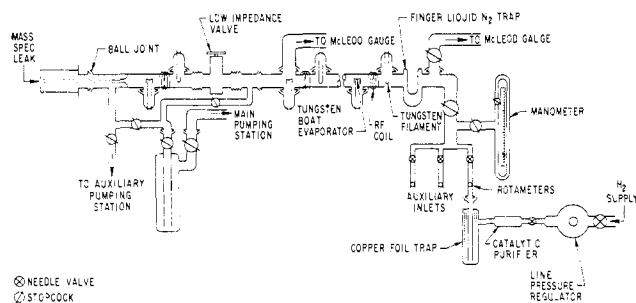(6) P. Breisacher and B. Siegel, *J. Am. Chem. Soc.*, **86**, 5053 (1964).

Figure 1. Diagram of flow system.

⊗ NEEDLE VALVE
∅ STOPCOCK

though gaseous gallanes and indanes had not been reported it was reasoned that if they were capable of stable existence they should form by reactions analogous to those already shown to lead to alane formation.

Experimental Section

The experiments consisted of the continuous passage of gaseous reaction mixtures obtained by the intersection of partially dissociated hydrogen and metal vapors along a line-of-sight path leading directly to the fast reaction inlet system of a Bendix 14-107 time-of-flight mass spectrometer. Salient features are shown in Figure 1, with details given below. An ultrapure grade of hydrogen was purified further by passage through a deoxo catalytic purifier and a liquid nitrogen cooled copper foil trap prior to passage into the metering system. The latter consisted of a tri-flat calibrated rotameter placed upstream of a micrometer needle valve. The hydrogen which was delivered from the tank at 3 p.s.i.a. was then passed over one more liquid nitrogen cooled finger trap before reaching the metal evaporators. The latter were placed at distances of 25.5, 86.0, and 173 cm. from the mass spectrometer leak. Throttling of the auxiliary pumping systems permitted pressure variations over the desired ranges. Pressures were measured at the midway point and at the beginning of the line-of-sight reaction tube by McLeod gauges. The vacuum system was entirely grease-free; stopcocks and ball and socket joints were made of Teflon, Viton A, and glass. A grease-free mass spectrometer shutoff valve of low impedance copper knife-edge seal design was used. The secondary tungsten filaments used for H-atom generation were 20-gauge tungsten held at 1350°. The radiofrequency generator was designed to deliver up to 250 w. of reflected energy at the helical coil antenna. The lead wires of the components were 0.186-in. diameter tungsten rod while the evaporator boats were made of 0.005-in. tungsten sheet. In the latter the depression at the center was 2 mm. deep and 8 mm. wide, enough to hold 2 g. of the particular metal used. The Ga and In used in these experiments were 99.999% pure; In was in the form of a wire and Ga was used as pellets and rods.

The experimental steps for data acquisition were as follows. The hydrogen pressure was adjusted (the mass flow was always the same at 1.8 cc./sec. measured at S.T.P.) to the desired value. If an auxiliary filament or radiofrequency discharge was to be employed, then these were activated to the desired temperature or power, respectively. A mass spectrum was then obtained with the filament supporter cold. Current was then ap-

plied to the metal and its temperature was increased in gradual increments. At each temperature the mass spectrum was recorded. Temperature measurements were made through thin quartz windows using a micro optical pyrometer.

Mass spectrometer sensitivity factors were repeatedly checked throughout the experiments by passing a stream of hydrogen at known pressure over the leak or using known gas mixtures introduced through the molecular leak inlet system. The residence times given in the next section were the computed flow times from the point of intersection of the hydrogen with the evaporating metal to the mass spectrometer leak, in milliseconds. The H·Gen. columns refer to the method of H atom generation, the R.F. representing the radiofrequency discharge method; fil., the tungsten filament leads used to heat the evaporator boats; and double fil., representing the latter and a secondary filament maintained at 1350°.

Results

The temperature range of the aluminum droplet when hydrides were observed was 1090 to 1300°.[6] This corresponds roughly to an equilibrium vapor pressure range of 10^{-6} to 10^{-4} atm.[7] Although the process was not strictly an equilibrium one, these data serve as a reference point for comparison with the gallium and indium runs. Comparable vapor pressures can be obtained at considerably lower temperatures for Ga and In; for Ga, about 926 to 1176°, and for In, about 818 to 1053°. One would thus expect to observe hydrides of Ga and In at lower evaporator temperatures than had been the case with aluminum. This behavior was in fact observed. Small peaks attributable to InH_3^+ and GaH_3^+ were observed at temperatures at which In^+ and Ga^+ mass peaks were first noted. However, in these runs the alane behavior, in which the hydride pressure increased with steadily increasing vapor pressure of aluminum, was never encountered. Instead the InH_3^+ and GaH_3^+ peaks remained at very low levels throughout the course of each run, even when the vapor pressures of the metals rose above the maximum 10^{-4} atm. previously attained with aluminum. There was no indication of the formation of the dimers Ga_2H_6 or In_2H_6.

In an effort to obtain higher partial pressures of gallanes and indanes, a wide range of reaction parameters was investigated. Thus, whereas the alane behavior had been noted at a hydrogen pressure of 0.3 mm. and a residence flow time of 39 msec., in the present runs the residence times were varied from only several milliseconds up to several hundred milliseconds. Further, the hydrogen pressures were also varied over a wider range. The dependence of residence time–pressure was studied by varying each independently of the other. Since it had been shown previously that the level of atomic hydrogen formed by collision of H_2 with the glowing filament is rate determining for the reaction between evaporating aluminum and hydrogen,[8] an effort was made to supplement the H atom concentrations by an additional glowing filament at 1350° or by passage of the H_2 through a radiofrequency discharge.

(7) R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley and Sons, Inc., New York, N. Y., 1963.

(8) B. Siegel, *J. Am. Chem. Soc.*, **82**, 1535 (1960).

The data for indium are given in Table I. The measure of the extent of InH_3 formation is taken as the ratio of ion intensities at mass peaks 118 to 2, multiplied by the pressure of H_2. The latter is essentially the observed pressure since the over-all hydrogen atom concentration is quite low, as was verified mass spectrometrically. This $p_{H_2}(InH_3^+/H_2^+)$ term would give the exact partial pressure of InH_3 if the ionization cross sections of H_2 and InH_3 were identical. Although this is probably not the case, so that $p_{H_2}(InH_3^+/H_2^+)$ is only an indication of the InH_3 pressure, this term permits a good comparison of the MH_3 pressures for alane, gallane, and indane, by comparing p_{H_2} (MH_3^+/H_2^+) for these hydrides. Certainly the cross sections for the various hydrides are identical within an order of magnitude. The pressures of InH_3 in Table I were obtained by averaging the numerous ion intensities for InH_3^+ obtained for each run, as the temperature was increased; the scatter in the data for these very small InH_3^+ mass peaks is reflected by the choice of only one significant figure for the final partial pressure term.

Table I. Indium Evaporations

Residence time, msec.	p_{H_2}, mm.	H·Gen.	p_{H_2} (InH_3^+/H_2^+), mm. $\times 10^6$
2.8	0.070	R.F. + fil.	0.4
6.4	0.030	Double fil.	0.6
7.8	0.200	R.F. + fil.	0.6
8.1	0.038	R.F. + fil.	0.8
8.6	0.220	R.F. + fil.	0.7
12.2	0.312	R.F. + fil.	3
12.8	0.060	Double fil.	2
55.0	0.110	Fil.	0.8
89.8	0.420	Double fil.	1
102.5	0.205	Fil.	2
106.5	0.213	Double fil.	0.9
147.5	0.295	Fil.	0.9
215.1	0.430	Fil.	0.2

It can be seen that the values for InH_3 fall within the range 10^{-7} to 10^{-6} mm. This is in marked contrast to the value of 5.1×10^{-4} mm. previously found for $p_{H_2}(AlH_3^+/H_2^+)$ and the 5.7×10^{-3} mm. value previously found for $p_{H_2}(Al_2H_6^+/H_2^+)$ at the higher Al vapor pressures. Clearly indane is found at levels three to four orders of magnitude lower than the aluminum hydrides, despite the wide range of reaction parameters investigated. There appears to be no discernible correlation of the InH_3 formation with each of the factors studied.

Comparable data for gallium are given in Table II. Since Ga has two important isotopes (39.9% Ga^{71} and 60.1% Ga^{69}) the mass peak at m/e 72 is formed from both Ga$^{69}H_3^+$ and Ga$^{71}H^+$. It was therefore convenient to consider only Ga$^{71}H_3^+$ and to obtain the total GaH_3^+ by multiplying the ion intensity at m/e 74 by 100/39.9. Despite the numerous runs in which $p_{H_2}(GaH_3^+/H_2^+)$ fell below 10^{-6} mm., it can be seen that about half the runs gave values of approximately 10^{-5} mm. Although this is still very much below the alane data, it does indicate that GaH_3 is formed in higher yields than InH_3, under the conditions described. In only three runs did $p_{H_2}(GaH_3^+/H_2^+)$

rise significantly above the 10^{-5}-mm. level. Perhaps it is significant that in each of these cases the residence time was 10.6 msec. or less, the highest GaH_3 level occurring at the lowest residence time of 2.3 msec. Despite the fact that many runs at low residence times gave considerably lower GaH_3 levels, we believe that the data indicate that higher yields of GaH_3 could be observed at very much lower residence times. This is consistent with the formation of a relatively unstable GaH_3 molecule. Aside from the possible significance of residence time, the other factors do not lead to a discernible correlation with GaH_3 formation.

Table II. Gallium Evaporations

Residence time, msec.	p_{H_2}, mm.	H·Gen.	p_{H_2} (GaH_3^+/H_2^+), mm. $\times 10^5$
2.3	0.060	R.F. + fil.	17
4.1	0.105	R.F. + fil.	<0.01
4.3	0.110	R.F. + fil.	<0.01
4.7	0.022	Fil. only	1.4
4.7	0.120	R.F. + fil.	7
4.9	0.125	R.F. + fil.	0.2
5.4	0.137	R.F. + fil.	<0.01
5.8	0.149	R.F. + fil.	0.08
5.9	0.151	R.F. + fil.	1
6.1	0.157	Fil. only	2
7.8	0.200	R.F. + fil.	0.07
8.0	0.205	R.F. + fil.	0.4
10.6	0.270	R.F. + fil.	6
11.3	0.053	Double fil.	0.2
12.0	0.305	R.F. + fil.	<0.01
20.5	0.450	Fil. only	2
25.6	0.120	R.F. + fil.	0.9
26.4	0.053	Double fil.	0.9
29.5	0.059	Fil. only	0.4
32.3	0.151	R.F. + fil.	<0.01
42.0	0.084	Fil. only	<0.01
49.4	0.231	Fil. only	<0.01
49.4	0.231	R.F. + fil.	0.7
52.5	0.105	R.F. + fil.	0.9
52.5	0.105	R.F. + fil.	0.9
77.4	0.155	R.F. + fil.	0.4
79.6	0.159	R.F. + fil.	0.3
157.6	0.315	R.F. + fil.	1
175.0	0.350	R.F. + fil.	0.9

By contrast to the fairly steady but low levels of GaH_3 and InH_3, an example of the behavior of AlH_3 is shown in Figure 2. The time axis reflects successive mass spectral scans, with each scan taking 3 to 5 min. Whereas the Al_2H_6 level rises steadily with increasing evaporator temperature, the AlH_3 level remains substantially constant and is shown as a continuous line while the Al_2H_6 data are plotted as circles. The temperature dependence of this curve has been previously reported.[6] The abrupt decreasing portion of the Al_2H_6 curve reflects only the fact that we are observing the behavior when the sample has completely evaporated.

Discussion

The large differences between the observed aluminum hydride levels and those found for the gallium and indium hydrides, as well as the differing behavior with increasing evaporator temperatures, clearly establishes that the gaseous aluminum hydrides are very much more
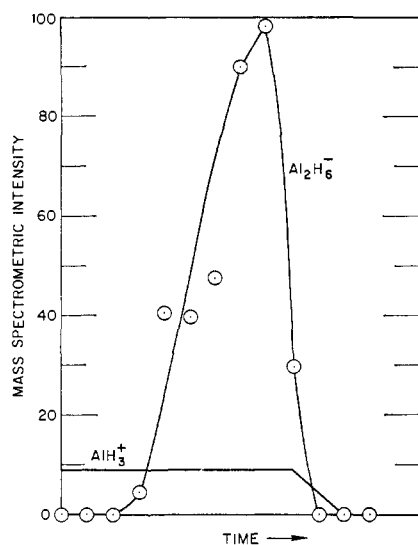
Figure 2. Formation of aluminum hydrides.

stable than the analogous gaseous hydrides of the other metals. The data also indicate that GaH_3 is somewhat more stable than InH_3. These relative stabilities of the gaseous hydrides tend to confirm the findings of ref. 4 and 5 as to the instability of the condensed state gallanes, especially since polymeric aluminum hydride has been shown to decompose appreciably at temperatures of about 80°.[9] On the basis of the present data it is extremely unlikely that the stabilities of the condensed gallanes could exceed that of $(AlH_3)_x$, as would be required if the stability data of Wiberg, et al.,[1,2] were correct. On this basis the reported stability of $(InH_3)_x$[3] also seems very unlikely.

A theoretical basis for the order of stabilities observed in the present study can be shown. There is a trend toward lower bond dissociation energies of the gaseous diatomic hydrides of the III-B elements with increasing atomic weight, as is shown in Table III; this is a general trend that is also observed for the hydrides of other groups of the periodic table. Because of this trend the difference between the dissociation energies for AlH and GaH is probably larger than that reflected by the average values given in the table, especially in view of the large uncertainty for the $D_0°$ of AlH. However, these data reflect only the bonding of the simple unhybridized molecules. In the MH_3 hydrides of the III-B metals the metal atoms are probably sp^2 hybridized and there should be a much greater difference in bond strength between metal–hydrogen bonds in AlH_3 and GaH_3 than in AlH and GaH, reflecting the differences in the hybridization energies of the metal atoms. There are numerous examples of this in the literature.[10] For example, the difference in bond energies between CH and SiH is

(9) A. C. Finholt, A. C. Bond, and H. I. Schlesinger, J. Am. Chem. Soc., 69, 1199 (1947).
(10) T. L. Cottrell, "Strengths of Chemical Bonds," Butterworth & Co., Ltd., London, 1958.

only 7 kcal./mole, as compared to 23 kcal./mole between sp^3 bonds in CH_4 and SiH_4. In the case of the III-B hydrides the bond energy for B–H bonds in BH_3 is 90 ± 2 kcal./mole,[11] while an estimated value of 72 ± 3 kcal./mole[12] has been advanced for AlH_3. One would predict a similarly large difference between AlH_3 and GaH_3. On this basis one would predict less stability for GaH_3 than for AlH_3, and that InH_3 would be even less stable than GaH_3.

Table III. Dissociation Energies of III-B Diatomic Hydrides

Diatomic hydride	$D_0°$, kcal./mole
BH	78 ± 0.9[a]
AlH	67 ± 4.6[b]
GaH	66 ± 1.7[c]
InH	58 ± 2.3[b]
TlH	46 ± 4.6[b]

[a] A. C. Hurley, Proc. Roy. Soc. (London), A261, 237 (1961). [b] A. G. Gaydon, "Dissociation Energies," Chapman and Hall, London, 1953. [c] M. L. Ginter and K. K. Innes, J. Mol. Spectry., 7, 64 (1961).

The fact that neither GaH_3 nor InH_3 dimerized in the experiments described above is consistent with the aluminum hydride data, since AlH_3 did not dimerize until the aluminum vapor pressures rose substantially above the minimum value required for AlH_3 formation.[6] Since in every experiment the GaH_3 and InH_3 levels were very much lower than the AlH_3 levels, one should not expect dimerization of either GaH_3 or InH_3.

The instabilities or short lifetimes of gaseous gallium and indium hydrides make it especially difficult to study these species by employing a steady-state flow system incorporating a heated evaporator such as that used here. Our data indicate that residence times well below 1 msec. would be required. It is very difficult to obtain such residence times in this type of a flow system. A better approach appears to be the use of transitory reaction initiators such as exploding wires or flash photolysis, in combination with line-of-sight inlet conditions such as used with the Bendix time-of-flight mass spectrometer. This would eliminate the need for steady-state flow conditions and the difficulty of achieving exceedingly low residence times, while providing a means of achieving sufficiently high levels of unstable species, even if only for a very short time interval. The fast flow technique described in the present study is clearly useful for the investigation of gas species that are relatively stable at low pressures but are difficult to obtain by other than atom techniques. However, as has been shown above, the relative stabilities of even quite unstable species may also be qualitatively ascertained by this method.

(11) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1963.
(12) G. T. Armstrong, U.S.N.B.S. Report 6484, July 1959.