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Preliminary communication

REACTION OF TRIMETHYLGALLIUM WITH TIN, SILICON, GERMANIUM AND ARSENIC FILMS

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Summary

The transfer of methyl groups from $(CH_3)_3Ga$ to tin, silicon and germanium films has been observed at 190, 230 and 285°C forming $(CH_3)_4Sn$, $(CH_3)_6Si_2$, $(CH_3)_3SiH$ and $(CH_3)_4Ge$, respectively.

During an investigation of some reactions of $(CH_3)_3Ga$ we observed that it reacts with a silicon mirror at about 250° to produce alkylsilanes. We report our results on this reaction and of that between $(CH_3)_3Ga$ and other metalloids. This type of alkyl group transfer is well known between many metallic systems where the reactions are carried out in organic solvents. In some reactions, such as that between $Hg(CH_3)_2$ and beryllium [1], the organometallic compound served as the liquid phase.

To our knowledge, no exchange reactions involving alkylborons, alkylaluminums or alkylgalliums have been reported. Further, we are unaware of any report of alkyl exchange between a metal (or metalloid) and an alkylmetal in the absence of a liquid phase except where free alkyl radicals were presumed to be the reactive species. The best known reaction of this type is that between $Pb(CH_3)_4$ and mirrors of lead, zinc, antimony, bismuth and beryllium [2].

In a typical experiment, a metalloid mirror (silicon, germanium, tin, arsenic) was deposited in a 80 ml reaction vessel from a 400° one hour pyrolysis of about 2 mmoles of the appropriate hydride (SiH_4, GeH_4, SnH_4, AsH_3). The H_2 and remaining hydride (< 0.2 mmol) were distilled off and the surface was baked for two hours at 400°*. The temperature was then lowered and $(CH_3)_3Ga$ (0.4 mmol) was expanded into the vessel. After two hours at the appropriate temperature, the products were distilled and analyzed

*It has been demonstrated that pure silicon is the final product from the pyrolysis of SiH_4 at these temperatures [3]. Since the silicon—hydrogen bond is stronger than the germanium—hydrogen tin—hydrogen or arsenic—hydrogen bonds [4], we have assumed that the above procedure also produced pure, germanium, tin and arsenic mirrors.

by infrared and mass spectrometry and by gas chromatography. In these pyrolyses, all of the $(CH_3)_3Ga$ was consumed. The observed volatile products are listed in Table 1.

TABLE 1

PRODUCTS FROM REACTION OF $(CH_3)_3Ga$ AND METALLOIDS

Metalloid	Lowest temp. for reaction	Products
Sn	190 [a]	$(CH_3)_4Sn$
Si	230 [b]	$(CH_3)_6Si_2/(CH_3)_3SiH = 10/1$
Ge	285 [c]	$(CH_3)_4Ge$
As	340 [d]	CH_4

[a] At 205°, about 0.02 mmol of product was produced. [b] No reaction at 220°, 0.06 mmol of product at 250°. [c] No reaction at 245°, 0.04 mmol of product at 285°. [d] No arsenic containing products.

When the reaction vessel was cleaned and a new mirror deposited, the first reaction consumed only about 10% of the $(CH_3)_3Ga$ and produced no products. However, after a fresh mirror was deposited, results as listed in Table 1 were obtained. Similar results could then be obtained over freshly deposited mirrors. Presumably, the first unsuccessful pyrolyses removed the last traces of H_2O.

Under our reaction conditions, methane was not obtained in the neat pyrolysis of $(CH_3)_3Ga$ below 285°. Trimethylgallium decomposes thermally to yield CH_3 radicals [5] which would abstract H atoms to produce CH_4. Therefore, CH_3 radicals were not present in our system in significant quantities below 285°. Thus the reaction of $(CH_3)_3Ga$ with metallic tin or silicon did not involve free CH_3 radicals and was undoubtedly a reaction between $(CH_3)_3Ga$ and the metallic film. Hurd and Rochow have previously demonstrated that CH_3 radicals do not react with silicon at this temperature [6].

Since the reaction with germanium occurs just at 285°, it is difficult to determine the mode of this reaction. It has been postulated that CH_3 radicals do react with a germanium surface [7].

The relative rates of the surface reaction are in the order: tin > silicon > germanium, arsenic. This order correlates with the electronegativities of the metalloids which are: 1.72, 1.74, 2.02 and 2.20, respectively [8]. The electronegativity of gallium is 1.82 [8]. The methyl group was readily transferred to the less electronegative tin and silicon (formally reduction by tin or silicon) and transferred with more difficulty to the more electronegative germanium (possibly via free methyl radicals) and not at all to arsenic with its still greater electronegativity.

References

1 A.B. Burg and H.I. Schlesinger, J. Amer. Chem. Soc., 62 (1940) 3425.
2 F.A. Paneth and W. Hofeditz, Ber., 62 (1929) 1335
3 J.H. Purnell and R. Walsh, Proc. Roy. Soc., Ser. A, 293 (1966) 543.
4 S.R. Gunn and L.G. Green, J. Phys. Chem., 65 (1961) 779.
5 M.G. Jacko and S.J.W. Price, Can. J. Chem., 41 (1963) 1560.
6 D.T. Hurd and E.G. Rochow, J. Amer. Chem. Soc., 67 (1945) 1057.
7 G.Ya. Zueva, N.V. Luk'yankina, and V.A. Po[illegible]renko, Izv. Akad. Nauk SSSR, Ser. Khim. 6 (1970) 1448, Chem. Abstr., 73 (1970) 131090j.
8 A.L. Allred and E.G. Rochow, J. Inorg. Nucl. Chem., 5 (1958) 264.