

nitrogen does not. Stabilization of transition states by d-orbitals has been suggested before.<sup>9</sup>

Phosphorus has d-orbitals which seem to lower the energy of transition states where a negative charge is developed on an atom next to the phosphorus atom.<sup>9a</sup> We investigated the reaction of *p*-nitrobenzyltriphenylphosphonium bromide<sup>3</sup> with sodium hydroxide. This salt has been prepared previously and allowed to react with sodium hydroxide in 50% alcohol.<sup>10</sup> Triphenylphosphine oxide and *p*-nitrotoluene were reported as products but no yields were given. An aqueous solution 0.05 *M* in phosphonium salt and 0.1 *M* in sodium hydroxide was allowed to reflux on a steam bath 72 hr. A yield of 97% of crude triphenylphosphine oxide was removed by filtration and after purification through an alumina column gave 88% of analytically pure material. A 56% yield of *p*-nitrotoluene was scraped from the reflux condenser. No *p,p'*-dinitrostilbene or *p*-nitrobenzyl alcohol could be found by thin layer chromatography. Phosphorus has low-lying d-orbitals but phosphonium salts react rapidly with hydroxide ion by a mechanism other than carbene formation.<sup>11</sup> Also, although there is a scarcity of data, there is an indication that triphenylphosphine may be a rather poor leaving group relative to dimethyl sulfide.<sup>12</sup>

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#### FORMATION OF GASEOUS TITANIUM(IV) HYDRIDE AND CHLOROHYDRIDES OF TITANIUM

Sir:

Titanium compounds in which Ti is in the II, III and IV oxidation states are known but the highest known hydride of titanium is crystalline TiH<sub>2</sub>; actually, the latter is non-stoichiometric and approaches TiH<sub>2</sub> as a limiting composition.<sup>1</sup> Titanium(II) compounds are generally ionic while those of Ti(IV) are usually covalent. There has long been speculation upon the possible existence of a TiH<sub>4</sub> hydride but this compound has never been prepared. In a recent review of hydride formation by atomic hydrogen reactions, it was pointed out that many hitherto unknown hydrides might be observed if atomic hydrogen reactions with volatile compounds containing metal atoms were studied with a time of flight mass spectrometer.<sup>2</sup> Using this technique we have now observed the formation of TiH<sub>4</sub> and also previously unknown chlorohydrides of Ti(IV). This has been accomplished by following the reaction products of the mercury-photosensitized decomposition of TiCl<sub>4</sub>-H<sub>2</sub> mixtures at low pressures.

In applying the time of flight mass spectrometer technique, it is particularly desirable to place the reactor directly adjacent to the spectrometer leak which is situated in the wall of the ionization chamber.

(1) D. Hurd, "Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952.

(2) B. Siegel, *J. Chem. Educ.*, **38**, 496 (1961).

One can use the Bendix fast reaction inlet system for this purpose. In this way the mass spectrometer analyzes the reaction gas composition directly adjacent to the leak since this composition is essentially frozen upon crossing the leak; once within the ionization chamber very few molecular collisions can occur. Mixtures of H<sub>2</sub>-TiCl<sub>4</sub> (9H<sub>2</sub>:1TiCl<sub>4</sub>) saturated with mercury were irradiated with light of 2537 Å. in a reaction cell situated as described above. Mass spectra of the product mixtures were taken at reactant pressures of 30, 8 and 4 mm. using an ionizing potential of 70 electron volts. Since the reactor was continually being pumped out through the mass spectrometer leak, constant pressure of reactants was maintained by continuous introduction of pre-mixed TiCl<sub>4</sub>-H<sub>2</sub> from a large reservoir.

The reaction is very much pressure-dependent. Using the relative intensities of the mass peak 188, which corresponds principally to the major fragment ion (Ti<sup>48</sup>Cl<sub>4</sub><sup>35+</sup>), as a measure of the extent of reaction, it was observed that this reference mass peak decreased only slightly at 30 mm. after the ultraviolet source was activated, but decreased 70-74% at the lower pressures. Clearly the extent of reaction is greater at lower pressures where the hydrogen atom concentrations are larger. The gaseous products of the reaction were identified by the appearance of new or intensified mass peaks after irradiation. At 30 mm. it was not possible to detect the formation of halohydrides of Ti. However, at 8 mm. we observed an increase in the ratio of mass peaks 120/118, corresponding mainly to Ti<sup>48</sup>Cl<sub>2</sub><sup>35</sup>H<sub>2</sub><sup>+</sup>/Ti<sup>48</sup>Cl<sub>2</sub><sup>35+</sup>, and a striking increase in the ratio of mass peaks 86/83, corresponding mainly to Ti<sup>48</sup>Cl<sup>35</sup>H<sub>3</sub><sup>+</sup>/Ti<sup>48</sup>Cl<sup>35+</sup>; whereas the latter ratio is 0.04 to 0.05 prior to irradiation, it increases to 0.45 after the source is activated. At 8 mm., TiClH<sub>3</sub> is a major component of the gas phase, and some TiCl<sub>2</sub>H<sub>2</sub> is also present.

At 4 mm. one again observes an increase in the mass peak ratio 86/83, rising from 0.05 to 0.47, indicating the presence of TiClH<sub>3</sub>. However, in contrast to the runs at 8 mm. where there was little increase in intensity at mass numbers 49 through 52, at 4 mm. one observes the appearance of new peaks at 52 and 51, indicating the presence of Ti<sup>48</sup>H<sub>4</sub><sup>+</sup> and Ti<sup>48</sup>H<sub>3</sub><sup>+</sup>; one also observes substantial increases in the mass ratios 50/48 and 49/48, mainly attributable to Ti<sup>48</sup>H<sub>2</sub><sup>+</sup> and Ti<sup>48</sup>H<sup>+</sup>. This certainly demonstrates that TiH<sub>4</sub> was formed, but the lower hydride peaks may be fragmentation patterns of TiH<sub>4</sub> rather than indicative of TiH<sub>3</sub>, TiH<sub>2</sub> and TiH.

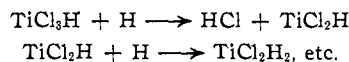
It is known that TiCl<sub>4</sub> can be reduced with H<sub>2</sub> at higher pressures<sup>3</sup> and temperatures, and also by electric discharge,<sup>4</sup> to form TiCl<sub>3</sub>(s) and TiCl<sub>2</sub>(s), as well as HCl. Since little change in the gas composition was noted at 30 mm. in our experiments, several experiments were performed in another apparatus to verify the extent of the mercury-photosensitized reaction at higher pressures. In particular, it was intriguing to determine whether crystalline subhalides of titanium could be prepared by this technique from TiCl<sub>4</sub> alone or TiCl<sub>4</sub> and H<sub>2</sub> at room temperature. However, no appreciable reactions were noted for short reaction times with TiCl<sub>4</sub> vapor alone or a 9:1 mixture of H<sub>2</sub>-TiCl<sub>4</sub> at 90 mm. These experiments were carried out in an infrared cell with NaCl windows in a plane perpendicular to one containing a quartz window. If reaction did proceed, then HCl would have been

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formed, but this gas could not be found as evidenced by the lack of infrared absorption at 2950 and 2850  $\text{cm}^{-1}$ . Nevertheless, upon standing for several weeks, a  $\text{TiCl}_4\text{-H}_2$  mixture at 90 mm. was observed to react slowly at room temperature to form the brown solid characteristic of the titanium subhalides.

Since the dissociation energy at 25° for the reaction  $\text{TiCl}_4(\text{g}) \rightarrow \text{TiCl}_3(\text{g}) + \text{Cl}$  is only 79 kcal./mole,<sup>5</sup> the excited mercury atoms are capable of producing this dissociation step, as well as  $\text{H}_2 \rightarrow 2\text{H}$ . Thus mercury photosensitization of the mixture  $\text{TiCl}_4 + \text{H}_2$  should lead to  $\text{TiCl}_3(\text{g})$ , Cl and H in primary steps. However, Cl undoubtedly reacts with the excess  $\text{H}_2$  to form  $\text{HCl} + \text{H}$  and thus  $\text{Hg}^*$ -induced decomposition of  $\text{TiCl}_4$  also leads to atomic hydrogen formation. The chlorohydride  $\text{TiCl}_3\text{H}$  can be formed by the simple step  $\text{TiCl}_3 + \text{H} \rightarrow \text{TiCl}_3\text{H}$ . Note that reaction between H and  $\text{TiCl}_4$  would lead to the formation of  $\text{HCl} + \text{TiCl}_3$ , furnishing more of the latter as precursor of the chlorohydride. At lower pressures where the concentrations of H are expected to be higher,  $\text{TiCl}_3\text{H}$  can be converted to  $\text{TiH}_4$  and higher chlorohydrides by reactions such as



At high pressures where the concentrations of H are small by comparison with  $\text{TiCl}_3(\text{g})$  or  $\text{TiCl}_2(\text{g})$ , it is not surprising that crystalline subhalides form rather than chlorohydrides or  $\text{TiH}_4$ . Under these conditions  $\text{TiCl}_3(\text{g}) \rightarrow \text{TiCl}_3(\text{s})$  and  $\text{TiCl}_2(\text{g}) \rightarrow \text{TiCl}_2(\text{s})$  are more probable steps than those leading to hydride formation.

(5) This value was calculated from thermochemical data in the JANAF Thermochemical Tables, Dow Chemical Co., Midland, Michigan, Dec. 31, 1961.

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### AFATOXINS B AND G

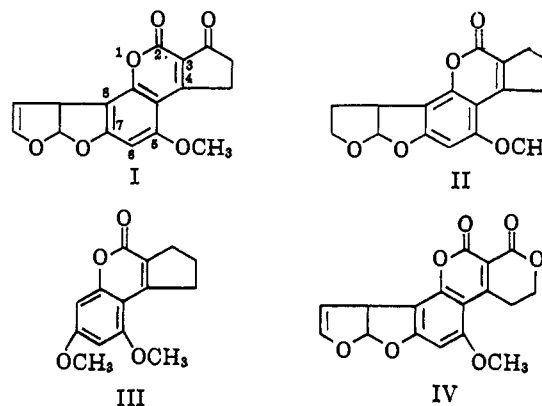
Sir:

Many outbreaks of an unusual toxicity in several domestic animal species have been reported in Britain.<sup>1</sup> The causative agents have been identified as metabolites of the fungus *Aspergillus flavus* Link ex Fries which infests feed ingredients during harvest or storage.<sup>2</sup> Preliminary reports have dealt with the isolation and characterization of two toxins produced by this mold.<sup>3-5</sup>

This communication is concerned with the isolation and structure elucidation of the two major toxic metabolites. The compounds were isolated from 200 mg. of crude extract generously provided by the U. S. Food and Drug Administration. This concentrate proved to contain substantially greater activity than similar extracts prepared previously in this Laboratory utilizing a different mold variant. The material was prepared as follows. Cultures of *A. flavus* Link ex Fries were grown on sterilized crushed wheat, extracted with chloroform and the toxins precipitated by adding 20 volumes of petroleum ether. Fractionation into individual components was accomplished by thin layer chromatography. The two major components (out of

fifteen discernible) appeared as blue-fluorescent and yellow-green fluorescent bands.

The substance exhibiting blue fluorescence,  $\text{C}_{17}\text{H}_{12}\text{O}_6$ , mol. wt. 312 (mass spec.)<sup>6</sup> had m.p. 268–269° dec.,  $[\alpha]_D^{25} \text{CHCl}_3 -558^\circ$ ;  $\lambda_{\text{max}}^{\text{EtOH}}$  223, 265, 362  $\text{m}\mu$  ( $\epsilon$  25,600; 13,400; 21,800);  $\nu_{\text{max}}^{\text{CHCl}_3}$  1760, 1665, 1630, 1600  $\text{cm}^{-1}$ . These constants demonstrated identity with the previously described aflatoxin B.<sup>3</sup> Catalytic reduction in ethanol over palladized charcoal was complete after three moles of hydrogen had been absorbed. The resulting product (II)  $\text{C}_{17}\text{H}_{16}\text{O}_6$ , m.p. 272–274°, mol. wt. 300 (mass spec.);  $[\alpha]_D^{25} \text{CHCl}_3 -312^\circ$ ;  $\nu_{\text{max}}^{\text{CHCl}_3}$  1705 (reduced intensity), 1625, 1600  $\text{cm}^{-1}$  gave important information concerning the structure of the toxin. Its ultraviolet spectrum  $\lambda_{\text{max}}^{\text{EtOH}}$  255, 264, 332  $\text{m}\mu$  ( $\epsilon$  8,500; 9,200; 13,900) had a shape identical with that of the synthetic coumarin (III), m.p. 182–184°, but all three maxima in the reduction product were displaced to longer wave lengths by 7  $\text{m}\mu$ . The changes in molecular composition and infrared absorption accompanying catalytic reduction are explainable if aflatoxin B contains a carbonyl group in a five membered ring and cross conjugated with the  $\alpha,\beta$ -unsaturated lactone function.



The nature of the sixth oxygen atom and of the remaining carbon atoms was revealed by the n.m.r. spectrum of aflatoxin B (all in  $\text{CDCl}_3$ ; chemical shifts in p.p.m. from tetramethylsilane) which had signals at 6.89 (doublet,  $J = 7$  c.p.s., 1H); 6.52 (triplet,  $J = 2.5$  c.p.s., 1H); 5.53 (triplet,  $J = 2.5$  c.p.s., 1H); 4.81  $\delta$  (triplets of doublet,  $J = 2.5$  and 7 c.p.s., 1H). Such a pattern can arise from the four protons of a dihydrofuran ring and agrees with that found in analogous situations.<sup>7</sup> Additional signals at 6.51 (singlet, 1H) and 4.02  $\delta$  (singlet, 3H) can be assigned to an aromatic and three methoxy protons while the remaining four protons exhibit  $A_2B_2$  type absorption at 3.42 and 2.61  $\delta$ , respectively. The spectrum of the reduction product (II) lacked signals for vinylic protons but the peaks due to the acetal (6.42, doublet,  $J = 5.5$  c.p.s.), aromatic (6.30, singlet) and methoxy protons (3.82  $\delta$ , singlet) were still present. Furthermore, the portion of the spectrum representing the six cyclopentane protons is identical in detail with that of the coumarin (III). To complete the argument the attachment of the four carbon side chain to the coumarin ring had to be considered. The n.m.r. spectrum of the synthetic coumarin (III) exhibits aromatic proton signals at 6.35 (doublet,  $J = 2.5$  c.p.s.) and 6.55  $\delta$  (doublet,  $J = 2.5$  c.p.s.).

Earlier experience<sup>7</sup> suggests that the high field signals are due to the  $\text{C}_6$  proton and because the aro-

(6) We wish to thank Professor K. Biemann and Mr. H. Schnoes for the mass spectra.

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