

To the 300th Anniversary of the founding of St. Petersburg University

## Thermal Decomposition of the Complex [tBu<sub>3</sub>PH][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]

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**Abstract**—The thermal stability of the [tBu<sub>3</sub>PH][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] complex, which is a product of molecular hydrogen activation by the tBu<sub>3</sub>P·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> frustrated Lewis pair (FLP), was studied using a static tensimetric method with a membrane null-manometer. It was found that heating [tBu<sub>3</sub>PH][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] to temperatures above 430 K is accompanied by thermal dissociation with passing into vapor of molecular hydrogen, pentafluorobenzene, and 2-methylpropene, as the main volatile products.

**Keywords:** tensimetry, tris(pentafluorophenyl)borane, Frustrated Lewis Pairs (FLP), donor-acceptor complex, thermal decomposition

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### INTRODUCTION

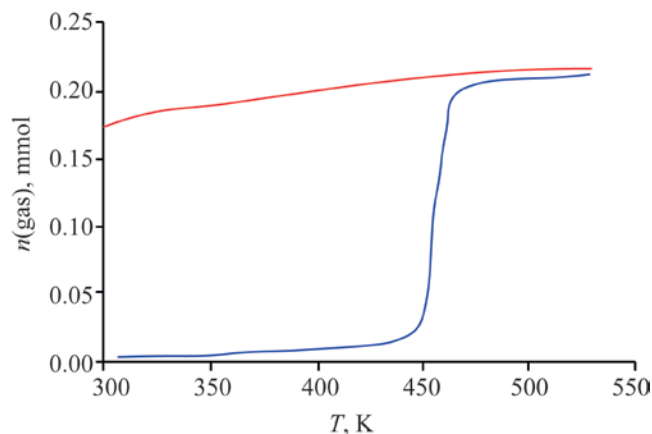
Activation of hydrogen molecules is an urgent task for many chemical processes using hydrogen as a reducing agent in synthetic chemistry. In 2006, D.V. Stefan's group discovered hydrogen binding by the (C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>2</sub>P(C<sub>6</sub>F<sub>4</sub>)·B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> system at room temperature [1]. Further studies have shown that combinations of strong acids and Lewis bases, which do not form classical donor-acceptor complexes due to steric hindrances, have a similar property [2]. Such systems were called Frustrated Lewis Pairs (FLP). A number of studies have shown the promise of FLP for the activation of small molecules (H<sub>2</sub>, CO, and CO<sub>2</sub>) in various reactions with alkenes, alkynes, ketones, and amines [3–10]. It was noted that hydrogen binding by FLPs is reversible upon heating and pressure lowering [1, 5, 9–10]. The thermodynamic characteristics of FLP·H<sub>2</sub> ↔ FLP + H<sub>2</sub> processes determined by quantum chemical calculations [5, 11–13] significantly depend on the choice of calculation methods. The experimental values of the thermodynamic characteristics of the processes are important for the correct choice of the method and the basis for quantum chemical calculations, which was previously noted for a similar system B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>·Py [14]. The study of FLP-activated hydrogen using TGA/DSC methods is usually hampered by the

high sensitivity of compounds to moisture and oxygen, and also by low hydrogen content by weight (less than 0.3% for the (C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>2</sub>P(C<sub>6</sub>F<sub>4</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>·H<sub>2</sub> system.

The system of tritertbutylphosphine tBu<sub>3</sub>P with trispentafluorophenylborane B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is a classic example of a frustrated Lewis pair that can absorb hydrogen at room temperature and atmospheric pressure in a toluene medium and form the compound [tBu<sub>3</sub>PH][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] [15, 16]. It was noted that hydrogen is not released from a solution of [tBu<sub>3</sub>PH][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] in toluene at temperatures up to 420 K [15]. At the same time, in the absence of a solvent and at low pressure, [tBu<sub>3</sub>PH][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] can dissociate with the hydrogen release. In this regard, the experimental study of [tBu<sub>3</sub>PH][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] dissociation processes occurring at elevated temperatures and under low pressure is provided. It is useful for choosing the correct methods of quantum chemical calculations. In this work, a mass spectrometric and tensimetric study of [tBu<sub>3</sub>PH][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] was performed to establish the limits of its thermal stability.

### RESULTS AND DISCUSSION

**The mass spectrometric study** showed that in the temperature range 310–480 K, the mass spectrum of vapor above [tBu<sub>3</sub>PH][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] contains ions with



**Fig. 1.** Temperature dependence of the amount of substance in the gas phase for the  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$  system. The heating curve is given by a blue line, and the cooling curve is red line. Heating rate 0.1 K/min, cooling rate 0.15 K/min.

isotopic distribution and  $m/z$  values corresponding to toluene ( $\text{C}_7\text{H}_8^+$ , 19%), pentafluorobenzene ( $\text{HC}_6\text{F}_5^+$ , 30%), and ditertbutylphosphine ( $\text{tBu}_2\text{PH}^+$ , 17%;  $\text{tBu}^+$ , 100%). This points to the release of solvent residues and thermal decomposition of the compound under study. In the temperature range 490–570 K, the mass spectrum of vapor over  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$  shows an increase in the absolute intensity of pentafluorobenzene ( $\text{HC}_6\text{F}_5^+$ , 100%) and ditertbutylphosphine ( $\text{tBu}_2\text{PH}^+$ , 52%;  $\text{tBu}^+$ , 58%), and also the appearance of ions corresponding to passing trispentafluorophenylborane to the gas phase [17]. Note that according to [14], trispentafluorophenylborane passes into the gas phase under similar evaporation conditions at significantly lower temperatures (370–380 K), which indicates the absence of free  $\text{B}(\text{C}_6\text{F}_5)_3$  in the condensed phase at temperatures up to 490 K. Ions indicating passing tritertbutylphosphine to the gas phase have not been detected. Thus,  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$  under nonequilibrium evaporation conditions undergoes thermal dissociation. In the temperature range 310–480 K, toluene impurities are evolved and slow decomposition with the elimination of pentafluorobenzene and ditertbutylphosphine is observed. At a temperature of 490 K, the thermal dissociation process is significantly intensified and boron-containing ions corresponding to the transition of  $\text{B}(\text{C}_6\text{F}_5)_3$  to the gas phase are established in the mass spectrum of vapor over  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ .

**The tensimetric study** was carried out by a static tensimetric method with a membrane null-manometer using an automatic tensimetric equipment [18]. The

accuracy of temperature measurement was 0.01 K and the accuracy of pressure measurement was 0.1 mmHg. The sample of  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ , 41(3) mg, 0.057(4) mmol, was placed in a valve in an argon atmosphere, evacuated, and soldered. The sample was introduced into the inner volume of the membrane chamber, 19.1(1) mL, by soldering the valve to the tensimeter. After evacuation of the internal volume of the tensimeters membrane chamber (residual pressure less than  $10^{-3}$  torr), the thin glass membrane of the valve was mechanically broken. Further the tensimeter was placed in a furnace and heated to 530 K at a rate of 0.1 K/min and then cooled to room temperature at a rate of 0.15 K/min. The temperature dependence of the amount of gas in the system is shown in Fig. 1.

When  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$  was heated from room temperature to 430 K, the number of gas moles in the system slow increased up to 0.013(1) mmol at 430 K. Further heating led to intense gas release in the temperature range of 430–480 K. When the temperature reached 530 K, 0.214(1) mmol of gas was released, which corresponds to 3.75(24) mol of gas per 1 mol of  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ . Cooling of the tensimeter led to partial condensation of gas in the system (0.042(1) mmol) the ratio  $n(\text{gas})/n([\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3])$  at 300 K being 3.02(24). When the tensimeter was cooled to the liquid nitrogen temperature (77.4 K), condensation of most of the gas phase was observed. The amount of non-condensable gas in the system was 0.044(4) mmol. The only possible non-condensable gas in the system is hydrogen. Calculations showed that 0.77(8) mol of hydrogen were released per 1 mol of  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ .

After removing the tensimeter from the furnace, the formation of a viscous light yellow liquid was visually observed. The volatile decomposition products were condensed into a glass ampoule with liquid nitrogen, but the light yellow liquid was practically not distilled. The ampoule was sealed from the system without defrosting. After defrosting the ampoule, a small amount of liquid was observed. The ampoule with a sample of volatile components was opened in an argon atmosphere in an InertLab 2GB glove box. Then 0.8 mL of  $\text{C}_6\text{D}_6$  was added to the liquid. The resulting solution was transferred to an NMR ampoule. NMR spectroscopy results  $\{^1\text{H NMR} (\text{C}_6\text{D}_6): 1.60 \text{ t} (J = 1.1 \text{ Hz}, 6\text{H}, 2\text{-methylpropene}), 4.75 \text{ m} (2\text{H}, 2\text{-methylpropene}), 5.80 \text{ m} (\text{HC}_6\text{F}_5); ^{19}\text{F}\{\text{H}\} \text{ NMR} (\text{C}_6\text{D}_6): -162.35 \text{ m} (\text{HC}_6\text{F}_5),$

–154.07 t ( $J = 20.8$  Hz,  $\text{HC}_6\text{F}_5$ ), –139.48 s, –139.13 m ( $\text{HC}_6\text{F}_5$ );  $^{31}\text{P}\{\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): –137.26 s) showed the presence of 2-methylpropene [19] and pentafluorobenzene [20] as the main products. Unidentified signals from fluorine and phosphorus nuclei indicate the presence of other compounds in the system.

The results of the tensimetric study indicate that at temperatures above 430 K, intensive processes are accompanied by the release of hydrogen, 2-methylpropene, and pentafluorobenzene from  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ . The release of 2-methylpropene was noted in [19], when studying the reaction of  $\text{tBu}_3\text{P}$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  with the formation of  $[\text{tBu}_3\text{PH}][\text{FB}(\text{C}_6\text{F}_5)_3]$  and  $p\text{-tBu}_2\text{PC}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_2$ . This indicates the beginning of hydrogen cleavage from  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$  with the formation of free  $\text{tBu}_3\text{P}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  at 430 K. The release of pentafluorobenzene is possible with further thermal decomposition of the resulting compounds. Our experimental results are in qualitative agreement with the results of quantum chemical calculations [13] and with the previously observed thermal stability of  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$  in toluene medium up to temperatures of 420 K [15].

## CONCLUSIONS

It has been established by the methods of mass spectrometry and static tensimetry with a membrane null-manometer that heating  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$  in vacuum above 430 K results in processes accompanied by the release of hydrogen, 2-methylpropene, and pentafluorobenzene. The evolution of 2-methylpropene points to the formation of free  $\text{tBu}_3\text{P}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  upon evolution of molecular hydrogen from the starting compound. The increase in the amount of gas in the system in the range 310–430 K may indicate the release of solvent residues and slow thermal decomposition of the sample. The experimental results are in qualitative agreement with the published data.

## EXPERIMENTAL

In order to exclude the interaction of moisture and oxygen in the air with the sample, all operations of the synthesis and sample taking were carried out using a Schlenk line or an InertLab 2GB glove box in a pure argon atmosphere (moisture and oxygen content less than 0.1 ppm). Deuterodichloromethane (Carl Roth, 99.8% D) was dried over  $\text{CaH}_2$ , after which it was distilled and stored

over activated zeolites of grade 4 Å. Toluene (Vecton, pure grade), deuterobenzene (Carl Roth, 99.5% D), and hexane (Vecton, pure grade) were dried over a Na/K eutectic alloy, distilled, and stored over activated zeolites of grade 4 Å. Tris(pentafluorophenyl)borane  $\text{B}(\text{C}_6\text{F}_5)_3$  was synthesized by a well-known technique [21] and purified by sublimation in vacuum. Tritertbutylphosphine  $\text{tBu}_3\text{P}$  (Sigma Aldrich, 98%) was used without additional purification. The purity of  $\text{tBu}_3\text{P}$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  was monitored by NMR spectroscopy. Hydrogen (99.99%) was additionally dried by passing through a trap cooled by liquid nitrogen.

NMR studies were performed on a Bruker AVANCE 400 device at room temperature. TMS, 1M  $\text{H}_3\text{PO}_4$ , and  $\text{CFCl}_3$  were used as external standards. The resonant frequency in  $^1\text{H}$  NMR is 400 MHz, in  $^{19}\text{F}\{\text{H}\}$  NMR is 376.5 MHz, and in  $^{31}\text{P}\{\text{H}\}$  NMR is 162 MHz. The chemical shift is indicated in ppm. The mass spectrometric study was performed on a Thermoscientific ISQ mass spectrometer with a DIP direct input controller. Ionization was carried out by electron impact at electron energy of 70 eV. The  $m/z$  interval was 15–1100 Da. The temperature range of the study was 310–570 K, the heating rate of the sample is 10 K/min. A sample (1–2 mg) in an InertLab 2GB glove box in an argon atmosphere was placed in a glass capillary sealed at one end (length 10 mm, diameter 2 mm, wall thickness 0.2 mm), after which it was transferred into a mass spectrometer.

The compound  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$  was synthesized according to the published method [16] by dissolving tris(pentafluorophenyl)borane (500 mg, 0.976 mmol) and tritertbutylphosphine (198 mg, 0.978 mmol) in 20 mL of toluene. The resulting solution was placed in a flask, which was then evacuated and filled with hydrogen at a pressure of 2 atm. An immediate formation of a white precipitate was observed. The solution was stirred for 2 h, after which the precipitate was filtered off and washed with hexane. After removal of volatile components in vacuum ( $10^{-1}$  torr), a powdered product weighing 184.1 mg was obtained. Yield 26%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 1.63 d ( $J = 15.8$  Hz, 27H,  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ ), 3.61 q ( $J = 89$  Hz, 1H,  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ ), 4.97 d ( $J = 283$  Hz, 1H,  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ ).  $^{19}\text{F}\{\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): –167.48 m ( $\text{C}_6\text{F}_5$ ), –164.56 t ( $J = 20.4$  Hz,  $\text{C}_6\text{F}_5$ ), –133.80 d ( $J = 30.2$  Hz,  $\text{C}_6\text{F}_5$ ).  $^{31}\text{P}\{\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 59.86 s. The results of NMR spectroscopy are qualitatively consistent with the literature data for  $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$  in  $\text{C}_6\text{D}_5\text{Br}$  [16].

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## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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