

## THE Hg ( $6^3P_1$ ) PHOTSENSITIZED DECOMPOSITION OF TRIETHYLBORANE

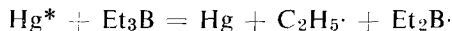
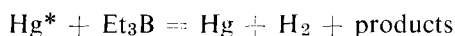
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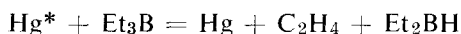
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### SUMMARY

The Hg ( $6^3P_1$ ) photosensitized decomposition of triethylborane at room temperature gives hydrogen, ethane, ethylene and butane as the main volatile products. To elucidate the reaction mechanism, the effect of added gases such as 1,3-butadiene, propylene, nitrous oxide, hexafluoroethane, carbon dioxide and deuterium were examined under various experimental conditions. It was found that the main primary processes can be represented by:



and probably:



with primary quantum yields of 0.3,  $\geq 0.3$  and  $\leq 0.07$  respectively.

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### INTRODUCTION

The only reported studies of a Hg atom photosensitized decomposition of organometallic compounds are those reported for the alkyl derivatives of mercury and silicon compounds<sup>1, 2</sup>. There are also some recent studies on the photolysis of organo-lithium and organo-aluminium compounds in the presence of mercury<sup>3, 4</sup>, but the mechanism does not seem to involve sensitized decomposition by the Hg ( $6^3P_1$ ). Trialkyl boron compounds are of particular interest because of the several reaction paths available and the possibility of specific interaction between the mercury triplet and the vacant *p* orbital of the central atom. In the present work we have carried out a study of the photosensitized decomposition of triethylborane.

## EXPERIMENTAL

A conventional high vacuum apparatus was employed, with a Pyrex reaction cell (250 cm<sup>3</sup>) provided with a quartz window 5 cm in diameter. A drop of mercury present in the reaction cell assured saturation with mercury vapour. A Corning 7910 glass filter was used to eliminate the 1849 Å radiation.

All runs were carried out at room temperature and with a total absorbed intensity of  $1.7 \times 10^{16}$  quanta/s.

Photolyses were carried out using a Phillips low pressure mercury lamp as source of 2537 Å radiation.

The reaction products were fractionated as follows: (a) non-condensable at solid nitrogen temperature. They were measured in a Toepler pump or analyzed by gas chromatography over a column of molecular sieve; (b) condensables at  $-100^\circ\text{C}$ . This fraction consists of the unreacted triethylborane and heavier reaction products. It was not analyzed; (c) condensables at solid nitrogen temperature. They were analyzed by gas-liquid chromatography (g.l.c.).

Triethylborane was an Ethyl Corporation product. Before each run it was degassed from a  $-100^\circ\text{C}$  bath.

1,3-Butadiene, propylene, nitrous oxide, ethane, hexafluoroethane, carbon dioxide and deuterium were all from Matheson. All reactants were thoroughly degassed and purified by trap-to-trap distillation, except deuterium, which was used without purification.

## RESULTS

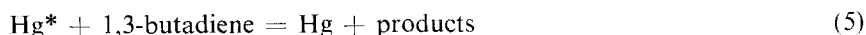
The rate constant for the quenching of the excited mercury atom by triethylborane (TEB) was determined by the method described by Cvetanovic<sup>5</sup>. Mixtures of nitrous oxide and ethane (1:1 ratio) were photolyzed in the presence of different amounts of TEB. Under these conditions, the rate of nitrogen production is determined by reactions (1) to (3):



and hence

$$(R_{\text{N}_2})_0 / (R_{\text{N}_2}) = 1 + (k_3/k_2) \times [(\text{Et}_3\text{B})/(\text{N}_2\text{O})] \quad (4)$$

where  $(R_{\text{N}_2})_0$  measures the rate of nitrogen production in the absence of TEB. From the results shown in Fig. 1,  $k_3/k_2 = 2.3$ . When the same method was applied to 1,3-butadiene, it was found that  $k_5/k_2 = 2.7$ , where reaction (5) is:



For this ratio, the value previously reported is 2.6<sup>6</sup>.

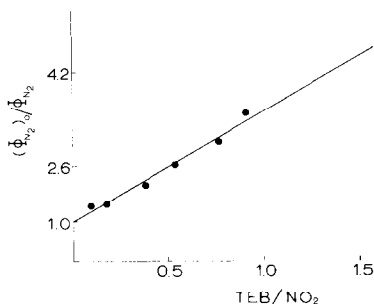


Fig. 1. Competitive quenching of Hg\* by TEB and N<sub>2</sub>O.

Since under our experimental conditions the  $(\Phi_{N_2})_0$  can be taken as unity<sup>5</sup>, the value of  $(R_{N_2})_0$  was employed as a measure of the absorbed intensity.

The  $(R_{N_2})_0$  was nearly independent of total pressure, showing that pressure broadening is not important under our experimental conditions.

In the photolysis of TEB, the main products analyzed were hydrogen, ethane, ethylene and butane. Traces of propane were also observed among the reaction products. Methane could not be detected. Both the amount of products and their distribution were nearly independent of TEB pressure from 5 to 23 Torr (see Fig. 2). The reproducibility of the ethane quantum yield was poor and minor amounts of this product were also observed in 'dark' runs. Therefore, no systematic analyses of this product were carried out.

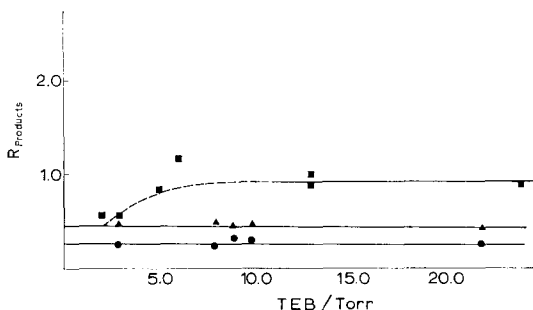


Fig. 2. Product yields as a function of TEB pressure. ●, Ethylene; ■, hydrogen; ▲, butane.

The rate of product formation was nearly independent of reaction time (see Fig. 3). Furthermore, successive photolyses, using the same TEB (up to 12.5% conversion) gave essentially the same product quantum yields.

The product distribution was also independent of light intensity. This effect is shown in Fig. 4.

The effect of added propylene and 1,3-butadiene upon the main products is shown in Fig. 5 and 6.

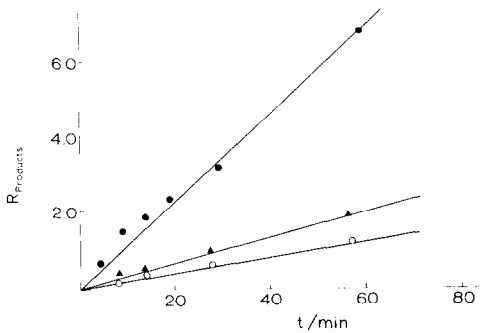


Fig. 3. Product yields as a function of reaction time.  
TEB pressure: 8 Torr. O, Ethylene; ●, hydrogen; ▲, butane.

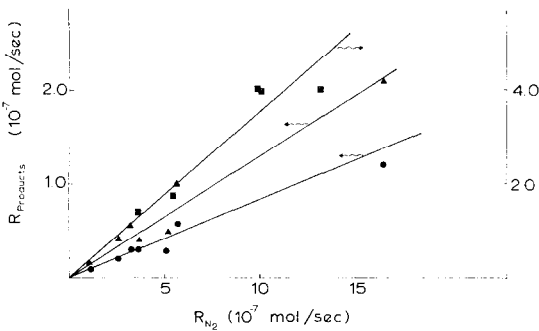


Fig. 4. Product yields as a function of light intensity.  
(Rates are given in mol/s.) ▲, Rate of butane production; ●, rate of ethylene production; ■, rate of hydrogen production.

The total decomposition quantum yield obtained at 8 Torr pressure was nearly 0.75. This yield was evaluated from:

$$\Phi_{\text{Dec.}} = \Phi_{\text{H}_2} + \Phi_{\text{C}_2\text{H}_4} + \Phi_{\text{C}_2\text{H}_6} + 2\Phi_{\text{C}_4\text{H}_{10}} \quad (6)$$

The uncertainty introduced by the 'dark' ethane is less than 0.05.

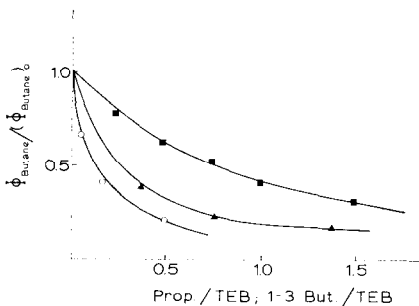


Fig. 5. Effect of added olefins on  $\Phi_{\text{Butane}}$ . O, 1,3-Butadiene added; ▲, propylene added; ■, calculated by applying eqn. (12) to propylene and 1,3-butadiene.

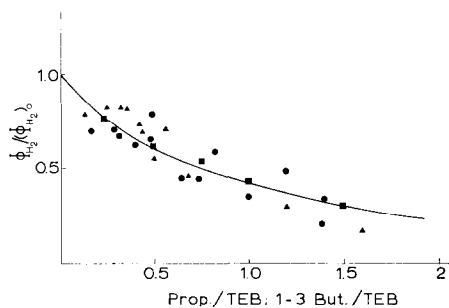


Fig. 6. Effect of added olefin on  $\Phi_{H_2}$ ; ▲, 1,3-Butadiene added; ●, propylene added; ■, calculated by applying eqn. (12) to propylene and 1,3-butadiene.

#### *The reactions of D atoms with triethylborane*

The mercury photosensitized decomposition of  $D_2$  in the presence of TEB and TEB/1,3-butadiene mixtures, was studied in order to investigate the reaction of D atoms with TEB. The method used was that of Cvetanovic<sup>7</sup>. Some of the results obtained are shown in Table 1.

TABLE 1

EFFECT OF ADDED GASES ON PRODUCT YIELDS

$P_{TEB}/Torr$	$P_{D_2}/Torr$	$P_{CO_2}/Torr$	$P_{1,3-But}/Torr$	$\Phi_{C_4H_{10}}$	$\Phi_{H_2}$	$\Phi_{H_2}^a$
5				0.139		
5	160			0.354		
7	150		2	<0.017		
4	150		3	<0.013		
8					0.30	
8		44			0.265	0.195
5		45			0.222	0.159
8		80			0.144	0.150
5		60			0.105	0.132
8		172			0.051	0.099

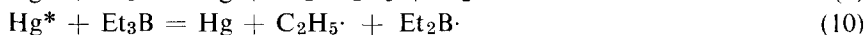
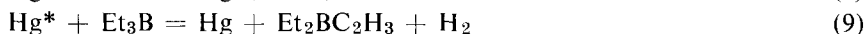
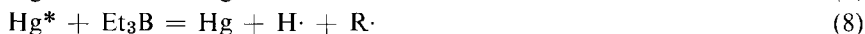
<sup>a</sup> Evaluated from eqn. (12) with  $(k_Q)_{CO_2}/k_3 \sim 0.1$ .  
Irradiation time: 15 min.  $I_a = 1.7 \times 10^{16}$  quanta/s.

#### DISCUSSION

The results shown in Figs. 2, 3 and 4, together with the fact that successive photolyses gave the same products indicate that secondary photolysis of primary products are unimportant. Furthermore, direct photolysis of TEB can also be disregarded since it only absorbs radiation at wavelengths shorter than 2100 Å<sup>8</sup>. The change in product quantum yields observed at low pressures is similar to

that reported in similar systems<sup>9</sup> and can be related to wall effects. Accordingly, a small decrease in  $(R_{X_2})_0$  was observed when mixtures of N<sub>2</sub>O and ethane were photolyzed at low pressures.

There are several ways in which the reported products can be produced in the system. The possible initial steps are:



All these reactions can be justified on thermochemical and mechanistic grounds. The relatively high cross-section found in the present work for reaction (3) (relative to that of a hydrocarbon of similar size) would be compatible with a specific interaction between the Hg\* and the central atom in TEB. It should be stated that a high rate of reaction (8), induced by the weakness of the C–H bond in TEB<sup>10</sup>, would also explain the high rate of reaction (3)<sup>11</sup>. Nevertheless, since some of the main products arise from other primary steps than reaction (8) (see following discussion) we have to conclude that a weak C–H bond cannot completely explain the high cross-section obtained.

In order to elucidate the source of the main products, some runs were carried out in the presence of carbon dioxide, propylene and 1,3-butadiene. If the only effect of the added gas were to quench the Hg\*, it can be derived that:

$$R/R_0 = \frac{1}{1 + [k_Q(Q)/k_3(\text{TEB})]} \quad (12)$$

where  $R$  is the rate of production of a given product and  $k_Q$  is the rate constant for the quenching of Hg\* by the quencher introduced. Values of  $R/R_0$  obtained by applying eqn. (12) have been included in Figs. 5 and 6 (propylene and 1,3-butadiene as quenchers) and Table 1. The values of  $k_Q$  for propylene and carbon dioxide were obtained from the literature<sup>6</sup>. In the runs with 1,3-butadiene, a small correction has to be introduced to take into account the molecular hydrogen produced in reaction (5)<sup>12</sup>. Nevertheless, the value of  $\Phi_{\text{H}_2}$  in this reaction is small and does not invalidate the use of eqn. (12). This fact is also supported by the low values that  $\Phi_{\text{H}_2}$  reaches at high 1,3-butadiene/TEB (see Fig. 6).

#### Source of hydrogen

Hydrogen can arise from reaction (8) followed by:



or from reaction (9). The results shown in Fig. 6 strongly argue against reaction (13) as the main hydrogen source since: (a) the decrease in  $\Phi_{\text{H}_2}$  can be accounted

by the quenching of Hg\* by the added gas; (b) the effect of butadiene is similar to that of propylene in spite of the fact that: (i) propylene gives hydrogen atoms when reacting with Hg\*<sup>13</sup>; and (ii) the addition of hydrogen atoms to 1,3-butadiene is faster than that to propylene<sup>14</sup>.

We can consider then that the main source of hydrogen is reaction (9) and that only a minor fraction of it could arise from reaction (13). On the other hand, the occurrence of reaction (13) with participation of 'hot' hydrogen atoms is against the accepted mechanism for the occurrence of reactions such as reaction (8)<sup>10</sup>. Furthermore, the effect of carbon dioxide upon  $\Phi_{H_2}$  (Table 1) does not indicate any 'hot' atom influence since it can also be accounted by the quenching of Hg\*. In agreement with this, hexafluoroethane, a poor Hg\* quencher, has very little effect upon  $\Phi_{H_2}$ .

There are several systems in which molecular hydrogen is produced in a Hg\* photosensitized decomposition<sup>15</sup>. In most cases, the mechanism involves a two step process: an initial energy transfer followed by a unimolecular decomposition of the excited molecule produced. In this case, the process could be assisted by the stability of the compound produced in reaction (9)<sup>16</sup>. The fact that the decomposition of the excited molecule follows in the present case a reaction path different from that of the thermal decomposition<sup>17</sup>:



can be associated with the high energy available after the initial energy transfer and the fact that:



has very likely a higher *A* factor than that associated with reaction (14) (rough calculations indicate that  $A_{15}/A_{14} \approx 12$ , the difference being mostly due to the fact that only one internal rotation is lost during reaction 15).

#### *Source of butane*

Butane can be produced molecularly in a reaction such as:



or by recombination of ethyl radicals. The data shown in Fig. 5 indicate that reaction (16) cannot be the only source of butane. Furthermore, the presence of ethylene, ethane (and some propane) is compatible with the production of ethyl radicals. The source of the ethyl radicals can be either reaction (10) or a secondary reaction of hydrogen atoms:



The data shown in Figs. 3 and 5 argue against the occurrence of reaction (18). The data obtained with 1,3-butadiene are particularly conclusive since, with the small amount of ethylene present, reaction (18) cannot be competing with:



Reaction (17) can be disregarded since the results shown in Table I indicate that small amounts of 1,3-butadiene suppress almost completely the butane production, when this is produced through reaction (17). We consider then that the most likely source of ethyl radicals is reaction (10) and that the decrease in  $\Phi_{\text{Butane}}$  shown in Figs. 3 and 5 is different from that predicted by eqn. (12), owing to secondary reactions of the ethyl radicals (i.e. addition to the olefins or recombination with the radicals produced in the quenching of  $\text{Hg}^*$  by propylene).

Reaction (10) can be considered as another example of a homolytic substitution on a boron atom. This type of reaction has been found to be extremely fast for several excited triplets<sup>18</sup>.

#### Source of ethylene

Under all our experimental conditions we found that  $\Phi_{\text{C}_2\text{H}_4} > 0.12 \Phi_{\text{Butane}}$  showing that there is another source of ethylene other than ethyl radical disproportionation. A reaction between hydrogen atoms and ethyl radicals can be disregarded since the ethylene quantum yield does not increase with light intensity (see Fig. 2). The same conclusion can be reached from the small effect of propylene and butadiene upon the  $\Phi_{\text{C}_2\text{H}_4}$ . Other possible ethylene sources are reaction (11) or reaction (10) followed by:



Both possible ethylene sources involve the production of  $\text{Et}_2\text{BH}$  and hence a decrease in  $\Phi_{\text{C}_2\text{H}_4}$  with conversion could be expected due to the occurrence of:



which is supposed to be extremely fast<sup>17</sup>. The lack of this effect as well as the fact that  $\Phi_{\text{C}_2\text{H}_4}$  does not increase when small amounts of propylene are added, indicates that this reaction is not important. The most likely explanation is that  $\text{Et}_2\text{BH}$  is scavenged by other olefins produced in the system (i.e.  $\text{Et}_2\text{BC}_2\text{H}_3$ ).

#### Source of propane

The presence of small amounts of propane suggests the occurrence of a primary process represented by:



followed by methyl-ethyl combination. From the relative amounts of propane and butane we can estimate that  $\Phi_{22} \approx 0.003$ .



*Physical quenching*

The amount of physical quenching (reaction 7) can be estimated from the total decomposition yield. In this way, only an upper limit can be obtained and this can be affected by large errors. The estimated quantum yield for the different primary reactions are given in Table 2.

TABLE 2

PRIMARY QUANTUM YIELDS

$\Phi_7$	$\Phi_8$	$\Phi_9$	$\Phi_{10}^a$	$\Phi_{11}^b$	$\Phi_{22}$
$\leq 0.3$	$< 0.1$	0.3	$\geq 0.3$	0.07	$\approx 0.003$

<sup>a</sup> Evaluated from  $\Phi_{10} = 2.24 \Phi_{\text{Butane}}$ .

<sup>b</sup> Evaluated from  $\Phi_{11} = \Phi_{C_2H_4} - \Phi_{\text{Butane}} \times 0.12$ .

Results obtained at 8 Torr of TEB.

The result for  $\Phi_{10}$  given in Table 2 can be an underestimation since ethyl radicals can be lost in reaction with other radicals present in the system.

From Table 2 and the preceding discussion it can be concluded that TEB shows a peculiar behaviour towards Hg\*. This fact can be rationalized in terms of an initial interaction between Hg\* and the empty *p* orbital of boron. Particularly reaction (10) would be similar to that shown by triplet states of several organic molecules. The fact that the interaction is mainly over the boron atom is stressed by the low value of  $\Phi_8$  and the high rate of reaction (3).

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