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THERMAL IODINATION OF TRIETHYLBORANE

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SUMMARY

The termal iodination of triethylborane in cyclohexane solution has been studied in the 100 to 140° temperature range. The rate of iodine consumption fits the equation:

$$\frac{-d[I_2]}{dt} = k\cdot[I_2]^{\frac{1}{2}}\cdot[TEB] \qquad (1)$$

This rate expression suggests a free radical mechanism.

An Arrhenius plot for k gives $A=10^{11}\ l^{\frac{1}{2}}\cdot mol^{-\frac{1}{2}}\cdot s^{-1}$ and $E=27$ kcal/mol. For the rate determinating step

$$I^{\bullet}+Et_3B \longrightarrow IBEt_2+Et^{\bullet} \qquad (2)$$

it can be derived that $\log k_2 \approx 9.5-9800/(4.6\times T)$.

INTRODUCTION

The kinetics of the reactions of halogens with alkylboron compounds has been very little studied[1]. Early reports regarding the iodination of trialkylboranes in the absence of catalysts have been qualitative[2] and inconsistent. In the iodination of pure tripropylborane[3] it was found that the main reaction products were IBR_2 and RI. The reaction was assumed to take place molecularly via a "four-membered ring complex". On the other hand, preliminary data obtained in this laboratory suggests that both the photochemical and thermal iodination of triethylborane are free radical reactions[4]. In the present work, a more complete investigation of the thermal reaction has been undertaken and the results obtained lend support to the free radical mechanism.

EXPERIMENTAL

Triethylborane (TEB) was an Ethyl Corporation product. Hopkin and Williams cyclohexane (chromatographic grade) and re-sublimed iodine (Merck) were employed.

The iodine consumption was followed colorimetrically. The iodine/cyclohexane solutions (3 cm^3) were thoroughly degassed by repeated freezing and melting under high vacuum. The required amount of gaseous TEB was then measured in a calibrated volume, added to the solution, degassed and the reaction tube sealed under vacuum. The volume above the solution was kept as small as possible to avoid changes in concentrations owing to evaporation to the gas phase.

The initial absorption obtained for a given iodine concentration was independent of the TEB concentration and was the same as that of a similar blank tube (without added TEB). This fact shows that the absorption-iodine concentration calibration curves obtained with pure cyclohexane/iodine mixtures can be employed to obtain the iodine concentration even where TEB is present in the solution.

The reaction tubes were totally immersed in a thermostatted oil bath (±0.2°). They were also kept in complete darkness. After a given reaction time, they were brought to room temperature and the iodine concentration determined colorimetrically. The light from the colorimeter was not enough as to induce a photochemical reaction as several consecutive readings over the same reaction tube gave the same iodine concentration.

Some of the runs were carried out in quartz cells that could be introduced into a UV spectrophotometer. The spectra of the reaction products could then be recorded without having to open the reaction cell. A band similar to that of ethyl iodide was the main feature of these spectra.

Some ethane was produced even in runs without iodine. It was mainly produced at very short contact times and can be attributed to a heterogeneous decomposition of TEB over the glass surface[5]. The amount of ethane produced was less than 5% of the initial TEB concentration.

After the total consumption of the iodine, the behavior of the reaction mixture was similar to that expected from previous work[3]:

(*a*). Iodine (more than 30% of the initial amount) was produced when the reaction tube was opened to the air. After a short induction period, this iodine was rapidly consumed. This "second" iodine consumption was autocatalytic in agreement with the expected oxidation of the unreacted TEB in the presence of iodine[6]. The intensity of the ethyl iodide UV band was markedly increased after this second decoloration.

(*b*). If the reaction mixture was extracted with water in the absence of air, hydrogen iodide in significant amounts could be found in the aqueous layer. On the other hand, if the reaction mixture was exposed to the air before the extraction, no hydrogen iodide could be detected.

All these results are compatible with the formation of ethyl iodide and Et_2BI in the presence of unreacted TEB.

EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1 data obtained for two runs carried out at 120° with similar TEB concentrations is given. The results previously reported[4] together with the catalytic effect of the light, suggested a free radical mechanism. For the thermal reaction, the most likely free radical mechanism will comprise reactions (1) to (3).

$$I_2 \rightleftarrows 2\,I^\bullet \tag{1}$$

$$I^\bullet + Et_3B \rightarrow IBEt_2 + Et^\bullet \tag{2}$$

$$Et^\bullet + I_2 \rightarrow EtI + I^\bullet \tag{3}$$

This simple free radical mechanism leads to products similar to those found in the

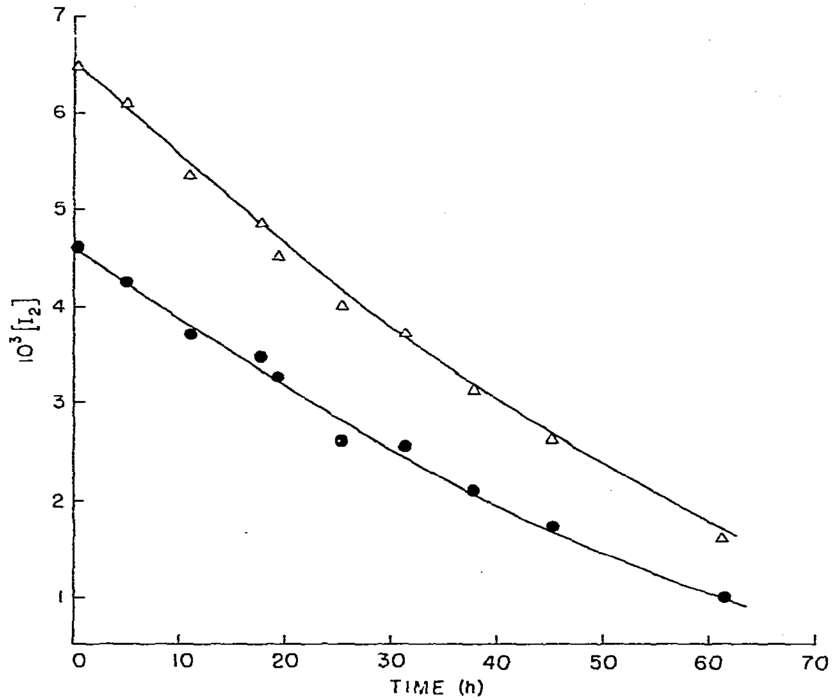

Fig. 1. Iodine consumption as a function of time. Temp. 100°. $[TEB]=9.1\times10^{-2}$ mol/l; $\triangle [I_2]_0 = 4.7\times10^{-3}$ mol/l; ● $[I_2]_0=6.5\times10^{-3}$ mol/l

iodination of tripropylborane[3] and is in agreement with the products observed in the present work. Furthermore, it has to be remarked that the propane reported as one of the reaction products in the previous work[3] can be easily explained by this mechanism as reaction (4) could compete with reaction (5) under the experimental conditions employed.

$$Pr^{\bullet} + Pr_3B \longrightarrow C_3H_8 + R^{\bullet} \tag{4}$$

$$Pr^{\bullet} + I_2 \longrightarrow PrI + I^{\bullet} \tag{5}$$

The proposed mechanism leads to equation (6)

$$-\frac{d[I_2]}{dt} = k\cdot[I_2]^{\frac{1}{2}}\cdot[TEB] \tag{6}$$

The validity of this expression was determined by working at several iodine and TEB concentrations.

Order in iodine

Working in excess TEB, eqn. (6) can be integrated to give eqn. (7).

$$[I_2]_0^{\frac{1}{2}} - [I_2]_t^{\frac{1}{2}} = \frac{k}{2}\cdot[TEB]_t \tag{7}$$

A plot of $\Delta[I_2]^{\frac{1}{2}}$ against time should then be linear and independent of the initial

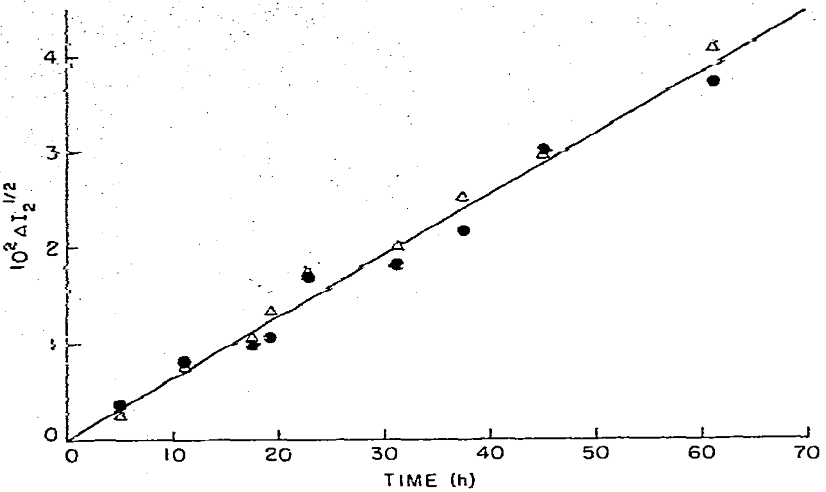

Fig. 2. Plot of $[I_2]_0^{\frac{1}{2}} - [I_2]_t^{\frac{1}{2}}$ against time. [TEB]$=9.1 \times 10^{-2}$ mol/l. Temp. 100°. △ $[I_2]_0 = 4.7 \times 10^{-3}$ mol/l; ● $[I_2]_0 = 6.5 \times 10^{-3}$ mol/l.

iodine concentration $[I_2]_0$. This type of plot is in Fig. 2. From this figure it can be concluded that the experimental data agrees with an order of $\frac{1}{2}$ in iodine and that the reaction shows a very clean behavior up to nearly 80% iodine consumption.

Order in TEB

The slope of plots like that of Fig. 2 allow the estimation of $p = k \cdot [\text{TEB}]$. A

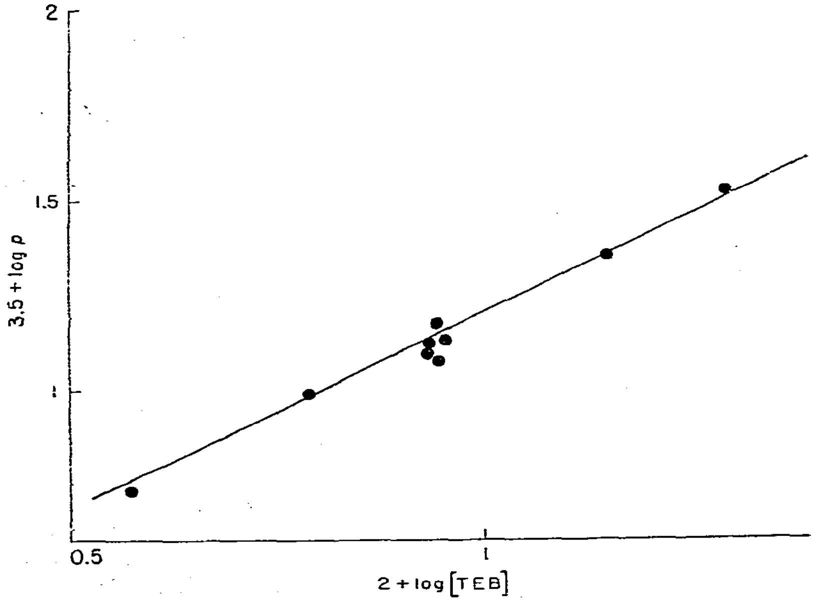

Fig. 3. Order in triethylborane: plot of log p against log [TEB]. Temp. 120°.

plot of log p against log [TEB] is shown in Fig. 3. The slope of this plot is 1.03, in complete agreement with the proposed mechanisms. Some runs were carried on until 30% of TEB was consumed. Eqn. (6) holds over the entire range, showing that impurities in the TEB cannot be playing any significant role in the iodine consumption.

TABLE 1

RATE CONSTANT FOR TRIETHYLBORANE IODINATION

Temp. (°C)	$[I_2]_0$ (10^{-3} mol/l)	$[TEB]_0$ (10^{-2} mol/l)	k (10^{-6} $l^{\frac{1}{2}}\cdot mol^{-\frac{1}{2}}\cdot s^{-1}$)
100	4.7	9.1	3.86
100	6.5	9.1	3.86
100	8.7	9.4	4.65
100	3.4	8.5	4.17
110	4.6	10.2	12.35
110	4.75	9.75	11.07
120	4.7	6.26	27.65
120	4.7	19.7	29.70
120	4.6	8.16	29.70
120	4.6	14.1	28.20
120	8.0	8.45	25.60
120	6.0	8.45	27.70
120	3.4	9.05	25.6
120	4.6	8.76	23.7
120	10.7	3.75	24.6
120	15.0	5.65	21.8
130	4.65	9.39	89.5
130	4.65	9.39	89.5
140	4.7	8.16	123.5
140	4.85	11.2	180.0

From the slopes p the values of $k = p/[TEB]$ can be directly obtained. The values of k so obtained are shown in Table 1. An Arrhenius plot for these values is shown in Fig. 4. The linearity of this plot supports the assumption that the same mechanism holds over all the temperature range. The Arrhenius parameters derived from Fig. 4 are:

$$A = 10^{11}\ l^{\frac{1}{2}}\cdot mol^{-\frac{1}{2}}\cdot s^{-1}$$

$$E = 27\ \text{kcal/mol}$$

Furthermore, the proposed mechanism implies that

$$k = K^{\frac{1}{2}}_{(I_2)}\cdot k_2$$

and then $E_2 = 27 - \frac{1}{2}\,\Delta H(I_2)$ and $A_2 = 10^{11} - \Delta S(I_2)/(2R)$.
If we accept that the values of $\Delta H(I_2)$ and $\Delta S(I_2)$ in cyclohexane solution are similar to those reported for the gas phase equilibrium[7], it can be estimated that

$$E_2 \approx 9.8\ \text{kcal/mol}$$

and

$$\log A_2 \approx 9.5\ l\cdot mol^{-1}\cdot s^{-1}$$

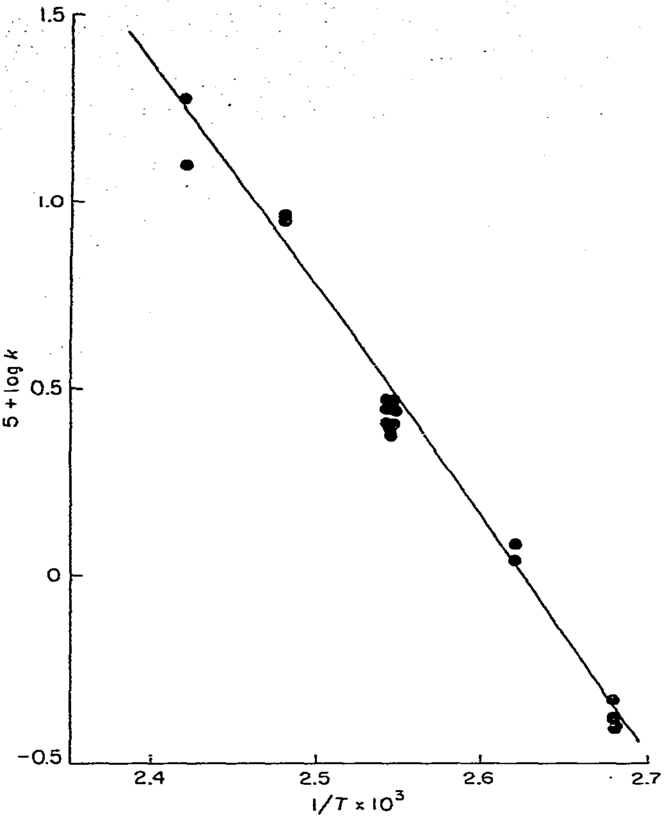

Fig. 4. Arrhenius plot for k.

The A factor is in agreement with that expected for an atom–molecule bimolecule reaction. Furthermore, the product distribution[3] points to the fact that $k_2 > k_8$· where reaction (8) represents the hydrogen abstraction reaction. The reaction of

$$I^{\bullet} + Et_3B \rightarrow HI + [C_2H_4BEt_2]^{\bullet} \quad (8)$$

iodine atoms with TEB appears then to be qualitatively different from that of bromine atoms. From this system it has been found[1] that $k_9 > k_{10}$, where:

$$Br^{\bullet} + TEB \rightarrow HBr + [C_2H_4BEt_2]^{\bullet} \quad (9)$$

and

$$Br^{\bullet} + TEB \rightarrow Et^{\bullet} + BrBEt_2 \quad (10)$$

REFERENCES

1 J. Grotewold, E. A. Lissi and J. C. Scaiano, *J. Organometal. Chem.*, 19 (1969) 431.
2 H. C. Brown, M. W. Rathke and M. M. Rogic, *J. Amer. Chem. Soc.*, 90 (1968) 5038.
3 L. H. Long and D. Dollimore, *J. Chem. Soc.*, (1953) 3902.
4 E. A. Lissi and E. Sanhueza, *J. Organometal. Chem.*, 26 (1971) C59.
5 E. Abuin, M. V. Encina and E. A. Lissi, unpublished results.
6 J. Grotewold, J. Hernandez and E. A. Lissi, *J. Chem. Soc. B*, (1971) 182.
7 J. Zimmerman and R. N. Noyes, *J. Chem. Phys.*, 18 (1950) 658.