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Preliminary communication

The reaction of triethylborane and iodine

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The reactions of alkylboron compounds with the halogens have been very little studied. The reaction of bromine with R_3B goes through a chain mechanism which involves bromine atoms as one of the chain carriers[1]. Hydrogen bromide is one of the main products[1,2], together with minor amounts of RBr. A mechanism involving reaction (1) and (2) with $k_1 > k_2$ was postulated to explain the experimental results. The reaction proceeded very rapidly at room temperature when Br atoms were produced photolytically.

$$Br^{\cdot} + R_3B \xrightarrow{k_1} R(-H)BR_2 + HBr \qquad (1)$$

$$Br^{\cdot} + R_3B \xrightarrow{k_2} BrBR_2 + R^{\cdot} \qquad (2)$$

On the other hand, the only results reported for the reaction of iodine with R_3B have been obtained either at high temperatures[3] or in the presence of a base as catalyst[4]. In the thermal reaction IR and IBR_2 have been reported as the main products. The

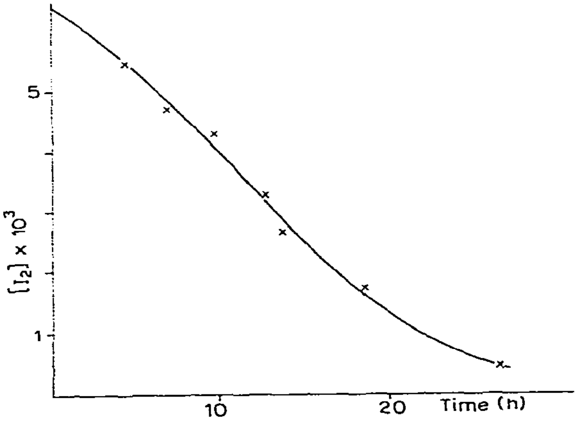

Fig.1. Iodine consumption as a function of time. ($\lambda > 3200$ Å, room temperature).

suggested mechanism involves a bimolecular reaction between an iodine molecule and R_3B.

We wish to report preliminary results on the thermal and photolytically initiated reaction of triethylborane (TEB) with iodine in cyclohexane solution, which show that these reactions go through a free radical mechanism.

When a mixture of TEB and iodine was irradiated with light of $\lambda > 3200$ Å at 20°, a noticeable decrease in iodine concentration could be detected colorimetrically.

In Fig.1 a typical plot of iodine concentration against time is given. From the shape of this curve it can be concluded that the reaction is autocatalytic. The rate constants were then obtained from the slopes at short reaction times. In Fig.2, plots of $\log_{10}$ (rate) against $\log_{10} I$, $\log_{10} I_2$ and $\log_{10}$ TEB are given. I is the light intensity. From the slopes of these plots it can be concluded that, at very short reaction times, the rate expression can be approximately given by:

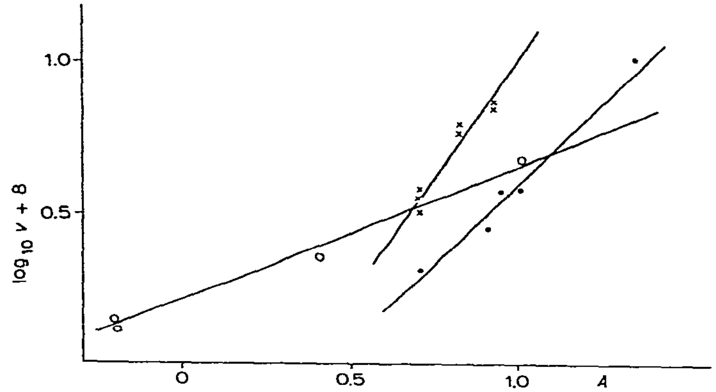

Fig.2. Van 't Hoff's order plots. ●, $A = \log_{10}(\text{TEB}) + 2$, $(I_2) = 5 \times 10^{-3}$; x, $A = \log_{10}(I_2) + 3$, $(\text{TEB}) = 8.7 \times 10^{-2}$; o, $A = \log_{10} I$, $(I_2) = 5 \times 10^{-3}$, $(\text{TEB}) = 11.0 \times 10^{-2}$. Concentrations are given in mole/liter, I is given in arbitrary units.

$$-\mathrm{d}(I_2)/\mathrm{d}t = k\, I^{1/2}\, (\text{TEB})(I_2)^{3/2} \qquad (3)$$

The dependence of the rate on the light intensity shows that the reaction must involve a photolytically generated transient. Furthermore, the one half order in I points to a free radical mechanism.

The products obtained are similar to those previously reported[3]. Ethyl iodide is one of the main products, together with another product (very likely $IBEt_2$) which liberates iodine when exposed to air.

The rate expression given by equation (3) is compatible with a free radical mechanism if the rate determining step involves a TEB molecule, an iodine atom and an iodine molecule (either free or complexed with one of the reactants). This reaction can also be considered as a reaction between I· and TEB assisted by an iodine molecule.

The thermal reaction can be studied at 120°, the reaction products being similar to those found in the photochemical reaction at low temperature. The rate expression can be accurately represented by:

$$-d(I_2)/dt = k(\mathrm{TEB})(I_2)^{1/2}$$

until very high conversions are reached, with

$$k = 2.72 \times 10^{-4}\ \mathrm{mole}^{-1/2} \cdot \mathrm{l}^{-1/2} \cdot \mathrm{sec}^{-1}$$

The rate expression is compatible with a mechanism involving reactions (4) to (6)

$$I_2 \rightleftarrows 2\,I^{\bullet} \qquad (4)$$

$$I^{\bullet} + \mathrm{TEB} = \mathrm{IBEt_2} + \mathrm{Et}^{\bullet} \qquad (5)$$

$$\mathrm{Et}^{\bullet} + I_2 = \mathrm{IEt} + I^{\bullet} \qquad (6)$$

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