Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

ON THE GAS PHASE REACTIONS OF BROMINE ATOMS WITH TRIETHYLBORANE

J. GROTEWOLD, E.A. LISSI AND J. C. SCAIANO
Laboratorio Central de Quimica, Universidad Tecnica del Estado Casilla 4587, Santiago (Chile)

(Received June 2nd, 1969)

As preliminary results obtained following the gas phase bromine/triethylborane reaction in an IR cell showed that an unusually fast reaction took place with hydrogen bromide evolution, we decided to study this system.

Halogen atoms can react with trialkylboranes through two different reaction paths, i.e.

$$\mathrm{Br} + \mathrm{RCH_2BR'_2} \rightarrow \mathrm{BrBR'_2} + \mathrm{R\dot{C}H_2} \qquad \mathrm{I}$$

or

$$\mathrm{Br} + \mathrm{RCH_2BR'_2} \rightarrow \mathrm{R\dot{C}HBR'_2} + \mathrm{HBr} \qquad \mathrm{II}$$

where R′ is an alkyl group and R may be an alkyl group or a hydrogen atom.

Substitution on the boron atom (type I reaction) may explain results obtained in liquid phase halogenation of trialkylboranes[1,2]. Furthermore, similar reactions between oxygenated free radicals and trialkylboranes have been postulated previously[3,4]. Type II reactions have only been reported in solution[1,5], but no kinetic study was carried out.

Both types of reactions were found to occur in our system, and kinetic data regarding the type II reaction are reported.

EXPERIMENTAL

As the reaction was extremely fast and to avoid most of the inconveniences found in the study of gas phase fast brominations[6], it was decided to employ a competitive method.

The apparatus employed was a conventional high vacuum system attached to a gas chromatograph. Grease-free stopcocks were used in the reaction vessel (600 cc) and wherever corrosive reagents were stored or measured. Further details on the experimental procedure have been previously reported[3].

Triethylborane (Ethyl Corporation) and cyclohexene (B.D.H.) were purified before each run by degassing them from suitable low temperature baths; inert gases were purchased from Matheson, and the toluene was a Hopkin and Williams product.

A mixture of bromine (Merck) and inert gas was prepared and kept wholly expanded in a 1000 cc container. For each run a cyclohexene/triethylborane mixture was prepared and introduced in the thermostatted reaction vessel. The contact time was varied from 12 to 30 minutes with no effect on the results, showing that the reaction was completed and that no secondary reaction is altering the results. The reaction products were then fractionated in traps at −120° and −196°. The inert gas (nitrogen, carbon monoxide or argon) was pumped out and measured with a Toepler pump, its amount being a measure of the quantity of bromine. The same technique was used in the runs with pure triethylborane.

The −196° fraction (hydrogen bromide and ethane) was measured manometrically; the hydrogen bromide was then absorbed on potassium hydroxide and the ethane was measured. Some GLC analysis of the −120° fraction showed that it contained unreacted triethylborane and cyclohexene, ethyl bromide and some unidentified products.

RESULTS AND DISCUSSION

The results obtained in the IR cell clearly showed that a photochemical process was involved. Triethylborane and bromine can be kept together without noticeable change in the spectra, provided that light is not admitted. If the system is illuminated, triethylborane is immediately consumed.

The following set of reactions can be postulated for a long chain process initiated photolytically (C_6H_{10} stands for cyclohexene):

$$Br_2 + h\nu \rightarrow Br^\bullet + Br^\bullet \tag{1}$$

$$Br^\bullet + C_6H_{10} \rightarrow C_6H_{10}Br^\bullet \tag{2}$$

$$Br^\bullet + Et_3B \rightarrow BrBEt_2 + Et^\bullet \tag{3}$$

$$Br^\bullet + Et_3B \rightarrow HBr + Et_2B\dot{C}HCH_3 \tag{4}$$

$$C_6H_{10}Br^\bullet + Br_2 \rightarrow C_6H_{10}Br_2 + Br^\bullet \tag{5}$$

$$C_6H_{10}Br^\bullet + HBr \rightarrow C_6H_{11}Br + Br^\bullet \tag{6}$$

$$Et^\bullet + Br_2 \rightarrow EtBr + Br^\bullet \tag{7}$$

$$Et^\bullet + HBr \rightarrow EtH + Br^\bullet \tag{8}$$

$$Et_2B\dot{C}HCH_3 + Br_2 \rightarrow Et_2BCHBrCH_3 + Br^\bullet \tag{9}$$

$$C_6H_{10} + Br \rightarrow C_6H_9^\bullet + HBr \tag{10}$$

From previous results[7,8], k_7/k_8, $k_9/k_{(-4)}$ and k_5/k_6 are probably greater than ten. Reaction (10) can be disregarded at room temperatures as in runs with pure cyclohexene no hydrogen bromide could be detected. Then, if we assume that reactions (−4), (6) and (8) are consuming a minor fraction of the hydrogen bromide formed, eqn. (11) will hold:

$$\frac{[HBr]}{[C_6H_{10}Br_2]} = \frac{k_4 \cdot [Et_3B]}{k_2 \cdot [C_6H_{10}]} \tag{11}$$

As our experimental results show that:

$$[EtBr] + [EtH] \ll [HBr]$$

the amount of dibromocyclohexane can be evaluated from eqn. (12):

$$[C_6H_{10}Br_2] = [HBr]_0 - [HBr] \tag{12}$$

where $[HBr]_0$ is the amount of hydrogen bromide evolved when only triethylborane is present. Then, eqn. (13) can be derived:

$$\frac{[HBr]_0}{[HBr]} = 1 + \frac{k_2 \cdot [C_6H_{10}]}{k_4 \cdot [Et_3B]} \tag{13}$$

This equation will give the right value of k_2/k_4 only when eqn. (11) holds. In Fig. 1, a plot of $[HBr]_0/[HBr]$ *vs.* $[C_6H_{10}]/[Et_3B]$ is shown. At low values of $[C_6H_{10}]/[Et_3B]$, the slope of the curve will approach the right value of k_2/k_4. The value so obtained was 4.5 at 26°. The curvature of the plot can be related to the occurrence of reaction (6). It should be remarked that if any error was introduced by hydrogen bromide consumption, the value of k_2/k_4 should have been even lower.

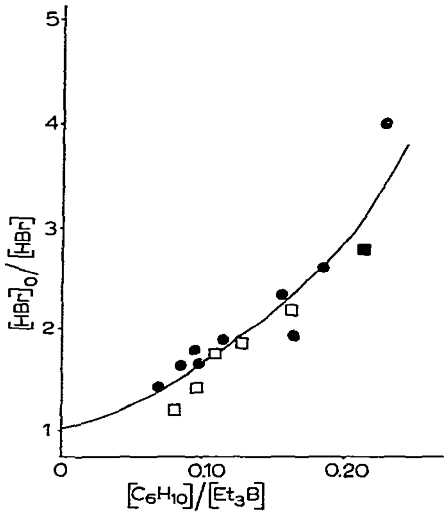

Fig. 1. Plot of $[HBr]_0/[HBr]$ *vs.* $[C_6H_{10}]/[Et_3B]$ at 26°. Pressure ranges: Et_3B, 15 to 26 mm Hg; C_6H_{10}, 1.9 to 5 mm Hg; Br_2, 0.4 to 0.8 mm Hg. Inert gases: ● carbon monoxide, $(CO/Br_2 = 8$ or $40)$; □ argon, $(A/Br_2 = 25)$; ■ nitrogen $(N_2/Br_2 = 12)$.

The run in which nitrogen was used as diluent (see Fig. 1), was carried out employing a sample of triethylborane that had been previously treated with 11% bromine. The fact that no difference could be detected when fresh or "*pre-treated*" triethylborane was used, rules out the possibility that the hydrogen bromide can be produced from a highly reactive impurity of triethylborane.

The occurrence of reaction (10) at temperatures higher than 50° did not allow the direct measurement of $(E_4 - E_2)$. However, the difference in activation energies can be estimated from our result at 26° by assuming a value for the pre-exponential factors ratio. From previous results on gas phase halogenations[9,10] it can be assumed that the pre-exponential factors ratio A_4/A_2 is *ca.* 24, which leads to $(E_4 - E_2) = 2.8 \pm 1.4$ kcal/mole. The estimated error was obtained assuming a factor of 10 as the indetermination of the A factors ratio. Then, taking E_2 as nearly zero[11], $E_4 = 2.8 \pm 1.4$ kcal/mole. Furthermore, an upper limit to E_4 can be derived from the information obtained in some runs carried out with toluene instead of TEB, where even at $[PhMe]/[C_6H_{10}] = 15$, no hydrogen bromide could be detected. This result contrast with those obtained using triethylborane, in which hydrogen bromide could be detected even at $[Et_3B]/[C_6H_{10}]$ of nearly three, showing that reaction (4) is at least 5 times faster than reaction (14)

$$PhCH_3 + Br^\cdot \rightarrow HBr + PhCH_2^\cdot \qquad (14)$$

From this information and assuming $A_4 = A_{14}$, as suggested by the constancy of A factors found for several C–H containing substrates[12,13], it can be concluded that $E_4 < 6.2$ kcal/mole[14].

From the preceding discussion and using the relationship derived by Marcus *et al.* between E_a and the C–H bond dissociation energy[15], an estimate of 80±3 kcal/mole for the secondary C–H bond energy in triethylborane can be derived. This unusually low value can be understood on the basis of the stabilization of the unpaired electron due to the presence of an adjacent vacant boron orbital. Comparing this result with the value for the secondary C–H bond in propane[16], it can be seen that the stabilization amounts to *ca.* 14.5 kcal/mole.

The fact that minor amounts of ethane and ethyl bromide are evolved, shows that reaction (3) takes place, but is remarkably slower than reaction (4). Thus, our results are similar to the qualitative determinations of Van Campen *et al.* for the bromination of tri-n-butylborane in solution[1].

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support from the Fund for Overseas Research Grants and Education, Inc.

REFERENCES

1 J. R. Johnson, H. R. Snyder and M. G. Van Campen Jr., *J. Amer. Chem. Soc.*, 60 (1938) 115.
2 L. H. Long and D. Dollimore, *J. Chem. Soc.*, (1953) 3902.
3 J. Grotewold, E. A. Lissi and J. C. Scaiano, *J. Chem. Soc., B*, (1969) 475.
4 A. G. Davies and B. P. Roberts, *J. Chem. Soc., B*, (1967) 17.
5 L. Zeldin and P. R. Girardot, *Abstr. 140th Nat. Meeting Amer. Chem. Soc.*, Chicago, Ill., September 1961, 15 N.
6 T. Berces and Z. G. Szabo, *Z. Phys. Chem. (Frankfurt am Main)* 56 (1967) 39.
7 G. C. Fettis and J. H. Knox, *Progr. Reaction Kinetics*, 2 (1964) 1.
8 G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, 12 (1944) 469.
9 P. G. Ashmore, F. S. Dainton and T. M. Sugden, *Photochemistry and Reaction Kinetics*, Cambridge University Press, Cambridge, 1967, p. 64.
10 G. Chiltz, P. Goldfinger, G. Huybrechts, G. Martens and G. Verbeke, *Chem. Rev.*, 63 (1963) 355.
11 H. Schmitz, H. J. Schumacher and A. Jäger, *Z. Phys. Chem., Abt. B*, 51 (1942) 281.
12 G. C. Fettis, J. H. Knox and A. F. Trotman-Dickenson, *Can. J. Chem.*, 38 (1960) 1643.
13 G. C. Fettis, J. H. Knox and A. F. Trotman-Dickenson, *J. Chem. Soc.*, (1960) 4177.
14 H. R. Anderson, H. A. Scheraga and E. R. Van Artsdalen, *J. Chem. Phys.*, 21 (1953) 1258.
15 A. O. Cohen and R. A. Marcus, *J. Phys. Chem.*, 72 (1968) 4249.
16 S. W. Benson, *J. Chem. Educ.*, 42 (1965) 502.