Rates of Primary Initiation of Trialkylborane Autoxidations

By P. B. Brindley* and J. C. Hodgson
(*Kingston Polytechnic, Kingston-upon-Thames, Surrey*)

Summary Rate constants (in $\text{M}^{-1}\,\text{s}^{-1}$) for the primary initiation stage of borane autoxidations have been found to be $1{\cdot}8 \times 10^{-3}$ for tri-s-butylborane, $0{\cdot}9 \times 10^{-3}$ for tri-isobutylborane, and $21{\cdot}9 \times 10^{-3}$ for tricyclohexylborane at 25° in benzene; the reaction is first order in borane and oxygen.

The discovery that the autoxidation of organo-boranes was a free radical process[1] has been followed by measurements which allowed estimates to be made of the initiation rates.[2–5]

$$\text{Initiation:}\quad R_3B + O_2 \xrightarrow{k_i} R\cdot + [\cdot O_2BR_2] \qquad (1)$$

$$\text{Propagation:}\quad R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot \qquad (2)$$

$$RO_2\cdot + R_3B \xrightarrow{k_p} RO_2BR_2 + R\cdot \qquad (3)$$

The methods used to measure the primary rate of initiation are open to uncertainty because of the unknown extent to which termination, peroxide decomposition (4), and induced decomposition (5) steps contributed to the measurements.

$$RO{\cdot}OBR_2 \longrightarrow RO\cdot + [\cdot OBR_2] \qquad (4)$$

$$R_3B + RO{\cdot}OBR_2 \longrightarrow \text{radicals} \qquad (5)$$

We now report accurate specific rate constants of primary initiation (k_i) for tricyclohexylborane, tri-s-butylborane and tri-isobutylborane, in benzene solution at 25°. The slow rate of oxygen absorption was measured during the early stages of reaction while under inhibition by galvinoxyl. Autoxidation initiations are not clearly understood and these results have significance beyond their fundamental importance to organoboron autoxidations. The reaction was first order in borane, first order in oxygen, and almost independent of galvinoxyl concentration.

At the steady state, equation (6) holds, where k_3 is for reaction (7) and G = galvinoxyl.

$$-\mathrm{d}[O_2]/\mathrm{d}t = k_i[R_3B][O_2]\{1 + k_2[O_2]/(k_2[O_2] + k_3[G])\} \qquad (6)$$

$$R\cdot + G \xrightarrow{k_3} RG \qquad (7)$$

The reaction between alkyl radicals and oxygen is known to be very fast.[6]† When $k_2[O_2] \gg k_3[G]$ equation (6) simplifies to equation (8). When $k_3[G] \gg k_2[O_2]$ the

$$-d[O_2]/dt = 2\,k_i[R_3B][O_2] \qquad (8)$$

equation becomes (9). The rate constant for thermal homolysis (4) of di-s-butyl-s-butylperoxyborane has been

$$-d[O_2]/dt = k_i[R_3B][O_2] \qquad (9)$$

given by Davies and Ingold *et al.*[4] as $k = 3{\cdot}8 \times 10^{-4}\ s^{-1}$ at 30° while our own measurements on di-n-butyl-n-butylperoxyborane ($k = 5{\cdot}0 \times 10^{-5}\ s^{-1}$; activation energy 10·7 kcal mol^{-1}) give values significantly different to those for dialkyl peroxides. The termination involving self reaction of s-butylperoxy-radicals at 30° was $1{\cdot}5 \times 10^6\ \text{M}^{-1}\ s^{-1}$ which, like k_p, has a small activation energy.[4] None of these reactions should significantly affect our measurements of k_i.

Values of k_i obtained from equation (8) were not truly constant and the ratios of k_3 to k_2 were determined by the method of successive approximations using a preliminary best value of k_i obtained from equation (8). The rate constants k_i were then calculated from equation (6) using the values $k_3/k_2 = 13{\cdot}5$ for $Bu^s{}_3B$, and 2·8 for $Bu^i{}_3B$. The initiation rate constants at 25° in benzene solution were, for $Bu^s{}_3B$, $k_i = 1{\cdot}8 \times 10^{-3}\ \text{M}^{-1}\ s^{-1}$; and $Bu^i{}_3B$, $k_i = 0{\cdot}9 \times 10^{-3}\ \text{M}^{-1}\ s^{-1}$; tricyclohexylborane [calc. from equation (9)], $k_i = 21{\cdot}9 \times 10^{-3}\ \text{M}^{-1}\ s^{-1}$.

A comparison of r_i values calculated in this way compared with those obtained using the relationship: $r_i{}' =$ (initial galvinoxyl conc.)/(induction period), indicates good agreement at high borane and high oxygen concentration but with low borane, low oxygen and high galvinoxyl concentrations the displacement reaction (3), and hence autocatalytic reactions (4) and (5), become significant towards the end of the inhibition period, and k_i calculated by this method was not constant. The induction period method appears to overestimate the initiation rate under these circumstances. Galvinoxyl is also removed by reactions (10) and (11).

$$G + RO{\cdot}OBR_2 \longrightarrow \text{products} \qquad (10)$$

$$G + O_2 \longrightarrow \text{products} \qquad (11)$$

Recently Brown *et al.*[5] and Grotewold *et al.*[7] have separately used iodine to inhibit borane oxidations. Again the extent to which competing reactions are involved is not clear and in this case there are additional reactions which can be postulated to give the alkyl iodide including an oxygen initiated iodine–borane chain reaction. Brown interprets his order for relative rates of tributylborane initiations as being due to steric crowding about the boron atom. The compounds we have studied so far do not enable us to generalise but the specific rate constants we have obtained do not suggest that steric control operates to the exclusion of electronic factors. We would like to correct any impression that our earlier rates for tributylborane initiation[2] can be compared with those in the presence of massive concentrations of iodine.[5b] The dependence on borane concentration has now been demonstrated and our rates were measured under radically different conditions to those of Brown and Midland.

Drs. H. C. Bailey and J. Betts are thanked for helpful discussions.

(*Received, 8th November* 1971; *Com.* 1934.)

---

† $k_p = 8 \times 10^4\ \text{M}^{-1}s^{-1}$ at 30° for tri-s-butylborane (ref. 4).

[1] A. G. Davies and B. P. Roberts, *J. Chem. Soc.* (*B*) 1967, 17; P. G. Allies and P. B. Brindley, *Chem. and Ind.*, 1967, 319.

[2] P. G. Allies and P. B. Brindley, *J. Chem. Soc.* (*B*) 1969, 1126.

[3] K. U. Ingold, *Chem. Comm.*, 1969, 911.

[4] A. G. Davies, K. U. Ingold, B. P. Roberts, and R. Tudor, *J. Chem. Soc.* (*B*) 1971, 698.

[5] H. C. Brown and M. M. Midland (a) *J. Amer. Chem. Soc.*, 1971, **93**, 1056; (b) *Chem. Comm.*, 1971, 699.

[6] Reaction rate of methyl radicals with oxygen in the vapour phase = $10^{12}\ \text{M}\ s^{-1}$ (Van den Berg and A. B. Callear, *Trans. Faraday Soc.*, 1971, **67**, 2017. Radical + radical reactions are *ca.* 10^7–$10^8\ \text{M}^{-1}\ s^{-1}$, hence k_3 is placed in this range—L. R. Mahoney, *J. Amer. Chem. Soc.*, 1967, **89**, 1895.

[7] J. Grotewold, J. Hernandez, and E. A. Lissi, *J. Chem. Soc.* (*B*), 1971, 182.