Kinetics and Rate Constants for Reactions associated with Organoborane Autoxidations

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The thermal decomposition of the peroxides $Bu^nOOBBu^n_2$, $(Bu^nOO)_2BBu^n$, and $(Bu^sOO)_2BBu^s$ occurs predominantly by a non-radical process with a low enthalpy and large negative entropy of activation. A minor homolytic decomposition was detected in vinyl acetate. The primary initiation, $R_3B + O_2 \xrightarrow{k_i}$ radicals, was also investigated and k_i was found to be $1.7 \pm 0.2 \times 10^{-5}$ for tri-s-butylborane; $0.9 \pm 0.1 \times 10^{-5}$ for tri-isobutylborane, and *ca.* 6.8×10^{-5} s^{-1} for tricyclohexylborane.

Following the discovery that the autoxidation of trialkylboranes was a free radical chain process of long chain length,[1,2] Davies *et al.*[3] carried out a thorough kinetic study of the propagation stages (i)—(iii). The radical

$$R\cdot + O_2 \xrightarrow{k_2} ROO\cdot \qquad \text{(i)}$$

$$ROO\cdot + R_3B \xrightarrow{k_p} \underset{\text{(I)}}{ROOBR_2} + R\cdot \qquad \text{(ii)}$$

$$ROO\cdot + ROOBR_2 \xrightarrow{k_{p'}} \underset{\text{(II)}}{(ROO)_2BR} + R\cdot \qquad \text{(iii)}$$

displacement reactions (ii) and (iii) at the electron deficient centre are examples of S_H2 reactions and $k_p > k_{p'}$ are both smaller than k_2. It was necessary for Davies *et al.* to carry out the organoborane autoxidation in the presence of pyridine because of the speed of step (ii); this caused the concentration of the free borane to be much reduced, the pyridine–borane complex not undergoing autoxidation. The propagation rate constants at 30 °C in iso-octane solvent were reported[3a] as k_p 2×10^6 for n-butyl and 8×10^4 l mol^{-1} s^{-1} for s-butyl, while $k_{p'}$ was 3×10^4 for n-butyl and 1×10^4 l mol^{-1} s^{-1} for s-butyl. In order to obtain these results the authors had to take into consideration the rate of the termination reaction between two peroxyl radicals.

The autoxidations are also strongly influenced by initiation processes and boron peroxide removing reactions, a knowledge of their magnitude being necessary for a full understanding of the overall process. This is particularly so in the case of organoborane-induced vinyl polymerisations about which there have been reports.[4] In many of these it is not clear whether free radicals were derived *via* peroxyboranes or even if free radicals were involved.

Yields of alkyl(bisalkylperoxy)boranes are high if dilute solutions and efficient gas–liquid mixing are employed[5,6] and although the peroxides have been characterised, their lability has not encouraged isolation and purification. We attempted purification by means of complex formation with ammonia and amines[7] without success and an attempt to purify n-butyl-(bis-n-butylperoxy)borane by distillation at ambient temperature and under high vacuum was unsuccessful because the distillation time could not be made small compared with its rate of decomposition. However, we were able to prepare, in high purity and in almost quantitative yield, hydrocarbon solutions of the normal and secondary butylperoxyboranes by means of carefully controlled autoxidation procedures. Taking advantage of an earlier observation that at —74 °C the autoxidation of tri-n-butylborane ceased completely after one mol. equiv. of oxygen had been absorbed[6] we obtained the unstable di-n-butyl-(n-butylperoxy)-borane. This technique did not work for tri-s-butylborane and the compound was not considered sufficiently pure for detailed kinetic investigations. Therefore, our choice of boron peroxides for study were limited to those compounds which we could prepare in a suitably pure state.

Isobutyl(bisisobutylperoxy)borane has been reported as being 30% decomposed after 2.5 h at room temperature by Davies *et al.*,[8] and they suggested that a 1,2-nucleophilic rearrangement was involved. In contrast organoperoxyborates $(ROO)_nB(OR)_{3-n}$ (n = 1—3), not having boron–carbon bonds, behave like dialkyl peroxides and only decompose at measurable rates at *ca.* 120 °C with activation energies in the range 30—35 kcal mol^{-1}, homolysis of the peroxy bond occurring.[9] We followed the rates of decomposition of butyl-n- and -s-butylperoxyboranes iodometrically and found an overall kinetic order close to unity. The mono- and di-peroxides decomposed at widely different rates and were not significantly affected by the presence of each other. The first-order rate constants (k/s^{-1}) were: $6.0 \times 10^3 e^{-11100 \pm 530/RT}$ for $Bu^n_2BOOBu^n$, $4.55 \times 10^4 e^{-14300 \pm 1070/RT}$ for $Bu^nB(OOBu^n)_2$, and $6.46 \times 10^5 e^{-15900 \pm 400/RT}$ for $Bu^sB(OOBu^s)_2$.

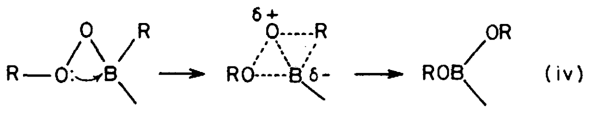
Good first-order plots were obtained over the first 40% of reaction. From the overall first-order rate constants, measured over a 30° temperature range in iso-octane solvent, were constructed Arrhenius graphs (Figure 1) and enthalpies and entropies of activation (Table 1) were calculated. It is significant that the enthalpies are considerably smaller than for dialkyl peroxides or

TABLE 1

Enthalpy and entropy of activation for the thermal decomposition of butyl(butylperoxy)boranes

Peroxyborane in iso-octane	t/°C	k/s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
$(Bu^nOO)_2B\,Bu^n$	70.6	3.78×10^{-5}	13.6 ± 1.07	−39.5
$(Bu^sOO)_2\,B\,Bu^s$	70.6	4.80×10^{-5}	15.2 ± 0.40	−34.1
$Bu^nOOB^2Bu^n_2$	25.1	4.68×10^{-5}	10.5 ± 0.53	−43.1

organoperoxyborates and this is in keeping with a synchronous, intramolecular rearrangement process where the energy required for bond breaking is compensated by energy release during bond formation. The values are in agreement with the results of Ta-Hsan Lee *et al.*[10] for diethyl(ethylperoxy)borane. The lower activation energy of the monoperoxy compound [11.1 ± 0.5 for $BuOOBBu_2$ compared to 14.3 ± 1.0 kcal mol^{-1} for $(BuOO)_2BBu$] reflects the smaller p_π–p_π interaction between oxygen atoms and boron. The large decrease in entropy of activation is attributed to a cyclic activated complex [reaction (iv)]. The Baeyer–Villiger conversion



of ketones to esters which involves rearrangement of the peroxy 'Criegee intermediate' has a similar large negative entropy of activation associated with a cyclic transition state.[11]

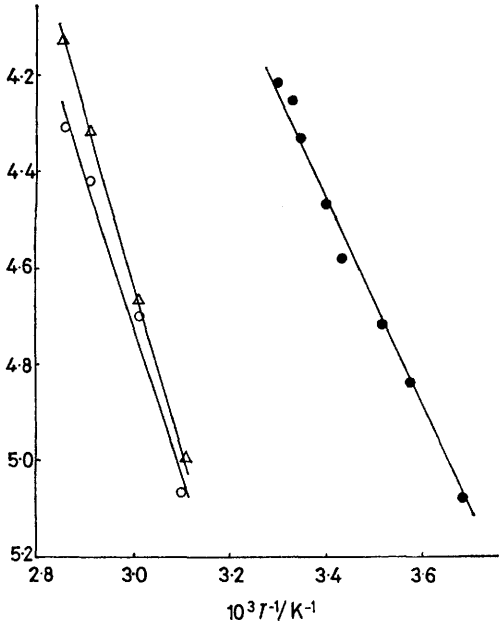


FIGURE 1 Arrhenius graphs for the decomposition of alkylperoxyboranes: ○, n-butylbis-n-butylperoxyborane; △, s-butylbis-s-butylperoxyborane; ●, di-n-butyl-n-butylperoxyborane

Since alkoxy(alkyl)alkylperoxyboranes ROOB(R)OR might be considered intermediates arising from intermolar decompositions of types (v) and (vi) the synthesis

$$(ROO)_2BR + ROOBR_2 \longrightarrow 2ROOB(R)OR \quad (v)$$

$$(ROO)_2BR + R_3B \longrightarrow ROOB(R)OR + ROBR_2 \quad (vi)$$

of 2-butoxy-s-butyl-s-butylperoxyborane from chloro-s-butoxy-s-butylborane and s-butyl hydroperoxide was carried out. The chloroborane was even more unstable than the previously reported n-butyl isomer.[12] The peroxide prepared from it was particularly difficult to purify although the method of preparation gave essentially the required compound. This peroxide was the most stable of the peroxides studied and was 10% decomposed after 24 h at 50 °C and it had a first-order rate constant of *ca.* 1×10^{-6} s^{-1}. It is considered unlikely that this peroxide significantly affected the decomposition rates of the peroxides (I) or (II).

The autocatalysis observed during organoborane autoxidation could be attributed to homolytic fission of the peroxy bonds and Davies and Ingold [3] report that the rate constant for reaction (vii) was 1.1×10^{-5} s^{-1} at

$$Bu^nOOBBu^n_2 \longrightarrow Bu^nO\cdot + \cdot OBBu_2 \quad (vii)$$

30 °C. Since vinyl acetate polymerises almost exclusively at a known rate [13] by a free radical mechanism [14] we chose to measure the rate of homolysis of our peroxide by using them to initiate the polymerisation of the monomer. s-Butylbis-s-butylperoxyborane showed a typical polymerisation (Figure 2), the rate increasing to a constant value. n-Butylbis-n-butylperoxyborane was unusual in that after an initial rapid polymerisation the rate slowed to a constant value; this is assumed to be due to traces of the less stable monoperoxide. Polymerisation in the presence of di-n-butyl-n-butylperoxyborane was autoaccelerating and since the measurements were made only over *ca.* 3.5% of reaction this effect cannot be attributed to an increase in viscosity of the solution. This last example did not allow calculation of an accurate polymerisation rate but an average value is given in Table 2.

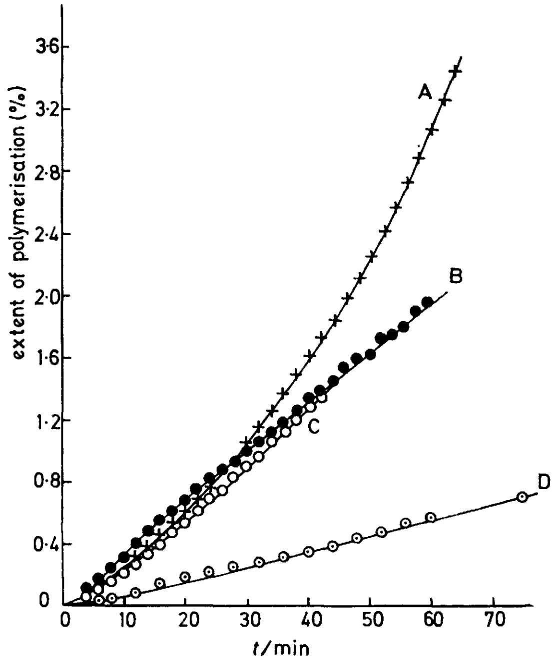


FIGURE 2 Polymerisations of vinyl acetate using organoperoxyborane initiators: A, di-n-butyl-n-butylperoxyborane at 25 °C; B, n-butylbis-n-butylperoxyborane at 60 °C; C, s-butylbis-s-butylperoxyborane at 60 °C; D, s-butylbis-s-butylperoxyborane at 50° C

It is notable that the homolytic rate constant k_d for reaction (viii) is much smaller than the overall rate constants determined iodometrically. The difference is too great to be attributed to low initiator efficiency and

$$\mathrm{BuOO\overset{|}{B}{-}Bu} \xrightarrow{k_d} \mathrm{BuO\cdot} + \mathrm{\cdot O\overset{|}{B}{-}Bu} \qquad \text{(viii)}$$

therefore it must be concluded that homolytic decomposition of alkyl organoperoxyboranes constitutes only a minor part of the overall disappearance of peroxide. There is an apparent contradiction with the homolytic rate constant given by Davies and Ingold [3a] (1.1×10^{-5} s^{-1} at 30 °C) but their results were measured in the presence of oxygen and galvinoxyl and may reflect induced decompositions.

TABLE 2

Polymerisation of vinyl acetate by butyl(butylperoxy)-boranes

Initiator	t/°C	Rate of polymerisation R_{p_1}/l mol^{-1} s^{-1}	Overall peroxide decomposition rate (l mol^{-1} s^{-1})	Initiation rate constant [a] k_{d_1}/s^{-1}
$(ROO)_2BR$ R = Bu^n	60.5	5.7×10^{-5}	2.00×10^{-5}	1.5×10^{-8}
$(ROO)_2BR$ R = Bu^s	60.5	7.5×10^{-5}	2.13×10^{-5}	2.6×10^{-8}
ROO BR_2 R = Bu^n	25.0	1.03×10^{-4}	4.68×10^{-5}	2.6×10^{-7}

[a] k_p 3 700 (at 60°), 1 012 s^{-1} (at 25°); k_t 7.4×10^7 (at 60°) 2.94×10^7 l mol^{-1} s^{-1} (at 25°).[11]

Another reaction which gives rise to loss of peroxide was reported when Murviss [15] noted that a significant reduction in peroxide concentration occurred when tri-n-hexylborane and autoxidised tri-n-butylborane were mixed under nitrogen; n-hexyl alcohol corresponding to the loss of peroxide was isolated after hydrolysis. This he interpreted in terms of a four-centre, bimolecular redox reaction. However, Hansen [16] concluded from polymerisation studies that the reaction was free radical in nature and more recently Davies and Ingold [3a] have demonstrated by e.s.r. spectroscopy that alkyl radicals are involved. It seems that it is this reaction which gives rise to the autocatalysis observed in organoborane autoxidations and Grotewold *et al.*[17] have proposed the mechanism in reactions (ix) and (x).

$$R_2BOOR + R_3B \longrightarrow R_2BOR + R_2BO\cdot + R\cdot \qquad \text{(ix)}$$

$$R_2BO\cdot + R_3B \longrightarrow R_2BOBR_2 + R\cdot \qquad \text{(xi)}$$

We attempted to follow iodometrically the corresponding reaction using di-n-butyl-n-butylperoxyborane but found that the reaction was almost complete after 30 s at 25 °C with no noticeable effect on lowering the temperature by 50°. An attempt to follow the reaction rate using u.v. spectroscopy by measuring the rate of disappearance of free radical trapping agents such as galvinoxyl or 2,2,6,6-tetramethylpiperidone nitroxide was also unsuccessful. Interaction occurred with the trapping agents and reaction was virtually complete in 15 s at 25 °C. Similar results were found with the n-butylbis-n-butylperoxyborane. The simple stoicheiometry suggested by Murviss was not obeyed. Both mono- and di-peroxides removed *ca.* 1.7 mole of borane in keeping with the Grotewold mechanism.

Consideration of the spontaneous initiation of borane autoxidation [reaction (xi)] is also relevant to this study.[3]

$$xR_3B + yO_2 \xrightarrow{k_1} \text{alkyl radical} \qquad \text{(xi)}$$

From the foregoing it can be argued that samples of borane, even if contaminated with traces of peroxide, will have rapidly lost the peroxide to yield non-radical forming products [equations (ix) and (xi)] on standing. Borane spontaneous initiation might be compared with the spontaneous initiation observed for hydrocarbon autoxidation [18] which was reported as being first order in oxygen and second order in hydrocarbon.

We have previously reported a very slow absorption of oxygen during the galvinoxyl inhibited iso- and s-butylborane autoxidation.[6] This we interpret as a measure of reaction (xi) and we have measured this slow oxygen absorption for these boranes and for tricyclohexylborane. Figure 3 is typical of the absorption and it can be seen that the linear part is followed by an autoaccelerating region. The latter corresponds to depleted galvinoxyl and the S_H2 propagation (ii) and Grotewold type initiation [(ix) and (xi)] become important. Although the reaction between oxygen and alkyl radicals (k_2) is known to be very fast, it is possible for galvinoxyl (G) to enter into competition for alkyl and alkylperoxyl radicals [reactions (xii) and (xiii)]. Assuming a steady state concentration of alkyl radicals, it can be shown that equation (xiv) obtains.

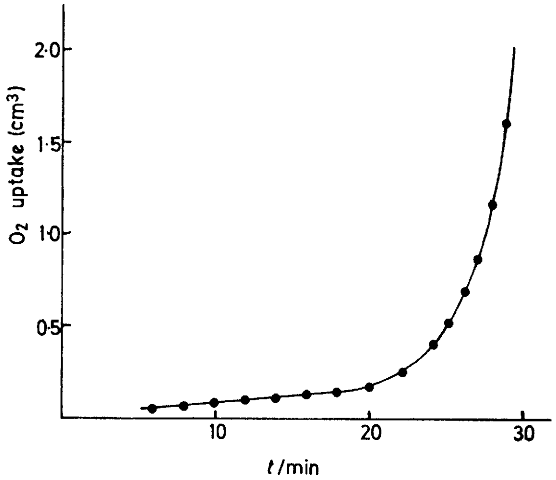


FIGURE 3 Galvinoxyl-inhibited autoxidation of tricyclohexylborane in benzene (50 ml) at 25 °C: $[R_3B]_0$ 2.9×10^{-3}M; $[G]_0$ 3.6×10^{-4}M; $[O_2]$ 1.6×10^{-3}M

$$R\cdot + G \xrightarrow{k_3} \text{RG stable products} \qquad \text{(xii)}$$

$$ROO\cdot + G \xrightarrow{k_4} \text{ROOG stable products} \qquad \text{(xiii)}$$

$$-\frac{d[O_2]}{dt} = k_1[R_3B]^x\,[O_2]^y\left(1 + \frac{k_2[O_2]}{k_2[O_2] + k_3[G]}\right) \qquad \text{(xiv)}$$

The order with respect to borane concentration was unity and with respect to oxygen the order was zero over the range studied. When k_3/k_2 is very large equation (xiv) simplifies to $-\mathrm{d}[O_2]/\mathrm{d}t = k_1[R_3B]$ and when it is zero $-\mathrm{d}[O_2]/\mathrm{d}t = 2k_1[R_3B]$. A somewhat

$$\log\left(\frac{-\mathrm{d}[O_2]}{\mathrm{d}t}\right) = \log[R_3B] + \log\left(1 + \frac{[O_2]}{[O_2 + k_3/k_2\,[G]]}\right) + \text{constant} \quad \text{(xv)}$$

better value for the rate constant k_1 could be obtained in the case of the tri-s- and tri-iso-butylborane by substituting various values of k_3/k_2 into equation (xv), until the best straight line was obtained. The result indicated that for tri-s-butylborane k_3/k_2 lay between 10 and 100 and probably between 20 and 40 whereas for tri-isobutylborane k_3/k_2 lay between 1 and 10 and probably between 1 and 3.

TABLE 3

Rate constants for the primary initiation of trialkylboranes in benzene at 25 °C

$10^2 \times [R_2B]$/M	$10^2 \times [O_2]$/M	$10^4 \times [G]$/M	$10^5 \times k_1/s^{-1}$ [a]	$10^8 \times R_i$/l mol^{-1} s^{-1}	$10^5 \times k_1/s^{-1}$ [c]
		Tri-s-butylborane			
0.76	0.75	1.5	1.9	14.0	1.9
0.76	0.36	1.5	1.9	11.7	1.6
0.76	0.16	1.5	1.5	7.7	1.0
0.76	0.16	2.9	1.7	12.9	1.7
0.36	0.16	2.9	1.5	10.6	3.1
1.48	0.16	2.9	1.4	22.8	1.6
2.10	0.16	2.9	2.2	46.7	2.2
0.76	0.16	7.3	1.7	13.9	1.9
		Tri-isobutylborane			
1.44	0.75	1.5	0.9	12.9	0.9
1.44	0.16	1.5	0.7	8.7	0.6
0.75	0.16	1.5	0.8	5.4	0.7
2.10	0.16	1.5	0.8	12.9	0.6
1.44	0.16	5.9	0.9	9.3	0.7
2.80	0.16	1.5	1.1	15.3	0.6
		Tri-cyclohexylborane			
0.29	0.16	3.6	6.2 [d]	19.9	6.8
0.26	0.16	0.7	8.6 [d]	3.35	1.3 [e]

[a] Calculated from equation (xiv) using $k_3/k_2 = 30$ for Bu^s_3B and 2 for Bu^i_3B [b] Calculated from $R_i = [G]/\tau$. [c] Calculated from equation (xviii). [d] Calculated from equation $\mathrm{d}[O_2]\mathrm{d}t = k_1[R_2B]$. [e] In iso-octane.

The mean rate constants then obtained from equation (xiv) with benzene as solvent, at 25 °C, were: tri-s-butylborane $1.7 \pm 0.2 \times 10^{-5}$ s^{-1} (k_3/k_2 taken as 30); tri-isobutylborane $0.9 \pm 0.1 \times 10^{-5}$ s^{-1} (k_3/k_2 taken as 2). This approach did not prove sufficiently accurate for tricyclohexylborane since it was the most difficult to inhibit and the value of k_3/k_2 *ca.* 100 must be viewed with caution, particularly since the rates are close to the diffusion controlled limit. Therefore the rate constant for initiation was established from the total induction period [equation (xviii)] and was 6.8×10^{-5} s^{-1} at 25 °C in benzene compared with a value of *ca.* 6×10^{-5} calculated from equation (xiv), assuming k_3/k_2 was very large. Estimates of primary rates of initiation based on the total induction period (τ) might be considered open to error. Removal of galvinoxyl by reactions other than (xii) and (xiii), particularly towards the end of the induction period, encourages peroxide formation [reaction (ii)] and its decomposition into radicals. This should give enhanced oxygen absorption. It is gratifying to find good agreement between the two methods (Table 3).

The primary initiation rates as determined by Brown and Midland [19] using iodine in high concentration are lower than our values. Our results are in keeping with the suggestion that iodine can be reformed from alkyl iodide,[3b] and with the low activation energy for the process.

It was reported by Allies and Brindley [6] that galvinoxyl does not interact significantly with borane in the absence of oxygen. The existence of a borane–oxygen complex has been reviewed by Murviss [15] and one must conclude that it is labile, short-lived intermediate. The ease of formation of four-co-ordinate boron compounds and their comparative stability towards alkyl and alkylperoxyl radicals [3b] encourages one in the belief that galvinoxyl does not compete in equation (xvi); the absence of autocatalysis during the early part of the initiation confirms that the galvinoxyl is acting as an inhibitor, not as a chain transfer agent.

An explanation for the primary initiation step assumes a rapid establishment of a borane–oxygen complex followed by a slow intramolecular rearrangement to peroxide and then its rapid decomposition to radicals under the influence of free borane.[15,16] Therefore, we

$$R_3B + O_2 \xrightleftharpoons{\text{fast}} R_3B{\cdot}O_2 \xrightarrow{\text{slow}} ROOBR_2 \quad \text{(xvi)}$$

$$ROOBR_2 + R_3B \xrightarrow{\text{fast}} R{\cdot} + R_2BO{\cdot} + \text{stable products} \quad \text{(xvii)}$$

suggest that the primary initiation rates are a measure of the rearrangement of the oxygen complex into the peroxyborane.

EXPERIMENTAL

Preparation of Butylperoxyboranes.— *Butylbisbutylperoxyborane.* Tri-n- or -s-butylborane (0.005 mol) in iso-octane

(50 ml) was treated with oxygen at 20 °C using a high speed stirrer for gas–liquid mixing. After 1 h the oxygen flow was replaced by nitrogen. Analysis for peroxide using sodium iodide in propan-2-ol and acetic acid showed a peroxide content of $>96\%$.

Di-n-Butyl-n-butylperoxyborane. This was prepared in an analogous manner at −74 °C over 15 min (Found: peroxide, 95%). All experiments were carried out on freshly prepared solutions and because of its instability all transfers were kept to a minimum.

s-Butoxy-s-butyl-s-butylperoxyborane. *Di-s-butoxy-s-butylborane* was prepared by the slow addition of an ether solution of s-butylmagnesium bromide (1.42 mol) to tri-s-butylborate (1.4 mol) in ether at −70 °C and had b.p. 54° at 1 mmHg, n_D^{20} 1.404 5 (Found: C, 67.5; H, 12.6; B, 4.9. $C_{12}H_{27}BO_2$ requires C, 67.4; H, 12.6; B, 5.1%). It was converted to chloro-s-butoxy-s-butylborane by the slow addition of redistilled boron trichloride (1 mol) at −70 °C using n-pentane solvent.[12] After warming to 0 °C the solvent and s-butyl chloride was removed under vacuum. Undecomposed dichloro-s-butoxyborane was removed as a lower boiling fraction during successive vacuum distillation. Chloro-s-butoxy- s-butylborane, b.p. 58—62° at 15 mmHg, n_D^{20} 1.400 7, was stored at −80 °C and flash distilled at low temperature immediately before use. s-Butyl hydroperoxide in pentane was added dropwise to chloro-s-butoxy-s-butylborane in pentane at 0 °C while aspirated by a slow current of argon until all the hydrogen chloride had been removed (Found: HCl, 103%). The crude peroxide (yield 75%) was purified by trap-to-trap evaporation at −180 °C to yield s-butoxy-s-butyl-s-butylperoxyborane.

Thermal Decomposition of Butylperoxyboranes.—Measurements were made over the first 40% of reaction using an iodometric method of analysis of samples. The analytical method was found to be both accurate and reproducible. Rate constants were evaluated using least squares plots and experiments were carried out using various initial concentrations of the peroxides in order to distinguish first-order from any possible second-order kinetics (Figures 1—3). s-Butoxy-s-butyl-s-butylperoxyborane was only studied briefly since it decomposed with a rate constant *ca.* 1×10^{-6} s^{-1} at 50 °C which was much slower than the butyl(butylperoxy)boranes.

Polymerisation of Vinyl Acetate.—The peroxyborane initiated polymerisation of vinyl acetate (purified under high vacuum) was studied by dilatometry. Ethyl acetate was chosen as a blank in order to demonstrate that the acetate group did not induce reaction. Typical results are shown in Figure 1 and the calculated rates of polymerisation of vinyl acetate R_p are listed in Table 2 for 8.5mM concentrations of peroxide. Using known rates of polymerisation propagation k_p and termination k_t [20] the initiation rates k_d were calculated using the relationship $k_d = R_p{}^2k_t/[I][M]k_p$ where M is vinyl acetate and I peroxyborane.

Rates of Initiation (*Table* 3).—These were carried out at constant pressure. The benzene solvent and oxygen, at the required partial pressure, were allowed to come to equilibrium at 25 °C with the stirrer running (apparatus described earlier [6]). Care was taken to check that oxygen absorption was independent of stirrer speed. The galvinoxyl solution (stabilised with 5% hydrogalvinoxyl) quickly followed by borane solution, were injected using calibrated syringes. Equilibrium was re-established after *ca.* 3 min and readings were taken on the gas burette. Plots of $-\log d[O_2]/dt$ against $\log [R_3B]$ [equation (xiv)] gave slopes of 1.1 and 1.05 for s-butyl- and isobutyl-boranes, respectively. In the case of tricyclohexylborane it was found more convenient to use relationship (xviii) based on (xvi) and

$$\tau = 2\,303 \log \{[R_3B]_0/([R_3B]_0 - [G]_0)\}/k_1 \quad \text{(xviii)}$$

(xvii) rather than equation (xiv). The number of radicals removed by one molecule of galvinoxyl is unity and $[R_3B]_0$ = concentration at zero time.

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