The Kinetics and Rate Constants for the Autoxidation of s-Butylboronic Anhydride

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Summary The kinetics of the self-initiated and di-t-butylperoxyoxalate initiated autoxidation of s-butylboronic anhydride have been studied and the rate constant for the peroxy-radical displacement of the s-butyl radical from boron has been measured.

THE autoxidation of a number of organoboron compounds in the liquid phase is an extremely rapid reaction which has recently been shown to occur by a free-radical chain process. The experimental evidence[1] for the free-radical nature of these oxidations is that they can be inhibited for significant periods by the addition of powerful free-radical traps such as galvinoxyl, and that stereoisomeric organoboron compounds are oxidized to nonstereospecific products. In addition, it has been shown by e.s.r. that alkoxy-radical can displace alkyl radical from a boron centre,[2] a reaction analogous to reaction (3). The following overall mechanism has been suggested:

Initiation: Production of $\mathrm{R\cdot}$ (1)

Propagation: $\mathrm{R\cdot + O_2 \rightarrow ROO\cdot}$ (2)

$$\mathrm{ROO\cdot + RB \xrightarrow{k_p} ROOB + R\cdot} \quad (3)$$

Termination: $\mathrm{R\cdot(ROO\cdot) + R\cdot(ROO\cdot) \rightarrow}$ Non-radical products (4)

If this mechanism is correct, the reaction should be subject to kinetic analysis in the same way as hydrocarbon autoxidations. Reaction (3), the radical displacement on boron, is of especial interest, particularly with regard to its rate constant as there are few rate constants known for radical displacement reactions and none for this particular reaction.

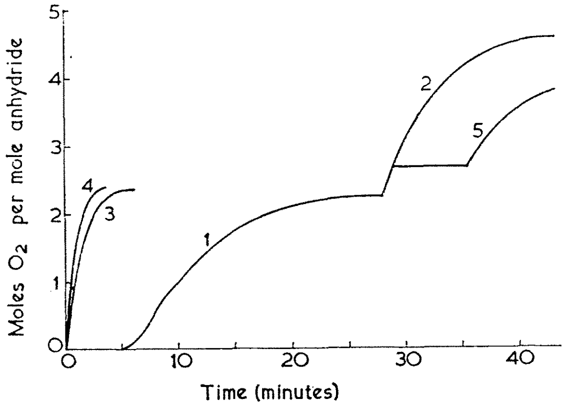
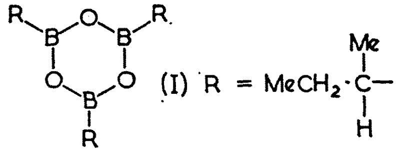


FIGURE. *The oxidation of* $3{\cdot}3 \times 10^{-3}$M-*s-butylboronic anhydride in iso-octane at* 30°. *Curve* 1: *Normal oxidation. Curve* 2: *A fresh sample of anhydride* ($3{\cdot}3 \times 10^{-3}$M) *added after* 28 min. *Curve* 3: *Oxidation initiated with* $1{\cdot}0 \times 10^{-2}$M-[DTBPO]. *Curve* 4: *Oxidation initiated with* $4{\cdot}0 \times 10^{-2}$M-[DTBPO]. *Curve* 5: $1{\cdot}5 \times 10^{-5}$M-[galvinoxyl] *added to reaction corresponding to Curve* 2 *after* 1 *min. oxidation.*

The absorption of oxygen by s-butylboronic anhydride (I) in iso-octane (chosen as a non-complexing solvent) at 30° is shown in curve 1 in the Figure. Autocatalytic oxygen absorption begins after an induction period, the curve showing a minor discontinuity at the point corresponding to the uptake of one mole of O_2 per mole of anhydride. A fresh sample of anhydride added to the fully oxidized anhydride (curve 2) is oxidized without any induction period.



(I) R = $\mathrm{MeCH_2{\cdot}C(Me)(H)}$—

In order to study the oxidation kinetics it is necessary to know the rate of chain initiation, R_i, at the point where the oxidation rate itself is measured. The initiation rate was determined by two independent methods. Firstly, it proved possible essentially to swamp out the self-initiation process by adding the thermal initiator di-t-butylperoxyoxalate[3] (DTBPO), see curves 3 and 4. Since the rate of production of free radicals at 30° from this compound is known, the oxidation is occuring at a known rate of chain initiation. Secondly, it was found that any oxidation could be stopped dead by the injection of galvinoxyl or 2,6-di-t-butyl-4-methoxyphenol (BMeOP). After a limited period the oxidation continued in the normal way (see *e.g.* curve 5). The rate of chain initiation at the point where the inhibitor is added is equal to n[inhibitor]/induction period, where n is the number of radicals trapped by the inhibitor (1·0 for galvinoxyl, 2·0 for BMeOP). The DTBPO addition and the inhibitor addition procedures gave results in qualitative and quantitative agreement with one another. The rate of oxidation was found to be proportional to the first power of the anhydride concentration and to the square root of the rate of chain initiation,and independent of the oxygen partial pressure (150—760 mm.). These kinetics correspond to those for the oxidation of most hydrocarbons at oxygen pressures above *ca.* 100 mm. and indicate that chain termination occurs by the self-reaction of two peroxy-radicals.[4]

Termination: $\mathrm{ROO\cdot + ROO\cdot \xrightarrow{2k_t}}$ Non-radical products (4′)

This means that reaction (3) is the rate controlling step for chain propagation and the overall rate can be represented by

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{Anhydride}]R_\mathrm{i}^{\frac{1}{2}}/(2k_\mathrm{t})^{\frac{1}{2}}.$$

The mean value of $k_\mathrm{p}/(2k_\mathrm{t})^{\frac{1}{2}} = 39{\cdot}6\,\mathrm{M}^{-\frac{1}{2}}\mathrm{s.}^{-\frac{1}{2}}$. Since $2k_\mathrm{t} = 1{\cdot}5 \times 10^6\,\mathrm{M}^{-1}\mathrm{s.}^{-1}$, for the self-reaction of s-butylperoxy-radical at 30°,[5] then $k_\mathrm{p} = 4{\cdot}8 \times 10^4\,\mathrm{M}^{-1}\mathrm{s.}^{-1}$, that is, $k_\mathrm{p} = 1{\cdot}6 \times 10^4\,\mathrm{M}^{-1}\mathrm{s.}^{-1}$ per carbon–boron bond. This propagation rate constant is much larger than the values found for hydrogen atom abstraction or peroxy-radical addition to double bonds in the oxidation of any hydrocarbon.[6] It will be interesting to discover the effect on k_p of the structure of the organoboron compound and the range of values which k_p may cover for different types of compound.

The self-initiation process in this autoxidation has also been examined. The natural induction period (curve 1) is greater in air than under 1 atm. of O_2 implying that the initial initiation process involves reaction of molecular oxygen with the substrate, either,

$$O_2 + \text{Anhydride} \rightarrow \text{Radicals} \tag{5}$$

or, $$O_2 + \text{Anhydride} \rightarrow \text{Peroxide} \rightarrow \text{Radicals} \tag{6}$$

The initiation process involving pre-oxidized anhydride (*i.e.*, curve 2 and, of course, curve 1 once significant oxidation has commenced) was studied by measuring R_1 by galvinoxyl addition during the second oxidation (*i.e.* curve 5) or by galvinoxyl addition immediately prior to the second anhydride addition. It was found that $R_1 \propto$ [oxidized anhydride]$^{0.5}$ [anhydride]. This can be rationalized by the assumption that the oxidized anhydride gives an unstable intermediate which is not trapped by galvinoxyl but either reacts with anhydride to give radicals or reacts with itself to give nonradical products:

$$\text{Oxidized anhydride} \xrightarrow{\text{slow}} \text{X} \tag{7}$$

$$\text{X} + \text{Anhydride} \rightarrow \text{R}\cdot \tag{8}$$

$$\text{X} + \text{X} \rightarrow \text{Non-radical products} \tag{9}$$

That is, $R_1 = k_8[\text{Anhydride}]\,(k_7[\text{Oxidized anhydride}]/2k_9)^{\frac{1}{2}}$ It seems likely that the relative importance of these, and perhaps other, self-initiation processes will be highly dependent on the structure of the organoboron compound and the experimental conditions.

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