Absolute Rate Constants for Homolytic Alkoxydealkylation at Boron

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Summary Absolute rate constants for the S_H2 process $RO\cdot + BBu_3 \rightarrow ROBBu_2 + Bu\cdot$ have been obtained by two competition techniques involving the analysis of products by g.l.c., or of the radical intermediates by e.s.r.

ALKOXY-radicals react with tri-n-butylborane by a bimolecular homolytic substitution (S_H2) at the boron centre (Equation 1).[1] We report values for the absolute rate constants for this reaction, which have been determined by two independent competition methods.

The first involved analysis of the products from the reaction of a t-alkyl hypochlorite with tributylborane. The reaction is rapid and can be totally inhibited by galvinoxyl; butyl chloride is the major product. This is consistent with a radical chain mechanism involving the propagation steps shown in Equations (1) and (2).

$$RCMe_2O\cdot + BBu_3 \xrightarrow{k_1} RCMe_2OBBu_2 + Bu\cdot \qquad (1)$$

$$Bu\cdot + ClOCMe_2R \rightarrow BuCl + \cdot OCMe_2R \qquad (2)$$

If the hypochlorite is suitably chosen ($R = Pr^i$), the S_H2 process (1) competes with the β-scission of the alkoxy-radical (Equation 3)[2] for which the rate can be derived from information in the literature.[2-4]

$$Pr^iCMe_2O\cdot \xrightarrow{k_3} Pr^i\cdot + Me_2CO \qquad (3)$$

The ratio of the two rate constants is given by the expression

$$\frac{k_1}{k_3} = \frac{[BuCl]}{[Me_2CO][Bu_3B]} \qquad (4)$$

The ratio $[BuCl]/[Me_2CO]$ was determined by g.l.c. for the reaction of 0·1M-tributylborane and 0·01M-1,1,2-trimethylpropyl hypochlorite in carbon tetrachloride at 40°. The average of eight determinations gave $k_1/k_3 = 9{\cdot}2 \pm 0{\cdot}9\ \text{M}^{-1}$; $k_3 = 4{\cdot}84 \times 10^6\ \text{s}^{-1}$, whence k_1 ($R = Pr^i$) $= 4{\cdot}5 \times 10^7\ \text{M}^{-1}\text{s}^{-1}$ at 40°.

The second method involved the simultaneous observation by e.s.r., and measurement of the relative concentrations, of the butyl radical resulting from the S_H2 reaction (1), and of the cyclopentyl radical produced by competitive hydrogen abstraction from cyclopentane† which occurs at a known rate (Equation 5).[2-4]

$$RCMe_2O\cdot + C_5H_{10} \xrightarrow{k_5} RCMe_2OH + C_5H_9\cdot \qquad (5)$$

t-Butoxy-radicals were generated (*cf.* ref. 1) by photolysing di-t-butyl peroxide or di-t-butyl hyponitrite (*ca.* 1M) in cyclopentane (*ca.* 8M) containing tributylborane (0·1M), when the spectra of both the butyl and cyclopentyl radicals were observed (Equations 1 and 5; $R = Me$).

The ratio of the rate constants for displacement at boron and abstraction of hydrogen from cyclopentane is given by Equation (6).

$$\frac{k_1}{k_5} = \frac{[C_5H_{10}][Bu\cdot]}{[Bu_3B][C_5H_9\cdot]} \qquad (6)$$

From eighteen experiments between − 5° and + 48°, an Arrhenius plot was obtained (Figure), whence

$$k_1/k_5 = (0{\cdot}034 \pm 0{\cdot}001)\exp[(5190 \pm 360)\boldsymbol{R}/T] \qquad (7)$$

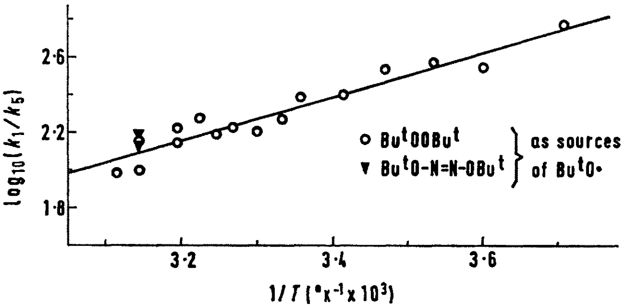

FIGURE. *Arrhenius plot describing* $C_5H_{10}:Bu^n{}_3B$ *competition for* $Bu^tO\cdot$ *radicals.*

At 40°, $k_5 = 5{\cdot}1 \times 10^4\ \text{M}^{-1}\text{s}^{-1}$, thus k_1 ($R = Me$) $= 7{\cdot}3 \times 10^6\ \text{M}^{-1}\text{s}^{-1}$.

The activation energy for hydrogen abstraction from cyclohexane is $6{\cdot}7 \pm 2{\cdot}7$ kcal mol^{-1};[3,4] if the value for cyclopentane is similar, it would suggest that the activation energy for the displacement reaction (1) is 2 ± 3 kcal mol^{-1}.

Similar values of k_1 were thus obtained for the two t-alkoxy-radicals by the two methods. This supports the validity of the two techniques, and the order of magnitude of the rate constants.

These results, together with the similar data which have recently been obtained for the reaction of alkylperoxy-radicals,[6] represent the only absolute rate coefficients for the reaction of oxygen-centred radicals at metal atoms, that have been recorded.

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† As far as we are aware, this is a novel application of the e.s.r. spectroscopy of alky radicals. The spectrum of the cyclopentyl radical, with similar coupling constants, has been previously observed by irradiating cyclopentane with high-energy electrons (ref. 5).

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