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# MECHANISM OF AUTOXIDATION OF ALKYL BORATES[1]

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**Abstract**—Autoxidation behaviour of cyclohexyl, benzyl, α- and β-phenethyl and benzhydryl borates has been studied and compared with the parent alcohols. Autoxidation of cyclohexanol proceeds autocatalytically in the presence of desiccating agent, $MgSO_4$, or tricyclohexyl borate, since the equilibrium constant for hydrolysis of the borate is large (ca. $10^4$ at 80°). Cobalt naphthenate is a catalyst, but cobaltous acetate suppresses the autoxidation. Alcohols, whose energies of activation for abstraction of α-H (hydrogen atom) range 7–10 kcal/mole, are autoxidized ca. 10 times as fast as their borates. Whereas alcohols, whose energies of activation are 3–4 kcal/mole, are autoxidized ca. 5 times as fast as their borates. Based on NMR data of α-proton, the inductive effect of boron exerted on one of α-H's in borate is evaluated to be 0·95 as a $\sigma^*$ value which is smaller than that of acetyl group ($\sigma^*$ 1·65). The higher stability of borate than acetate may be due to the steric requirement in $B(OR)_3$.

Liquid-phase autoxidation of normal, branched-chain and cyclic paraffins affords often poor selectivity of products. Scipioni[2] has reported that addition of boric acid in the autoxidation system brings about the suppression of further oxidation of intermediary alcohol to ketone, carboxylic acid or fission products. A number of patents and reports concerning the preparation of alcohols by autoxidation of paraffins in the presence of boric acid,[3] boric anhydride[4] or borate[5] have appeared, which were proved to be of industrial importance.[6] The observed increase in the selectivity of alcohol in the presence of boron compounds seems to be caused by the formation of borate stabilized against autoxidation.

## RESULTS AND DISCUSSION

*Autoxidation of cyclohexanol.* The appropriate conditions and conversions for autoxidation of cyclohexanol as a typical alcohol with some additive are illustrated in Fig. 1.

In the autoxidation of cyclohexanol without additive, a long induction period (ca. 3·5 hr) together with rather rapid slow-down of oxygen uptake was observed (Curve 1). But on addition of $MgSO_4$ the quenching of oxygen uptake ceased as seen in Curve 2. On addition of a small amount of $(t\text{-}BuO)_2$ as an initiator, the induction period disappeared, but the oxygen absorption became slow (Curve 3). In this case also, $MgSO_4$ was an effective drying agent and resulted in the acceleration of oxygen absorption which probably accompanies autocatalysis (Curve 4).

A number of examples of autoxidation inhibited by water are known. In the present experiments, $MgSO_4$ absorbs water produced by the reaction to form $MgSO_4 \cdot H_2O$

which is stable at the reaction temperature of 120°. Cooper *et al.*[7] explained the mechanism for the inhibition with water by means of the following equations.

$$HOO\cdot + H_2O \rightleftarrows \cdot OO^- + H_3O^+ \tag{1}$$

$$\cdot OO^- \rightarrow \cdot OO\cdot + e \tag{2}$$

Active radical, HOO·, is destroyed by $H_2O$, giving less active radical ·OO·. But details of reason are still unknown.

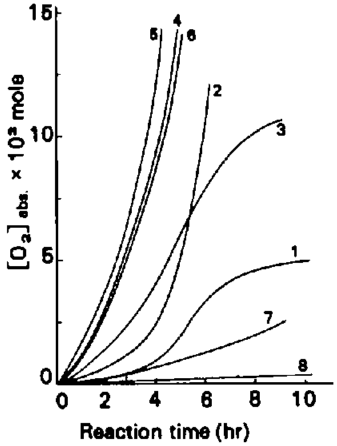


FIG. 1 Autoxidation of cyclohexanol (0·1 mole) at partial pressure of $O_2$ of 680 mmHg at 120°

1. None; 2. $MgSO_4$, 2 g; 3. $(t\text{-}BuO)_2$, 0·3 wt%; 4. $MgSO_4$, 2 g and $(t\text{-}BuO)_2$, 0·3 wt%; 5. $MgSO_4$, 2 g and $(t\text{-}BuO)_2$, 0·6 wt% 6. Co naphthenate, 0·5 mole% as Co; 7. Co $(OAc)_2\cdot 6H_2O$, 0·5 mole % as Co; 8. AcOH, 1 ml.

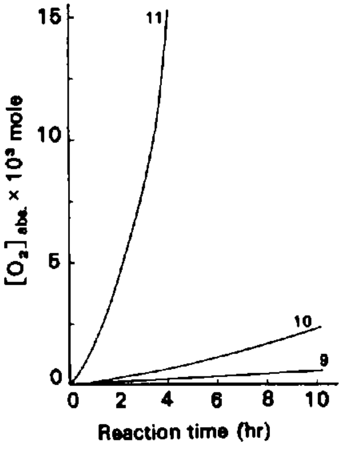


FIG. 2 Autoxidation of tricyclohexyl borate (0·033 mole) with additives at partial pressure of $O_2$ of 680 mmHg at 120°

9. None; 10. $MgSO_4$, 2 g and $(t\text{-}BuO)_2$, 0·6 wt%; 11. Cyclohexanol, 0·1 mole.

It is of interest to note that a two-fold increase of the amount of $(t\text{-BuO})_2$ results in a $\sqrt{2}$ fold increase of initial rate of oxygen absorption (Curve 5).

The effect of metallic ions was also examined. Cobalt naphthenate displays a catalytic effect (Curve 6) but cobaltous acetate suppresses the reaction (Curve 7). Addition of acetic acid also inhibits the reaction effectively (Curve 8). These results suggest that acetate ion inhibits the autoxidation.

*Autoxidation of tricyclohexyl borate.* In a comparison of the rate of autoxidation of cyclohexanol with that of its borate, the number of α-H (hydrogen atom) in both reactants should be equal; hence, 0·033 mole of the borate was used for the comparison with the runs using 0·1 mole of cyclohexanol. Typical results are shown in Fig 2.

The borates are stable without $(t\text{-BuO})_2$ (Curve 9), and even in the presence of the peroxide (Curve 10). The rate increases markedly on addition of 0·1 mole of cyclohexanol (Curve 11). The observed rate is greater than that of oxidation of 0·1 mole cyclohexanol (Curve 4 in Fig 1). This is explained by Eq. 3, i.e., the facile removal of water by borate, which is more effective than $MgSO_4$, and an increased amount of cyclohexanol, which is more oxidizable than the borate, results in the acceleration of apparent oxygen absorption.

$$\frac{1}{3}(C_6H_{11}O)_3B + H_2O \overset{K}{\rightleftarrows} C_6H_{11}OH + \frac{1}{3}H_3BO_3 \qquad (3)$$

The Karl–Fischer estimation of $H_2O$ formed in Eq. 3 gave the equilibrium constant ($K$) of ca. $10^4$ (at 80°). This figure justifies the above discussion and also suggests that either addition of borate and boron anhydride or removal of water in the autoxidation of paraffins is effective to raise the yield of alcohol.

Reviewing the above data (Figs 1 and 2), experiments described below were carried out with addition of $MgSO_4$ and $(t\text{-BuO})_2$, and the reproducible results are shown in Curves 4, 5, 10 etc.

*Autoxidation of some alcohols and their esters.* In addition to cyclohexanol, a number of alcohols with activation energy of α-H abstraction in the range 10–3 kcal/mole were chosen for the study of effect of boron on autoxidation. Comparison of alcohols with their borates was done by the estimation of the initial rate of oxygen absorption in order to avoid further oxidation of carbonyl compounds formed initially (Table 1).

TABLE 1. RATE CONSTANTS OF AUTOXIDATION OF ALCOHOLS ($k_H$), BORATES ($k_B$) AND ACETATES ($k_{Ac}$) AT 120° (EXCEPT *170°) WITH PARTIAL PRESSURE OF $O_2$, 680 mmHg. 0·1 MOLE OF ALCOHOL (X = H) OR ACETATE (X = Ac) AND 0·033 MOLE OF BORATE (X = B) WERE USED FOR THE MEASUREMENTS OF OXYGEN ABSORPTION IN THE PRESENCE OF $MgSO_4$ (2 g) AND $(t\text{-BuO})_2$ (0·6 wt%).

$k_X$ is expressed as $[O_2]_{abs} \times 10^3$ mole/α-H eq.mole/hr.

| $RCH_2OX$ | $k_H$ | $k_B$ | $k_{Ac}$ | $k_H/k_B$ | $k_{Ac}/k_B$ |
|---|---|---|---|---|---|
| $PhCH_2CH_2OX$ | 4·83 | 0·59 | 1·27 | 8·13 | 2·13 |
| $C_6H_{11}OX$ | 15·3 | 1·66 | 4·35 | 9·24 | 2·62 |
| $PhCH_2OX$ | 12·1 | 1·16 | — | 10·43 | — |
| $Ph_2CH(OX)$* | 20·1 | 4·63 | 6·32 | 4·32 | 1·37 |
| $PhCH(OX)CH_3$ | 23·6 | 5·11 | — | 4·58 | — |

Activation energies of α-H abstraction in β-phenethyl, cyclohexyl and benzyl alcohols in the autoxidation initiated by benzoyl peroxide or UV light (sensitized by $TiO_2$) are ca. 7–10 kcal/mole.[8] The rate constant for oxidation of these borates is ca. 1/10 of that of corresponding alcohols. On the other hand, activation energies of α-H abstraction in benzhydryl and α-phenethyl alcohols are 3–4 kcal/mole[8] and their borates are oxidized rapidly (the rate constants are ca. 1/5 of those of the corresponding alcohols). Oxidation rates of carboxylates are higher than the corresponding borates, e.g., the rate constants of acetate are 1/3–1/4 of those of alcohols, but this is independent of the rate of α-H abstraction, which suggests that its acetyl group exerts the inductive effect alone to retard the autoxidation.

*Inductive effect and steric hindrance of boron.* The results in Table 1 show that borates are more resistant to autoxidation than acetates. No quantitative information on the electron-attracting inductive effect of boron is available in the literature; hence the effect of boron was examined by NMR chemical shift of α-proton as shown in Table 2. The inductive effect of boron is exerted on three symmetrical alkoxy groups in the borate.

TABLE 2. NMR CHEMICAL SHIFT (τ) OF α-PROTON OF ALCOHOLS (X = H), BORATES (X = $B_{1/3}$) AND ACETATES (X = Ac). SOLVENT, $CDCl_3$; REFERENCE, TMS.

| $RCH_2OX$ | H | $B_{1/3}$ | Ac |
|---|---|---|---|
| $PhCH_2CH_2OX$ | 6·36 | 6·13 | 5·84 |
| $C_6H_{11}OX$ | 6·40 | 6·00 | 5·35 |

Since one of α-protons would be affected by one third of the inductive effect of boron, $\sigma^*$ value of $B_{1/3}$ is obtained from the linear plot of $\tau$ *vs* $\sigma^*$. The $\sigma^*$ values for H and Ac are known[9] to be 0·49 and 1·65, respectively. Therefore, the $\sigma^*$ values of $B_{1/3}$ are evaluated as 0·97 and 0·94 from the $\tau$'s of α-protons of β-phenethyl and cyclohexyl borates, respectively.

In spite of the smaller inductive effect of boron (average value $\sigma^*$ of $B_{1/3}$ is 0·95), borates are more resistant to autoxidation than acetates ($k_B < k_{Ac}$). Such a phenomenon may be explained as follows. When one of α-H in $B(OR)_3$ is abstracted, then a gross inductive effect of B is exerted largely on the remaining two α-H's in $(OR)_2$, and this results in difficult abstraction. Assuming the inertness of the remaining two α-H's, another effect of boron was examined by plotting $\log k_x$ *vs* $\sigma^*$ after multiplying $k_B$ by three (the number of reactive α-H in borate is assumed to be 1/3 of that in free alcohol or acetate). Values of $\log k_B$ deviate downwards from linear plots of $\log k_H$ and $\log k_{Ac}$ *vs* $\sigma^*$. The deviation corresponds to the steric effect of boron. Molecular models of the borates also show the steric hindrance to α-H.

*Mechanistic difference between sterically hindered alcohols and their borates in autoxidation.* Benzyhydryl borate, which is more sterically hindered than β-phenethyl and cyclohexyl borates, is more reactive (Table 1) and this suggests that autoxidation of alcohols may proceed by the following two mechanisms.[8]

Mechanism A

$$\mathrm{RR'CHOH} \xrightarrow{k_1} \mathrm{RR'\dot{C}OH}$$

$$\mathrm{RR'\dot{C}OH} + \mathrm{O_2} \xrightarrow{k_2} \mathrm{RR'C}\begin{matrix}\diagup \mathrm{OO\cdot} \\ \diagdown \mathrm{OH}\end{matrix} \quad (\mathrm{AOO\cdot})$$

$$\mathrm{AOO\cdot} \xrightarrow{k_3} \mathrm{RR'CO} + \mathrm{HOO\cdot}$$

$$\mathrm{HOO\cdot} + \mathrm{RR'CHOH} \xrightarrow{k_4} \mathrm{HOOH} + \mathrm{RR'\dot{C}OH}$$

$$\mathrm{HOO\cdot} + \mathrm{HOO\cdot} \xrightarrow{k_5} \mathrm{HOOH} + \mathrm{O_2}$$

$$\mathrm{HOO\cdot} + \mathrm{AOO\cdot} \begin{array}{l} \xrightarrow{k_6} \mathrm{HOOH} + \mathrm{RR'CO} + \mathrm{O_2} \\ \xrightarrow{k_7} \mathrm{AOOH} + \mathrm{O_2} \end{array}$$

$$\mathrm{AOO\cdot} + \mathrm{AOO\cdot} \begin{array}{l} \xrightarrow{k_8} \mathrm{AOOH} + \mathrm{RR'CO} + \mathrm{O_2} \\ \xrightarrow{k_9} \mathrm{AOOA} + \mathrm{O_2} \end{array}$$

On the other hand, alcohols having reactive α-H such as α-phenethyl alcohol (activation energy for α-H abstraction is 3·4 kcal/mole) may be autoxidized via another pathway, where α-H is abstracted by peroxy radical (AOO·) instead by hydroperoxy radical (HOO·).

Mechanism B

$$\mathrm{AOO\cdot} + \mathrm{RR'CHOH} \xrightarrow{k'_3} \mathrm{AOOH} + \mathrm{RR'\dot{C}OH}$$

$$\mathrm{RR'\dot{C}OH} + \mathrm{RR'\dot{C}OH} \begin{array}{l} \xrightarrow{k_{10}} \mathrm{RR'CHOH} + \mathrm{RR'CO} \\ \xrightarrow{k_{11}} (\mathrm{RR'COH})_2 \end{array}$$

$$\mathrm{RR'\dot{C}OH} + \mathrm{HOO\cdot} \begin{array}{l} \xrightarrow{k_{12}} \mathrm{RR'CO} + \mathrm{HOOH} \\ \xrightarrow{k_{13}} \mathrm{AOOH} + \mathrm{O_2} \end{array}$$

$$\mathrm{RR'\dot{C}OH} + \mathrm{AOO\cdot} \xrightarrow{k_{14}} \mathrm{RR'CO} + \mathrm{AOOH}$$

Mechanism B explains the predominant formation of organic-peroxide and dependence of rate on partial pressure of oxygen.[8]

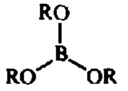
The present autoxidation of α-phenethyl and benzhydryl alcohols may proceed by mechanism B, while the autoxidation of their borates may go by way of mechanism A accompanied by some degradation, since the peroxy radical bound to $(RO)_2B$- seems to be too bulky to attack on another bulky borate molecule.

In fact, virtually no organic peroxide was identified in the oxidation mixture of borates.

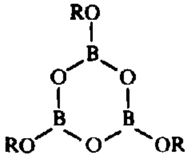
## EXPERIMENTAL

*Materials.* Commercial alcohols except benzhydrol were purified by repeated fractional distillation under $N_2$ and qualified before use by GLC, IR and refractometry. Benzhydrol was prepared by Grignard reaction of benzaldehyde and PhMgBr.[11] Tricyclohexyl,[12] tribenzyl[13] and tri-α-phenethyl borates[13] were prepared by known methods. Tri-β-phenylethyl borate was prepared by heating a mixture of β-phenethyl alcohol (244 g, 2 mole) and boric acid (30 g, 0·5 mole) to 110° under reduced press to remove water formed. After heating for 7 hr, the reaction mixture was fractionated, b.p. 232–235° (2·5 mm), hygroscopic liquid

165 g; IR $\lambda_{max}^{neat}$: 1480, 1340, 743 cm$^{-1}$ (lit[14–16] on assignments for IR spectra bands of borates); NMR (CDCL$_3$) τ: 7·33 (2 H), 6·13 (2 H), 2·95 (5 H); $n_D^{20}$ 1· 490, $n_D^{25}$ 1·5470. Tribenzylhydryl borate was prepared by refluxing a mixture of benzhydrol (46 g), boron trioxide (2·5 ~~g)~~and xylene (100 ml) for 5 hr. After removal of water formed and solvent as azeotrope, the residue was powdered and washed with ether (30 ml) and then with CCl$_4$ (100 ml), giving crystals (44 g), m.p. 168·7–169·0°; IR $\lambda_{max}^{KBr}$: 1490, 1330, 750 cm$^{-1}$. (Found: C, 83·21; H, 5·78. C$_{39}$H$_{33}$O$_3$B requires: C, 83·57; H, 5·93%). All borates may have structure I, but not II.



I



II

Cyclohexyl acetate was prepared by the reaction of cyclohexanol and glacial AcOH according to Vogel[17] in a yield of 58·4%; b.p. 174° [lit.[17] 172° (752 mm)], $n_D^{20}$ 1·4473. β-Phenethyl acetate was prepared by heating a mixture of pure β-phenethyl alcohol (36 g, 0·3 mole), Ac$_2$O (30 g, 0·3 mole) and ZnCl$_2$ (0·3 g) at 150° for 24 hr. Distillation at 118·0–118·3° (20 mm) [lit.[18] 118–120° (13 mm)] gave 29 g (58·9 %) of colourless liquid (lit.[19] yellow liquid); IR $\lambda_{max}^{neat}$: 1745 (vs, $\nu_{c=o}$), 1245 (vs. broad, $\nu_{c-o}$), 1030 cm$^{-1}$(s); $n_D^{20}$ 1·4855 (lit.[18] $n_D$ 1·5108). Benzhydryl acetate was prepared by refluxing a mixture of benzhydrol (40 g), AcOH (80 g) and Ac$_2$O (40 g) for 15 hr; the product of 35 g (71·3 %) after fractionation at 168·5° (10 mm) [lit.[20] 184° (23 mm)] gave colourless liquid (lit.[20] m.p. 41–42°); IR $\lambda_{max}^{neat}$: 1735 (vs, $\nu_{c=o}$), 1225 (s, $\nu_{c-o}$), 1015 (M) cm$^{-1}$; NMR (CDCl$_3$) τ: 8·15 (3 H), 3·75 (1 H), 2·87 (10 H); $n_D^{20}$ 1·5483. (Found: C, 79·50; H, 6·26. C$_{15}$H$_{14}$O$_2$ requires: C, 79·62; H, 6·24%). Cobalt naphthenate and acetate, *t*–butyl peroxide and catalase (from bovine liver) were of guaranteed grade. O$_2$ and N$_2$ were of 99·7% and 99·9 % pure, respectively.

*Rate measurements.* The kinetic experiment was carried out by measuring O$_2$ absorption with an apparatus shown in Fig 3. Substrates (0·1 mole of alcohol or acetate or 0·033 mole of borate) and additives

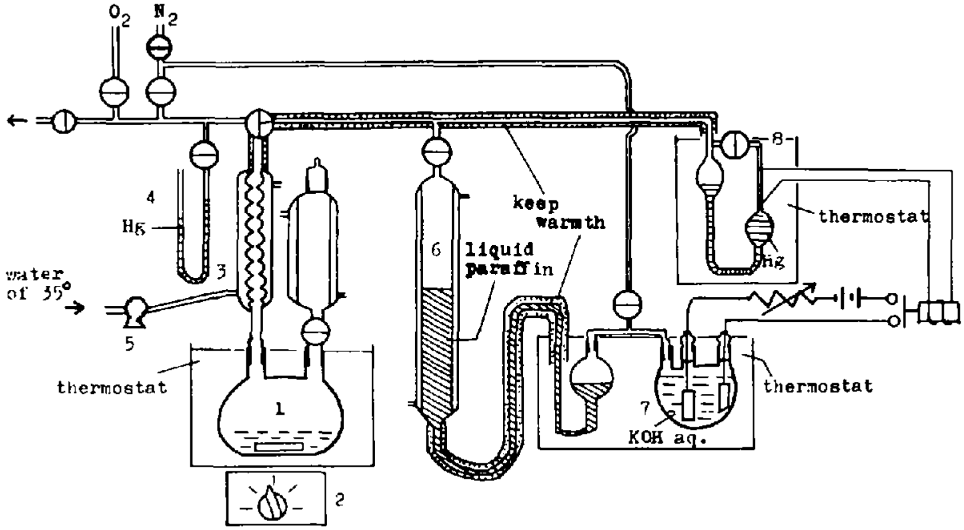


FIG. 3 Apparatus for the kinetic study of autoxidation.
1. Reactor 2. Magnetic Stirrer 3. Condenser 4. Manometer 5. Pump 6. Gas Burette
7. Electrolytic Cell 8. Regulator

were placed in a reactor 1 dipped in a thermostat at 120°. A mixture of $O_2$ and $N_2$ at atm press with a partial press of $O_2$ of 680 mm Hg was introduced and the mixture was stirred magnetically by stirrer 2 (800 rpm) in Fig 3. It was confirmed that the agitation of over 500 rpm made the rate of dissolution of $O_2$ into the reaction mixture faster than the rate of chemical reaction. The rate was measured by gas burette 6.

*Reaction products criterion.* The main product after 1 hr was carbonyl compound (90%) which was estimated acidimetrically by $NH_2OH \cdot \frac{1}{2}H_2SO_4$ and 0·1 N KOH with bromophenol blue as an indicator.[21] Analysis by a gas chromatograph of Yanagimoto GCG-550 F equipped with 2 m column of 3% PEG No. 6000 on celite 545 also proved that carbonyl compound was the main product. Peroxides were estimated by iodometry, where $H_2O_2$ was decomposed preliminarily by catalase.

*NMR analysis.* All samples were dissolved in $CDCl_3$ and analysed by a 60 Mc JEOL Minimer.

*Estimation of K in Eq. 3.* Water formed from cyclohexanol of $5 \times 10^{-2}$ mole and boric acid of $1{\cdot}67 \times 10^{-2}$ mole at 80° was estimated by a Yanagimoto potentiometric titrimeter with Pt electrodes at polarization current of 5 μA with Karl–Fischer reagent.

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