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# Mechanistic aspects of benzylic bromide formation and oxidation during the cobalt acetate bromide catalyzed oxidation of alkylbenzenes in carboxylic acids

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## Abstract

The formation and fate of benzylic bromides during the cobalt acetate bromide catalyzed oxidation of toluene and 4-chlorotoluene were investigated in carboxylic acid solvents. The rate of formation of benzylic bromides depends on the substrate and catalyst concentrations while the conversion of ionic bromide to benzylic bromides is strongly influenced by the type of solvent and the presence of nucleophilic ligands and metal co-catalysts. The observed effects are best explained in terms of a chain carrier comprising both cobalt acetate and bromide. Oxidation of benzylic bromides under the reaction conditions results in the formation of benzal bromides, benzaldehydes, benzoic acid and molecular bromine. An electron transfer process is proposed to explain the oxidation of benzylic bromides.

*Keywords:* Alkylbenzenes; Benzylic bromides; Cobalt acetate bromide; Oxidation

## 1. Introduction

Several important industrial processes for the liquid phase oxidation of alkylbenzenes to the corresponding carboxylic acids are based on cobalt catalyst systems<sup>1</sup>. The application of this technology however, varies widely and includes, inter alia, the use of activator substances such as ketones, aldehydes or ozone [1,2], the use of promoters such as ionic bromides [3–6], the use of co-catalysts such as zirconium(IV) and hafnium(IV) acetates [7], and the use of high cobalt(III) acetate concentrations in the absence

of any activators, promoters or co-catalysts [8]. The use of a bromide-promoted catalyst system offers several advantages such as its applicability to a variety of substrates, the fact that it suffers virtually no inhibition problems and the use of relatively small amounts of metal catalyst. The major disadvantage of such systems is their corrosive nature which necessitates the use of expensive construction materials such as titanium or Hastelloy C in production facilities [9].

Despite the fact that the oxidation of hydrocarbons in carboxylic acid solutions, catalyzed by cobalt acetate bromide, have been studied by several workers [3–8], many aspects concerning the exact role played by bromide and/or bromide containing intermediates are still unclear. It is generally accepted that the profound synergistic effect

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<sup>1</sup> The patent literature on these oxidations runs into hundreds of patents and literature references will be restricted to publications dealing with mechanisms and related aspects.

of bromide ions on metal catalysis can be attributed to the enhancement in the rate of the propagation step, since the rate of oxidation of alkylbenzenes far exceeds the values calculated from the propagation and termination rate constants [5,10].

Several proposals regarding the synergistic effect of bromide appear in the literature. These include changes effected by bromide on the cobalt(III) redox potential due to co-ordination effects [11,12], redistribution of the cobalt monomer–dimer equilibrium [11], the formation of bromine atoms which may act as powerful hydrogen abstractors [4,13], and the formation of a cobalt–bromide complex which act as the chain transfer agent [6,14]. None of the above, however, adequately explain the following aspects concerning bromide promoted autoxidations:

- the nature of organic bromides formed during the course of such reactions,
- the rate and extent of conversion of ionic bromide to organic bromide,
- the observation that in continuous reactions, the cobalt catalyst maintains a relatively high activity, despite the presence of bromide as an ‘unreactive’ organic bromide,
- the detection of molecular bromine in cobalt acetate bromide (CAB) catalyzed oxidations only at low substrate concentrations, and
- the effect of co-catalysts and/or solvent/ligands on bromide-promoted oxidations.

Despite the importance of organic bromide intermediates, formed during catalyzed oxidations of alkylbenzenes (since their formation probably involves the interaction of an ‘active’ catalyst species and an activated form of the substrate) very little attention has been paid to the formation and fate of organic bromides in such reactions. A better understanding of the bromine cycle in CAB catalysed oxidations is important from both a fundamental (mechanistic) and engineering (reactor and process) point of view. In this work we report the results on a study of the factors affecting the formation of benzylic bromides, their fate and their effect on catalytic activity during cobalt ace-

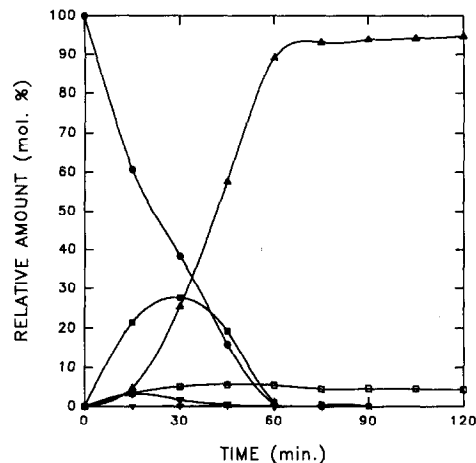


Fig. 1. Product distribution for CAB catalyzed oxidation of toluene. (mol%, based on toluene. For experimental details see Table 3, subscript b.) Symbols: ● – toluene; ▽ – benzyl alcohol; ▼ – benzyl acetate; □ – benzyl bromide; ■ – benzaldehyde; △ – benzoic acid.

tate bromide catalyzed air oxidations of toluene and chloro-substituted toluenes.

## 2. Results

The change in concentration of substrate and products in a typical oxidation reaction of toluene is shown in Fig. 1. The formation of intermediates such as benzyl alcohol, benzyl acetate, benzaldehyde, as well as the reaction product, benzoic acid, have been discussed in detail elsewhere [11] and needs no further comment. The variation in the concentrations of benzyl bromide, and benzal bromide towards the end of the reaction, which is of direct interest to this investigation, is shown more clearly in Fig. 2, together with the variation in the concentration of ionic bromide (determined as  $\text{Br}^-$  by cyclic voltametry). Fig. 2 shows that ionic bromide (or catalyst bound bromide) is rapidly converted to benzyl bromide, the concentration of which decrease at low substrate concentrations. Prior to the onset of benzyl bromide disappearance there is good correlation between the total amount of bromide added and the bromide appearing as ionic and benzyl bromide, but after the onset of benzyl bromide disappearance, this correlation deteriorates rapidly. During the latter stages of the oxidation reaction, traces of benzal bromide

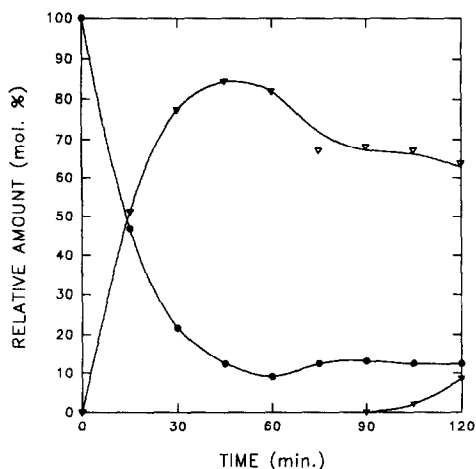


Fig. 2. Variation of bromine containing compounds for toluene oxidation. (mol%, based on total  $\text{NH}_4\text{Br}$ . For experimental details, see Table 3, subscript b.) Symbols: ● – bromide; ▽ – benzyl bromide; ▼ – benzal bromide.

Table 1  
Types of organic bromides

Substrate <sup>b</sup>	Organic bromide	Yield <sup>a</sup> (mol%)
$\text{C}_6\text{H}_5\text{CH}_3$	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	87.5
2- $\text{ClC}_6\text{H}_4\text{CH}_3$	2- $\text{ClC}_6\text{H}_4\text{CH}_2\text{Br}$	99.2
4- $\text{ClC}_6\text{H}_4\text{CH}_3$	4- $\text{ClC}_6\text{H}_4\text{CH}_2\text{Br}$	97.9
2,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{CH}_3$	2,4- $\text{Cl}_2\text{C}_6\text{H}_3\text{CH}_2\text{Br}$	99.5
4- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$	4- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Br}$	<sup>c</sup>
4- $\text{HOOC}_6\text{H}_4\text{CH}_3$	4- $\text{HOOC}_6\text{H}_4\text{CH}_2\text{Br}$	<sup>c</sup>
4- $\text{MeOC}_6\text{H}_4\text{CH}_3$	4- $\text{MeOC}_6\text{H}_4\text{CH}_2\text{Br}$	<sup>c</sup>

<sup>a</sup> Based on total  $\text{NH}_4\text{Br}$  added;

<sup>b</sup> Substrate (ca. 26 mmol);  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.48 g; 1.93 mmol);  $\text{NH}_4\text{Br}$  (0.19 g; 1.94 mmol);  $\text{C}_6\text{H}_5\text{NO}_2$  (3.0 g; 24 mmol);  $\text{HOAc}$  (30  $\text{cm}^3$ );  $\text{O}_2$  flow rate (30  $\text{cm}^3 \cdot \text{min}^{-1}$ );

<sup>c</sup> Not determined.

(identified by GC–mass spectrometry and co-injection of authentic samples) appear in the reaction mixtures. At termination of the reaction, approximately 15% of the initial bromide is unaccounted for and may be ascribed to the formation of molecular bromine (which may be observed visually during the latter stages of the reaction).

### 2.1. Nature of organic bromides

In order to establish the nature of the most important organic bromides formed during the CAB-catalyzed oxidations of alkyl-benzenes, a number of alkyl aromatic substrates were oxidized

in acetic acid in the presence of cobalt(II) acetate and ammonium bromide (Table 1). Reaction products were identified by GC–MS and confirmed by co-injection of authentic samples. The results confirm previous reports that benzylic bromides are the major organic bromides formed during CAB catalyzed oxidations [4,15–19]. No nuclear brominated compounds could be detected in any of the oxidation reactions investigated. When molecular bromine is introduced into the reaction mixtures in the same quantities and under the same reaction conditions in the presence of cobalt(II) acetate, significant amounts of nuclear brominated compounds may, however, be observed for substrates with activating substituents on the ring ( $-\text{OMe}$ ,  $-\text{CH}_3$  etc) [12,19].

### 2.2. Factors influencing benzylic bromide formation

The variation in the rate of 4-chlorobenzyl bromide formation during the CAB-catalyzed air oxidation of 4-chlorotoluene, as a function of 4-chlorotoluene concentration, is shown in Fig. 3 together with the variation in the rate of 4-chlorotoluene consumption. Results, obtained from the oxidation of toluene show similar behaviour, i.e. an increase in the rate of benzylic bromide

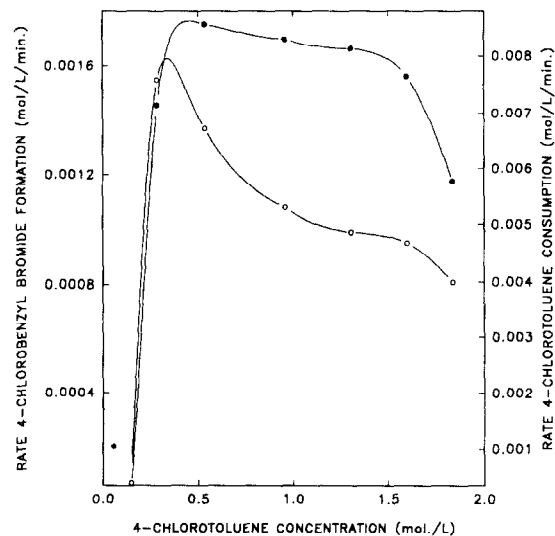


Fig. 3. Effect of substrate concentration. (For experimental details, see Table 2, subscript a.) Symbols: ● – 4-chlorotoluene consumption; ○ – 4-chlorobenzyl bromide formation.

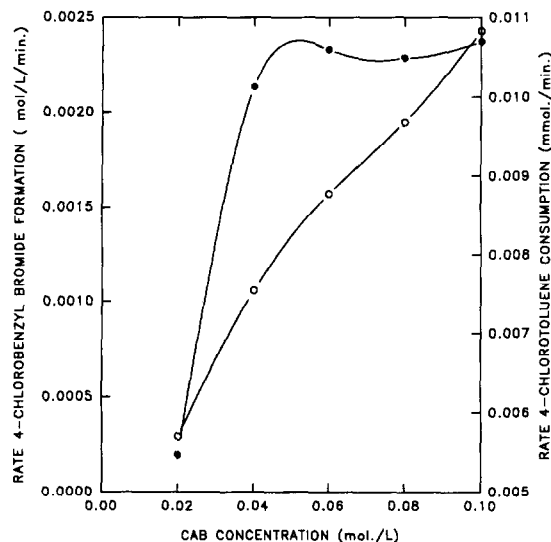


Fig. 4. Effect of CAB concentration. (For experimental details, see Table 2, subscript c.) Symbols: ● – 4-chlorotoluene consumption; ○ – 4-chlorobenzyl bromide formation.

formation with increasing substrate concentration. At higher substrate concentrations, the rates of benzylic bromide formation are suppressed significantly. The close correspondence in the curves for benzyl bromide formation and toluene consumption, especially at lower substrate concentrations, suggests that these two processes are related. Fig. 4, which compares the rates of 4-chlorobenzyl bromide formation and 4-chlorotoluene consumption as a function of CAB concentration, shows that 4-chlorobenzyl bromide formation is directly related to CAB concentration. When the rate of benzylic bromide formation is measured as a function of bromide/cobalt ratio, a linear relationship (Fig. 5) is obtained in the range 0–2.0. At  $\text{Br}^-/\text{Co}$  ratios above 2.0, the rate decreases rapidly. The increase in benzylic bromide formation with increasing  $\text{Br}^-/\text{Co}$  ratios may be ascribed to an increase in  $\text{Co(II)(OAc)Br}$  formation since not all of the bromide added to cobalt(II) acetate solutions in acetic acid is coordinated [20]. A higher  $\text{Br}^-/\text{Co}$  ratio, therefore, should increase the proportion of bromide coordinated to cobalt in the form  $\text{Co(II)(OAc)Br}$ . The decrease in the rate of benzyl bromide formation at high  $\text{Br}^-/\text{Co}$  ratios is probably the result of catalyst deactivation due to  $[\text{CoBr}_4]^{2-}$  formation as proposed by Bawn and Wright [15].

The effect of substrate concentration, CAB concentration and  $\text{Br}^-/\text{Co}$  ratio on the conversion of ionic bromide to benzyl bromide during the CAB catalyzed oxidation of toluene, is illustrated in Table 2. (The ‘yields’ of benzyl bromide reflected in Table 2 are the maximum amounts of benzyl bromide formed in any one particular reaction, while the corresponding values for toluene conversion were obtained from the same sample taken for benzyl bromide analysis.) The conversion of ionic bromide to benzyl bromide varies with substrate and CAB concentrations, but is, apparently, unaffected by the  $\text{Br}^-/\text{Co}$  ratio. It is also of interest to note that the conversion of toluene in these reactions is virtually unaffected by the above reaction variables. The only exception appears to be at high initial substrate concentrations, where a significant reduction in toluene conversion is observed.

The extent of ionic to benzylic bromide conversion is also dependent upon the nature of the substrate, the type of carboxylic acid solvent used, the nature of the catalyst, as well as the presence of nucleophilic ligands (Table 3). Thus, a change from acetic to propionic acid results in a dramatic decrease in the conversion of ionic bromide to 4-chlorobenzyl bromide during the CAB catalyzed

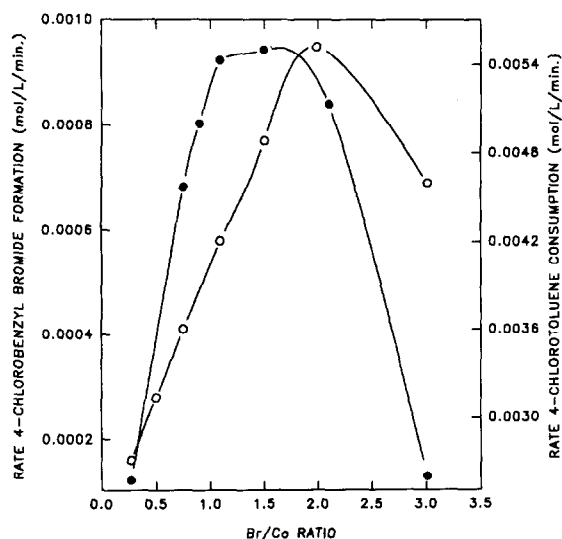


Fig. 5. Effect of  $\text{Br}^-/\text{Co}$  Ratio. (For experimental details, see Table 2, subscript d.) Symbols: ● – 4-chlorotoluene consumption; ○ – 4-chlorobenzyl bromide formation.

Table 2  
Bromide to benzylbromide conversion

[C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> ] <sup>a</sup> (mol·dm <sup>-3</sup> )	Yield <sup>b</sup> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (mol%)	Conversion C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (mol%)	[CAB] <sup>c</sup> (mol·dm <sup>-3</sup> )	Yield C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (mol%)	Conversion C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (mol%)	Br <sup>-</sup> /Co ratio <sup>d</sup>	Yield C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (mol%)	Conversion C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (mol%)
0.29	62.7	92.3	0.02	65.7	87.0	0.25	81.6	93.2
0.56	71.2	95.6	0.04	71.8	94.0	0.50	83.8	92.8
0.80	85.0	95.5	0.06	89.4	95.2	0.75	85.3	91.0
1.16	82.5	86.4	0.08	85.7	91.3	0.90	84.3	91.7
1.88	80.3	70.5	0.10	76.8	94.5	2.0	81.3	92.8

<sup>a</sup> C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (0.862 g to 5.54 g); Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.48 g; 1.93 mmol); NH<sub>4</sub>Br (0.19 g; 1.94 mmol); C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (3.0 g; 24 mmol); HOAc (30 cm<sup>3</sup>); O<sub>2</sub> flow rate (30 cm<sup>3</sup>·min<sup>-1</sup>).

<sup>b</sup> Based on NH<sub>4</sub>Br.

<sup>c</sup> C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (2.4 g; 26 mmol); Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.149 g to 0.748 g); Co:Br<sup>-</sup> ratio (1:1); C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (3.0 g; 24 mmol); HOAc (30 cm<sup>3</sup>); O<sub>2</sub> flow rate (30 cm<sup>3</sup>·min<sup>-1</sup>).

<sup>d</sup> C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (12.0 g; 130.2 mmol); Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (2.4 g; 9.64 mmol); NH<sub>4</sub>Br (0.236 g to 1.89 g); C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (15.0 g; 121.8 mmol); HOAc (30 cm<sup>3</sup>); O<sub>2</sub> flow rate (30 cm<sup>3</sup>·min<sup>-1</sup>).

oxidation of 4-chlorotoluene without affecting the rate of 4-chlorotoluene oxidation, or the extent of oxidation significantly. It is not clear whether this

difference is related to differing amounts of bromide coordinated to the cobalt in the two different solvents [20]. The presence of nucleophilic

Table 3  
Bromide to benzylic bromide conversion

Substrate	Solvent	Catalyst	NaOAc/CAB ratio	Pyridine/CAB ratio	Rate RCH <sub>2</sub> Br formation (mol·dm <sup>-3</sup> ·min <sup>-1</sup> ) × 10 <sup>-3</sup>	Bromide conversion <sup>a</sup> (mol%)
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> <sup>b</sup>	CH <sub>3</sub> COOH	CAB	0	0	1.89	84.3
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>c</sup>	CH <sub>3</sub> COOH	CAB	0	0	0.94	97.9
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> <sup>d</sup>	CH <sub>3</sub> CH <sub>2</sub> COOH	CAB	0	0	0.83	59.9
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>e</sup>	CH <sub>3</sub> CH <sub>2</sub> COOH	CAB	0	0	0.49	64.8
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>f</sup>	CH <sub>3</sub> COOH	CCB <sup>m</sup>	–	–	0.78	90.0
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>g</sup>	CH <sub>3</sub> COOH	CMB <sup>n</sup>	–	–	0.53	89.3
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>h</sup>	CH <sub>3</sub> COOH	CAB	5	0	0.22	57.0
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>i</sup>	CH <sub>3</sub> COOH	CAB	10	0	–	34.5
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>j</sup>	CH <sub>3</sub> COOH	CAB	0	0.5	0.61	91.7
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>k</sup>	CH <sub>3</sub> COOH	CAB	0	1	0.41	85.2
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>l</sup>	CH <sub>3</sub> COOH	CAB	0	4	0.017	20.4

<sup>a</sup> Based on NH<sub>4</sub>Br.

<sup>b</sup> C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (2.4 g; 26 mmol); HOAc (30 cm<sup>3</sup>); C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (3.0 g; 24 mmol); Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.48 g; 1.93 mmol); NH<sub>4</sub>Br (0.17 g; 1.73 mmol); O<sub>2</sub> flow rate (30 cm<sup>3</sup>·min<sup>-1</sup>).

<sup>c</sup> 4-ClC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> (1.26 g; 9.95 mmol); Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.248 g; 0.996 mmol); NH<sub>4</sub>Br (0.09 g; 0.996 mmol); C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (0.63 g; 5.12 mmol); HOAc (30 cm<sup>3</sup>); O<sub>2</sub> flow rate (30 cm<sup>3</sup>·min<sup>-1</sup>).

<sup>d</sup> As in b, using 30 cm<sup>3</sup> CH<sub>3</sub>CH<sub>2</sub>COOH.

<sup>e</sup> As in c, using 30 cm<sup>3</sup> CH<sub>3</sub>CH<sub>2</sub>COOH.

<sup>f</sup> As in c, but using CeBr<sub>3</sub>·6H<sub>2</sub>O (0.122 g; 0.250 mmol) in place of NH<sub>4</sub>Br.

<sup>g</sup> As in c, but using MnBr<sub>2</sub>·4H<sub>2</sub>O (0.071 g; 0.248 mmol) in place of NH<sub>4</sub>Br.

<sup>h</sup> As in c, and NaOAc·3H<sub>2</sub>O (0.677 g; 4.975 mmol).

<sup>i</sup> As in c, and NaOAc·3H<sub>2</sub>O (1.355 g; 9.957 mmol).

<sup>j</sup> As in c, and pyridine (0.039 g; 0.493 mmol).

<sup>k</sup> As in c, and pyridine (0.079 g; 0.999 mmol).

<sup>l</sup> As in c, and pyridine (0.315 g; 3.98 mmol).

<sup>m</sup> CCB = Co(OAc)<sub>2</sub>·4H<sub>2</sub>O + CeBr<sub>3</sub>·6H<sub>2</sub>O.

<sup>n</sup> CMB = Co(OAc)<sub>2</sub>·4H<sub>2</sub>O + MnBr<sub>2</sub>·4H<sub>2</sub>O.

ligands such as acetate and pyridine clearly reduce the rate of 4-chlorobenzyl bromide formation. In contrast to the effect of solvent, where the overall rate and extent of oxidation was virtually unaffected by the nature of the solvent, nucleophilic ligands significantly reduce the rate of oxidation (Table 3) so that in these cases, the lower rates of benzylic bromide might be interpreted in terms of an overall reduction in reaction rate.

### 2.3. Effect of benzylic bromide formation on catalyst activity

Although it has previously been shown that benzylic bromides promote the cobalt acetate catalyzed oxidation of alkyl aromatic compounds [15], they are rather poor promoters compared to ionic bromides. For example, the rate of 4-chlorotoluene consumption over the first 30 min of the CAB catalyzed oxidation of 4-chlorotoluene (using  $\text{NH}_4\text{Br}$  as bromide source) is ca.  $2.10 \times 10^{-1} \text{ mmol} \cdot \text{min}^{-1}$ . Replacing  $\text{NH}_4\text{Br}$  with 4-chlorobenzyl bromide results in a rate, measured under similar conditions, of ca. only  $7.80 \times 10^{-3} \text{ mmol} \cdot \text{min}^{-1}$ . (It is of interest to note that the promoting effect of benzylic bromides generally improves with time, for example, the rate of 4-chlorotoluene consumption in the latter reaction increases to  $7.0 \times 10^{-2} \text{ mmol} \cdot \text{min}^{-1}$  at 4-chlorotoluene conversions  $> 50 \text{ mol}\%$ . Whether this improvement in promoting effect of benzylic bromides is the result of the interaction of benzylic bromide with cobalt catalyst or the result of the slow formation of benzylic acetates with resultant release of bromide, (which occurs even in the absence of cobalt catalyst), has not been established unequivocally.)

A more elegant way to demonstrate the effect of benzylic bromide formation on catalyst activity is to compare the rates of substrate consumption in consecutive oxidations (of the same substrate) for that part of the reaction where ionic bromide is being converted into benzylic bromide (stage 1) and that part of the reaction where the benzylic bromide concentration has reached a steady state (stage 2). Such comparisons may be achieved by

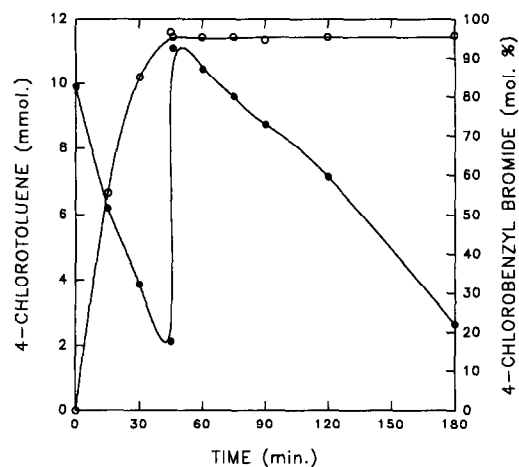


Fig. 6. Consecutive oxidation of 4-chlorotoluene. ( $4\text{-ClC}_6\text{H}_4\text{CH}_2\text{Br}$ , mol% based on  $\text{NH}_4\text{Br}$ . For experimental details, see Table 4, subscript d.) Symbols: ● – amount 4-chlorotoluene; ○ – mol% 4-chlorobenzyl bromide.

simply restoring the substrate concentration to its original value at the point of maximum benzylic bromide formation. The fact that the conversion of ionic to benzylic bromide remains virtually constant after the addition of substrate in these reactions (Fig. 6), allows calculation of the two reaction rates. The results of these comparisons for the oxidation of toluene and 4-chlorotoluene (Table 4), clearly show a reduction in reaction rate in the second stage of the reaction where the benzylic bromide functions as the bromide source. In reactions where both substrate and ionic bromide is added to the reaction mixture at the point of maximum bromide formation, a good correlation with the first stage rate is obtained.

### 2.4. Fate of benzylic bromides

Benzylic bromides, formed during CAB catalyzed oxidations of alkyl aromatic compounds, are converted to the corresponding benzal bromide and benzoic acid at low substrate concentrations (Fig. 1). To gain further insight into this reaction, the oxidations of benzyl bromide and 4-chlorobenzyl bromide were investigated. The use of CAB as catalyst in acetic acid solvent, results in the formation of the corresponding benzyl acetate ( $< 5 \text{ mol}\%$  conversion after 3 h) as the only reaction product. In the presence of cobalt acetate

Table 4  
Reaction rates <sup>a</sup> for consecutive oxidations

Substrate	Stage	Experiment	Control
toluene	1	$-1.81 \times 10^{-2}$ <sup>b</sup>	$-1.92 \times 10^{-2}$ <sup>c</sup>
	2	$-9.77 \times 10^{-3}$ <sup>b</sup>	$-1.47 \times 10^{-2}$ <sup>c</sup>
4-chlorotoluene	1	$-7.07 \times 10^{-3}$ <sup>d</sup>	$-6.87 \times 10^{-3}$ <sup>e</sup>
	2	$-1.80 \times 10^{-3}$ <sup>d</sup>	$-7.06 \times 10^{-3}$ <sup>e</sup>

<sup>a</sup> Substrate disappearance, mol · dm<sup>-3</sup> · min<sup>-1</sup>.

<sup>b</sup> C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (2.4 g; 26 mmol); Co(OAc)<sub>2</sub> · 4H<sub>2</sub>O (0.48 g; 1.93 mmol); NH<sub>4</sub>Br (0.19 g; 1.94 mmol); C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (3.0 g; 24 mmol); HOAc (30 cm<sup>3</sup>); O<sub>2</sub> flow rate (30 cm<sup>3</sup> · min<sup>-1</sup>); addition of 1.74 g C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (18.9 mmol) after 45 min reaction time.

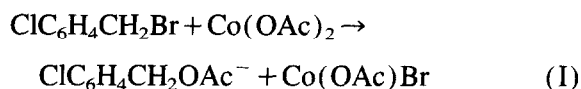
<sup>c</sup> As in b, but adding 0.186 g (1.9 mmol) of NH<sub>4</sub>Br together with toluene after 45 min reaction time.

<sup>d</sup> 4-ClC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> (1.27 g; 10.03 mmol); Co(OAc)<sub>2</sub> · 4H<sub>2</sub>O (0.250 g; 1.0 mmol); NH<sub>4</sub>Br (0.10 g; 1.02 mmol); C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (0.65 g; 5.3 mmol); HOAc (30 cm<sup>3</sup>); O<sub>2</sub> flow rate (30 cm<sup>3</sup> · min<sup>-1</sup>); addition of 1.07 g (8.5 mmol) 4-ClC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> after 45 min reaction time.

<sup>e</sup> As in d, but adding 0.06 g (0.61 mmol) NH<sub>4</sub>Br in addition to the 4-chlorotoluene after 45 min reaction time.

alone, benzyl bromide and 4-chlorobenzyl bromide are, however, both rapidly oxidized (Fig. 7). In both cases, short induction periods (10–30 min) are observed in acetic acid (not shown) and, for the oxidation of benzyl bromide, complete catalyst deactivation is observed after the reaction of 1 mol equiv. of benzyl bromide (relative to Co(OAc)<sub>2</sub>). In propionic acid, no induction period and no catalyst deactivation are observed in either case. The oxidation of 4-chlorobenzyl bromide leads to the formation of 4-chlorobenzal bromide and 4-chlorobenzoic acid as the major oxidation products, together with molecular bromine which may be observed visually in the reaction medium. (Due to the partial entrainment of molecular bromine in the gas stream, it was not possible to determine the rate, or extent of Br<sub>2</sub> formation during these reactions.) Small amounts of 4-chlorobenzaldehyde (< 2.0 mol%) may be detected during the initial stages of the reaction, while 4-chlorobenzyl acetate (< 2.0 mol%) may be observed during the latter part of the reaction. The appearance of 4-chlorobenzyl acetate only during these latter stages of the reaction (> 50% 4-chlorobenzyl bromide conversion) suggests that a ligand exchange reaction (Eq. (I)) between a cobalt acetate species and 4-chlorobenzyl bro-

midate [4,16] cannot be an important pathway in the oxidation of benzylic bromides.



Oxidation through intermediate benzylic alcohols also appears unlikely. Only trace amounts of 4-chlorobenzyl alcohol are detected during the oxidation of 4-chlorobenzyl bromide (see Fig. 7). In addition, formation of benzyl alcohol from benzyl bromide in acetic acid solutions have previously been suggested to be unimportant. [21]

It is of interest to note that, while the initial rates of benzylic bromide oxidation in acetic and propionic acids are virtually identical (eg. over the first 30 min during the oxidation of 4-chlorobenzyl bromide the average rates of 4-chlorobenzyl bromide consumption are  $4.44 \times 10^{-2}$  mmol · min<sup>-1</sup> and  $4.47 \times 10^{-2}$  mmol · min<sup>-1</sup> in acetic and propionic acids, respectively), the relative product distributions differ markedly. In acetic acid, one 4-chlorobenzal bromide is formed for ca. every two 4-chlorobenzoic acids during the initial 30 min of the oxidation of 4-chlorobenzyl bromide. In propionic acid, the ratio of 4-chlorobenzal bro-

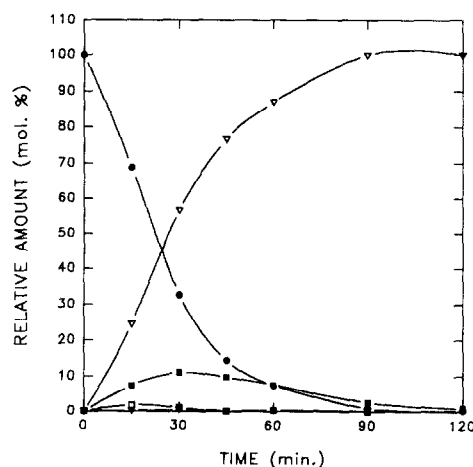
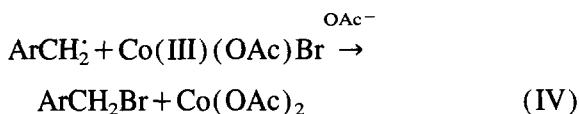
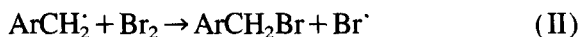


Fig. 7. Product distribution for cobalt (II) acetate catalyzed oxidation of 4-chlorobenzyl bromide. (mol% based on substrate. Reaction conditions: 4-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br (0.409 g; 1.99 mmol); C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (0.63 g; 5.12 mmol); Co(OAc)<sub>2</sub> · 4H<sub>2</sub>O (0.248 g; 0.996 mmol); propionic acid (30 cm<sup>3</sup>); reaction temp. 95°C; O<sub>2</sub> flow rate (30 cm<sup>3</sup> · min<sup>-1</sup>.) Symbols: ● – 4-chlorobenzyl bromide; ▽ – 4-chlorobenzoic acid; ▼ – 4-chlorobenzyl alcohol; □ – 4-chlorobenzaldehyde; ■ – 4-chlorobenzal bromide.

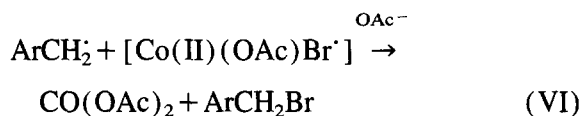
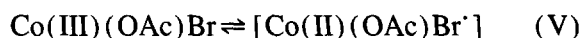
mide to 4-chlorobenzoic acid, over the same reaction period, is ca. 1:5. For benzyl bromide oxidation, the ratio of benzal bromide to benzoic acid is 1:1 and 1:2 for acetic and propionic acids, respectively. These observations are probably the result of a lower rate of oxidation of the resultant benzal bromide in acetic than in propionic acid.

### 3. Discussion

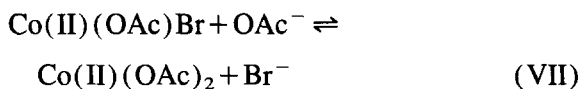
Several proposals appear in the literature to explain the formation of benzylic bromides during CAB catalyzed oxidations of alkyl aromatic compounds in carboxylic acids. These include the reaction of benzylic radicals with bromine (Eq. (II)) [15], benzylic radicals with bromine radicals (Eq. (III)) [15], and the reaction of benzylic radicals with cobalt(III) acetate bromide (Eq. (IV)) [6].



Arguments against the formation of free bromine radicals have been offered in terms of the observed activities and selectivities of CAB catalyzed oxidations of alkyl aromatic compounds in carboxylic acids, as well as the difference in the chain lengths obtained in reactions catalyzed by CAB and molecular bromine [6]. The absence of nuclear brominated compounds in oxidations of alkylbenzenes catalyzed by CAB suggests the absence of molecular bromine, albeit in small quantities, and hence the absence of reactions leading to the formation of free bromine radicals. The observed dependence of benzylic bromide formation on catalyst and substrate concentrations, solvents, nucleophilic ligands and the presence of other metal co-catalysts, is best explained in terms of the formation of a chain carrier complex comprising both cobalt and bromide as proposed by Kamiya [6] (Eq. (V)).



Thus, an increase in CAB concentration leads to an increase in the rate of 4-chlorobenzyl bromide formation, since CAB concentration and  $[\text{Co(II)(OAc)Br} \cdot]$  concentration will be directly related. An increase in substrate concentration will promote reaction between the 'active' catalyst (or chain carrier)  $[\text{Co(II)(OAc)Br} \cdot]$  and substrate above reaction of active catalyst and benzylic radicals, the concentration of which will always be at a low value due to reaction with molecular oxygen. The rate of benzylic bromide formation will consequently be suppressed relative to the formation of oxidation products. The effect of added nucleophiles such as acetate ions may possibly be explained in terms of a ligand exchange reaction (Eq. (VII)).

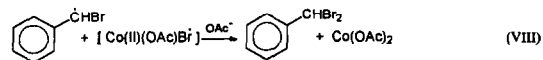


A high, free acetate concentration forces the equilibrium to the right, thereby reducing the rates of  $\text{Co(II)(OAc)Br}$  formation and, consequently,  $[\text{Co(II)(OAc)Br} \cdot]$  formation.

Benzal bromide formation during the cobalt(II) acetate catalyzed oxidation of benzyl bromide may be explained by the reaction of an initially formed bromobenzyl radical ( $\text{Ar} \cdot \text{CHBr}$ ) with active catalyst (Eq. (VIII), Scheme 1) in a manner similar to the formation of benzyl bromide.

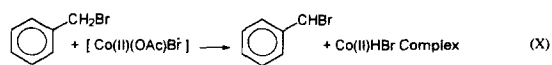
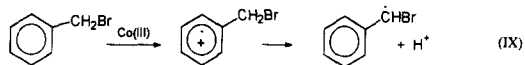
The formation of bromobenzyl radicals may proceed either by an electron transfer mechanism (Eq. (IX)) or a hydrogen abstraction mechanism (Eq. (X)) as depicted in Scheme 2.

Although it might be expected that mixtures of  $\text{Co(OAc)}_2$  and  $\text{NH}_4\text{Br}$  may catalyze the oxidation of benzylic bromides by hydrogen abstraction as

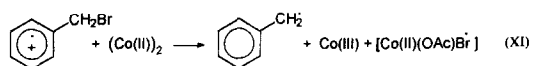


Scheme 1.

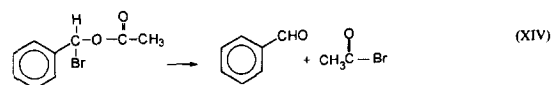
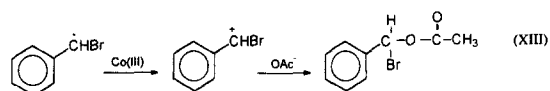
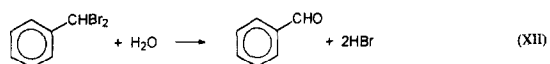




Scheme 2.



Scheme 3.



Scheme 4.

depicted in equation (X), virtually no oxidation is observed even after prolonged reaction periods. This not only suggests that electron transfer is probably the preferred route in benzylic bromide oxidation, but also that bromine transfer from benzylic bromide to cobalt catalyst may be important in oxidations catalyzed by cobalt(II) acetate alone. Such bromine transfer may be considered to occur from an initially formed radical cation to a cobalt(II) species with simultaneous electron transfer between  $[\text{Br}^{\cdot+}]$  and cobalt(II) (Eq. (XI), Scheme 3). The benzylic radical so formed may then be oxidized via the aldehyde to the acid in the conventional way.

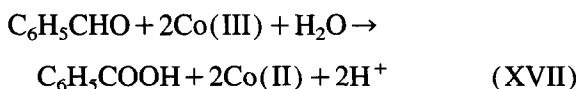
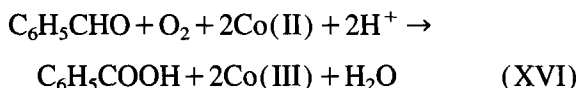
Alternative routes to aldehyde during benzylic bromide oxidations include (Scheme 4) the hydrolysis of benzal bromide (Eq. (XII)) and oxidation of bromobenzyl acetate, which in turn can be formed by further oxidation of bromobenzyl radicals (Eqs. (XIII) and (XIV)) in a manner

similar to the formation of benzyl acetates from benzylic radicals [22].

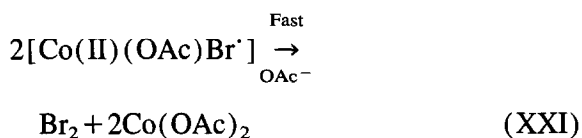
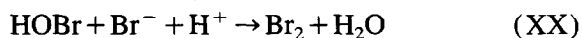
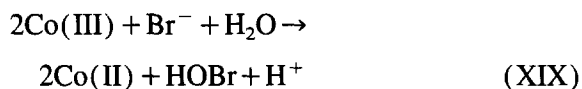
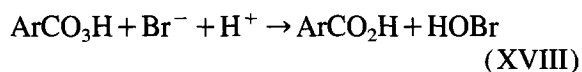
It might, however, be expected that in the case of hydrolysis, benzaldehyde be present in small, yet significant amounts throughout the course of the reaction as a result of the production of water during the oxidation process. Fig. 7 shows that benzaldehyde formed during the reaction has virtually disappeared by the time the benzal bromide content reaches its maximum value. Although bromobenzyl acetate is observed in small quantities during the oxidation of benzyl bromide by cobalt(III) acetate in both  $\text{N}_2$  and  $\text{O}_2$  atmospheres, no bromobenzyl acetate could be detected during oxidation reactions catalyzed by cobalt(II) acetate.

The conversion of ionic bromides to benzylic bromides during CAB catalyzed oxidations of alkyl aromatic compounds (Table 1), together with the observed correlation between ionic bromide added at the start of the reaction and total benzylic plus 'ionic' bromide during the reaction, suggests that bromine ( $\text{Br}_2$ ) formation during the CAB catalyzed oxidations of alkyl aromatic compounds is essentially the result of the oxidation of benzylic bromides. Although benzal bromide is decomposed to benzoic acid and molecular bromine in carboxylic acids in an oxygen atmosphere (both in the presence and absence of cobalt(II) acetate), this reaction appears to be too slow to account for the rapid formation of benzoic acid and bromine at the start of benzylic bromide oxidations. Fig. 7 clearly shows that whilst benzal bromide concentration increases at the start of benzylic bromide oxidations (indicating a lower rate of consumption than formation), the benzoic acid increases at an even higher rate. Thus, apart from its formation from benzal bromide by oxidative decomposition (Eq. (XV)), benzoic acid (and molecular bromine) must also be formed by an alternative route. The most logical explanation appears to be the interaction of benzyl bromide with cobalt catalyst in the manner predicted by Eq. (XI). The resultant benzylic radical may then be oxidized in the normal way to aldehyde, which is then further oxidized to the acid by one or both

of the processes depicted in Eqs. (XVI) and (XVII) [20].



The low aldehyde concentrations detected during the oxidation of benzylic bromides, together with the high rate of benzoic acid formation, is probably indicative of a very high rate of aldehyde formation and oxidation. Molecular bromine may be formed from free, or catalyst bound ionic bromide in a number of ways during this rapid oxidation of aldehyde [20]. These possibilities are illustrated in Eqs. XVIII to XXI.



#### 4. Conclusion

The bromine cycle in CAB catalyzed oxidations of alkyl aromatic hydrocarbons is considerably more complex than previously reported [23]. Apart from termination (and regeneration) reactions to (and from) benzylic bromides, the bromine cycle must also include oxidation reactions of benzylic bromides to benzal bromide and molecular bromine. A cycle which attempts to include these additional steps is proposed in Fig. 8. Evidence for the regeneration of active bromine from benzylic bromides, as proposed by Eq. (XI),

will be explored in more detail in a future paper.

## 5. Experimental

### 5.1. Materials

Chemicals used in oxidation and analytical procedures were purchased from either Merck or Riedel-de Haen, and used as received. Benzyl acetate and 4-chlorobenzyl acetate was prepared by the esterification of benzyl alcohol and 4-chlorobenzyl alcohol respectively, with acetic acid in the presence of sulphuric acid. Products were purified by vacuum distillation. Benzyl bromide and 4-chlorobenzyl bromide were prepared by the bromination of toluene and 4-chlorotoluene, respectively, with molecular bromine in carbon tetrachloride at reflux under UV irradiation. Benzyl bromide was purified by column chromatography and 4-chlorobenzyl bromide by recrystallisation from ethanol. Benzal bromide and 4-chlorobenzal bromide were prepared from the corresponding benzyl bromides in a similar manner.

### 5.2. Analytical

GLC analyses were performed on a Varian 3300 gas chromatograph with a 25 m × 0.32 mm Carbowax 20 M capillary column and FID data were acquired by means of a personal computer equipped with DAPA, version 1.30. HPLC analyses were performed on a Beckman System Gold HPLC and data collected by personal computer with System Gold Data Acquisition software. HPLC conditions for analysis of 4-chlorotoluene and its oxidation products were: injector volume (25 μl manual loop injection), column (Spherisorp (Phase Sep) C<sub>18</sub> 5 μm, 25 cm × 4.6 mm), mobile phase (methyl cyanide:water (pH = 3.00 with H<sub>3</sub>PO<sub>4</sub>) 45:55 for 6 min, then linear gradient to 70:30 over 5 min and hold), flow rate (1 ml · min<sup>-1</sup>), detector (220 nm). The internal stan-

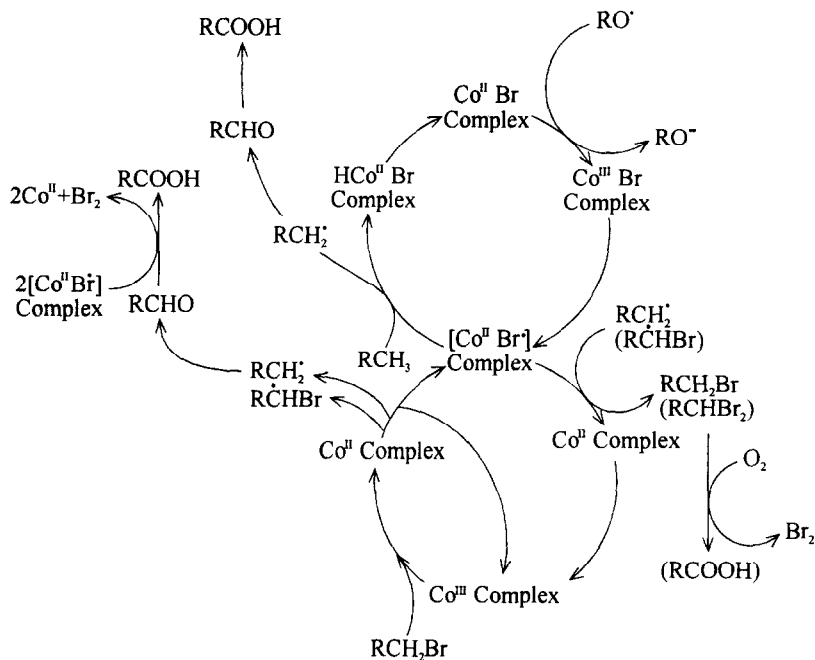
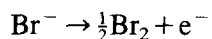


Fig. 8. Proposed bromine cycle.

standard method (nitrobenzene) was used for both GC and HPLC analysis.

Ionic bromide analyses were performed by cyclic voltammetry on a BAS CV-27 cyclic voltammetry system linked to an  $x$ - $y$  recorder and BAS CV-27 electrochemical cell equipped with a platinum working electrode, platinum wire auxiliary electrode, and a Ag/AgCl reference electrode. Voltamograms were recorded by scanning the working electrode potential between 0 V ( $E_i$ ) and +1.3 V at a scan rate of  $60 \text{ mV} \cdot \text{S}^{-1}$  and sensitivity of  $0.05 \text{ mA} \cdot \text{V}^{-1}$ . A calibration curve, for  $\text{Br}^-$  analysis, was prepared by recording the voltamograms of standard KBr solutions in  $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ KClO}_4$  supporting electrolyte over the range  $6 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ – $8 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$  and measuring  $i_{\text{pa}}$  at +1.0 V for the half reaction:



Proton magnetic resonance spectra were recorded on a Varian EM360A spectrometer and gas-chromatographic-mass-spectrometric determinations on a VG Trio 1000 instrument and Carlo Erba GC 6000 fitted with an OV-1701 column. Infrared spectra were recorded using a Shimadzu FTIR 4200 spectrophotometer.

### 5.3. Oxidation procedures

Catalyst, internal standard (nitrobenzene) and substrate were weighed into a  $100 \text{ cm}^3$  two necked, round bottom flask and  $30.0 \text{ cm}^3$  of the appropriate solvent added. The flask was fitted with a condenser and allowed to equilibrate in a preheated oil bath ( $85^\circ\text{C}$  for toluene and benzyl bromide oxidations,  $95^\circ\text{C}$  for 4-chlorotoluene, and 4-chlorobenzyl bromide oxidations) whilst stirring the mixture magnetically at a rate of 1000 rpm. Oxygen, at a preset flow rate of  $30 \text{ cm}^3 \cdot \text{min}^{-1}$ , was introduced and timing of the reaction commenced. Consecutive oxidations were performed as described above but substrate added at the point of maximum benzylic bromide formation, determined previously from batch reactions. Aliquots ( $0.2 \text{ cm}^3$  for GC analysis and  $0.5 \text{ cm}^3$  for HPLC analysis) were removed at regular intervals and treated as follows: for GC analysis, cobalt was precipitated with malonic acid and  $10 \text{ cm}^3$  of diethyl ether added prior to filtering over  $\text{Na}_2\text{SO}_4$ ; for HPLC analysis, samples were simply diluted with methyl cyanide ( $10 \text{ cm}^3$ ) and further diluted prior to analysis. Samples for ionic

bromide analysis were diluted with  $0.1 \text{ mol} \cdot \text{dm}^{-3}$   $\text{KClO}_4$  prior to analysis.

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