

AUTOXIDATION REACTIONS CATALYZED BY COBALT ACETATE BROMIDE

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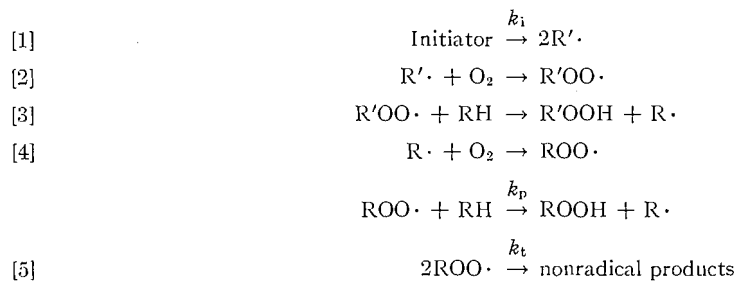
Dedicated to Professor R. B. Sandin on the Occasion of his Sixty-Eighth Birthday

ABSTRACT

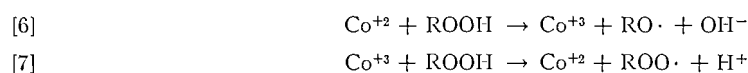
Cobalt acetate bromide in acetic acid solution is an extraordinarily active catalyst for the autoxidation of hydrocarbons. Carboxylic acids and ketones are readily prepared in high yields at moderate temperatures and at atmospheric pressure. In addition, benzylic and allylic groups can be converted to esters of the corresponding alcohols, and the oxidation of tetralin can be controlled to give either α -tetralone or 1,2-dihydronaphthalene as the major product. A mechanism for these reactions is postulated.

INTRODUCTION

The autoxidation of aralkyl hydrocarbons has received considerable attention in recent years, and the mechanism (eqs. [1]–[5]) is now well understood (1).



In the presence of heavy metal salts this reaction sequence is modified principally by reactions [6] and [7], which increase the rate of free radical production (2) and have a profound effect on the products of the reaction.



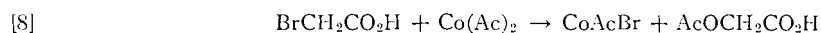
For compounds having a methyl group on an aromatic ring, these degradation reactions eventually result in a carboxyl group, and this is the basis of some commercial processes for the production of such acids.

In a previous report (3) we described the ozone-initiated cobalt-catalyzed autoxidation of aralkyl hydrocarbons. Ozone oxidizes cobalt(II) to cobalt(III) and thus serves to initiate the cyclic sequence in eqs. [6] and [7]. As soon as oxidation of the aralkyl hydrocarbon begins, the ozone may be stopped since the peroxy intermediates will reoxidize cobalt(II) efficiently. Thus, ozone serves the same function as acetaldehyde and methyl ethyl ketone in the processes described by Hull (4) and Brill (5).

In this system, *p*-xylene and *m*-xylene are readily oxidized to the corresponding toluic acids. Continued oxidation results in high yields of corresponding dibasic acids. However, when *o*-xylene is subjected to this system, the principal product is *o*-toluic acid, and

o-phthalic acid is formed only in amounts equivalent to the cobalt ion in solution. Apparently *o*-phthalic deactivates the catalyst, since the reaction proceeds only very slowly.

We hypothesized that *o*-phthalic acid was influencing the oxidation potential of the Co(II)–Co(III) couple by chelation with cobalt ions. If so, the propagation reactions (eqs. [6] and [7]) would be affected and the rates decreased. To circumvent this retardation by *o*-phthalic acid, we decided to run the reaction in the presence of acids stronger than acetic and *o*-phthalic. Among the many acids tried, α -bromoacetic acid was unique in that it allowed *o*-xylene to be rapidly oxidized in high yield to *o*-phthalic acid. The reaction mixture became deep blue and the effect was soon found to be due to a bromine ion presumably formed via reaction with cobalt acetate.



No ozone was necessary in this reaction.

This paper describes the scope of cobalt acetate bromide (CAB) catalyzed autoxidations and the results of our study on the mechanism of the reaction. The effect of bromine on metal-catalyzed autoxidations, principally as a route to the phthalic acids, has been the subject of intensive work in other laboratories (6), and a comparison with these results is made.

DISCUSSION AND RESULTS

The addition of an equimolar amount of hydrogen bromide to cobalt(II) acetate in acetic acid solution gives a catalyst that is extraordinarily active for the autoxidation of methylene or methyl groups adjacent to an aromatic ring to ketones or carboxylic acids, respectively (7). Thus, *p*-xylene can be readily oxidized to terephthalic acid at atmospheric pressures and at temperatures as low as 60–100 °C. Tetralin is oxidized rapidly at room temperature to α -tetralone. Phenacyl esters can be prepared from the corresponding β -phenethyl esters and oxidation of methylphenyl acetate yields methylphenyl glyoxylate. Further examples are described in the Experimental section. All of these reactions are performed at atmospheric pressure and moderate temperatures (25–120 °C) and thus are readily adaptable to conventional equipment in the laboratory.

Most metal-catalyzed autoxidation reactions require only trace amounts of catalyst and, in fact, the catalytic effect reaches a maximum value at relatively low concentrations (8). In the CAB system, concentrations of catalyst of at least 0.1 *M* are necessary for optimum reaction rates. Below this concentration the rates drop off rapidly. This can be qualitatively demonstrated by oxidizing *p*-xylene at various catalyst concentrations and observing the point at which terephthalic acid, which is insoluble in the reaction mixture, first precipitates (Fig. 1).

In most metal ion autoxidation systems, the anion associated with the metal ion is of minor importance in determining the activity of the metal ion as a catalyst. Obviously, the anion can play a role in aiding solubility of the salt or in increasing or decreasing the oxidation–reduction potential of the metal ions. In general, however, these effects are small. Bromine, however, is unique in that, when used in conjunction with cobalt(II) ion, it yields a catalyst of increased activity. Other metal ions such as manganese and cerium also show this effect, but to a more limited extent. Moreover, we discovered that the ratio of the atoms of bromine to the atoms of cobalt in the catalyst system and the molar concentration of the catalyst have a profound and unexpected effect on the low-temperature oxidation reaction. Therefore, we have devoted considerable study to defining the scope of the reaction and to elucidating the mechanism of the reaction.

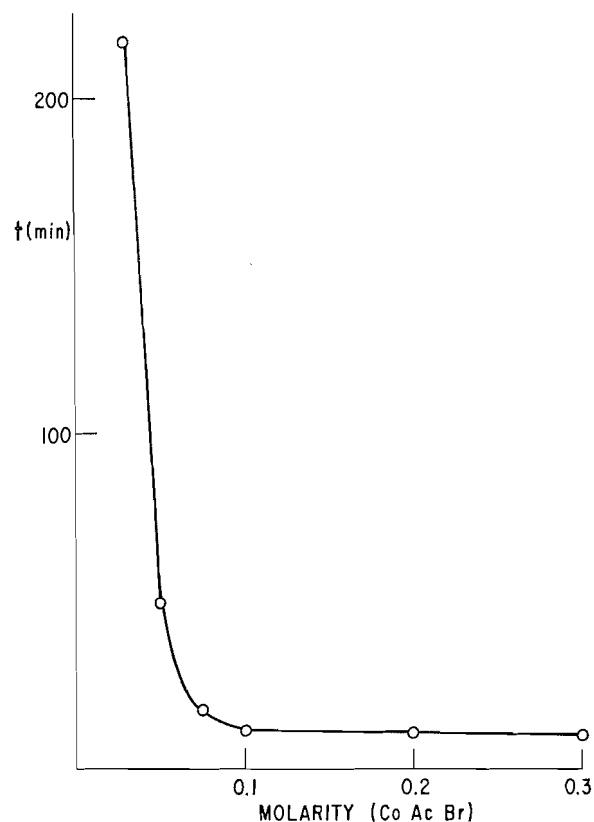


FIG. 1. Oxidation of *p*-xylene (0.4 *M*) at 90 °C in acetic acid. [CoAcBr] = 0.1 *M*; *t* = time in minutes for the appearance of terephthalic acid.

Any explanation devised to account for the uniqueness of the CAB system must account for the following facts. (i) The rates of autoxidation are greatly enhanced by the presence of the bromine, much more so than if the metal ions were present alone. (ii) The nature of the products in a given autoxidation can be profoundly altered. Thus, for example, *p*-xylene is converted easily and at temperatures as low as 60 °C to terephthalic acid. (iii) Bromine is unique in its effect. None of the other halogens or their compounds approach it in activity.

Since bromine has such a profound effect on autoxidations it seemed important to establish unequivocally that the free-radical nature of the reaction was preserved in the presence of the bromine-containing catalyst. It might be imagined, for example, that the addition of bromine had completely changed the reaction to such an extent that we were no longer dealing with a free-radical chain reaction. Indeed, in the early phases of the investigation, it was found that hydrocarbons such as toluene, xylene, and cumene could be autoxidized in the presence of CAB without the addition of the usual free-radical initiator. However, when highly purified hydrocarbons were treated in this manner, induction periods were observed which were apparently dependent on the degree of purity. Moreover, these induction periods could be removed by (a) exposing the purified hydrocarbons to air and light before the oxidation or (b) adding hydroperoxides or α, α -azo-bisisobutyronitrile (AIBN) as an initiator. Further, and significantly, it was found

that addition of such a typical free-radical chain inhibitor as 2,6-di-*t*-butyl-*p*-cresol (DBPC) inhibited the oxidations. These findings offer strong support to the idea that the autoxidations in the presence of CAB follow the typical free-radical chain mechanism operative in normal initiated autoxidations.

Since the mechanism for initiated autoxidations is composed of three distinct parts, namely, initiation, propagation, and termination, it is conceivable that CAB could have an effect on any or all of these steps. To determine its effect on the initiation step, we have studied rates of initiation in the AIBN-initiated autoxidation of cumene in the presence and in the absence of CAB. The results of this phase of the investigation, which was carried out as described in ref. 9 for cobalt(II) ions themselves, are presented in Table I.

TABLE I
Inhibited oxidations of cumene (1.03 *M*) in acetic acid initiated by azo-bisisobutyronitrile (0.097 *M*) at 60 °C

[Co ⁺⁺] (mole l ⁻¹) × 10 ³	[Br ⁻] (mole l ⁻¹) × 10 ³	[DBPC]* (mole l ⁻¹) × 10 ³	Time of inhibition (min)	Rate† (mole l ⁻¹ s ⁻¹) × 10 ⁶
—	—	—	2	4.89
8.0	—	—	2	5.72
16.0	—	—	2	6.96
—	—	1.77	48	4.89
—	—	3.54	93	4.89
8.0	8.0	1.77	48	38.6
16.0	16.0	1.77	48	76.0
16.0	16.0	3.54	93	76.0
14.0‡	14.0‡	1.77	47	5.30

*Initial concentration of 2,6-di-*t*-butyl-*p*-cresol.

†Rate following the inhibition period.

‡Initial concentration of cobaltous acetate chloride.

As is evident from the data in Table I, the lengths of the inhibition periods in the presence and in the absence of CAB are identical within experimental error. From this fact, the important conclusion can be drawn that the rate of free-radical production is the same in the presence as it is in the absence of the added CAB, and therefore the CAB has no effect on the initiation reaction. Stated somewhat differently, it can be concluded that there is no direct reaction between CAB, oxygen, and hydrocarbon which leads directly to free-radical production, and therefore an enhanced rate of oxidation (10). It follows that the explanation for the bromine effect must be sought either in the propagation reaction and (or) the termination reaction.

First, let us consider the possibility that the main function of the CAB is to enhance the rate of autoxidation by speeding up the propagation reaction. As shown in Table I, the rates of oxidation in the presence of CAB are substantially faster than those in the absence of CAB. Moreover, this rate enhancement must be intimately bound up with the bromine since, as shown by the data in Table I, those runs containing cobalt(II) ions with no bromine show only a slight rate enhancement. Moreover, as shown by the last experiment in Table I, cobaltous acetate chloride shows virtually no rate enhancement. Based on the earlier work of Vaughan, Rust, and their co-workers (11) we were led to consider the possibility that bromine could enhance the rate of autoxidations independent of the metal ion. To this end we studied the effect of anhydrous hydrogen bromide on the initiated oxidation of cumene. The results of this phase of the study are presented in Fig. 2.

As shown in Fig. 2, anhydrous hydrogen bromide enhances the rate of oxidation of cumene markedly. Indeed, in the initial stages of oxygen absorption the rates are increased

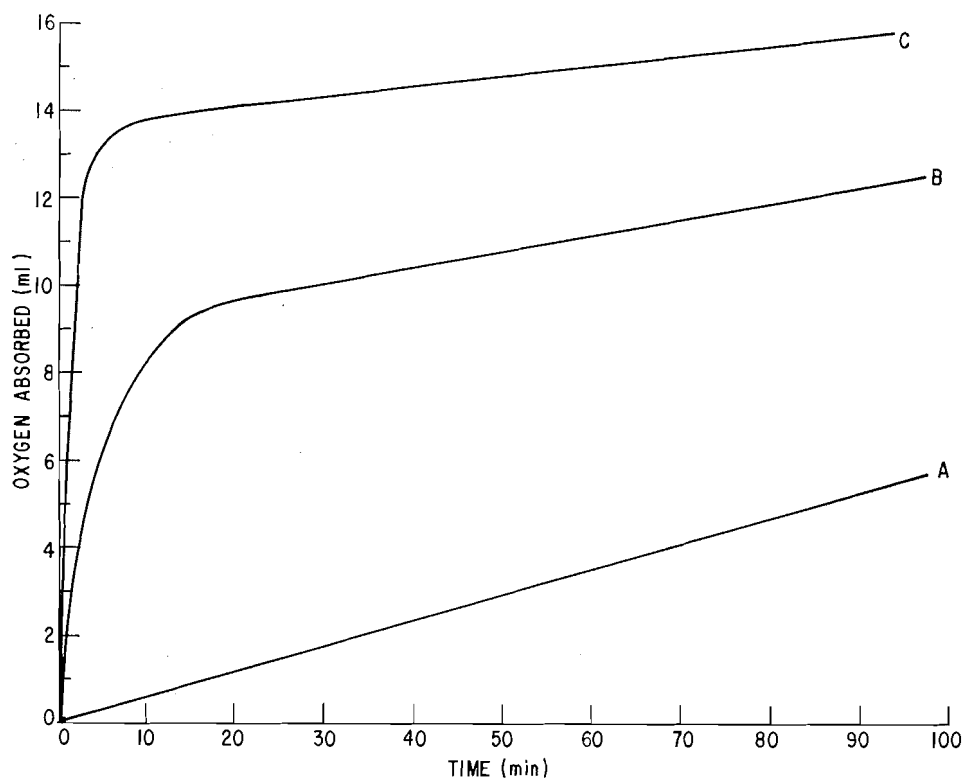
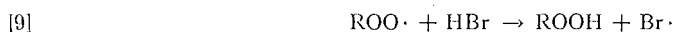


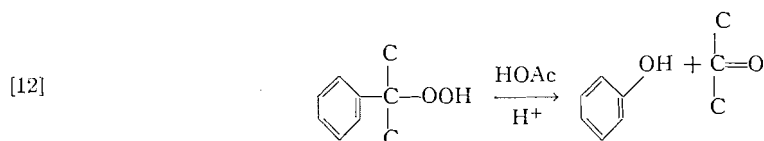
FIG. 2. The effect of hydrogen bromide on the AIBN-initiated oxidation of cumene. Curve A, AIBN-initiated rate, no HBr; curve B, AIBN plus 0.022 *M* HBr; curve C, AIBN plus 0.04 *M* HBr.

by 3–4 orders of magnitude. This rate enhancement is best explained on the basis of eqs. [9], [10], and [11] as postulated by Vaughan, Rust, and co-workers.

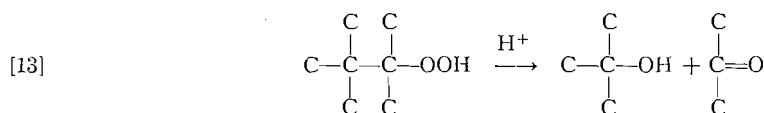


Moreover, reaction [9] would not be expected to be important in the case of anhydrous hydrogen chloride since the bond energy for this substance is some 15 kcal/mole higher than that for anhydrous hydrogen bromide (12). Obviously, hydrogen iodide possesses a low enough bond energy to participate in the propagation step. However, because of the facile oxidation of iodide ion to molecular iodine, a well-known scavenger of free radicals, this substance actually functions as an inhibitor. Thus, the oxidation curves presented in Fig. 2 show that the rates of oxygen absorption can be greatly enhanced quite independently of the cobalt(II) ions.

As shown in Fig. 2, the initially fast rates continue only for a relatively short time and ultimately approach a value which is, in fact, slower than the AIBN-initiated rate of oxidation of cumene. This is due, at least in part, to the production of phenolic inhibitors, apparently arising from the heterolytic rearrangement of cumene hydroperoxide (eq. [12]). As pointed out earlier, the reaction is a free-radical chain process and, hence, is subject to inhibition by phenolic-type inhibitors. However, this is not the whole story, because even



triptane shows this same kind of behavior and the products of the acid-catalyzed rearrangement of triptane hydroperoxide (*tert*-butyl alcohol and acetone, eq. [13]) are not oxidation inhibitors. Rather, what appears to be the case is that the bromine is actually consumed, causing the reaction to "run downhill."



Support for this idea is gained by the fact that addition of more hydrogen bromide to a triptane oxidation where the rate has fallen off to a very low value causes a resumption in the rate. Thus, a solution of triptane (1.03 *M*) in benzene containing anhydrous hydrogen bromide (0.06 *M*) and AIBN (0.097 *M*) absorbs approximately 15 ml of oxygen in 10 min, after which oxidation virtually ceases. If, at this point, the solution is again made 0.06 *M* with respect to anhydrous hydrogen bromide, oxidation can be resumed and an additional 15 ml of oxygen will be absorbed in 10 min time. This cycle can be repeated several times. To account for this behavior, we suggest the following reactions.

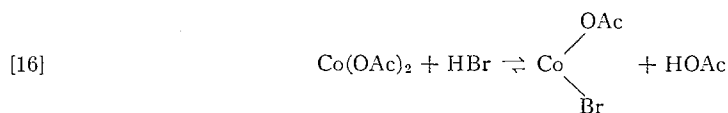


Each time reaction [15] takes place, bromine will be "lost" as a catalyst and, providing those reactions are efficient enough, all of the bromine can be used up in reactions of this kind.

More recently, McIntyre and Ravens (13) have oxidized aralkyl hydrocarbons to carboxylic acids in high yield in aqueous hydrogen bromide with oxygen in the temperature range 180–200 °C. These reactions, in all probability, proceed by the same mechanism as those described by Rust and Vaughan. The intermediate hydroperoxides formed in both cases would be thermally decomposed to the aldehyde and alcohol. Lorand and Edwards (14) have, for example, prepared *p*-methylbenzyl hydroperoxide and find it rapidly decomposes above 130 °C. In reactions studied by Rust and Vaughan, a significant side reaction is the formation of the benzyl bromide; however, in the aqueous system, as pointed out by McIntyre and Ravens (13), any bromides formed would be rapidly hydrolyzed to the alcohol and subsequently oxidized to the acid under the reaction conditions.

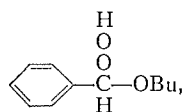
From the results described, it appears that the rate enhancement can be explained on the basis that the rate of the propagation reaction is greatly increased by the presence of bromine atoms. It remains, however, to assign a role to the metal ions. From the nature of the products (phthalic acid from xylene, acetophenone from ethyl benzene, etc.) it is clear that reactions [6] and [7] are operative in this system and one function of the metal ions is to degrade the intermediate hydroperoxides. This will, of course, lead to rate enhancement since the rate of free-radical production is increased. However, as shown previously (9) for cobalt(II) ions, this rate enhancement is not strikingly large. We feel that the major function of the metal ions in this system can best be explained on the basis of equilibrium [16]. As shown, this equilibrium is shifted well to the right and thus one

function of the cobalt(II) ions is to keep the concentration of free hydrogen bromide at a

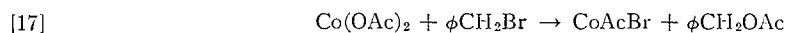


very low value, thus preventing any heterolytic rearrangement of hydroperoxides to phenol.

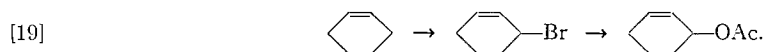
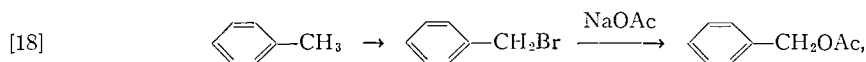
It is interesting to note that in the oxidation of benzyl *n*-butyl ether an appreciable by-product is benzaldehyde. Increasing the concentration of bromide ion (and hence increasing the acidity of the reaction mixture) increases the amount of benzaldehyde formed. The intermediate hydroperoxide,



which has an acetal structure, would be expected to be readily cleaved by acid to benzaldehyde in competition with the cobalt-catalyzed decomposition to butyl benzoate. Secondly, cobalt(II) must also have the ability of preventing bromine from being consumed by reactions such as [14] and [15]. Since the above equilibrium is shifted to the right, the concentration of free hydrogen bromide will be low and, thus, the concentration of bromine atoms will be low. This situation will make the recombination reaction [14] slow. Addition of cobalt(II) acetate to a warm solution of benzyl bromide in acetic acid immediately generates the intense blue color caused by cobalt acetate bromide. Thus, the cobalt acetate is able to reconvert benzylic bromide back to ionic bromine and keep the catalyst active.

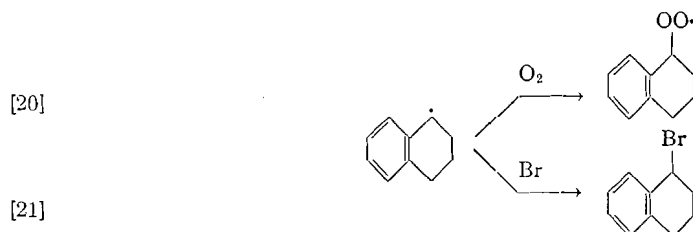


Interestingly, it was observed that when these reactions became too anhydrous the catalyst rapidly lost its activity, as evidenced by the change in color of the solution from blue to pink and the presence of lachrymatory materials in the reaction mixture, presumably benzyl bromides. Also, if the reactions were deliberately performed under anhydrous conditions with sodium acetate added, the blue color of the reactions was maintained and a major product was the allylic or benzylic ester, e.g.



A useful method for the preparation of allylic and benzylic esters in moderate yields using inexpensive reagents is thus afforded.

The oxidation of tetralin is of particular interest. This oxidation takes place rapidly at room temperature to give α -tetralone as the major product. However, on distillation of the product the fraction containing unreacted tetralin also contained appreciable amounts of 1,2-dihydronaphthalene and naphthalene. The intermediate α -tetralyl radical can react in either of the following ways.



The reaction with oxygen eventually gives α -tetralone; however, under the present reaction conditions the bromotetralin would dehydrohalogenate to 1,2-dihydronaphthalene. Subsequent oxidation of 1,2-dihydronaphthalene could give, in the same manner, naphthalene or α -naphthol. The latter would inhibit the oxidation and consume bromine, and indeed in the latter stages of the reaction the blue color of the active catalyst is invariably lost. When the oxidation is starved for oxygen the major product then becomes 1,2-dihydronaphthalene. Presumably, if the reaction were performed at higher oxygen pressures, this side reaction could be eliminated.

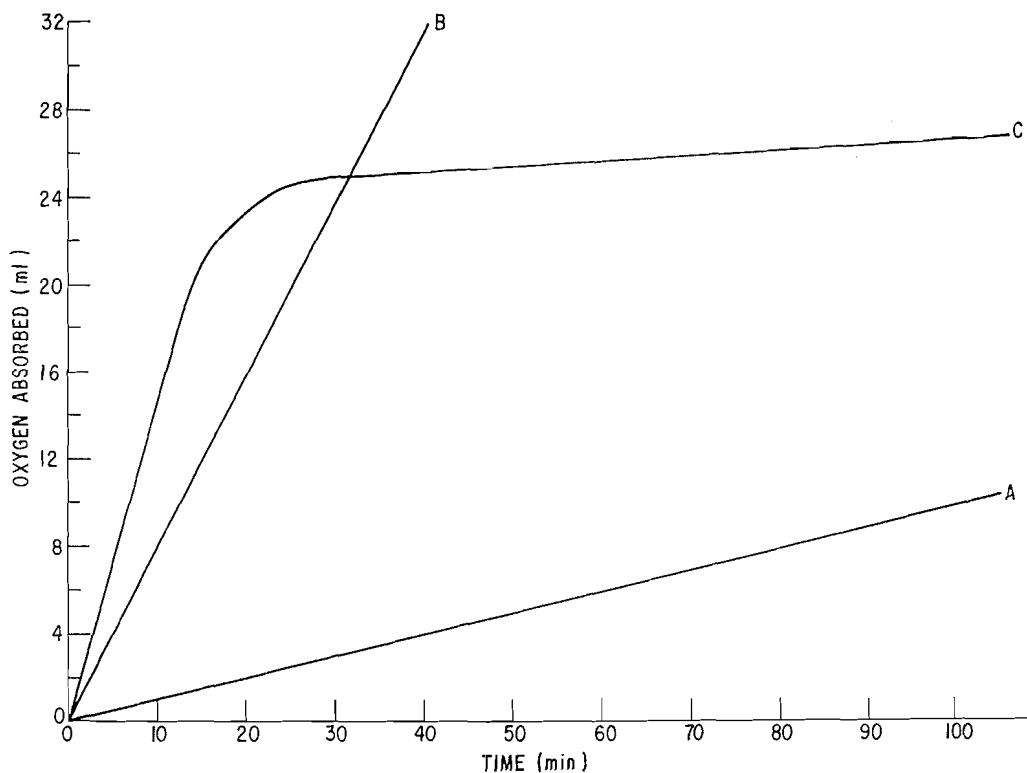


FIG. 3. Oxidation of cumene. (A) AIBN-initiated oxidation; (B) AIBN plus CAB; (C) AIBN plus cobalt(II) bromide.

If the equilibrium situation depicted in eq. [16] actually prevails, it should follow that increases in the bromine to cobalt ratio should cause increases in the rates of oxygen absorption. As shown by the typical oxidation curves in Fig. 3, this prediction is borne out. Thus, curve A shows the AIBN-initiated rate of oxidation of cumene in the absence of

cobalt(II) acetate bromide. Curve B shows the marked rate enhancement observed in the presence of cobalt(II) acetate bromide (prepared from equimolar amounts of cobalt(II) acetate and anhydrous hydrogen bromide). Finally, curve C shows the even greater enhancement observed in the *initial* rate of oxygen absorption caused by cobalt(II) bromide. However, as shown in Fig. 3, the initially rapid oxidation observed in the presence of cobalt(II) bromide is sustained for only a very short period and quickly falls to a value lower than the AIBN-initiated rate of oxidation itself. We interpret this result to mean that the concentration of hydrogen bromide present in the equilibrium depicted in eq. [15] has now increased to such an extent that phenolic inhibitors are formed and the oxidation will not proceed to completion. By way of comparison, it should be noted that curve B shows no evidence of departure from linearity and, in fact, oxidations in the presence of equimolar amounts of cobalt(II) acetate and hydrogen bromide proceed readily to completion. Thus, from a practical standpoint, when the reaction is run below 120 °C the optimum catalyst is obtained when quantities of cobalt(II) acetate and hydrogen bromide are in the range encompassing equimolar amounts.

EXPERIMENTAL

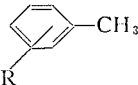
Most of the reactions described represent only one experiment and no attempt has been made to optimize the reactions.



The general reaction conditions employed are illustrated by the oxidation of *o*-bromotoluene to *o*-bromobenzoic acid.

The reaction flask consisted of a 1-l round-bottomed flask equipped with an oxygen inlet tube and thermometer and a condenser which also served as a gas exit tube. Efficient oxygen-liquid mixing was obtained with a Vibromixer stirrer. Flowmeters were attached to the inlet and exit tubes to measure the oxygen consumption to indicate when the reactions were completed.

Oxidation of $R-CH_3$ to $R-COOH$

To the reaction flask was added 25 g (0.1 mole) of cobalt(II) acetate, 27 g (0.1 mole) of 30% hydrogen bromide in acetic acid, 500 ml of acetic acid, and 86.5 g (0.5 mole) of *o*-bromotoluene. Oxygen (600 ml/min) was bubbled through the vigorously stirred reaction mixture, which was initially heated to 90°, at which point the reaction became exothermic and kept the reaction at the temperature of reflux. The reaction was continued for 2 h, during which time the temperature rose to a maximum of 112°. At the end of this period, oxygen was no longer being absorbed. The reaction mixture was cooled and made up to 1 l with ice water. From the solution, *o*-bromobenzoic acid (90.5 g, 91% yield) separated, m.p. 146.5–148°. There was no depression in a mixed melting point with an authentic sample. In a similar fashion the carboxylic acids in Table II were prepared.

TABLE II
Oxidation of 

R	Product	Yield	m.p.	N.E.
H-	Benzoic acid	86	121	
<i>p</i> -Cl-	<i>p</i> -Chlorobenzoic acid	88	240	
<i>o</i> -Cl-	<i>o</i> -Chlorobenzoic acid	86	141	
<i>p</i> -Me-	Terephthalic acid	71.5*	>300	86.3
	Oxydibenzoic acid	87*	>300	131.2
	Benzophenone dicarboxylic acid	76*	>300	132.2
<i>m</i> -Me-	Isophthalic acid	67*	>300	86.5
<i>p</i> -Et-	4-Acetylbenzoic acid	78		157

*The dibasic acid is insoluble in the reaction mixture. By dilution of the filtrate with water the monocarboxylic acid is obtained.

Phenacyl Benzoate

To a 250-ml flask was added 5 g (0.02 mole) of cobalt acetate, 4 ml (0.02 mole) of 30% hydrogen bromide in acetic acid, 22.6 g (0.1 mole) of β -phenethylbenzoate, and 100 ml of acetic acid. Oxygen (600 ml/min) was passed through the vigorously stirred solution for 75 min, during which time the temperature of the reaction mixture was raised from 60 °C to 80 °C. The reaction mixture was poured into 1 l of ice water and the solid removed by filtration. The solid was dissolved in ether and washed with potassium carbonate solution to remove benzoic acid. The ether layer was dried and evaporated to yield 17.0 g (0.071 mole, 71% yield) of phenacyl benzoate, m.p. 121 °C.

n-Butyl Benzoate

Oxygen (600 ml/min) was passed through a vigorously stirred solution of 5 g (0.02 mole) of cobalt acetate, 4 ml (0.02 mole) of 30% hydrogen bromide in acetic acid, and 32.8 g (0.2 mole) of benzyl-*n*-butyl ether in 100 ml of acetic acid. Over a period of 11 min, the temperature rose from 30 to 100 °C. The reaction was continued for a further 50 min and then poured into 1.5 l ice water and extracted with ether. The ether was washed with potassium carbonate solution and then dried, evaporated, and distilled to yield 21.5 g (0.12 mole, 60% yield) of *n*-butyl benzoate, b.p. 60° at 0.5 mm, n_D^{20} 1.4975. From the potassium carbonate layer after acidification there was obtained 7.5 g (0.61 mole, 31% yield) of benzoic acid.

A series of three reactions were run in a similar fashion except that the temperature was kept below 45 °C and at different bromine to cobalt ratios, and the neutral portion of the product was examined by vapor phase chromatography for benzaldehyde.

Br/Co	Benzaldehyde, % yield
1	13.7
1.5	15.2
1.9	28.5

n-Hexyl Caproate

To a 500-ml flask equipped as previously described with the addition of a Dean-Stark trap was added 150 g (1.47 moles) of *n*-hexanol, 50 g of benzene, 5 g (0.02 mole) of cobalt acetate, and 3.27 g (0.01 mole) of cobalt bromide. Oxygen (1 000 ml/min) was passed through the vigorously stirred solution at reflux and water was collected in the Dean-Stark trap. Over a 2-h period the temperature of the reaction mixture rose from 89 to 143 °C and a total of 24 ml of water was collected. The reaction mixture was cooled and dissolved in 300 ml of ether, then washed with cold dilute hydrochloric acid to remove the cobalt salts. The ether layer was washed with cold dilute potassium carbonate solution, then dried, and distilled to yield 14.9 g (0.15 mole) of *n*-hexanol and 56.9 g (0.28 mole) of *n*-hexyl caproate. The potassium carbonate layer was acidified and after distillation there was obtained 26.7 g (0.23 mole) of caproic acid.

Methylphenylglyoxylate

To a 1-l flask was added 600 ml of acetic acid, 10 g (0.04 mole) of cobalt(II) acetate, 2.6 g (0.008 mole) of cobalt(II) bromide, and 75 g (0.5 mole) of methylphenylacetate. Oxygen (800 ml/min) was bubbled through the vigorously stirred reaction mixture at the temperature of reflux for 80 min. The reaction mixture was flooded with ice water and extracted with ether. The ether layer was washed with cold potassium carbonate solution, dried ($MgSO_4$), and distilled. There was obtained 46.5 g (0.31 mole) of methylphenylacetate, b.p. 77° at 6 mm, and 12.7 g (0.08 mole, 41% yield) of methylphenylglyoxylate, b.p. 102.5–106° at 6.5 mm, DNP m.p. 175.5–176° (lit. (15) 174°).

Benzyl Acetate

To a 1-l three-necked round-bottomed flask equipped with gas inlet tube, Vibromixer stirrer, thermometer, and water condenser which also served as a gas exit was added 20 g (0.08 mole) of cobalt(II) acetate, 8 g (0.08 mole) of sodium bromide, 3.3 g (0.04 mole) of sodium acetate, 200 ml of acetic acid, 186 g (1.82 moles) of acetic anhydride, and 138 g (1.5 moles) of toluene. Oxygen was bubbled through the vigorously stirred solution. The temperature was raised and, when the reaction mixture reached about 70°, it became exothermic and rose rapidly to 109°, and oxygen was absorbed by the solution at a rate of 600 ml/min. The reaction was continued for 65 min and then poured into ice water and extracted with ether. The ether layer was washed with sodium bicarbonate solution to remove acetic acid (and any benzoic acid present), then dried over anhydrous magnesium sulfate, and filtered. The ether was distilled off on the steam bath and 158.9 g of a light yellow oil remained. This was examined quantitatively by vapor phase chromatography (v.p.c.) using known solutions for calibration. The product contained 97.2 g of unreacted toluene, 30 g of benzyl acetate (44.7% yield), 10.1 g of benzaldehyde (21.5%), and 15.6% of an unidentified product. The remainder (19.2%) probably is principally benzoic acid which was not isolated.

p-Methylbenzyl Acetate

In a similar fashion 160 g (1.5 moles) of *p*-xylene was oxidized for 160 min to yield 185.4 g of a yellow oil containing 102 g (0.96 mole) of *p*-xylene, 23 g of *p*-tolualdehyde (0.21 mole, 39%), and 52 g (0.31 mole, 57%) of *p*-methylbenzyl acetate.

α -Methylbenzyl Acetate

Oxidation of ethylbenzene (159 g, 1.5 moles) gave 35 g (0.33 mole) of ethyl benzene, 35 g (0.29 mole, 25% yield) of acetophenone, and 25 g (0.15 mole, 13% yield) of α -methylbenzyl acetate. The products isolated by v.p.c. were identified by comparison of their infrared spectra with those of the known compounds.

3-Acetoxy cyclohexene

To a 500-ml three-necked round-bottomed flask equipped with thermometer, Vibromixer stirrer, and water condenser which also served as a gas exit was added 200 g (0.08 mole) of cobalt(II) acetate, 8 g (0.08 mole) of sodium bromide, 26.5 g of sodium acetate, 200 ml of acetic acid, 186 g of acetic anhydride, and 123 g (1.5 moles) of cyclohexene. Oxygen was bubbled through the vigorously stirred solution (600 ml/min) at reflux temperature. Over a period of 5 h the pot temperature rose from 80 to 111 °C.

The reaction mixture was flooded with water and extracted with ether. The ether layer was washed with sodium bicarbonate solution, then dried over magnesium sulfate, filtered, and evaporated. There was obtained 96.0 g of a sweet-smelling oil which was distilled to yield 23 g of 3-acetoxy cyclohexene, b.p. 53 °C at 6 mm, n_D^{20} 1.4618 (literature n_D^{20} 1.4609). Vapor phase chromatography showed it was a pure material.

 α -Acetoxymethylstyrene

Oxidation of α -methylstyrene (177 g, 1.5 moles) gave by v.p.c. 98 g (0.83 mole) of α -methylstyrene, 54 g (0.45 mole, 62% yield) of acetophenone (identified by comparison of infrared spectrum), and 28 g (0.16 mole, 24% yield) of α -acetoxymethylstyrene. A sample was isolated for analysis; n_D^{20} 1.5329 (lit. 1.5281).

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.75, 74.61; H, 6.61, 7.04.

 α -Tetralone

To a 2-l round-bottomed flask equipped as described previously was added 750 ml of acetic acid, 25 g (0.1 mole) of cobalt(II) acetate tetrahydrate, and 30 g (0.092 mole) of cobalt(II) bromide hexahydrate. Oxygen in excess was kept passing through the vigorously stirred solution maintained at 40° with an ice bath and "jackomatic". Over a 30-min period was added 330 g (2.5 moles) of tetralin dissolved in 255 g of acetic anhydride. The reaction was very exothermic and up to 1 200 ml/min of oxygen was absorbed during this period. The reaction was continued for 30 min,* then flooded with ice water, and extracted with ether. The ether layer was washed with cold sodium carbonate solution, then dried ($MgSO_4$), and distilled. A fraction (86 g), b.p. 40–50 °C at 0.5 mm, and 168 g (1.15 moles), b.p. 90–95 °C at 0.5 mm, were obtained. The latter fraction was α -tetralone, m.p. 6.5 °C.

A number of smaller scale runs were performed and analyzed by vapor phase chromatography (Perkin-Elmer K column). In all cases, in addition to α -tetralone and unreacted tetralin, naphthalene (0.5–3%) and 1,2-dihydronaphthalene (10–15%) were identified. The latter was isolated by preparative vapor phase chromatography, b.p. 63 °C at 3.2 mm, n_D^{20} 1.5829, m.p. –8 °C.

Oxidation of Tetralin to 1,2-Dihydronaphthalene

To a 500-ml wide-mouthed Erlenmeyer flask equipped with a gas inlet tube, thermometer, and a Vibromixer was added 10 g (0.04 mole) of cobalt(II) acetate tetrahydrate, 10.8 g (0.04 mole) of 30% hydrogen bromide in acetic acid, 250 ml of propionic acid, and 66 g (0.05 mole) of tetralin. Air (50 ml/min) was bubbled through the stirred reaction mixture for 16 h. The reaction mixture was then flooded with water, extracted with ether, washed with cold sodium bicarbonate solution, and dried ($MgSO_4$), and the ether removed on the steam bath to leave 67 g of a light orange oil.

The oil was analyzed by vapor phase chromatography and contained tetralin, 67%; 1,2-dihydronaphthalene, 21%; naphthalene, 5%; and α -tetralone, 5%. This is a 71% yield of 1,2-dihydronaphthalene based on the tetralin consumed.

Rate and Inhibition Studies

The rate and inhibition studies were carried out exactly as described in ref. 10.

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*When reactions are continued longer the blue color of the catalyst is lost, indicating that consumption of the bromide ion and considerably larger amounts of high-boiling residue are obtained in the reaction.

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