

Articles

Mechanistic Role of Benzylic Bromides in the Catalytic Autoxidation of Methylarenes

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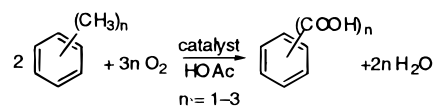
Different pathways for benzylic bromide transformations were examined under conditions of cobalt–bromide catalysis in acetic acid. It has been shown that benzylic bromides participate in the catalytic cycle through their catalyzed and noncatalyzed oxidation, through their reaction with Co(III), and through cobalt(II)-catalyzed solvolysis. The rates of the direct reduction of Co(III) by several benzylic bromides were measured under an argon atmosphere; the reaction occurs by a mechanism involving two forms of Co(III). The same reaction under an oxygen atmosphere initiates the cobalt–bromide-catalyzed oxidation of benzyl bromide, thus leading to the regeneration of inorganic bromide and the fast reduction of Co(III). Solvolysis of benzylic bromides plays only a minor role in the regeneration of inorganic bromide in glacial acetic acid.

Introduction

Cobalt–bromide catalysis constitutes the basis for a major industrial application, known as the MC/Amoco process, for oxidation of alkylaromatics to the corresponding carboxylic acids (Scheme 1).^{1,2} The crucial components of the system include bromide salts and one or more transition metals as catalyst, notably Co and Mn, in acetic acid. Although the process has been known for almost 50 years, many aspects of it are not well understood despite a significant amount of literature on the subject^{3–9} and its commercial importance.^{10–12}

From the mechanistic point of view, the most striking feature of cobalt–bromide catalysis is the 3-orders-of-magnitude increase in the oxidation rate resulting from addition of bromide ions, as compared to the cobalt-only-catalyzed oxidation. Zakharov^{3,9,13} explained these surprisingly high oxidation rates by the generally accepted branching sequence (Scheme 2) which exists in the presence of cobalt and bromide ions in protic solvents. Cobalt–bromide catalysis is based on two reactions, namely, the reaction of peroxy radicals with Co(II), leading to formation of hydroperoxide and Co(III), and the subsequent

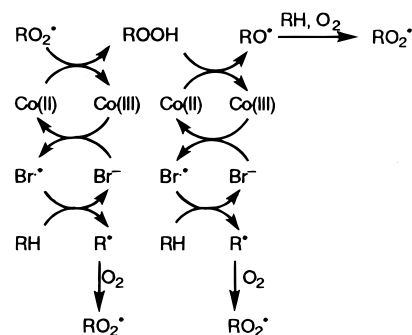
Scheme 1. Catalytic Formation of Arenecarboxylic Acids



Catalyst = Co(OAc)₂/Mn(OAc)₂/NaBr or HBr

T = 50–300 °C, P = 1–25 atm

Scheme 2. Generally Accepted Scheme for Chain Branching for Peroxyl Radical Buildup



reduction of Co(III) by bromide ions. A hydrogen atom is then abstracted from the hydrocarbon by a “bromine atom”, or more likely a Co–Br complex. These steps constitute the sequence that leads to branching of the radical-chain process. One peroxy radical is multiplied to three, as shown in Scheme 2.³

The bromide salt improves the rate of the cobalt-catalyzed autoxidation of hydrocarbons.⁴ Equally important, the metal–bromide catalysts can be operated at significantly higher temperatures than metal-only catalysts,¹⁰ thereby decreasing the rate of HOAc oxidation. During the oxidation process, as much as 99% of the initial inorganic bromide is converted to benzylic bromide, the concentration of which remains about the same

- (1) Partenheimer, W. *Catal. Today* **1995**, 23, 69.
- (2) Sheldon, R. A. In *Advances in Organobromine Chemistry II*; Desmurs, J.-R., Gerard, B., Goldstein, J., Eds.; Elsevier: New York, 1995; p 278–302.
- (3) Zakharov, I. V.; Geletii, Y. V.; Adamyan, V. A. *Kinet. Catal.* **1988**, 29, 924–929.
- (4) Geletii, Y. V.; Zakharov, I. V.; Strizhak, P. E. *Kinet. Catal.* **1985**, 26, 736–741.
- (5) Heiba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1969**, 91, 6830–6837.
- (6) Jones, G. H. *J. Chem. Soc., Chem. Commun.* **1979**, 536–537.
- (7) Jones, G. H. *J. Chem. Res., Synop.* **1981**, 228–229.
- (8) Jones, G. H. *J. Chem. Res., Synop.* **1982**, 207.
- (9) Zakharov, I. V.; Kumpan, Y. V. *Kinet. Catal.* **1993**, 34, 922–927.
- (10) Partenheimer, W. In *Catalysis of Organic Reactions*; Blackburn, D. W., Ed.; Marcel Dekker: New York, 1990; p 321.
- (11) Partenheimer, W. *Chem. Ind.* **1990**, 75, 357.
- (12) Landau, R. S., A. *Chem. Eng. Prog.* **1968**, 64, 20.
- (13) Zakharov, I. V.; Geletii, Y. V. *Petroleum Chem. USSR* **1986**, 26, 234–246.

until the oxidation of the hydrocarbon is nearly complete.^{1,14–17} Whereas inorganic bromide salts are active, covalently bound bromides, such as ArCH_2Br , have been reported to be catalytically inactive because their solvolysis to inorganic bromide is so slow (reaction 1).¹¹ Benzylic bromides have been reported



to be catalytically inactive, their participation in catalysis limited because solvolysis is so slow (reaction 1).¹¹ It is apparent from the literature, however, that benzyl bromide¹⁷ and *p*-nitrobenzyl bromide¹⁴ can be oxidized to carboxylic acids and HBr under the conditions of cobalt–bromide catalysis. The mechanism of benzylic bromide oxidation has not been well studied. The only report applies to benzyl bromide itself, which produces benzoic and hydrobromic acids accompanied by small amounts of benzal bromide and traces of molecular bromine.¹⁷ The reaction stopped when 1 equiv of benzyl bromide relative to cobalt had been oxidized, which was attributed to CoBr_2 being less reactive than CoOAcBr .¹⁷

To resolve the issues of benzylic bromide participation more completely, we undertook a study of the kinetics of the reactions of PhCH_2Br and other benzylic bromides with Co(III) . In addition, the related reactions occurring in the autocatalytic oxidation of benzylic bromides in the presence of cobalt(II) or cobalt(III) were investigated.

Experimental Section

Oxygen consumption in the reactions during benzyl bromide oxidation was measured with a manometric apparatus similar to the one described in the literature.¹⁸ The reaction rates were calculated from the change in the volume of oxygen in a buret connected to the reaction vessel. The range of reliably measurable rates was between $\sim 0.5 \times 10^{-6}$ and $5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ with a 5 mL solution volume; the range could be expanded by changing the solution volume. All experiments were carried out at ambient pressure. The concentration of bromide ions was determined electrochemically by cyclic voltammetry in acetic acid using a BAS-100 electrochemical analyzer with a Pt working electrode and a saturated calomel reference electrode (SCE). The peak current at 1.0 V vs SCE, calibrated with standard bromide solutions, was used to determine $[\text{Br}^-]$.

The progress of the reaction between Co(III) and benzyl bromide was determined by monitoring the decrease of the Co(III) absorption at 450 nm. Spectra were recorded using either a Shimadzu UV-2101PC or a Applied Photophysics DX-17MV sequential stopped-flow spectrophotometer. Rate constants were measured under pseudo-first-order conditions ($[\text{PhCH}_2\text{Br}] > 10[\text{Co(III)}]$). The absorbance–time data were fitted to first-order kinetics by a nonlinear least-squares program. In all instances the solutions were thermostated at the desired reaction temperature. Molecular bromine was determined spectrophotometrically at 400 nm ($\epsilon_{400} = 200 \text{ L mol}^{-1} \text{ cm}^{-1}$).

Commercial samples of cobalt(II) acetate tetrahydrate, glacial acetic acid, hydrobromic acid, and benzylic bromides were used without further purification. Cobalt(III) solutions were prepared by the ozonolysis of cobalt(II) acetate solutions to approximately 60% completion.¹⁹

Results and Interpretation

Reduction of Co(III) by PhCH_2Br . This reaction was studied in glacial acetic acid under argon and oxygen atmo-

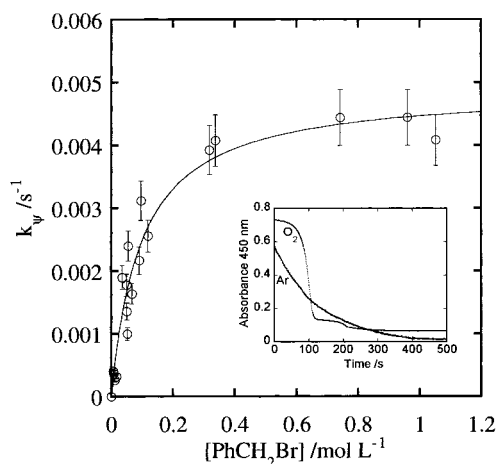


Figure 1. Benzyl bromide concentration dependence of the pseudo-first-order rate constant for the Co(III) /benzyl bromide reaction (50 °C, glacial acetic acid, $[\text{Co(III)}] = 1\text{--}3 \text{ mmol L}^{-1}$). Inset: Absorbance–time profile for the reaction between benzyl bromide and Co(III) under argon and oxygen atmospheres ($[\text{Co(III)}] = 1.9 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{PhCH}_2\text{Br}] = 1.34 \text{ mol L}^{-1}$, glacial acetic acid, 70 °C).

spheres at 23–80 °C with $1\text{--}3 \text{ mmol L}^{-1} \text{ Co(III)}$ and $0\text{--}1.34 \text{ mol L}^{-1} \text{ PhCH}_2\text{Br}$. Typical kinetic curves are presented in Figure 1. Under argon, the kinetic data fit well to a first-order rate law ($[\text{PhCH}_2\text{Br}] > 10[\text{Co(III)}]$). If traces of oxygen remained, the progress curves showed induction times which degraded the fit to first-order kinetics. Under the conditions described here, Co(OAc)_2 was the only product detected ($\epsilon_{522} = 13 \text{ L mol}^{-1} \text{ cm}^{-1}$). No bromide was detected as either the CoBr_2 complex ($\epsilon_{676} = 400 \text{ L mol}^{-1} \text{ cm}^{-1}$) or CoBr^+ ($\epsilon_{550} = 24 \text{ L mol}^{-1} \text{ cm}^{-1}$) on the time scale of these experiments,²⁰ nor was Br_2 detected ($\epsilon_{400} = 200 \text{ L mol}^{-1} \text{ cm}^{-1}$), an indication that net oxidation of hydrogen bromide by Co(III) had not occurred.

Figure 1 also displays the rate constant determined in the absence of O_2 as a function of PhCH_2Br . The rate of reduction of Co(III) increases with the PhCH_2Br concentration before reaching a plateau above $\sim 0.3 \text{ mol L}^{-1}$. This observation is consistent with the fact that two different forms of Co(III) exist in solution, each with a different reactivity toward PhCH_2Br .^{1,6,7,21–26} The ozonolysis method used to prepare Co(III) produces Co(III) . Our data suggest that Co(III) does not react with PhCH_2Br . Rather, Co(III) participates in an unfavorable equilibrium with a minor but more reactive form, Co(IIIa) . Various workers have published structural information on the identities of Co(IIIa) and Co(IIIb) . Co(IIIa) is likely a dimer or monomer $[\text{Co(OAc)}_3(\text{HOAc})_n]$,^{6,7} while Co(IIIb) has been shown to be a hydroxo-bridged dimer.²⁵ Further details can be found in the cited papers. Scott and Chester²⁷ observed a similar Co(III) equilibrium in which Co(III) and Co(IIIa) oxidized toluene at different rates. Our data suggest a model in which Co(IIIa) only reacts with the benzyl bromide. Scheme 3, the products of which have been identified by Dugmore and co-workers, can be proposed.¹⁷

(20) Sawada, K.; Tanaka, M. *J. Inorg. Nucl. Chem.* **1977**, *39*, 339.

(21) Sumner, C. E., Jr.; Steinmetz, G. R. *J. Am. Chem. Soc.* **1985**, *107*, 6124–6126.

(22) Szymanska-Buzar, T.; Ziolkowski, J. J. *J. Mol. Catal.* **1979**, *5*, 341.

(23) Ziolkowski, J. J.; Pruchnik, F.; Szymanska-Buzar, T. *Inorg. Chim. Acta* **1973**, *7*, 473–476.

(24) Roelofs, M. G.; Wasserman, E.; Jensen, J. H.; Nader, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 6329.

(25) Chipperfield, J. R.; Lau, S.; Webster, D. E. *J. Mol. Catal.* **1992**, *75*, 123.

(26) Blake, A. B.; Chipperfield, J. R.; Lau, S.; Webster, D. E. *J. Chem. Soc., Dalton Trans.* **1992**, 3719.

(27) Scott, E. J.; Chester, A. W. *J. Phys. Chem.* **1972**, *76*, 1520.

(14) Brodskii, M. S.; Yalter, Y. A.; Gervits, M. Y.; Kruglik, A. E. *Kinet. Katal.* **1979**, *20*, 274.

(15) Bukharkina, T. V.; Gavrilenko, N. D.; Digurov, N. G.; Knyazeva, N. A. *Kinet. Katal.* **1978**, *19*, 402.

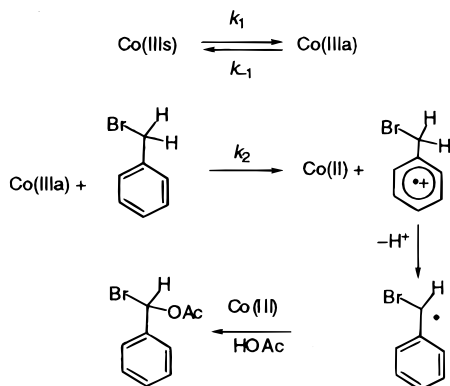
(16) Scherbina, F. F. *Zh. Obshch. Khim. (Engl. Transl.)* **1988**, *58*, 1188.

(17) Dugmore, G. M.; Powels, G. J.; Zeelie, B. *J. Mol. Catal.* **1995**, *99*, 1.

(18) Emanuel, N. M.; Denisov, E. T.; Maizus, Z. K. *Liquid-Phase Oxidation of Hydrocarbons*; Plenum Press: New York, 1967; p 350.

(19) Lande, S. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1968**, *90*, 5196.

Scheme 3. Oxidation of Benzyl Bromide by Co(IIIa) under Argon

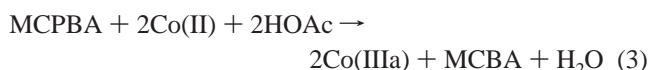


We propose that the reaction consists of the outer-sphere oxidation of benzyl bromide to its radical cation, proton dissociation from the radical center, and further oxidation of the resultant benzyl radical. Reactions such as this have been proposed before,¹⁷ but have not been verified experimentally. If the highly reactive Co(IIIa) species is assumed to be at a steady-state concentration, then eq 2 can be derived. Part-

$$-\frac{d[\text{Co(IIIa)}]}{dt} = \frac{(k_1 k_2 / k_{-1}) [\text{PhCH}_2\text{Br}] [\text{Co(IIIa)}]}{1 + (k_2 / k_{-1}) [\text{PhCH}_2\text{Br}]} \quad (2)$$

heimer and Gipe²⁸ found $k_{-1} = 0.095 \text{ s}^{-1}$ at 50°C . From eq 2, $k_1 = (4.9 \pm 0.3) \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 1.0 \pm 0.2 \text{ L mol}^{-1} \text{ s}^{-1}$ ($50.0 \pm 0.1^\circ\text{C}$, glacial acetic acid). The value of k_2 represents the rate constant for the bimolecular reaction between Co(IIIa) and benzyl bromide.

To verify this interpretation of the complex kinetics and the association of k_2 with the reaction of Co(IIIa), we sought to measure the rate constant k_2 directly. According to these data, the reaction of Co(IIIa) with benzyl bromide will proceed so rapidly that the stopped-flow technique will be required. Jones⁶ showed that Co(IIIa) could be generated directly by oxidizing Co(II) with *m*-chloroperbenzoic acid (MCPBA) (eq 3). However,



conversion of Co(IIIa) to Co(IIIb) is rapid enough to preclude the simple preparation of Co(IIIa) solutions for use in stopped-flow studies of the reaction between Co(IIIa) and PhCH₂Br. The sequential stopped-flow method provides the means for the generation of Co(IIIa) and the study of its subsequent reaction with PhCH₂Br on the stopped-flow time scale. Stoichiometric quantities of Co(II) and MCPBA were reacted in the "premixing loop" of the instrument, where it was aged for 0.1–5.0 s to allow complete oxidation of Co(II) according to eq 3. Then, Co(IIIa) was mixed with PhCH₂Br in the observation cell of the stopped-flow spectrophotometer ($[\text{PhCH}_2\text{Br}] > 10[\text{Co(IIIa)}]$). The reaction was monitored at 450 nm in glacial acetic acid at $50.0 \pm 0.1^\circ\text{C}$. The reaction was shown to be first order with respect to each of the reactants. Any Co(IIIb) produced in the premixing loop was reduced much more slowly by PhCH₂Br than Co(IIIa), giving rise to pure first-order kinetics rather than biexponential kinetics. For the Co(IIIa)–PhCH₂Br reaction,

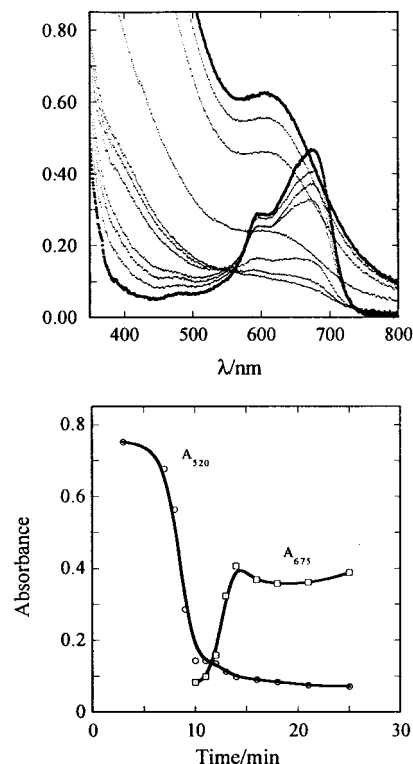


Figure 2. Kinetics showing (lower) the absorbance–time profile from one reaction at 50°C between PhCH₂Br (1.6 mol L^{-1}) and Co(III) (1.9 mmol L^{-1}) in the presence of oxygen, at 520 and 675 nm. These wavelengths monitor the respective loss of Co(III) and the buildup of CoBr₂ (and thus HBr), and (upper) the repetitive scans from which absorbance values were read. The times at which spectral scans were taken are those at which the points were plotted on the upper kinetic curve.

Table 1. Second-Order Rate Constants for the Reactions of Benzylic Bromides with Co(IIIa) at $50.0 \pm 0.1^\circ\text{C}$ and 450 nm in Glacial Acetic Acid

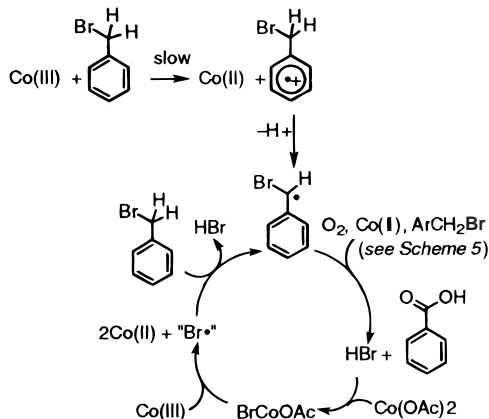
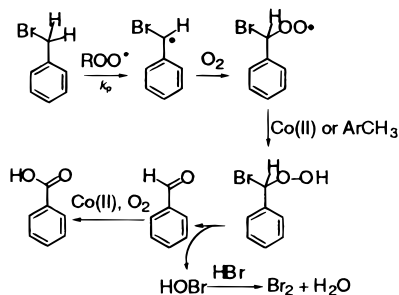
compound	$k_2/\text{L mol}^{-1} \text{ s}^{-1}$	compound	$k_2/\text{L mol}^{-1} \text{ s}^{-1}$
α -bromo- <i>p</i> -toluic acid	18	<i>p</i> -methylbenzyl bromide	2.0
<i>o</i> -methylbenzyl bromide	2.3	benzyl bromide	0.9
<i>m</i> -bromobenzyl bromide	2.2	<i>m</i> -methylbenzyl bromide	0.8
<i>p</i> -fluorobenzyl bromide	2.2	<i>p</i> -bromobenzyl bromide	0.7

this direct determination gives $k_2 = 0.9 \pm 0.1 \text{ L mol}^{-1} \text{ s}^{-1}$ ($50.0 \pm 0.1^\circ\text{C}$, glacial acetic acid), which agrees with the value $1.0 \text{ L mol}^{-1} \text{ s}^{-1}$ from the fit to eq 2.

The reactions of several other benzylic bromides with Co(IIIa) were studied using the sequential stopped-flow technique ($50.0 \pm 0.1^\circ\text{C}$, 450 nm, in glacial acetic acid). Values for k_2 , summarized in Table 1, are remarkable for their lack of variation. Except for α -bromo-*p*-toluic acid, the substituted benzylic bromides vary in their reactivity with Co(IIIa) by, at most, a factor of about 3. The enhanced reactivity of α -bromo-*p*-toluic acid can be attributed to displacement of an acetate ligand at Co(IIIa) by α -bromo-*p*-toluic acid, leading to a more rapid, inner-sphere electron-transfer reaction.

Figure 2 depicts the absorbance changes during the reaction between Co(III) and benzyl bromide in an oxygen atmosphere, which are different from those of the reaction under argon. The reaction under O₂ is characterized by a short induction period, after which Co(III) disappears several times more rapidly than under Ar. In addition, bromide ions are released during the course of the oxidation, as seen from the absorbance increase

(28) Parteneheimer, W.; Gipe, R. K. *Nature of the Co–Mn–Br Catalyst in the Methylaromatic Compounds Process*; American Chemical Society Symposium Series 523; American Chemical Society: Washington, DC, 1993; pp 81–88.

Scheme 4. Proposed Scheme for the Autocatalytic Reduction of Co(III) by Benzyl Bromide**Scheme 5.** Proposed Scheme for the Catalyzed and Uncatalyzed Autoxidation of Benzyl Bromide

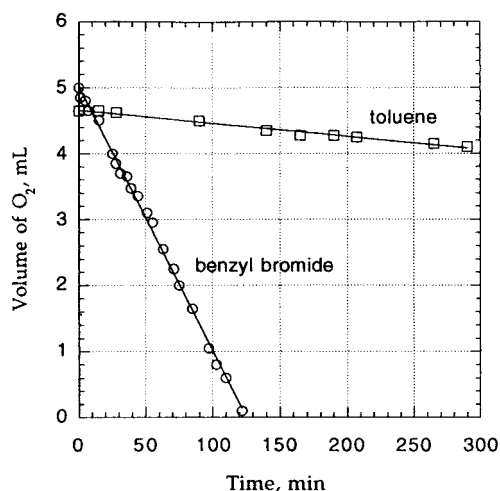
at 676 nm, indicating the formation of CoBr_2 . Under O_2 , benzyl radicals react with oxygen to form a peroxy radical that starts an autocatalytic process, similar to the one observed for the case of other, nonbrominated, alkylaromatic hydrocarbons.¹ This catalytic oxidation releases hydrogen bromide that in turn reduces Co(III) much faster than benzyl bromide does. The overall proposed reaction sequence is shown in Scheme 4. The mechanism of the release of HBr is discussed later.

Autoxidation of Benzyl Bromide. It should be noted the catalytic oxidation of benzyl bromide does not necessarily proceed by the oxidation step depicted in Schemes 3 and 4. We have thus explored further the oxidation of benzyl bromide under conditions in which (a) cobalt-free experiments were performed to evaluate the oxidizability of benzylic bromides by the $\text{ArCH}_2\text{OO}^\bullet$ radical and (b) only Co(II) and no Co(III) is initially present.

Oxidizability of Benzyl Bromide. Data taken at 30 °C were used to suggest that benzyl bromide is quite susceptible to free-radical autoxidation.²⁹ The experiments were not satisfactorily reproducible, however, owing to the instability of intermediate aralkylbromohydroperoxides. We performed Co-free measurements at 80 °C in glacial acetic acid using azoisobutyronitrile (AIBN) as the initiator. The rate of the initiated chain oxidation of hydrocarbons is described by eq 4, where the rate constant

$$v = (k_p/(2k_t)^{1/2})v_{in}^{1/2}[\text{RH}] = \alpha v_{in}^{1/2}[\text{RH}] \quad (4)$$

k_p refers to the propagation step (the reaction between RO_2^\bullet and ArCH_3 or ArCH_2Br , Scheme 5) and k_t to the termination step (recombination of two peroxy radicals).¹⁸ The initiation rate is designated v_{in} , referring to the decomposition of AIBN, which can be assumed to be constant. The parameter α , equal

**Figure 3.** Kinetics of oxygen consumption during AIBN-initiated oxidation of benzyl bromide and toluene in HOAc. Both experiments were carried out at 80 °C, $[\text{AIBN}] = 0.01 \text{ M}$, $[\text{benzyl bromide}] = 0.841 \text{ M}$, and $[\text{toluene}] = 0.939 \text{ M}$. The Y axis shows the volume of oxygen in the manometric apparatus.

to $k_p/(2k_t)^{1/2}$, is commonly used to compare the oxidizability of hydrocarbons.¹⁸ In these experiments the data were referenced to toluene: where v_{BB} and v_{tol} are the respective initial rates of

$$\frac{\alpha_{\text{BB}}}{\alpha_{\text{tol}}} = \frac{v_{\text{BB}}}{v_{\text{tol}}} \frac{[\text{PhCH}_3]}{[\text{PhCH}_2\text{Br}]} \quad (5)$$

oxidation (rates of oxygen consumption) of benzyl bromide and toluene by the $\text{ArCH}_2\text{OO}^\bullet$ radical. Figure 3 shows the kinetic plots of oxygen consumption during the AIBN-initiated oxidation of benzyl bromide ($[\text{PhCH}_2\text{Br}] = 0.841 \text{ M}$) and toluene ($[\text{toluene}] = 0.939 \text{ M}$) in glacial acetic acid ($v_{\text{tol}} = (1.8 \pm 0.1) \times 10^{-3} \text{ mL of O}_2 \text{ min}^{-1}$; $v_{\text{BB}} = (40 \pm 3) \times 10^{-3} \text{ mL of O}_2 \text{ min}^{-1}$). From these data

$$\alpha_{\text{BB}}/\alpha_{\text{tol}} = 22 \pm 1 \quad (6)$$

This shows that PhCH_2Br is significantly easier to oxidize than toluene. Values of $\alpha/\alpha_{\text{tol}}$ for other intermediates of toluene oxidation are (PhCH_2OH) 85 and (PhCHO) 29 000.³⁰

Oxidation of PhCH_2Br with the Co/Br Catalyst. The consumption of oxygen during oxidation of PhCH_2Br by the cobalt–bromide catalyst occurs following an initial induction period, after which the reaction attains its maximum rate of oxygen consumption. The oxidation of PhCH_2Br in the presence of Co(II) and oxygen is characterized by the continuous accumulation of bromide ions, as signaled by buildup of the CoBr_2 complex, which was detected spectrophotometrically at 675 nm, Figure 4. Thus, PhCH_2Br is easily oxidized in the presence of cobalt(II), and this process leads to the effective recovery of bromide ions. Molecular bromine is also formed during the oxidation of PhCH_2Br in the presence of oxygen. Bromine accumulated to about the 3–8 mM level, after which oxygen consumption stopped. To examine this inhibiting effect further, bromine was added at the outset of the reaction. Figure 5 shows that Br_2 may be responsible for the inhibition of the catalytic cycle. Alternatively, bromine may consume Br^- , forming the tribromide anion. If it is assumed that tribromide is less active, or inactive, then the lowering of the bromide concentration would also produce the observed deactivation. In either case, Br_2 acts as an inhibitor of the catalytic cycle.

(29) Howard, J. A.; Korcek, S. *Can. J. Chem.* **1970**, *48*, 2165.(30) Sheldon, R. A.; Kochi, J. K. *Adv. Catal.* **1976**, *25*, 272.

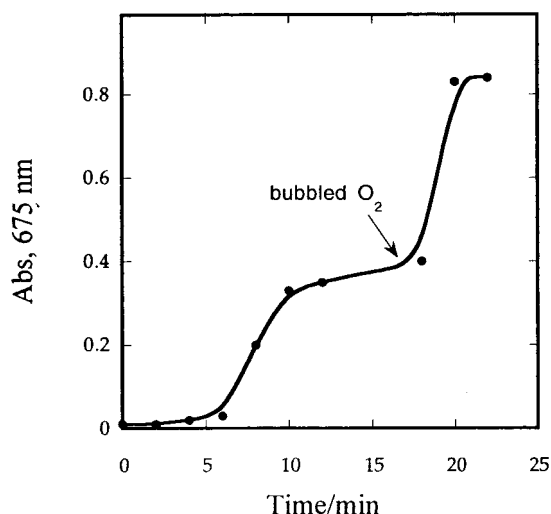


Figure 4. Time course of the absorbance at 676 nm during the oxidation of benzyl bromide by O_2 . Oxygen was present from the outset, but the supply was replenished after ca. 16 min. This absorbance is due to $CoBr_2$, which thus serves as an optical monitor for the buildup of bromide. Conditions $[PhCH_2Br] = 0.841 \text{ mol L}^{-1}$, $[Co(OAc)_2] = 2.0 \times 10^{-3} \text{ mol L}^{-1}$ 70°C .

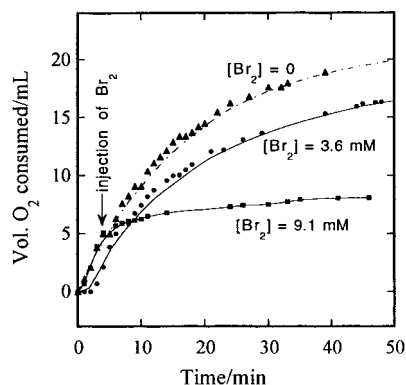
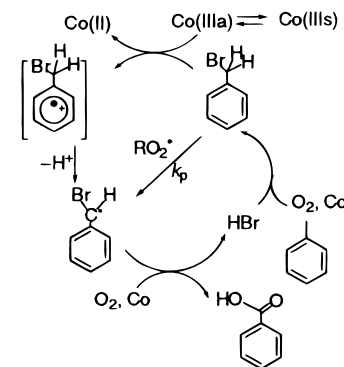


Figure 5. Kinetics of oxygen consumption during the oxidation of benzyl bromide in acetic acid, catalyzed by cobalt(II), illustrating the inhibiting effect of molecular bromine. ($[Co(II)] = 0.02 \text{ mol L}^{-1}$, $[PhCH_2Br] = 0.836 \text{ mol L}^{-1}$, 70°C). The point of injection of Br_2 is indicated, shortly after the rate decreased dramatically.

Solvolytic of $PhCH_2Br$ Catalyzed by Cobalt(II). Partenheimer has shown that solvolysis of $PhCH_2Br$, eq 1, is negligible over a 24 h period at 50°C in glacial acetic acid.¹¹ Here, we have duplicated this result and have shown that eq 1 is catalyzed by $Co(OAc)_2$. The solvolysis of $PhCH_2Br$ (0.081 mol L^{-1}) in glacial acetic acid at 50°C was first evaluated without $Co(OAc)_2$ present. To make this measurement, aliquots were removed at given times, to which $2.0 \times 10^{-3} \text{ mol L}^{-1} Co(OAc)_2$ was added as a spectrophotometric indicator of the bromide concentration. We agree with Partenheimer's findings:¹¹ solvolysis is negligible over the time course of this experiment. Solvolysis was also examined with $Co(OAc)_2$ added to the solution at the beginning. ($[Co(OAc)_2 \cdot 4H_2O] = 2.0 \times 10^{-3} \text{ mol L}^{-1}$, glacial acetic acid, 50°C). The solvolysis of benzyl bromide to benzyl acetate and HBr occurs much more quickly in the presence of cobalt(II) owing to the catalytic removal of bromide by cobalt(II) and the subsequent formation of stable bromocobalt(II) species. The shape of the resulting curve is accurately predicted from the formation constants of bromocobalt(II) complexes.²⁰ Manganese(II) acetate does not catalyze the solvolysis of benzyl bromide.

Scheme 6. Proposed Role of the $PhCH_2Br$ Intermediate in Autoxidation of Toluene



Discussion

Reaction Mechanism. The rates of reduction of $Co(III)$ in the presence of $PhCH_2Br$ and oxygen are much higher than the rate of anaerobic reduction of $Co(III)$ by $PhCH_2Br$ or the rate of $PhCH_2Br$ solvolysis. The rate of reduction of $Co(III)$ by $PhCH_2Br$ under argon becomes comparable to that under oxygen once allowance is made for a more active cobalt species, $Co(IIIa)$. The rate of solvolysis is many orders of magnitude lower than those of the other reactions.

The induction period is an important feature of the cobalt-catalyzed oxidation of $PhCH_2Br$ in the presence of oxygen. During this interval, small concentrations of bromocobalt(II) species accumulate as a result of $PhCH_2Br$ solvolysis. The formation of $Co^{II}Br_n$ starts a catalytic process similar to the oxidation of nonbrominated compounds, during which $PhCH_2Br$ is oxidized to benzoic acid and further HBr released, increasing the rate of oxidation. The increase in hydrogen bromide leads to the increase in the oxidation rate, explaining the autocatalytic kinetics after the induction period (see Figure 4). Scheme 5 shows the proper reaction sequence for the oxidation of $PhCH_2Br$ with and without the catalyst. An important difference between the oxidation of nonbrominated alkylaromatics and the oxidation of $PhCH_2Br$ is the release of HBr .

We suggest that hydrogen bromide is produced as shown in Scheme 5, thus not only regenerating hydrogen bromide effectively, but also generating alkyl radicals needed for the propagating steps of the chain reaction.

The major pathways by which $PhCH_2Br$ participates in the catalytic cycle are the free-radical oxidation catalyzed by $Co(II)$ and the direct oxidation by $Co(IIIa)$. Reaction of $PhCH_2Br$ with $Co(IIIb)$ is much less kinetically favorable than the competing reactions of $Co(IIIb)$ with inorganic bromides. We have shown that uncatalyzed solvolysis of $PhCH_2Br$ occurs too slowly to be very effective at restoring catalytic concentrations of hydrogen bromide. However, solvolysis catalyzed by $Co(II)$ is considerably faster. $PhCH_2Br$ is easily formed and oxidized, suggesting that part of the oxidation of methylarenes occurs through the formation of intermediate $PhCH_2Br$, as shown in Scheme 6. The oxidation of benzylic bromides by $Co(IIIa)$ does not follow a Hammett relationship, but the overall reaction of methylarenes with metal-bromide catalysts does. Therefore, the contribution of benzylic bromides to the overall rate is probably small.

Summary

The $Co-Br$ catalyst oxidizes $PhCH_2Br$. Under anaerobic conditions, $PhCH_2Br$ is oxidized easily by $Co(IIIa)$ and imper-

ceptibly by Co(III)s. These new results show that Co(IIIa) participates in an unfavorable *equilibrium* with Co(III)s. In the absence of O₂, neither Br₂ nor HBr is formed, whereas the aerobic oxidation initiates the catalytic oxidation of PhCH₂Br. The autoxidation reaction releases the inorganic bromide needed to sustain the efficient reduction of Co(III). The oxidation of methylarenes proceeds in part through the formation of PhCH₂-Br.

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