

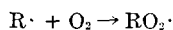
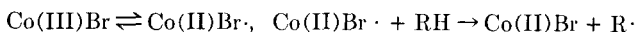
## Catalysis by Cobalt and Bromide Ions in the Autoxidation of Alkylbenzenes in Acetic Acid

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Relative activities of 11 hydrocarbons toward the active species in the autoxidation catalyzed by cobalt and bromide ions in acetic acid were measured using a competitive oxidation method, and the active species was as selective as alkylperoxy radical and more selective than bromine radical. The rates of oxidation of single hydrocarbons and some spectroscopic data are also presented and discussed. It was concluded that the main propagation step in the autoxidation catalyzed by cobalt and bromide ions in acetic acid can be written as follows;



### INTRODUCTION

Although the catalysis of cobalt and bromide ions in the autoxidation of acetic acid solution of hydrocarbons has been studied by several workers (1-6), it has still many points to be elucidated.

The profound synergistic effect of bromide ion on the metal catalysis can be attributed to the enhancement in the rate of propagation step, since the rate of oxidation of methylbenzenes far exceeds the value calculated (3, 7) from the propagation and termination rate constants.

In this paper, we report that the propagating catalyst should be cobalt acetate bromide on the basis of the relative reactivity of various hydrocarbons toward the active species and some spectroscopic results.

### EXPERIMENTAL METHODS

#### *Materials*

Acetic acid, chlorobenzene, hydrocarbons, alkali bromides and cobaltous acetate  $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$  were of reagent grade and used as received. Cobaltic acetate was pre-

pared by bubbling the ozone containing air through cobaltous acetate solution of acetic acid. It contained 10 mole% of cobaltous acetate.

#### *Reduction Rate of Cobaltic Ion*

Solution I (acetic acid solution of cobaltic acetate) and solution II (acetate acid solution of an alkali bromide and hydrocarbons), which were repeatedly degassed and kept in separate vessels, were simultaneously injected into a quartz cell under nitrogen atmosphere. Electronic spectra were measured by Hitachi-124 and Hitachi-RSP-2 rapid scan spectrophotometers. Generally the absorbance at 630 nm showed a small fluctuation within 10 sec after mixing. The fluctuation was ascribed to the formation of a new cobalt complex, so that the reduction rate of cobaltic ion was calculated by measuring the absorbance after 15 sec of standing.

#### *Relative Reactivity of Hydrocarbons in the Oxidation*

For example, a mixture composed of 30 ml acetic acid, 10 ml chlorobenzene (internal standard), 10 ml hydrocarbon A (mostly

ethylbenzene) and 10 ml hydrocarbon B was submitted to the oxidation after adding cobaltous acetate and alkali bromide under vigorous agitation at 1 atm oxygen atmosphere and 60°C except otherwise stated.

In some cases three hydrocarbons, as shown in Fig. 2, were submitted to the oxidation for comparison. Every 5 or 10 min the aliquot of solution (5 ml) was taken into 20 ml water in a 30 ml flask. After shaking and settling hydrocarbon phase it was analyzed with g.c. equipped with digital integrator using Carbowax 20 M column.

The oxygen absorption apparatus has been described elsewhere (3).

## RESULTS AND DISCUSSION

### Reduction Rate of Cobaltic Acetate Bromide Under Nitrogen Atmosphere

When bromide ion lower than cobalt ion was added to the acetic acid solution, the electronic spectra ( $\lambda_{\max}$  630 nm) of cobaltic ion changed slightly, and have shown a gradual decrease as the oxidation of hydrocarbon proceeded. When a higher concentration of bromide ion than cobalt ion was added, the shape of absorption spectra from 500 to 700 nm changed markedly, and the rate of oxidation could not be determined by the decrease of absorbance because of interruption due to cobalt dibromide. Therefore, the electronic spectra were measured at a lower ratio of alkali bromide to cobaltic acetate using alkylbenzenes as the substrate. Typical spectra of acetic acid solution of cobaltic acetate bromide in the course of oxidation are shown in Fig. 1.

In the presence of  $5 \times 10^{-3} M$  cobaltic acetate and  $2 \times 10^{-3} M$  calcium bromide at 30°C, the rate of reduction of Co(III) was 0.45, 0.95, 1.6, and  $2.3 \times 10^{-5} M/\text{sec}$  at toluene concentration of 0, 0.05, 0.1, and 0.2 M, respectively.

The decrease of Co(III) concentration in the absence of substrate may be due to the self-decomposition of unstable cobaltic acetate bromide. In spite of some deviations from straight line, the rate of reduction of Co(III) was roughly first order with respect to the concentration of toluene.

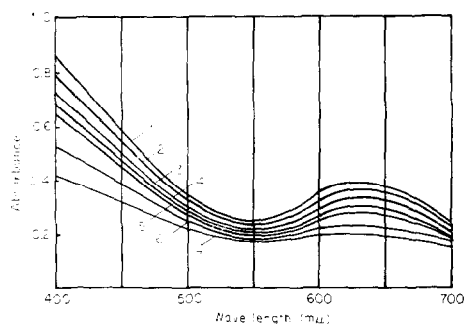


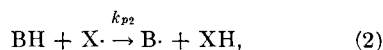
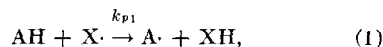
FIG. 1. Change of visible spectra of acetic acid solution of  $5 \times 10^{-3} M$  cobaltic acetate and  $2 \times 10^{-3} M$   $\text{CaBr}_2$  in the oxidation of  $5 \times 10^{-2} M$  cumene. Absorbance after: (1) 10 sec, (2) 20 sec, (3) 40 sec, (4) 70 sec, (5) 170 sec, (6) 1030 sec, (7) 2000 sec.

The rate of reduction of Co(III) was also roughly first order with respect to cobaltic ion over the concentration range from  $1 \times 10^{-3}$  to  $5 \times 10^{-2} M$  at molar ratio of bromide to cobalt ions 0.8. Then, the second order rate constant was calculated as about  $1 \times 10^{-4} M^{-1} \text{sec}^{-1}$ .

It should be mentioned that the rate of direct oxidation (4) with cobaltic acetate in acetic acid in the absence of oxygen increases by a factor of 100 in the presence of bromide ion.

### Relative Reactivity of Hydrocarbon Toward the Active Species in the Autoxidation Catalyzed by Cobalt and Bromide Ions

In the autoxidation catalyzed by cobalt and bromide ions in acetic acid the chain carrier can not be peroxy radical (3, 7) but a bromine compound independent of substrate. Therefore, the rates of disappearance of two hydrocarbons in the competitive oxidation can be expressed as follows, when the hydrogen abstraction is rate determining:



$$-d[\text{AH}]/dt = k_{p1}[\text{AH}][\text{X} \cdot], \quad (3)$$

$$-d[\text{BH}]/dt = k_{p2}[\text{BH}][\text{X} \cdot], \quad (4)$$

$$\begin{aligned} (-d[\text{AH}]/dt)/[\text{AH}] / (-d[\text{BH}]/dt)/[\text{BH}] \\ = k_{p1}/k_{p2}. \end{aligned} \quad (5)$$

Thus, the relative reactivity of substrate can be obtained by calculating the rate of oxidation of each fraction. In the absence of oxygen, the formed alkyl radicals will be converted to the esters such as benzyl acetate (14) in the presence of cobaltic ion.

However, in the presence of oxygen, the formation of peroxy radical will occur preferentially. Indeed, toluene was mainly oxidized to benzaldehyde and benzoic acid, and ethylbenzene to acetophenone and methylphenyl carbinol, and cumene to acetophenone and cumyl alcohol. The oxidation of ethylbenzene proceeded most smoothly, since any oxidation products other than acetophenone and methylphenyl carbinol were not detected and the molar ratio of acetophenone to methylphenyl carbinol showed a constant value of 6:1 independent of reaction conditions. Therefore, ethylbenzene was mostly used as the standard compound for obtaining relative reactivity.

The relative concentration of substrates was plotted against reaction time. As shown in Fig. 2, very good straight lines were obtained at conversions below 5%, and so the value of  $-d[RH]/dt[RH]$  was calculated from the slope of  $-\Delta[RH]/[RH]/\Delta t$ .

The relative reactivities of various hydrocarbons at 60°C shown in Table 1 indi-

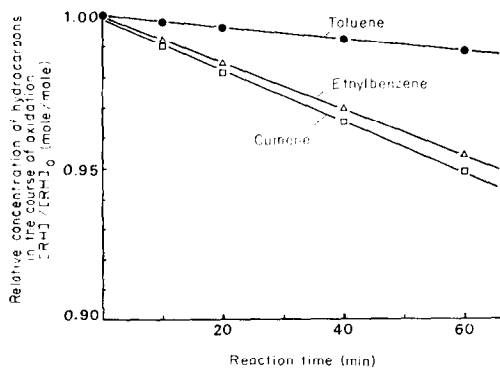


FIG. 2. Consumption of alkylbenzenes in the autoxidation catalyzed by 0.02 *M* Co(OAc)<sub>2</sub> and 0.04 *M* NaBr in acetic acid at 60°C. Oxidized solution was composed of 40 ml acetic acid, 10 ml chlorobenzene, 10 ml toluene, 10 ml ethylbenzene and 10 ml cumene.

TABLE I  
RELATIVE REACTIVITY OF HYDROCARBONS  
TOWARD THE ACTIVE SPECIES IN THE  
AUTOXIDATION CATALYZED BY  
COBALT AND BROMIDE IONS  
IN ACETIC ACID

Hydrocarbon	Relative reactivity (per active hydrogen)		
	Catalyst <sup>a</sup> composed of 0.02 <i>M</i> Co(OAc) <sub>2</sub> and 0.04 <i>M</i> NaBr at 60°C	Cumyl peroxy radical (8) at 30°C	Bromine radical (9) at 40°C
Cyclohexane	0.33	0.1	0.0074
<i>p</i> -Chlorotoluene	0.42		
Toluene	1.00	1.00	1.00
Mesitylene	1.17		
<i>p</i> -Xylene	1.50	1.60	
Pseudocumene	2.54		
<i>p</i> -Methoxytoluene	3.42		
Durene	3.83		
Ethylbenzene	8.33	9.3	17
Cumene	16.8	15.9	37
Tetralin	34.2	36.4	

<sup>a</sup> No significant differences in the relative reactivity were observed at Co(OAc)<sub>2</sub> 0.01 to 0.05 *M* and NaBr 0.02 to 0.1 *M*.

cate that the active species has a similar selectivity as cumylperoxy radical for many substrates and is less selective than bromine radical.

It should be mentioned that in this experiment we used sodium bromide as bromide ion source in order to exclude the effect of hydrogen bromide.

When the reaction temperature was changed within the range of 40–80°C, small differences in the relative reactivities of toluene, ethylbenzene, and cumene were observed at 0.02 *M* Co(OAc)<sub>2</sub> and 0.04 *M* NaBr, that is, 1.0:8.1:16.1 at 40°C, and 1.0:6.7:14.1 at 80°C.

When 0.02 *M* calcium bromide was used instead of 0.04 *M* sodium bromide, the relative reactivities of toluene, ethylbenzene, and cumene at 60°C were 1.0:9.0:19.1.

Therefore, the type of alkali bromide

seems to affect the relative reactivity a little, although the rate of oxidation of hydrocarbons (5) was affected considerably.

According to the data in Table 1, the Hammett plot showed a  $\rho$  value of  $-0.6$ . The relative reactivities of *p*-bromotoluene and *p*-nitrotoluene were negligibly small compared with that of toluene and the reactivity of *p*-chlorotoluene was a little smaller than the value extrapolated from Hammett relationship of substituted toluenes with electron releasing groups.

The above results probably show that the oxidation of chlorobenzene, internal standard for g.l.c. analysis, proceeded very slowly and apparently made the rate of oxidation of substituted toluenes with electron withdrawing groups a little lower than the true value.

As shown in Table 2, the relative rates of autoxidation of single hydrocarbons were quite different from the relative reactivities obtained by competitive oxidation.

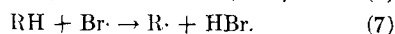
It is interesting that the rate of oxidation of substituted toluenes with electron with-

drawing groups shows higher values than those expected from the smaller reactivity in the hydrogen abstraction step. These results are attributable mainly to the difference in the rate of termination reaction between substituted toluenes. However, the differences in the rate of autoxidation of toluene, ethylbenzene, cumene, and tetralin can be partly ascribed to the complexed situation in the rates of formation and decomposition of hydroperoxide. For example, the rate of decomposition of tetralin hydroperoxide (3) catalyzed by cobalt increased 20% in the presence of bromide ion, but that of cumyl hydroperoxide (10) was suppressed remarkably.

#### Reaction Mechanism

It has been confirmed by many workers that the profound synergistic effect of bromide ion in the metal-catalyzed autoxidation of hydrocarbon in acetic acid was not due to the enhancement in the rate of chain initiation but due to the enhancement in the rate of propagation step.

Hay and Blanchard (2) proposed the following chain propagation reactions as confirmed by Rust and Vaughan (11), since the azobisisobutyronitrile (AIBN) initiated autoxidation of cumene was remarkably increased by the addition of hydrogen bromide.



The author (5) also confirmed that the rate of oxidation of tetralin initiated with 0.01 *M* AIBN at 50°C was increased by a factor of 40 in the presence of 0.02 *M* HBr, but the effect almost disappeared after a very short time, corresponding to the chain length of about 1.5. Therefore, free hydrogen bromide can not be so effective catalyst as a mixture of cobalt and bromide ion, since one bromide ion in the presence of cobaltous acetate can oxidize 25 toluenes before deactivation.

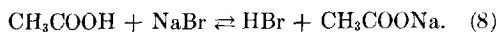
According to Fujita, Ito and Suga (12) the acidity of acetic acid solution of 0.05 *M* cobaltous acetate did not increase in the presence of sodium bromide in contrast to the case of hydrogen bromide.

TABLE 2  
RELATIVE RATE OF OXIDATION OF  
HYDROCARBONS CATALYZED BY  
0.02 *M* Co(OAc)<sub>2</sub> AND 0.04 *M*  
NaBr IN ACETIC ACID  
AT 60°C

Hydrocarbon (4.0 <i>M</i> )	Relative rate of oxidation	Relative rate per active hydrogen
Toluene	1.00	1.00
<i>p</i> -Toluic acid methyl ester	0.48	0.48
<i>p</i> -Methoxytoluene	0.96	0.96
<i>p</i> -Chlorotoluene	1.05	1.05
<i>p</i> -Toluic acid <sup>a</sup>	1.10	1.10
<i>m</i> -Xylene	1.73	0.87
<i>o</i> -Xylene	1.87	0.94
<i>p</i> -Xylene	1.96	0.98
Mesitylene	2.10	0.70
Pseudocumene	4.53	1.51
Durene	4.74	1.19
Ethylbenzene	1.17	1.76
Cumene	1.58	4.74

<sup>a</sup> Oxidation of toluene and *p*-toluic acid was carried out and compared at substrate concentration of 0.35 *M*.

Indeed, the rate of oxidation of tetralin in acetic acid initiated with 0.01 *M* AIBN increased only slightly by adding 0.03 *M* sodium bromide at 50°C. These results support that the equilibrium constant of reaction (8) is very small.

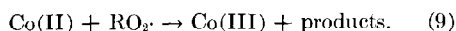


Hay and Blanchard (2) explained that hydrogen bromide was converted to inactive organic bromide rapidly but could be regenerated by the reaction of organic bromides with cobalt acetate.

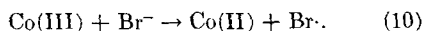
Although bromide ion can be regenerated by the reaction of organic bromide and cobalt ion (2, 4), and also by the oxidative decomposition (13) of organic bromide, the rate of regeneration is extremely low at 80°C.

For example, the rate of dehalogenation of *p*-methyl benzylbromide catalyzed by 0.03 *M* cobalt bromide in acetic acid at 70°C was  $3.8 \times 10^{-4}$  *M*/hr, which can be compared with the rate of oxidation of *p*-xylene  $8 \times 10^{-3}$  *M*/hr at the same conditions. Thus, the participation of hydrogen bromide in the propagating step can be discarded.

Therefore, the catalytic effect of cobalt and bromide ions can be attributed to the participation of cobaltous ion in the propagation step. As summarized by Howard (14), cobaltous ion reacts very rapidly with peroxy radicals in a neutral solvent.

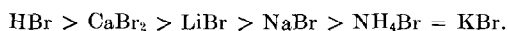


According to our experiments, cobaltous acetylacetonate in chlorobenzene reacted with equimolar amount of 2-cyano-2-propyl peroxy radical yielding cobaltic ion. It seems quite reasonable that Ravens (1) and Bawn and Wright (6) proposed that the reactions (9) and (10) played an important part in the cobalt bromide catalysis.



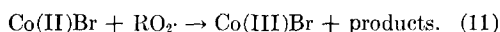
However, reaction (10) cannot be the rate determining step according to the following experimental results: (a) The rate of oxidation catalyzed by cobalt and bromide ions was only proportional to the

concentration of bromide ion (3-5) at the molar ratio of Br/cobalt below 2:1. (b) When 0.01 *M* of various inorganic bromide ions was added as alkali salts to an acetic acid solution of 0.01 *M* cobaltous acetate in the absence of oxygen, the absorbance\* at 610 nm due to cobaltous acetate bromide decreases in the following order:



The above order corresponds well to that of the rate of autoxidation of ethylbenzene (3), that is, the rate of oxidation is not proportional to the concentration of bromide ion but to that of cobaltous monobromide.

Furthermore, the reaction (9) was found to be very slow in acetic acid solution. The absorption spectrum at 630 nm due to cobaltic ion was hardly detected after 1 hr, when  $1.1 \times 10^{-8}$  *M*/sec of 2-cyano-2-propyl peroxy radical was formed in acetic acid in the presence of 0.01 *M* cobaltous acetate under oxygen atmosphere. In contrast, when 0.01 *M* sodium bromide was added to the same solution, cobaltic ion concentration was observed to increase with the rate of  $1.2 \times 10^{-8}$  mole/l sec just with the same rate of peroxy radical formation. The easiness of reaction (11) can be attributed to the steric effect of ligand and electrophilic property of bromine atom.



This result demonstrates that reaction (9) should be replaced by reaction (11) as a reaction scheme.

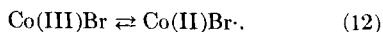
The relative reactivity of alkylbenzenes toward the active species in the cobalt bromide catalysis (Table 1) indicates that the active species resembles a free radical rather than cobaltic acetate (15, 16), and that carbon-hydrogen bond dissociation energy plays an important role in the reaction. Heiba, Dessau and Koehl (16) and Onopchenko, Schulz and Seekircher (17) observed that cobaltic acetate chloride was formed when lithium chloride was added

\* The absorption at 610 nm due to Co(II)Br was much weaker than that at 630 nm by Co(III).

to the acetic acid solution of cobaltic acetate and its activity was much higher than that of cobaltic acetate and resembles that of a chlorine radical.

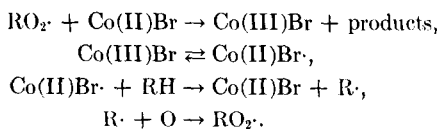
Kasahara, Saito and Izumi (18) reported that the oxidation of  $\alpha$ -methylstyrene by manganic acetate and potassium bromide proceeded selectively via allylic hydrogen abstraction, yielding  $\alpha$ -phenyl allyl acetate.

The active species in cobalt bromide catalysis may be expressed as  $\text{Co(II)Br}\cdot$  because of its reactivity.



It seems inadequate to consider the chain carrier as free bromine radical, because the chain length of bromide ion in cobalt bromide catalysis is as high as 25 in the autoxidation of toluene (4) and this value is quite high compared with the value of 1.5 in the catalysis by hydrogen bromide.

In conclusion, cobalt acetate monobromide should be the true catalyst and the chain carrier instead of peroxy radical in the autoxidation catalyzed by cobalt and bromide ions, and the propagating step can be written as follows.



Thus, a cobaltic acetate bromide will oxidize catalytically a number of alkylbenzenes. But, bromide ion will be slowly converted to an inactive form of organic

bromide by the reaction of  $\text{Co(III)Br}$  with alkyl radicals.

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