Studies on the Liquid Phase Oxidation of Nitroalkylbenzenes Catalyzed by Transition Metal and Bromide Ions

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The liquid phase autoxidation of nitroalkylbenzenes catalyzed by transition metal and bromide ions in acetic acid was investigated at 55—85 °C. A remarkable synergistic effect was found on the mixtures of metal catalysts composed of cobalt and other transition metals, the maximum reaction rate being observed at the molar ratio of Co : Mn : Br = 1 : 0.005—0.01 : 1—2. The rate of oxygen absorption of *p*- or *m*-nitroalkylbenzenes was affected by the partial pressure of oxygen, showing deviation from the first order dependency on the substrate concentration in contrast to the case of ordinary alkylbenzenes. The results can be explained by the retardation effect due to nitro compounds which might result from the reaction with alkyl radicals and the deactivation of metal catalysts. *o*-Nitroalkylbenzenes except nitroethylbenzene show a great resistivity against the oxidation. The retardation effect can be ascribed to the inhibiting effect due to inactive free radicals and also to the various reduced products resulting from the intramolecular reaction of nitro groups and active radicals. It was found that the autoxidation of *p*-nitrotoluene catalyzed by Co–Mn–Br catalyst proceeds very rapidly at temperatures as low as 85 °C, yeilding mostly *p*-nitrobenzoic acid along with a small amount of *p*-nitrobenzaldehyde.

The autoxidation of alkylbenzenes catalyzed by transition metal and bromide ions in acetic acid has been studied by many workers.(2–6) The liquid phase oxidation of nitroalkylbenzenes is important from the viewpoint of chemical industry, it is also interesting theoretically because of the difficulty of the reaction due to electron-withdrawing tendency of the nitro group, though this has not been clarified. Chervinskii and Kovalev reported the oxidation of *p*-nitrotoluene catalyzed by transition metal stearates and tetrabromoethane in propionic or butyric acids at 140—160 °C,(7,8) but we have confirmed that the selectivity of the reaction is low because of complicated side reactions. They reported the oxidation of nitrosubstituted *o*-xylenes,(9) but did not clarify the effect of the nitro group. Several patents which have been published for the oxidation of *p*- or *m*-nitrotoluenes(10–15) with severe conditions attached, do not furnish satisfactory data for a theoretical approach on the effect of the nitro group.

We have thoroughly studied the effect of the nitro group in the autoxidation of nitroalkylbenzenes catalyzed by transition metal and bromide ions in acetic acid and found that the oxidation proceeds easily at temperatures as low as 85 °C under restricted reaction conditions.

Experimental

Materials. Acetic acid, various metal acetates and alkali bromides of reagent grade were used. Nitrotoluenes, 2,4-dimethylnitrobenzene, *p*-nitroethylbenzene and nitrobenzene were purified by the usual method: distillation or recrystallization after washing with dilute sulfulic acid, aqueous alkali, water and drying. Chlorobenzene and *o*-dichlorobenzene were distilled after being dried over calcium chloride. *p*-Chlorotoluene, *o*-nitroethylbenzene, *o*-nitroacetophenone, *o*-nitrobenzaldehyde, *p*-nitrobenzaldehyde and other organic compounds of reagent grade were used after treatment with active alumina, when necessary.

Procedure. The rate of oxygen absorption was measured under atmospheric oxygen according to the method of Kamiya,(16,17) but in the case of the experiment under positive pressure, it was determined by measuring the very small pressure variation in a constant volume reactor.

Analysis. A gas chromatograph (Shimadzu GC-4BP-TF) was mainly used for analysis of the reaction products. The conditions were as follows, Column: 3% Silicone OV-17, on Chromosorb WHP, 1.5 m, 145 °C, Detector: FID, 250 °C, N_2-Flow rate: 40 ml/min, Injection temperature: 260 °C.

Results and Discussion

Feature of the Metal Catalyst. Oxidation of *p*-nitrotoluene and *p*-chlorotoluene was carried out in acetic acid in the presence of various catalysts. The steady state rate of oxidation is shown in Fig. 1. The general feature of the oxygen absorption curves was not affected by the concentration of catalyst or

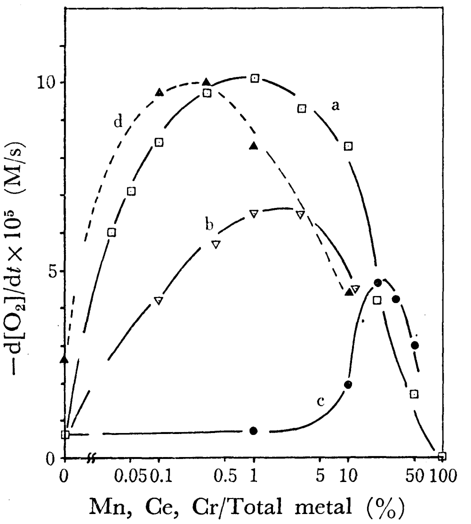


Fig. 1. Relation between catalyst composition and the rate of oxidation in acetic acid.
Total metal 3.6×10^{-2} M, NaBr 6.1×10^{-2} M, 85 °C. a: *p*-Nitrotoluene 1.69 M, $Co(OAc)_2 \cdot 4H_2O$, $Mn(OAc)_2 \cdot 4H_2O$, b: *p*-nitrotoluene 1.69M, $Co(OAc)_2 \cdot 4H_2O$, $Ce(OAc)_3 \cdot H_2O$, c: *p*-nitrotoluene 1.69M, $Co(OAc)_2 \cdot 4H_2O$, $Cr(OAc)_3 \cdot H_2O$, d: *p*-chlorotoluene 1.69M, $Co(OAc)_2 \cdot 4H_2O$, $Mn(OAc)_2 \cdot 4H_2O$.

substrate, a straight line being obtained until a considerable amount of substrate was consumed. The activity of catalysts decreased in the order, Co–Mn–Br> Co–Ce–Br> Co–Cr–Br, no appreciable catalysis being observed in other combinations of metal ions. Maximum reaction rates were obtained in metal mixtures of Co–Mn, Co–Ce, and Co–Cr at molar ratios of 99 to 1, 98 to 2 and 75 to 25, respectively. However, the Co–Mn ratio reported in the oxidation of *p*-xylene and ethylbenzene catalyzed by Co–Mn–Br is 80 to 20.[5)] In the following experiments, Co–Mn–Br catalyst was mainly used at the molar ratio of Co : Mn : Br=99 : 1 : 170 because of its high activity. With regard to the molar ratio of bromide ion to total metal ions, no significant difference was observed between the ratios from 1 : 1 to 2 : 1. The effect of counter cation on bromide ion was striking. In the case of alkali earth metal ions (*e. g.* Mg^{2+}, Ca^{2+}, and Ba^{2+}), the initial reaction rate was considerably high but decreased very soon, in similar way to that in the oxidation of ordinary alkylbenzenes.[18)]

Effect of Catalyst Concentration. The oxygen absorption rate is nearly of second order in catalyst at lower concentrations, but independent of the catalyst concentration above 3.6×10^{-2} M. This effect is not so significant in the oxidation of ordinary alkylbenzenes catalyzed by Co–Br catalyst.[19,20)] The difference is related to the substrates, but not to catalysts, because this effect was not so remarkable in the oxidation of ethylbenzene catalyzed by Co–Mn–Br catalyst. Since odd electron density at the benzylperoxyl radical center should decrease by electron-withdrawing substituents, the reaction of *p*-nitrobenzylperoxyl radical with metal ion at low oxidation state ($Me^{2+}+RO_2\rightarrow Me^{3+}\cdot RO_2$) leading to chain termination should be accelerated. Thus no increase of oxidation rate was observed with increasing catalyst concentration.

Effect of the Partial Pressure of Oxygen. The effect of oxygen partial pressure is shown in Fig. 2, indicating a slight positive effect on the rate of oxidation of nitrotoluenes. However, in the case of ordinary alkylbenzenes below 100 °C, this effect is negligible at pressures above 0.5 atm.[5,22)] Since the reaction of substituted benzyl radical with molecular oxygen has been concluded to have no significant effect due to substituents,[23,24)] the effect of partial pressure of oxygen is attributable to the following inhibiting effect due to the nitro group.

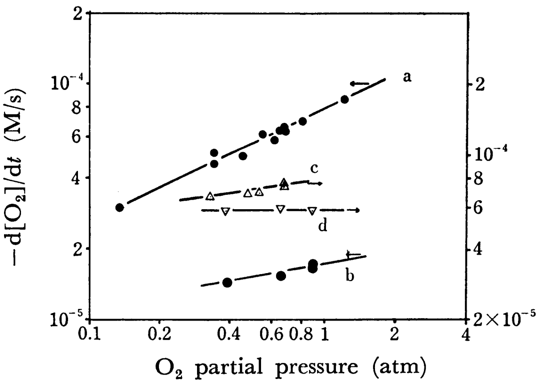
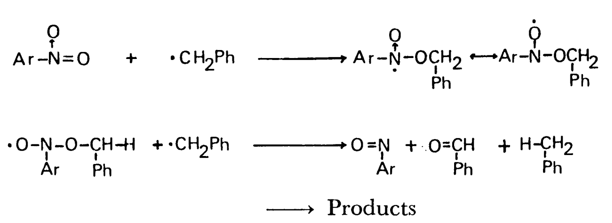


Fig. 2. The rate of oxidation of *p*-nitrotoluene, *m*-nitrotoluene, and *p*-chlorotoluene catalyzed by Co–Mn–Br catalyst in acetic acid as a function of oxygen partial pressure.
$Co(OAc)_2\cdot4H_2O$: $Mn(OAc)_2\cdot4H_2O$: NaBr=99 : 1 : 170, total metal 1.2×10^{-2} M.
a: *p*-Nitrotoluene 1.69 M, 85 °C, b: *p*-nitrotoluene 1.69 M, 65 °C, c: *m*-nitrotoluene 1.69 M, 85 °C, d: *p*-chlorotoluene 1.69 M, 65 °C.

According to Jackson and Waters,[25)] *O,N*-dibenzyl-*N*-phenylhydroxylamines, *N*-benzylanilines, anilines and resinous materials were obtained, after toluene, aromatic nitro compounds and *t*-butyl peroxide had been allowed to react at the reflux point for 80 h. They postulated the following mechanism for the reaction.



Scheme 1.

Aromatic nitro compounds are known to be oxidizing agents which become reduced in the course of reaction, the reduced products acting as inhibitor or retarder in radical polymerization.[26–28)]

Since there exist more than 1000-fold excess of nitro groups as compared with oxygen in *p*-nitrotoluene oxidation, a small portion of active radicals may react with nitro groups, even if the reaction betwen *p*-nitrobenzyl or *p*-nitrobenzoyl radicals and oxygen proceeds rapidly. Accordingly, various inhibitors could be formed in the solution, and the reaction rate would decrease by reduction in oxygen partial pressure.

Substrate Concentration. Although the rate of oxidation of *p*-nitrotoluene is of first order with respect to substrate at concentrations below 0.3 M, the order decreases with increase in concentration. However, the first order dependency is observed at high concentration region in the oxidation of ethylbenzene, *p*-xylene and toluene.[5)] The inhibition effect due to nitrobenzene in the oxidation of *p*-nitrotoluene was examined, acetic acid being replaced partly by nitrobenzene. The decrease in oxidation rate of *p*-nitrotoluene by nitrobenzene addition corresponds to the negative deviation from linearity at high concentration of *p*-nitrotoluene (Fig. 3). Although chlorobenzene or *o*-dichlorobenzene was similarly treated in place of nitrobenzene, they exhibited positive effect for the *p*-nitrotoluene oxidation. When the same amount of nitrobenzene as substrate was added in the oxidation of *p*-chlorotoluene, correlation between the rate of oxidation and concentration of substrate were similar to those of *p*-nitroethylbenzene and *p*-nitrotoluene. The anomality in the oxidation of nitroalkylbenzenes compared with the case of hydrocarbons having no nitro substituent can be explained in terms of the effect of the aromatic nitro group.

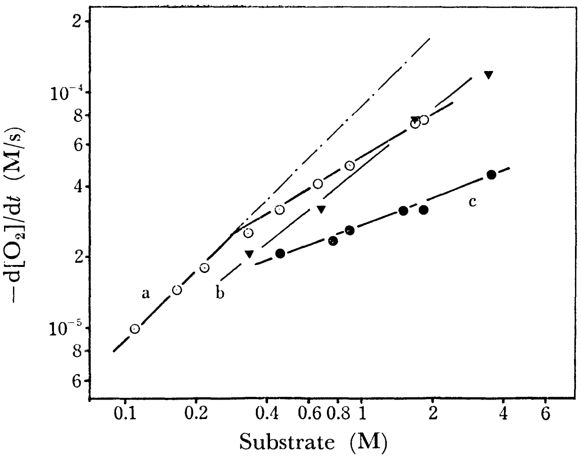


Fig. 3. The rate of oxidation of *p*-nitrotoluene *m*-nitrotoluene, and *p*-nitroethylbenzene catalyzed by Co-Mn-Br catalyst in acetic acid as a function of substrate concentration.
$Co(OAc)_2\cdot 4H_2O$: $Mn(OAc)_2\cdot 4H_2O$: NaBr = 99 : 1 : 170, total metal 1.2×10^{-2} M.
a: *p*-Nitrotoluene 85 °C, b: *m*-nitrotoluene 85 °C, c: *p*-niroethylbenzene 55 °C.

Two possibilities have been suggested for the negative effect of the nitro group in *p*-nitrotoluene oxidation;[7,8] interruption of the chains, and complex formation with catalyst, which has low activity in chain initiation.

Although the reaction conditions or catalyst composition differ from those of Chervinskii and Kovalev, our results support their view.

While there is no evidence for complex formation between catalyst and nitro compounds as well as its inactivity, the aromatic nitro compounds having high dielectric constants may coordinate to metal ion and deactivate the catalyst as in the action of water. The effect of substrate concentration in the oxidation of nitroalkylbenzenes should be due to the catalyst deactivating tendency by the complex formation and the chain terminating inclination by the reaction with active radical.

Reaction Products. Main products were *p*-nitrobenzaldehyde, *p*-nitrobenzoic acid and water in the oxidation of *p*-nitrotoluene in acetic acid. Small amounts (1—2% selectivity) of *p*-nitrobenzyl bromide and *p*-nitrobenzyl acetate were formed simultaneously. The total yield of these products per reacted nitrotoluene was 101%, and 69.5% of inorganic bromide ion initially added was found to be converted into organic bromide (*p*-nitrobenzyl bromide) at 48% conversion of *p*-nitrotoluene. The relation between oxidation products of *p*-nitrotoluene and the reaction time is shown in Fig. 4. Main products in the oxidation of *p*- or *o*-nitroethylbenzene in propionic acid were nitroacetophenones, 1-(nitrophenyl)ethanols, and water. As in the case of *p*-nitrotoluene, 1-(nitrophenyl)ethyl bromides and 1-(nitrophenyl)ethyl propionates were formed. The relation between the oxidation products and the reaction time is shown in Fig. 5. In all cases, the esters are considered to be formed through the following pathways.

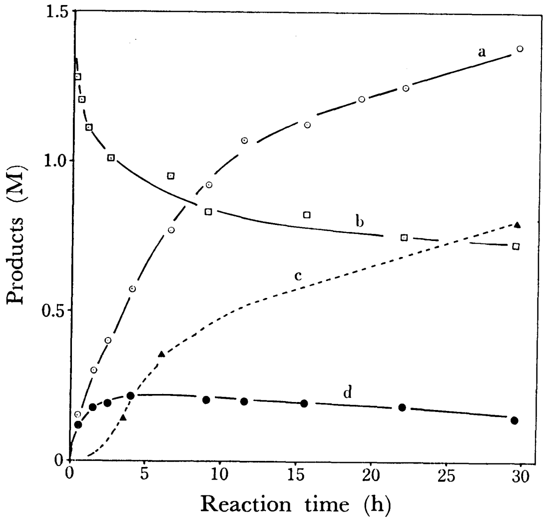


Fig. 4. Products distribution in the oxidation of *p*-nitrotoluene at 85 °C in acetic acid.
$Co(OAc)_2\cdot 4H_2O$: $Mn(OAc)_2\cdot 4H_2O$: NaBr = 99 : 1 : 170, total metal 1.2×10^{-2} M, *p*-nitrotoluene 1.69 M.
a: Absorbed O_2, b: *p*-nitrotoluene, c: *p*-nitrobenzoic acid, d: *p*-nitrobenzaldehyde.

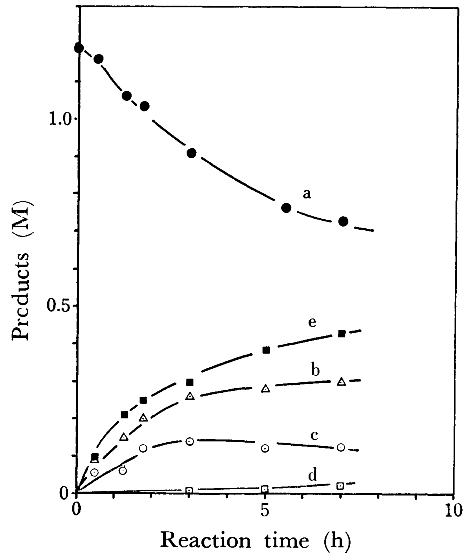
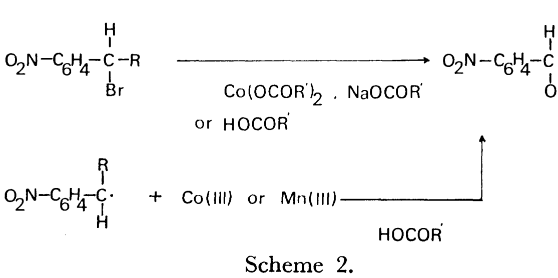


Fig. 5. Products distribution in the oxidation of *p*-nitroethylbenzene at 90 °C in propionic acid.
$Co(OAc)_2\cdot 4H_2O$: $Mn(OAc)_2\cdot 4H_2O$: NaBr = 99 : 1 : 170, total metal 1.2×10^{-2} M, *p*-nitroethylbene 1.19 M.
a: *p*-Nitroethylbenzene, b: *p*-nitroacetophenone, c: 1-(*p*-nitrophenyl)ethanol, d: 1-(*p*-nitrophenyl)ethyl propionate, e: absorbed O_2.



Scheme 2.

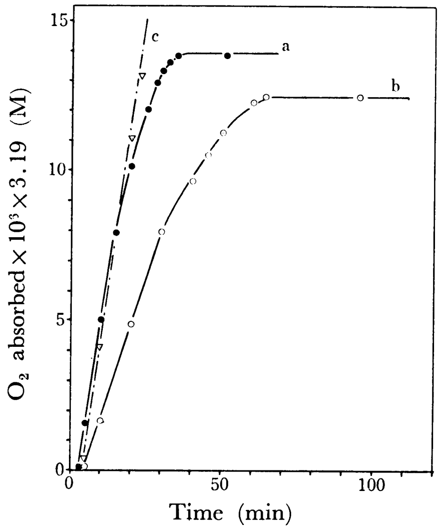
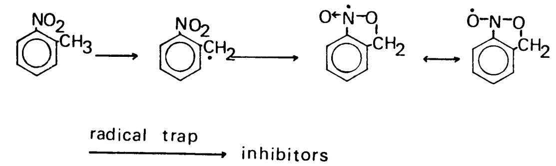


Fig. 6. Oxygen absorption curves of the *p*-nitrotoluene oxidation in the presence of *o*-nitrotoluene or *o*-nitroacetophenone at 85 °C in acetic acid.
$Co(OAc)_2 \cdot 4H_2O$: $Mn(OAc)_2 \cdot 4H_2O$: NaBr = 99 : 1 : 170, total metal 1.2×10^{-2} M.
a: *o*-Nitrotoluene addition, b: *o*-nitroacetophenone addition, c: *p*-nitrotoluene only, 1.69 M.

Oxidation of o-*Nitroalkylbenzenes*. When *o*-nitrotoluene was allowed to the oxidation catalyzed by Co–Mn–Br catalyst, the reaction did not proceed. As shown in Fig. 6, the oxidation of *p*-nitrotoluene in the presence of equal amounts of *o*-nitrotoluene or *o*-nitroacetophenone stops at low conversion (a few persent), as does the oxidation of 2,4-dimethylnitrobenzene. This suggests that *o*-nitrosubstituted toluene and acetophenone produce inhibitors during oxidation.

Intramolecular reaction should take place in the case of *o*-nitroalkylbenzenes. Intramolecular reaction proceeds advantageously as compared to intermolecular reaction. The reaction intermediates are supposed to form five or six membered rings.

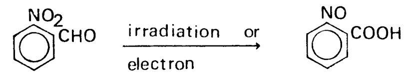


Scheme 3.

o-Nitrobenzaldehyde or *o*-nitroacetophenone formed as primary oxidation products are subjected to similar reactions. Inhibiting effect due to *o*-nitrotoluene or *o*-nitroacetophenone can be explained in terms of the intramolecular reaction between active radical and nitro group.

The oxidation of 2,4-dimethylnitrobenzene was carried out in acetic acid under the following conditions. Substrate concentration = 1.51 M, molar ratio of $Co(OAc)_2 \cdot 4H_2O$, $Mn(OAc)_2 \cdot 4H_2O$ and NaBr = 99 : 1 : 170, and 65 °C. When the catalyst concentration (total metal) decreased in the order 2.4×10^{-2} M, 1.2×10^{-2} M and 8×10^{-3} M, the oxidation stopped at 10 min, 70 min and did not stop over 150 min, respectively. The oxidation of 2,4-dimethylnitrobenzene stops at lower conversion as concentration of the catalyst increases. Reasons for this might be as follows. I) The metal catalyst itself stops the autoxidation chain by the reaction with peroxyl radical. II) The metal catalyst produces inhibitors in the course of the reaction.

The following reaction has been reported in studies of photochemical reaction[29)] and mass spectrometry of the *o*- or *peri*-nitro substituted aromatics.[30)]



Scheme 4.

The electron of the metal may enhance the rate of reaction, and a direct reaction between the catalyst and the nitro group can not be discarded.
However, when *o*-nitrobenzaldehyde or nitrobenzene was treated with equal amount of Co–Mn–Br catalyst at 80 °C in acetic acid in the absence of oxygen, no change took place. The effect of phenols which can be produced by the acid catalyzed decomposition of hydroperoxides should be negligible in acetic acid, where strong acid is absent. Thus, the inhibition effect at high concentration of catalyst on the oxidation of 2,4-dimethylnitrobenzene can be ascribed mainly to the chain termination due to metal ions. This can be correlated to the discussion on the effect of catalyst concentration.

The oxidation of *o*-nitroethylbenzene proceeded until 45% conversion. The rate of *o*-nitrocumene was extremely low as compared with that of *p*-isomer. Thus, of the *o*-nitro-substituted toluene, ethylbenzene and cumene, the oxidation of only *o*-nitroethylbenzene proceeded fairly rapidly. This can be attributed to:
I) The reactivity of *o*-nitroethylbenzene is expected to be higher than that of *o*-nitrotoluene or *o*-nitrocumene, since one of the secondary benzylic hydrogen atoms should be free from hydrogen bonding with the oxygen atom of nitro group. This would overcome the negative effect due to the nitro group.
II) The primary oxidation products, *o*-nitroacetophenone and 1-(*o*-nitrophenyl)ethanol, are relatively stable against autoxidation.

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