Autoxidation of Toluic Acids Catalyzed by Cobalt and Bromide Ions in Acetic Acid

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The effect of toluic acid concentration on the rate of autoxidation of toluic acids catalyzed by cobalt acetate and sodium bromide was elucidated. *p*-Toluic acid has shown a similar reactivity against oxidation to *m*-toluic acid, but a much different one from *o*-toluic acid. Although the rate of oxidation of *p*-toluic acid at 0.023 M cobalt increased with increasing *p*-toluic acid concentration and appeared to reach a limiting value, it was of first order with respect to the substrate concentration over wide range of concentration in the presence of 0.058 M cobalt. While, the rate of oxidation of *o*-toluic acid has shown higher values than the other toluic acids at substrate concentrations below 1.5 M and a maximum value at substrate concentration 0.75 M, suggesting that *o*-toluic acid can be oxidized easily but retards the catalysis by cobalt bromide. It was found that benzenecarboxylic acids remarkably retard the catalysis by cobalt and bromide ions, and the rate of oxidation of toluic acids is higher than that of toluene at such a low substrate concentrations as 0.34 M. The ease of oxidation of toluic acids can be attributed to the smaller rate constant of termination of carboxy benzyl peroxy radicals according to the polar and steric effects.

Although the rate of oxidation of alkylbenzenes[1–3] in acetic acid catalyzed by cobalt and bromide ions is of first order with respect to substrate concentration as in the cases of ordinary autoxidation reaction, that of *p*-toluic acid was reported to be independent of toluic acid concentration according to Ravens,[4] Bawn and Wright.[5] There has never been presented any successful explanations for this interesting result on *p*-toluic acid. Previously,[6] we have shown that the relative reactivity of substituted toluenes in this catalysis can be correlated by the polar effect of the substituent and is largely different from the relative rate of oxidation of single component. We intended to clarify the effect of benzenecarboxylic acids on the catalysis by cobalt and bromide ions and also to make clear the substituent effect on the rate of oxidation of substituted toluenes.

Experimental

Acetic acid, sodium bromide, cobaltous acetate $Co(OAc)_2 \cdot 4H_2O$, benzoic acid, phthalic acid, and three isomers of toluic acids were of reagent grade and used as received.

The oxygen absorption apparatus has been described elsewhere.[6]

Results and Discussion

The oxygen absorption curves in Fig. 1 shows that the rate of oxidation of toluic acids catalyzed by cobalt and bromide ions in acetic acid reaches a maximum and steady value within ten minutes of reaction.

In the cases of *m*- and *p*-toluic acids, the rate of oxidation slowly decreased after the absorption of considerable amount of oxygen and the solution became turbid indicating the formation of insoluble dibasic acids. The decrease in the rate of oxidation can be attributed to the decrease in the concentration of bromide ion, since it has been accepted[3,8,9] that bromide ion is slowly converted to an inactive form of organic bromide in the autoxidation of alkylbenzenes catalyzed by cobalt bromide.

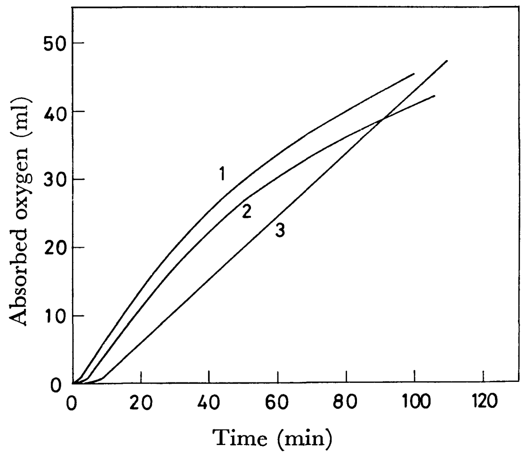

Fig. 1. Oxygen absorption curves of 2.4 M toluic acids in the autoxidation catalyzed by 0.023 M $Co(OAc)_2$ and 0.046 M NaBr in acetic acid at 85 °C.
1: *p*-Toluic, 2: *m*-Toluic, 3: *o*-Toluic acids.

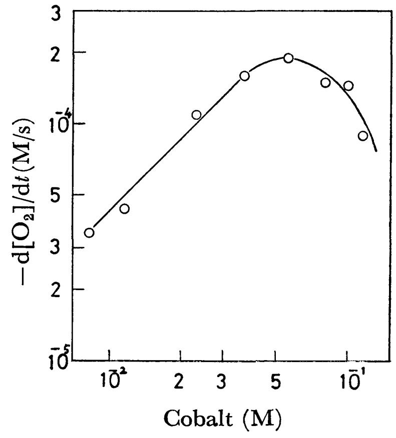

Fig. 2. The rate of oxidation of 0.65 M *p*-toluic acid catalyzed by cobaltous acetate and sodium bromide in acetic acid as a function of the concentration of cobalt acetate at the molar ratio of cobalt to bromide ion 2 and 85 °C.

However, in the case of *o*-toluic acid the oxygen absorption curve has shown a complete straight line for a long time. This might be due to the slower formation of organic bromides from the bromide ion than the other toluic acids, since Nakayama[7] observed a very small amounts of organic bromides in the oxidation of *o*-xylene to *o*-phthalic acid.

The steady rate of oxidation of *p*-toluic acid was nearly of first order with respect to cobalt concentration below 0.05 M in the presence of twice concentration of sodium bromide, as shown in Fig. 2. And the rate of oxidation was increased with increasing bromide ion until the ratio of cobalt to bromide ion became two. Hence, the oxidation was carried out at cobalt concentrations below 0.058 M and at the ratio of cobalt to bromide ions 2.

The steady rate of oxidation of three toluic acids as a function of substrate concentration is shown in Figs. 3, 4 and 5. When 0.023 M of cobalt acetate was used, the rates of oxidation of *p*- and *m*-toluic acids increased with increasing toluic acid concentration at concentrations below 1.0 M, and approached to a limiting value. The reactivity of *p*-toluic acid seems entirely the same as that of *m*-toluic acid. On the other hand, *o*-toluic acid has shown a maximum rate at 0.75 M and started to decrease as the substrate concentration was further increased.

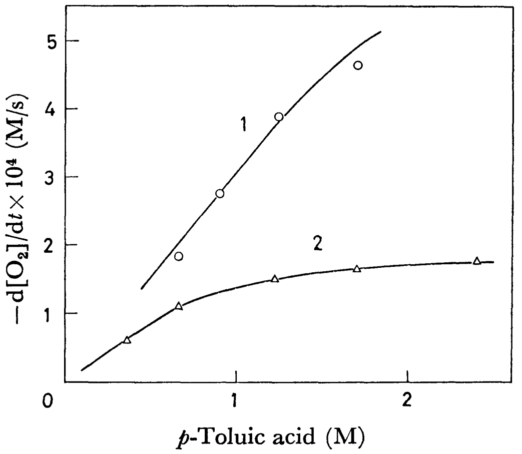

Fig. 3. The rate of oxidation of *p*-toluic acid catalyzed by cobaltous acetate and sodium bromide in acetic acid as a function of the concentration of *p*-toluic acid at 85 °C.

1: $Co(OAc)_2$ 0.058 M and NaBr 0.116 M
2: $Co(OAc)_2$ 0.023 M and NaBr 0.046 M

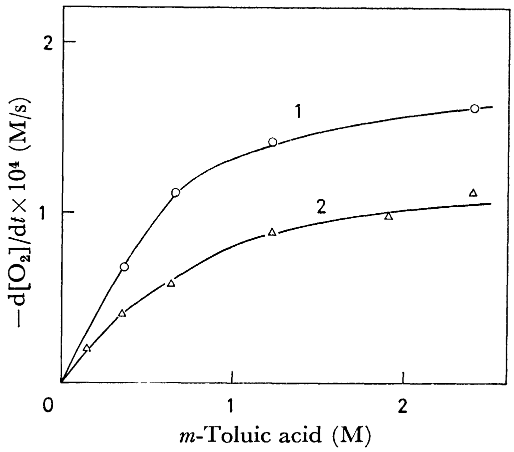

Fig. 4. The rate of oxidation of *m*-toluic acid catalyzed by cobaltous acetate and sodium bromide in acetic acid as a function of the concentration of *m*-toluic acid at 85 °C.

1: $Co(OAc)_2$ 0.023 M and NaBr 0.046 M
2: $Co(OAc)_2$ 0.023 M and NaBr 0.023 M

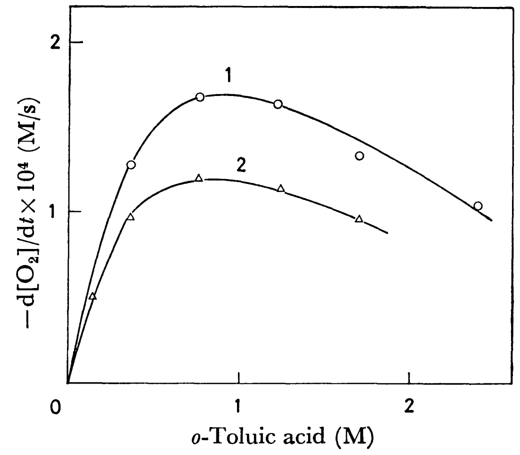

Fig. 5. The rate of oxidation of *o*-toluic acid catalyzed by cobaltous acetate and sodium bromide in acetic acid as a function of the concentration of *o*-toluic acid at 85 °C.

1: $Co(OAc)_2$ 0.023 M and NaBr 0.046 M
2: $Co(OAc)_2$ 0.023 M and NaBr 0.023 M

o-Toluic acid was oxidized faster than *p*- and *m*-toluic acids by a factor of two, but it seems to deactivate the catalyst remarkably.

When the concentration of cobalt acetate was increased from 0.023 M to 0.058 M, the rate of oxidation of *p*-toluic acid showed an almost linear relation against the substrate concentration over a wide range of concentration, suggesting that *p*-toluic acid suppressed the catalytic effect due to cobalt and bromide ions. The retardation effect due to *o*-phthalic and benzoic acids on the oxidation of *o*-toluic acid was further studied as shown in Table 1. The addition of 0.54 M *o*-phthalic acid has shown a considerable retardation effect, but further addition of phthalic acid higher than 1.0 M presented no additional retardation effect according to the low solubility in acetic acid.

It was confirmed that isophthalic and terephthalic acids have no effect on the rate of oxidation of toluic acids because of very low solubility.

In contrast, benzoic acid, which was quite stable against oxidation, has shown a quite clear retardation effect on the cobalt bromide catalysis. The rate of oxidation of *o*-toluic acid decreased by factors of two and three in the presence of 1.28 and 2.44 M of benzoic acid, respectively.

Since the rate of oxidation is nearly first order with respect to cobalt, 1.28 M of benzoic acid can be considered to deactivate 0.01 M cobalt ion.

As reported previously,[6] cobaltous acetate bromide was oxidized by 2-cyano-2-propyl peroxy radical quantitatively in acetic acid solution, yielding cobaltic

TABLE 1. RETARDATION EFFECT OF BENZENECARBOXYLIC ACIDS ON THE RATE OF OXIDATION OF *o*-TOLUIC ACID IN ACETIC ACID SOLUTION AT 85 °C

o-Toluic acid (M)	0.75	0.75	0.75	0.75	0.67	0.67	0.75
Benzoic acid (M)	0	1.28	1.86	2.44	—	—	—
o-Phthalic acid (M)	—	—	—	—	0	0.54	0.91
$Co(OAc)_2$ (M)	0.023	0.023	0.023	0.023	0.023	0.023	0.023
NaBr (M)	0.046	0.046	0.046	0.046	0.023	0.023	0.046
$-d[O_2]/dt$ (M/s) × 10^4	1.70	0.84	0.83	0.58	1.20	0.89	1.39

ion. It was confirmed that the rate of formation of cobaltic ion by peroxy radical decreased by a factor of three in the presence of 2.4 M benzoic acid.

Coordinated benzoic acid to cobaltous ion may retard the reaction of cobalt with peroxy radical and the formation of cobaltic ion because of steric hindrace, and so retard the successive oxidation of toluic acid.

In order to exclude the retardation effect due to toluic acids, the relative rate of oxidation of toluic acids at concentration of 0.34 M is compared with the other rates of substituted toluenes as shown in Table 2. It is surprizing that toluic acids are apparently more reactive than toluene or methoxy toluene.

TABLE 2. RELATIVE RATE OF OXIDATION OF SUBSTITUTED TOLUENES CATALYZED BY 0.023 M $Co(OAc)_2$ AND 0.046 M NaBr IN ACETIC ACID AT 85 °C

Substituted toluene (0.34M)	Relative rate of oxidation
Toluene	1.00
p-Xylene[a]	1.96
p-Methoxytoluene[a]	0.96
p-Chlorotoluene[a]	1.05
o-Chlorotoluene[a]	1.03
p-Toluic acid	1.10
m-Toluic acid	1.15
o-Toluic acid	2.30

a) Ref. 6.

Apparently, the rate of oxidation of toluene was much higher than those of toluic acids at higher substrate concentration, for example, it was about 2.4 times as fast as those of *m*- and *p*-toluic acids at concentration of 2.4 M and 85 °C.

Previously,[6] we have shown that the relative rates of autoxidation of substituted toluenes were quite different from the relative reactivities obtained by the competitive oxidation and we ascribed these results to the difference in the rate of termination reaction between substituted benzyl peroxy radical. An electron withdrawing substituent such as carboxyl group will decrease the rate of hydrogen abstraction step as in the case of ordinary free radical reaction, but it seems also to reduce considerably the rate of bimolecular reaction of benzyl peroxy radicals. Although we can not present any measured values about the termination rate constant of substituted toluenes, the polar effect seems to be a good explanation for the results given in Table 2. In addition, the bimolecular reaction of 2-carboxy benzyl peroxy radical can be expected to be slower than that of 4-carboxy benzyl peroxy radical because of steric hindrance. However, the steric effect of chlorine atom on the rate of termination seems not so large as the carboxyl group.

In order to elucidate the steric effect of carboxyl group, the mixing effect of toluic acids was studied and shown in Table 3. The rate of oxidation of an equimolar mixture of *m*- and *p*-toluic acids was nearly equal to those of twice amount of single components, because the rates of oxidation of 0.68 M and 1.22 M *p*-toluic acid were 1.10×10^{-4} and 1.50×10^{-4} M/s, respectively, and those of 0.68 M and 1.22 M *m*-toluic acid were 1.12×10^{-4} and 1.43×10^{-4} M/s.

It can be concluded that *m*- and *p*-toluic acids have similar reactivities in the autoxidation reaction. On the other hand, the rate of oxidation of 0.34 M *o*-toluic acid decreased from 1.30 to 1.21 or 1.18×10^{-4} M/s by the addition of 0.34 M *m*-toluic or *p*-toluic acids. These results can only be explained on the basis of cross termination between two different peroxy radicals as in the case of cumene and tetralin.[10] The retardation effect due to *m*- and *p*-toluic acids should be much smaller than by *o*-toluic acid according to Figs. 3—5.

The higher rate of oxidation of *o*-toluic acid than *p*-toluic acid can be attributed to the smaller termination rate constant (k_t) of the derived peroxy radical. However, in the presence of *p*-toluic acid, the cross termination between different peroxy radicals will be predominant and the rate constant of cross termination will be larger than k_t of *o*-toluic acid and similar to k_t of *p*-toluic acid, since no more significant steric effect can be expected in the bimolecular reaction between different peroxy radicals. Thus, a mixture of *o*- and *p*-toluic acids will present a similar rate of oxidation as a mixture of *m*- and *p*-toluic acids.

Incidentally, we observed similar antagonistic effect in the oxidation of a mixture composed of *p*-toluic acid and toluene, that is, the rate of oxidation of 0.86 M toluene catalyzed by 0.023 M $Co(OAc)_2$ and 0.046 M NaBr just increased from 1.35 to 1.43×10^{-4} M/s by adding 0.34 M *p*-toluic acid.

TABLE 3. MIXING EFFECT OF TOLUIC ACIDS ON THE RATE OF OXIDATION AT $Co(OAc)_2$ 0.023M, NaBr 0.046 M AND 85 °C IN ACETIC ACID

p-Toluic acid (M)	0.34	0.68	1.22	—	—	—	—	0.34	0.34	0.61	—	—
m-Toluic acid (M)	—	—	—	0.34	0.68	1.22	—	0.34	—	0.61	0.34	0.61
o-Toluic acid (M)	—	—	—	—	—	—	0.34	—	0.34	—	0.34	0.61
$-d[O_2]/dt$(M/s) × 10^4	0.62	1.10	1.50	0.66	1.12	1.43	1.30	1.13	1.21	1.43	1.18	1.48

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