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Photooxidation of Alkylbenzenes in the Presence of Bromides

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Synopsis. In the presence of organic bromides, toluene was oxidized photochemically by molecular oxygen, producing benzaldehyde as the major product. A modified procedure using hydrobromic acid and bubbling air also gave benzaldehyde with high efficiency and can be applied for the synthetic purpose. Similarly ethylbenzene gave acetophenone.

In relation to the recent study on the photolysis of polybromobenzenes in several organic solvents,[1–3] the photochemical behavior of aromatic bromides in alkylbenzenes was examined. For this purpose, some aromatic bromides were photolyzed in toluene and ethylbenzene in the presence or absence of molecular oxygen, the results being given in Table 1. Time-conversion curves of the two typical runs are shown in Fig. 1. In order to supply air or oxygen, the gas was bubbled into the irradiated solution at a rate of 40 ml min^{-1} with effective mixing.[4]

The photooxidation proceeded predominantly in the runs (runs 1 to 9) carried out under aerobic conditions. When the aerobic photolysis (run 1) was compared to an anaerobic reaction carried out with the same system under similar conditions (run 10), formation of a more than stoichiometric amount of benzaldehyde was shown to be very characteristic of the reaction under aerobic conditions (run 1), suggesting the involvement of a very efficient path of oxidation on the benzylic hydrogen of toluene. In contrast to the quite different behavior of toluene under the two conditions, nearly the same amounts of benzene were produced from bromobenzene in these conditions (runs 1 and 10). This suggests that the initial photolytic cleavage of C–Br bonds should proceed with nearly equal rates indifferent to the presence of oxygen. Thus produced bromine atom can be expected to abstract the benzylic hydrogen from toluene, generating benzyl radical from which all secondary products are derived. In the presence of molecular oxygen, benzyl radical can be assumed to react very rapidly with oxygen initiating the oxidation via a free radical chain mechanism commonly known as autoxidation,[5,6] which can produce a more than stoichiometric amount of benzaldehyde and other benzylic compounds. Further oxidation producing benzoic acid proceeds far less significantly under these conditions (Fig. 1(a)). A trace of 1,2-diphenylethane was detected in addition to the products in Fig. 1(a) and Table 1.

Photooxidation products of ethylbenzene in the presence of bromobenzene are given in the runs 2 and 3 in Table 1. Overall features of the reactions are similar to the corresponding reactions of toluene, giving acetophenone as the major products. A measurable amount of 1-phenylethanol was also obtained as a minor product (as shown in the time-conversion curve

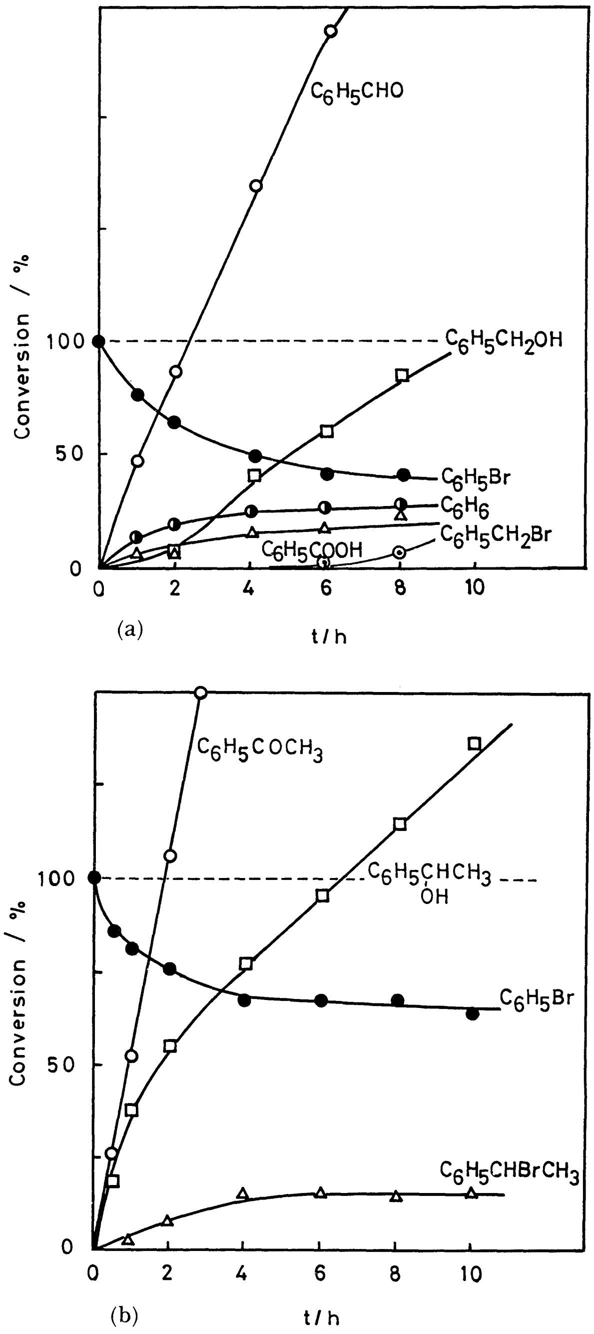

Fig. 1. Time-conversion curves for the photooxidation of (a) toluene and (b) ethylbenzene by air in the presence of bromobenzene (—●—).

Table 1. Products of the Photochemical Reactions of Various Bromides in the Presence of Alkylbenzenes as Solvents[a]

Run	Reactant		Reaction conditions			Conversion[b]	Product (Yield/%)[b]
No.	Halogen compd	Alkylbenzene	Atmosphere	Lamp	Period	%	
1	C_6H_5Br (0.06 mol^{-1})	$C_6H_5CH_3$	Air	L	4 h[d]	47.5	C_6H_6 (26.5), $C_6H_5CH_2Br$ (16.7), C_6H_5CHO (233), $C_6H_5CH_2OH$ (43.3)
2	C_6H_5Br (0.20 mol l^{-1})	$C_6H_5C_2H_5$	Air	L	4 h	21.2	$C_6H_5COCH_3$ (43.6), $C_6H_5CH(OH)CH_3$ (42.0), $C_6H_5CHBrCH_3$ (12.4)
3	C_6H_5Br (0.20 mol^{-1})	$C_6H_5C_2H_5$	O_2	L	4 h[e]	29.0	$C_6H_5COCH_3$ (165), $C_6H_5CH(OH)CH_3$ (85.4), $C_6H_5CHBrCH_3$ (15.5)
4	$C_6H_5CH_2Br$ (0.10 mol^{-1})	$C_6H_5CH_3$	Air	L	8 h	33.0	C_6H_5CHO (192), C_6H_5COOH (9.0), $C_6H_5CH_2OH$ (30.1)
5	HBr 47% aq. (2 ml)	$C_6H_5CH_3$	Air	L	8 h		C_6H_5CHO (66.8), $C_6H_5CH_2Br$ (25.5), $C_6H_5CH_2OH$ (7.7)
6	HBr 47% aq. (2 ml)	$C_6H_5CH_3$	Air	H	8 h		C_6H_5CHO (79.3), $C_6H_5CH_2Br$ (8.5), $C_6H_5CH_2OH$ (12.2)
7	HBr 47% aq. (2 ml)	$C_6H_5C_2H_5$	Air	L	10 h		$C_6H_5COCH_3$ (42.7), $C_6H_5CH(OH)CH_3$ (40.8), $C_6H_5CHBrCH_3$ (16.5)
8	HBr 47% aq. (2 ml)	$C_6H_5C_2H_5$	O_2	L	10 h		$C_6H_5COCH_3$ (40.2), $C_6H_5CH(OH)CH_3$ (39.0), $C_6H_5CHBrCH_3$ (20.7)
9	HBr 47% aq. (2 ml)	$C_6H_5C_2H_5$	O_2	H	8 h		$C_6H_5COCH_3$ (48.7), $C_6H_5CH(OH)CH_3$ (33.9), $C_6H_5CHBrCH_3$ (12.1)
10[c]	C_6H_5Br (0.06 mol^{-1})	$C_6H_5CH_3$	N_2	L	4 h	52.0	C_6H_6 (26.7), $C_6H_5CH_2Br$ (5.3), $CH_3C_6H_4C_6H_5$ (14.0, isomeric mixture)

a) 70 ml. b) Conversions and yields (%) in reference to the bromides are given. c) Very small amount of benzaldehyde was detected as a product which was probably formed by O_2 present as an impurity of N_2 gas. d) Amount of benzaldehyde attained 280% after 10 h's irradiation. e) Amount of acetophenone attained 230% after 10 h's irradiation.

for run 2 in Fig. 1(b)). Small amounts of meso and racemic 2,3-diphenylbutanes were detected in the gas chromatogram of the products. Similar reaction could be initiated by the photolysis of benzyl bromide (run 4) with a rate considerably slower than the run 1.

Aiming at the synthesis of benzaldehyde, a new procedure for the oxidation of toluene by hydrogen peroxide has recently been developed.[7] Thus, the procedure of our photolytic oxidation was modified taking into account the synthetic application. If bromine atom would play a crucial role in initiating and propagating the reaction, the oxidation leading to the corresponding carbonyl compounds could be expected to proceed similarly by use of hydrogen bromide as the source of bromine atom. In this expectation, the photooxidation of alkylbenzenes in the presence of hydrogen bromide was examined (runs 5—9). When these runs were carried out in the presence of 47% hydrobromic acid, two immiscible liquid layers coexist. But we could perform the reaction without difficulty by mixing the two heterogeneous layers with bubbling air. Composition of the products is very similar to those of the corresponding reactions initiated by the photolysis of bromobenzene or benzyl bromide. In the runs using hydrogen bromide, immiscible aqueous hydrogen bromide layer can be removed very easily after the completion of the oxidation. The aqueous bromide layer can be recycled and the similar photooxidation can be repeated many times without considerable loss of bromine compound. This might be advantageous for the possible synthetic application of the reaction. Formation of the carbonyl compound seemed to be favored by use of high-pressure lamp judging from the higher yields of benzaldehyde and acetophenone in the runs 6 and 9, respectively.

In order to examine the photolytically induced reactions in the presence of other halides, irradiations of hydrochloric acid, hydroiodic acid, chlorobenzene, and *p*-diiodobenzene were carried out in the presence of toluene under the similar aerobic conditions. Photooxidation leading to benzaldehyde took place in neither cases and toluene was recovered almost intact. This fact showed that the photooxidation of alkylbenzene proceeds only in the presence of organic or inorganic bromides, suggesting the participation of bromine atom (free radical) as the initiator and the chain carrier of the photooxidation.[5] Under anaerobic conditions, bibenzyl (PhCHRCHRPh) and benzyl bromide (PhCHRBr) tend to be produced more favorably.[8] The ratio of benzyl alcohol to benzoyl compound ([PhCHROH]/[PhCOR]) was also increased by the insufficient supply of oxygen.

In conclusion, this procedure for the photooxidation of alkylbenzenes can produce benzaldehyde or alkyl phenyl ketones in enough yields to be used for the practical synthetic purpose, if the contact of molecular oxygen to the reactive free radical species is effected efficiently.

Experimental

Photoreactions were carried out using a 30 W low-pressure mercury arc lamp (Rikokagaku UVL-30L). In some runs, a 100 W high-pressure mercury arc (Rikokagaku UVL-100H) was used.

Routine gas chromatographic analyses of the products were carried out by a Shimadzu GC-6A or a GC-4B-PTF apparatus equipped with a Silicone SE 30 or a PEG 20M stainless steel column (3 mm×2 m). Gas chromatography/mass spectrometry measurements were carried out by a Shimadzu LKB-9000B mass spectrometer.

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4) Rate of the photolytic cleavage of C–Br bond in bromobenzene was not affected considerably by aeration. Preliminarily examined rates of its conversion after 4 h are 47.0% in N_2 atmosphere and 45.2%, 43.0% and 48.1%, respectively, when the bubbling rates of air are 30 ml min^{-1}, 40 ml min^{-1} and 50 ml min^{-1}.

5) The reaction mechanism seemed essentially the same with that of the thermal autoxidation. [M. C. Ford and D. Mackay, *J. Chem. Soc.*, **1958**, 1290; D. A. S. Ravens, *Trans. Faraday Soc.*, **55**, 1768 (1959). J. Bett, *Quart. Revs.*, **25**, 265 (1971).]

6) Participation of bromine atom as the chain carrier has been discussed in a) P. Hurst and G. Skirrow, *Proc. R. Soc. London, Ser. A*, **268**, 405 (1962) and b) J. E. McIntyre and D. A. S. Ravens, *J. Chem. Soc.*, **1961**, 4082.

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8) In a run (No. 10) on bromobenzene under the nitrogen atmosphere, the products and their composition were similar to those of the photolysis (under anaerobic conditions) in benzene except for the formation of benzyl bromide which is expected to be formed as the secondary product. The products obtained after 24 h's irradiation were comprised of 55.7% of benzene (dehalogenation product), 5.9% of 2-methyl-, 6.3% of 3-methyl-, and 4.8% of 4-methylbiphenyl (arylation products) in addition to benzyl bromide. (Percentages were given in reference to the starting bromobenzene.) The relative reactivities of the sites from the observed isomeric distribution showed that the phenylation occurred rather randomly and more favorably at the para-position in comparison with the reported partial rate factors of free radical phenylation.[9]

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