The rate was also measured by estimation of α-iodopropionic acid. The pipetted out mixture was poured into water, and unreacted iodine was removed by washing with aqueous $Na_2S_2O_3$. The residual mixture was esterified by an ethereal solution of diazomethane. The resulting methyl α-iodopropionate was identified and estimated by means of GLC by using a Yanagimoto GCG-550 gas chromatograph equipped with a copper column packed with PEG 20 M (10%) on Chromosorb (WAW (60–80 mesh) and employing methyl caprate as an internal standard.

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Registry No. Propionic acid, 79-09-4; iodine, 7553-56-2; chlorosulfonic acid, 7790-94-5; methyl α-iodopropionate, 56905-18-1.

Photoinduced Decomposition of Peracetic Acid in Ethylbenzene

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The photolysis of peracetic acid in ethylbenzene has been conducted by using three sorts of light sources at room temperature. Photolyses at both 2537-Å light and over 2900-Å light give substantially the same products, namely, carbon dioxide, oxygen, water, methane, ethane, methanol, propylbenzene, ethyltoluenes, phenethyl alcohols, ethylphenols, and 2,3-diphenylbutane. The distribution of products depends on light wavelength; products from methyl radical (propylbenzenes) were formed preferentially in 2537-Å photolysis, while those from hydroxyl radical (phenethyl alcohols) were preferred in >2900-Å photolysis. This difference is discussed in relation to the mechanism of peracetic acid decomposition.

The photolysis of peracetic acid in aromatic hydrocarbons was initiated by two pathways: one path is the singlet–singlet energy transfer from excited aromatic solvent (ArH) to peracetic acid followed by its decomposition to methyl and hydroxyl radicals and carbon dioxide (2537-Å photolysis) and the other path is the direct decomposition of peracid (>2900-Å photolysis). In 2537-Å photolysis, methylated aromatic compounds were preferred to hydroxylated products, while in >2900-Å photolysis, the formation of hydroxylated compounds was favored. These facts suggest a difference of radical concentration with wavelength.[1,2]

In this experiment, we controlled the decomposition rate of peracid to compare the reactivity of radicals at the same or different radical concentration. The data which follow summarize our data on the photolysis of peracetic acid in ethylbenzene using 2537-Å (30 W) and >2900-Å (300 W and 1 kW) light sources. Products and effects of conditions on the product distribution suggest the mechanism of photolysis.

Results and Discussion

The products resulting from the photolysis of peracetic acid (1) in ethylbenzene are listed in Tables I and II; Table I shows the results with a 30-W low-pressure Hg lamp (2537-Å light) and Table II shows the results with 300-W (>2900-Å light) and 1-kW high-pressure Hg lamps (>2900-Å light). These products were identified by GLC and GC/MS comparison with authentic samples.

The yields of propylbenzenes indicate the summation of those of two isomers, propyl- and isopropylbenzene, the latter predominates markedly. Ethyltoluenes, which were formed by an attack of methyl radical on the ring, include three isomers in the order ortho > meta > para in both 2537-Å and >2900-Å photolyses.

Hydroxylation of the side chain gives α- and β-phenethyl alcohols, where the yields are α >> β. Hydroxylation of the ring gives three isomers of ethylphenols with the order of yields ortho > para > meta. 2,3-Diphenylbutanes, coupling products of α-phenethyl radicals, were composed of *dl* and meso isomers with comparable yields.

The light wavelength affects largely the distribution of products; methylated compounds (propylbenzenes and ethyltoluenes) are more favored with 2537-Å light (Table I) than with >2900-Å light (Table II), while the yields of phenethyl alcohols were much higher with >2900-Å than with 2537-Å light. On the other hand, the light intensity gave only a small effect on the distribution of products as apparent from Table IIa (300 W) and Table IIb (1 kW).

The product distribution was little affected by irradiation time except for the yields of oxygen, water, and methanol in both 2537-Å and >2900-Å photolyses. These results show that a further reaction, such as oxidation of α-phenethyl alcohol to acetophenone, does not occur under these conditions.

To study the dependency of radical concentration on the yields, we changed the initial concentration of peracetic acid (1) from 0.4 mmol/25 mL to 13.7 mmol/25 mL. Tables III and IV show the results in 2537-Å (30 W), > 2900-Å (300 W), and >2900-Å (1 kW) photolyses.

In 2537-Å photolysis, the yields of ethane, methanol, and propylbenzenes decrease while the yields of phenethyl alcohols and 2,3-diphenylbutanes increase with decreasing peracid concentration; however, the yields of ethyltoluenes and ethylphenols are almost unchanged. The yields of methylated compounds (propylbenzenes and ethyltoluenes) are higher than those of hydroxylated compounds (phenethyl alcohols and ethylphenols).

In >2900-Å (300 W) photolysis, the yields of propylbenzenes (3–4%) are much lower than those (22–28%) in 2537-Å photolysis. Also radical addition to the ring (ethyltoluenes and ethylphenols) with >2900-Å light is less favored than that with 2537-Å light, whereas the yields of

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[1] Y. Ogata and K. Tomizawa, *J. Org. Chem.*, **43**, 261 (1978).

[2] Y. Ogata and K. Tomizawa, *J. Org. Chem.*, **43**, 1920 (1978).

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Table I. Time Dependence of Product Yields in 2537-Å Light Decomposition[a]

	irradn time, h				
	0.5	1.0	2.0	4.0	6.0
amt of 1 decomposed[b]	5.69	8.98	16.8	28.2	36.4
products[c]					
carbon dioxide	5.66 (99.5)	9.00 (100.2)	16.7 (99.4)	28.0 (99.3)	36.0 (98.9)
oxygen	0.08 (2.8)	0.19 (4.2)	0.42 (5.0)	0.73 (5.2)	1.24 (6.8)
water	1.67 (29.3)	2.48 (27.6)	5.91 (35.2)	10.5 (37.2)	14.5 (39.8)
methane	2.20 (38.7)	3.41 (38.0)	6.42 (38.2)	10.4 (36.9)	13.7 (37.6)
ethane	0.23 (8.1)	0.43 (9.6)	0.67 (8.0)	0.85 (6.0)	1.09 (6.0)
methanol	0.83 (14.6)	1.28 (14.3)	2.13 (12.7)	3.10 (11.0)	3.53 (9.7)
propylbenzenes[d]	1.72 (30.2)	2.74 (30.5)	4.91 (29.2)	8.01 (28.4)	10.2 (28.0)
ethyltoluenes[e]	0.35 (6.2)	0.54 (6.0)	0.54 (3.2)	1.61 (5.7)	1.97 (5.4)
phenethyl alcohols[f]	0.49 (8.6)	0.77 (8.6)	1.76 (10.5)	3.13 (11.1)	4.36 (12.0)
ethylphenols[e]	0.13 (2.3)	0.41 (4.6)	0.94 (5.6)	1.75 (6.2)	2.29 (6.3)
2,3-diphenylbutane	0.29 (10.2)	0.53 (11.8)	1.08 (12.9)	2.13 (15.1)	2.80 (15.4)

[a] Initial concentration of peracetic acid (1) was 5.58 mmol/25 mL (0.223 M). [b] Amount in 10^{-1} mmol. [c] Amount in 10^{-1} mmol and percent (moles of product/moles of decomposed peroxide) × 100, except for O_2, ethane, and 2,3-diphenylbutane where this number is doubled. [a] Total amounts of propyl- and isopropylbenzenes. [e] Total amounts of ortho, meta, and para isomers. [f] Total amounts of α and β isomers.

Table II

(a) Time Dependence of Products Yields in >2900-Å (300 W) Light Decomposition[a]

	irradn time, h				
	1.0	2.0	4.0	7.0	10.0
amt of 1 decomposed[b]	5.13	8.75	15.9	25.0	31.8
products[c]					
carbon dioxide	5.01 (97.7)	8.14 (93.0)	14.8 (93.1)	23.7 (94.8)	29.6 (93.1)
oxygen	0.10 (3.9)	0.19 (4.3)	0.47 (5.9)	1.09 (8.7)	1.69 (10.6)
water	0.91 (17.7)	1.33 (15.2)	2.70 (17.0)	4.04 (16.2)	4.80 (15.1)
methane	3.65 (71.2)	6.21 (71.0)	11.5 (72.3)	18.3 (73.2)	22.6 (71.1)
ethane	0.09 (3.5)	0.15 (3.4)	0.26 (3.3)	0.44 (3.5)	0.53 (3.3)
methanol	0.32 (6.2)	0.55 (6.3)	0.86 (5.4)	1.19 (4.8)	1.34 (4.2)
propylbenzenes[d]	0.31 (6.0)	0.53 (6.1)	1.07 (6.7)	1.50 (6.0)	2.13 (6.7)
ethyltoluenes[e]	0.07 (1.4)	0.09 (1.0)	0.19 (1.2)	0.33 (1.3)	0.35 (1.1)
phenethyl alcohols[f]	2.23 (43.5)	4.00 (45.7)	7.19 (45.2)	12.2 (48.8)	15.6 (49.1)
ethylphenols[e]	0.04 (0.8)	0.05 (0.6)	0.10 (0.6)	0.13 (0.5)	0.19 (0.6)
2,3-diphenylbutane	0.27 (10.5)	0.54 (12.3)	0.98 (12.3)	1.71 (13.7)	2.13 (13.4)

(b) Time Dependence of Product Yields in >2900-Å (1 kW) Light Decomposition[a]

	irradn time, h				
	0.5	1.0	2.0	3.0	4.0
amt of 1 decomposed[b]	8.47	15.0	25.9	34.4	39.9
products[c]					
carbon dioxide	8.40 (99.2)	14.2 (94.7)	24.7 (95.4)	33.0 (95.9)	39.1 (98.0)
oxygen	0.14 (3.3)	0.32 (4.3)	0.76 (5.9)	1.31 (7.6)	1.68 (8.4)
water	1.73 (20.4)	3.39 (22.6)	5.10 (19.7)	6.91 (20.1)	7.26 (18.2)
methane	5.54 (65.4)	9.86 (65.7)	17.4 (67.2)	22.9 (66.6)	26.7 (66.9)
ethane	0.19 (4.5)	0.31 (4.1)	0.54 (4.2)	0.69 (4.0)	0.80 (4.0)
methanol	1.40 (16.5)	2.15 (14.3)	3.50 (13.5)	3.96 (11.5)	4.05 (10.2)
propylbenzenes[d]	0.37 (4.4)	0.60 (4.0)	1.19 (4.6)	1.41 (4.1)	1.48 (3.7)
ethyltoluenes[e]	0.10 (1.2)	0.21 (1.4)	0.31 (1.2)	0.34 (1.0)	0.40 (1.0)
phenethyl alcohols[f]	3.50 (41.3)	6.42 (42.8)	11.2 (43.2)	14.9 (43.3)	18.8 (47.1)
ethylphenols[e]	0.10 (1.2)	0.21 (1.4)	0.36 (1.4)	0.45 (1.3)	0.46 (1.2)
2,3-diphenylbutane	0.87 (20.5)	1.73 (23.1)	3.15 (24.3)	4.11 (23.9)	5.07 (25.4)

[a] Initial concentration of peracetic acid (1) was 5.58 mmol/25 mL (0.223 M). [b] Amount in 10^{-1} mmol. [c] Amount in 10^{-1} mmol and percent (moles of product/moles of decomposed peroxide) × 100, except for O_2, ethane, and 2,3-diphenylbutane where this number is doubled. [d] Total amounts of propyl- and isopropylbenzenes. [e] Total amounts of ortho, meta, and para isomers. [f] Total amounts of α and β isomers.

phenethyl alcohols (40–50%) with >2900-Å light are much higher than those (16–20%) in 2537-Å photolysis.

With >2900-Å (1 kW) photolysis, the yield of methanol is comparable to that in 2537-Å photolysis but is higher than that with >2900 Å (300 W) photolysis, while the yields (40–50%) of phenethyl alcohols are comparable to those with >2900-Å (300 W) photolysis but are much higher than those in 2537-Å photolysis. The yields of propylbenzenes, ethyltoluenes, and ethylphenols with 1 kW are slightly higher than those with 300 W.

Effect of Light Intensity. The half-time for decomposition of peracetic acid with >2900-Å light is fourfold shorter with a 1-kW lamp than with a 300-W lamp, which indicates a higher concentration of radicals with a 1-kW lamp, because the yields of coupling products (especially ethane, methanol, and 2,3-diphenylbutane) are higher with a 1-kW lamp.

The yields of phenethyl alcohols with a 1-kW lamp are slightly higher at higher peracid concentration than with a 300-W lamp, but at lower peracid concentration, their yields are similar, which suggests the preferential formation of phenethyl alcohols via the induced decomposition with α-phenethyl radical (see below).

Effect of Wavelength of Light. The 2537-Å light

Table III. Effect of Peracetic Acid (1) Concentration on Product Yields in 2537-Å Irradiation

	run					
	1	2	3	4	5	6
init concn of 1,[a] × 10^{-1} M	5.49	3.13	2.23	1.57	0.078	0.042
irradn time, h	8.0	6.0	6.0	5.0	5.0	4.0
amt of 1 decomposed[b]	76.6 (55.8)	40.6 (51.9)	36.4 (65.2)	30.3 (77.3)	15.6 (79.6)	7.12 (68.5)
products[b]						
oxygen	3.22 (8.4)	1.52 (7.5)	1.24 (6.8)	1.29 (8.5)	0.81 (10.4)	0.46 (12.9)
water	23.9 (31.2)	14.5 (35.7)	14.5 (39.8)	12.2 (40.3)	6.01 (38.5)	2.87 (40.3)
methane	27.0 (35.2)	15.7 (37.4)	13.7 (37.6)	11.5 (38.0)	6.16 (39.5)	2.87 (40.3)
ethane	4.14 (10.8)	2.05 (10.0)	1.09 (6.0)	1.12 (7.4)	0.55 (7.1)	0.24 (6.7)
methanol	12.8 (16.7)	5.89 (14.5)	3.53 (9.7)	2.79 (9.2)	1.17 (7.5)	0.50 (7.0)
propylbenzenes[c]	20.3 (26.5)	11.5 (28.3)	10.2 (28.0)	8.00 (26.4)	3.92 (25.1)	1.57 (22.1)
ethyltoluenes[d]	3.68 (4.8)	2.28 (5.6)	1.97 (5.4)	1.30 (4.3)	0.58 (3.7)	0.26 (3.7)
phenethyl alcohols[e]	12.9 (16.8)	7.27 (17.9)	4.36 (12.0)	4.73 (15.6)	2.63 (16.9)	1.40 (19.7)
ethylphenols[d]	3.75 (4.9)	1.83 (4.5)	2.29 (6.3)	1.67 (5.5)	0.59 (3.8)	0.30 (4.2)
2,3-diphenylbutane	5.74 (15.0)	4.42 (21.8)	2.80 (15.4)	4.02 (26.5)	2.12 (27.2)	0.99 (27.8)

[a] Amount of sample is 25 mL. [b] Amount in 10^{-1} mmol; parentheses denote percent (moles of product/moles of decomposed peroxide) × 100, except for O_2, ethane, and 2,3-diphenylbutane where this number is doubled. [c] Total amounts of propyl- and isopropylbenzenes. [d] Total amounts of ortho, meta, and para isomers. [e] Total amounts of α and β isomers.

Table IV

(a) Effect of Peracetic Acid (1) Concentration on Product Yields in >2900-Å Irradiation[a]

	run					
	1	2	3	4	5	6
init concn of 1,[b] × 10^{-1} M	5.49	3.13	2.23	1.57	0.078	0.042
irradn time, h	14.0	12.0	10.0	9.0	8.0	7.0
amt of 1 decomposed[c]	96.8 (70.5)	74.3 (74.3)	31.8 (57.0)	28.6 (73.0)	14.2 (72.4)	6.78 (65.2)
products[c]						
oxygen	3.87 (8.0)	2.44 (8.4)	1.69 (10.6)	1.66 (11.6)	0.98 (13.8)	0.52 (15.3)
water	19.6 (20.2)	10.3 (17.7)	4.80 (15.1)	4.35 (15.2)	1.55 (10.9)	0.77 (11.4)
methane	63.2 (65.3)	39.2 (67.5)	22.6 (71.1)	19.1 (66.8)	9.78 (68.9)	4.64 (68.4)
ethane	2.00 (4.1)	1.22 (4.2)	0.53 (3.3)	0.59 (4.1)	0.27 (3.8)	0.12 (3.5)
methanol	9.32 (9.6)	4.22 (7.3)	1.34 (4.2)	2.35 (8.2)	0.88 (6.2)	0.41 (6.0)
propylbenzenes[d]	4.26 (4.4)	2.47 (4.3)	2.13 (6.7)	0.95 (3.3)	0.39 (2.7)	0.19 (2.8)
ethyltoluenes[e]	1.22 (1.3)	0.64 (1.1)	0.35 (1.1)	0.24 (0.8)	0.14 (1.0)	0.06 (0.9)
phenethyl alcohols[f]	37.9 (39.2)	23.8 (41.0)	15.6 (49.1)	12.3 (43.0)	6.72 (47.3)	3.52 (51.9)
ethylphenols[e]	1.30 (1.3)	0.67 (1.2)	0.19 (0.6)	0.24 (0.8)	trace	trace
2,3-diphenylbutane	7.16 (14.8)	5.20 (17.9)	2.13 (13.4)	3.16 (22.1)	1.67 (23.5)	0.92 (27.1)

(b) Effect of Peracetic Acid (1) Concentration on Product Yields in >2900-Å Irradiation[g]

	run					
	1	2	3	4	5	6
init concn of 1,[b] × 10^{-1} M	5.49	3.13	2.23	1.57	0.078	0.042
irradn time, h	6.0	6.0	4.0	4.0	2.0	2.0
amt of 1 decomposed[c]	85.7 (62.4)	62.7 (80.2)	39.9 (71.5)	30.4 (77.6)	12.5 (63.8)	9.34 (89.8)
products[c]						
oxygen	2.44 (5.7)	1.88 (6.0)	1.68 (8.4)	1.49 (9.8)	0.77 (12.3)	0.55 (11.8)
water	18.3 (21.4)	12.7 (20.3)	7.26 (18.2)	4.74 (15.6)	2.03 (16.2)	1.20 (12.8)
methane	56.0 (65.3)	41.3 (65.9)	26.7 (66.9)	20.3 (66.8)	8.40 (67.2)	6.39 (68.4)
ethane	2.23 (5.2)	1.60 (5.1)	0.80 (4.0)	0.65 (4.3)	0.24 (3.8)	0.17 (3.6)
methanol	14.2 (16.6)	7.58 (12.1)	4.05 (10.2)	2.83 (9.3)	0.94 (7.5)	0.67 (7.2)
propylbenzenes[d]	5.31 (6.2)	3.19 (5.1)	1.48 (3.7)	1.23 (4.0)	0.43 (3.4)	0.31 (3.3)
ethyltoluenes[e]	1.65 (1.9)	0.96 (1.5)	0.40 (1.0)	0.36 (1.2)	0.09 (0.7)	0.08 (0.9)
phenethyl alcohols[f]	38.9 (45.4)	27.7 (44.2)	18.8 (47.1)	14.1 (46.4)	6.46 (51.7)	4.55 (48.7)
ethylphenols[e]	1.82 (2.1)	1.05 (1.7)	0.46 (1.2)	0.36 (1.2)	0.11 (0.9)	0.10 (1.1)
2,3-diphenylbutane	12.1 (28.2)	7.75 (24.7)	5.07 (25.4)	4.62 (30.4)	1.82 (29.1)	1.53 (32.8)

[a] Irradiated with a 300-W high-pressure Hg lamp. [b] Amount of sample is 25 mL. [c] Amount in 10^{-1} mmol; parentheses denote percent (moles of product/moles of decomposed peroxide) × 100, except for O_2, ethane, and 2,3-diphenylbutane, where this number is doubled. [d] Total amounts of propyl- and isopropylbenzenes. [e] Total amounts of ortho, meta, and para isomers. [f] Total amounts of α and β isomers. [g] Irradiated with a 1-kW high-pressure Hg lamp.

should be absorbed by ethylbenzene; excited ethylbenzene may then transfer energy to peracid[1,2] and/or may react with peracid to form "exciplex", while the >2900-Å light excites mainly peracetic acid alone.

A marked difference of yields exists in propylbenzenes, 22–28% in 2537-Å photolysis, 3–7% in >2900-Å (300 W) photolysis, and 3–6% in >2900-Å (1 kW) photolysis.

Rates of decomposition of peracid (Tables I and II) are in the order 2900Å (1 kW) > 2537 Å > 2900 Å (300 W); hence, the above yields of propylbenzenes cannot be explained by decomposition rate of peracid or radical concentration; instead they depend on wavelength.

Reaction Mechanism. As stated above, the initial steps of photolysis are dependent upon wavelength. These steps are given in eq 1–4.

For 2537 Å

$$\mathrm{PhCH_2CH_3} \xrightarrow{h\nu\ (2537\ \text{Å})} \mathrm{[PhCH_2CH_3]^*} \qquad (1)$$

$$\mathrm{[PhCH_2CH_3]^* + CH_3CO_3H \rightarrow PhCH_2CH_3 + [CH_3CO_3H]^*} \qquad (2)$$

$$\mathrm{[CH_3CO_3H]^* \rightarrow CH_3CO_2\cdot + HO\cdot \rightarrow CH_3\cdot + CO_2 + HO\cdot} \qquad (3)$$

For >2900 Å

$$\mathrm{CH_3CO_3H} \xrightarrow{h\nu\ (>2900\ \text{Å})} \mathrm{CH_3CO_2\cdot + HO\cdot \rightarrow CH_3\cdot + CO_2 + HO\cdot} \qquad (4)$$

If 2537-Å excited ethylbenzene, $[\mathrm{PhCH_2CH_3}]^*$, plays only a role of transferring excited energy to peracid in 2537-Å irradiation, eq 3 should give $\mathrm{CH_3\cdot}$, $\mathrm{HO\cdot}$, and $\mathrm{CO_2}$, the same as in >2900-Å irradiation (eq 4). In view of half-time of peracid decomposition (Tables I and II), the concentration of radicals with 2537-Å light is lower than that with >2900-Å (1 kW) light and is higher than that with >2900-Å (300 W) light.

The assumption that the radical concentration determines the distribution of products is inconsistent with the observed higher yields of propylbenzenes and the lower yields of phenethyl alcohols at 2537 Å than those at >2900 Å.

Furthermore, molecular oxygen is formed from acetylperoxy radical which is produced by induced decomposition of peracetic acid with radicals (eq 5)[2,3] and/or from the thermolysis of $\mathrm{H_2O_2}$ which is produced by $\mathrm{HO\cdot}$ radical coupling (eq 6).

$$\mathrm{CH_3CO_3{-}H + R\cdot \rightarrow CH_3CO_3\cdot + RH} \qquad (5)$$

$$\mathrm{2HO\cdot \rightarrow H_2O_2 \rightarrow H_2O + 0.5O_2} \qquad (6)$$

The latter process (eq 6) seems to be minor, because $\mathrm{H_2O_2}$ decomposes rapidly to $\mathrm{HO\cdot}$ radical on irradiation.[4] The yield of $\mathrm{O_2}$ formed by eq 5 and 6 is lower at 2537 Å than that at >2900 Å. On the other hand, the yield of $\mathrm{H_2O}$, which is formed mainly by H-atom abstraction with $\mathrm{HO\cdot}$, is higher at 2537 Å than at >2900 Å, which shows the contribution of induced decomposition of peracetic acid by radicals (e.g., eq 5) to decrease $\mathrm{HO\cdot}$ concentration at 2537 Å is less.

Radical $\mathrm{CH_3CO_3\cdot}$ (eq 5) produces $\mathrm{CH_3\cdot}$ and $\mathrm{CO_2}$ in addition to $\mathrm{O_2}$, as reported by Kenley and Traylor.[3] Therefore, 1 mol of $\mathrm{CH_3CO_3H}$ should produce an equimolar amount of $\mathrm{CH_3\cdot}$ at both 2537 Å and >2900 Å.

Although the radical $\mathrm{CH_3\cdot}$ is much less reactive than $\mathrm{HO\cdot}$[5], the yields of methylated compounds (propylbenzenes) at 2537 Å are much higher than those at >2900 Å. These results suggest that an alternative pathway producing propylbenzene should exist at 2537 Å. We reported previously that the fluorescence from excited toluene was quenched by peracetic acid.[1] Hence quenching correlates with the singlet energy transfer to peracid and/or the formation of "exciplex" leading to methylation via H-atom abstraction by $\mathrm{HO\cdot}$ followed by an attack of $\mathrm{CH_3\cdot}$ (eq 7 and 8).

$$\mathrm{[PhCH_2CH_3]^* + CH_3CO_3H \rightarrow [PhCH_2CH_3{\cdot}CH_3CO_3H]ex} \qquad (7)$$

$$\mathrm{[PhCH_2CH_3{\cdot}CH_3CO_3H]ex \rightarrow PhCH(CH_3)_2 + CO_2 + H_2O} \qquad (8)$$

α-Hydrogen abstraction of side chain of ethylbenzene by radicals ($\mathrm{CH_3\cdot}$ or $\mathrm{HO\cdot}$) occurs (eq 9), since energy for

$$\mathrm{PhCH_2CH_3 + R\cdot \rightarrow Ph\dot{C}HCH_3 + RH} \qquad (9)$$

$$\mathrm{Ph\dot{C}HCH_3 + CH_3\cdot \rightarrow PhCH(CH_3)_2} \qquad (10)$$

$$\mathrm{Ph\dot{C}HCH_3 + HO\cdot \rightarrow PhCH(OH)CH_3} \qquad (11)$$

$$\mathrm{2Ph\dot{C}HCH_3 \rightarrow CH_3CH(Ph)CH(Ph)CH_3} \qquad (12)$$

$$\mathrm{Ph\dot{C}HCH_3 + CH_3CO_2{-}OH \rightarrow PhCH(OH)CH_3 + CH_3CO_2\cdot} \qquad (13)$$

a secondary H-atom abstraction is lower than that of a primary one. In fact, the yield of α-phenethyl alcohol is much higher than that of the β isomer, and only 2,3-diphenylbutane was produced via coupling of α-phenethyl radical. Also α-phenethyl radical couples with $\mathrm{CH_3\cdot}$, $\mathrm{HO\cdot}$, or itself to give isopropylbenzene (eq 10), α-phenethyl alcohol (eq 11), and 2,3-diphenylbutane (eq 12), respectively, and induces decomposition of peracetic acid (eq 13) to give α-phenethyl alcohol.

The high yield of α-phenethyl alcohol at >2900 Å may be due to eq 13 rather than eq 11, because the yield is much higher than those of ethane, methanol, and 2,3-diphenylbutane formed by coupling.

Since $\mathrm{O_2}$ exists in this system and participates as a scavenger of alkyl radicals, alcohols (α-phenethyl alcohol and methanol) may be formed via peroxide (eq 14 and 15).

$$\mathrm{Ph\dot{C}HCH_3 + O_2 \rightarrow PhC(OO\cdot)HCH_3 \rightarrow \underset{\mathbf{2}}{PhC(OOH)HCH_3} \rightarrow PhCH(OH)CH_3, PhCOCH_3, PhCHO} \qquad (14)$$

$$\mathrm{CH_3\cdot + O_2 \rightarrow CH_3OO\cdot \rightarrow CH_3OOH \rightarrow CH_3OH, CH_2O} \qquad (15)$$

Peroxide **2** gives acetophenone and benzaldehyde as well as α-phenethyl alcohol; acetophenone and benzaldehyde (whose yields were included in those of α-phenethyl alcohol in all tables) were detected only at a high conversion (over 60%) and a high concentration (0.5 M) of peracid. Therefore, the contribution of eq 14 and 15 to the formation of alcohols would be small. This may be due to fast evolution of $\mathrm{O_2}$ out of the solution along with $\mathrm{CO_2}$.

The lower yields of phenethyl alcohols at 2537 Å may be due to the decrease of $\mathrm{HO\cdot}$ radical concentration by a preferential formation of water via "exciplex" (eq 7 and 8) and by the reaction of excited ethylbenzene with peracid, exemplified by eq 16.

$$\mathrm{[C_6H_5CH_2CH_3]^* + CH_3CO_3H \rightarrow HOC_6H_4CH_2CH_3 + CH_3CO_2\cdot} \qquad (16)$$

In fact, the yields of ethylphenols at 2537 Å were higher than those at >2900 Å. Also, the yields of ethyltoluenes, which are formed via addition of $\mathrm{CH_3\cdot}$ radical to the ring, are higher at 2537 Å than those at >2900 Å.

These phenomena suggest that the reactivity of the ring with radical is increased by photoexcitation.

On the other hand, slightly higher yield with a 1-kW lamp than with a 300-W lamp in runs 1–4 is attributable to an increase of radical concentration leading to coupling (eq 11).

The formation of oxygen indicates the induced decomposition (eq 5) as stated above. This is consistent with the higher total yields of methane and water than those of aromatic products; i.e., H-atom of peracid contributes as another H-atom source.

Yields of ethylphenols were low (4–5% at 2537 Å and 1–2% at >2900 Å), with orientation of ortho > para > meta. The higher yields of ethylphenols at 2537 Å than

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(3) R. A. Kenley and T. G. Traylor, *J. Am. Chem. Soc.*, **97**, 4700 (1975).

(4) The half-time of the decomposition of $\mathrm{H_2O_2}$ in ethylbenzene–methanol (ca. 1–10 mmol/25 mL) was below 6 h at 2537 and >2900 Å (1-kW lamp), while the thermolysis of $\mathrm{H_2O_2}$ in the dark at room temperature is negligible after 1 day.

(5) J. K. Kochi, "Free Radicals", Vol. 1, Wiley, New York, N.Y., 1973, pp 70–83.

those at >2900 Å may be ascribed to the reaction of excited ethylbenzene with peracid at 2537 Å as stated above but not the increase of HO· radical concentration. For comparison with the reaction of pure HO· alone, the photolysis of H_2O_2 in ethylbenzene was done. α-Phenethyl alcohol, ethylphenols, and 2,3-diphenylbutane in a ratio of 17.5:52.5:30.0 were obtained in 2537-Å photolysis, where isomer distribution of ethylphenols was ortho > para > meta. With >2900-Å (1 kW) photolysis, α-phenethyl alcohol, ethylphenols, and 2,3-diphenylbutane in a ratio of 19.1:51.6:29.3 were obtained, where isomeric ethylphenols are in the order ortho > para > meta, and the order with H_2O_2 is consistent with that with peracetic acid. Hence, the yields of ethylphenols with H_2O_2 are higher than that of 2,3-diphenylbutane. The higher yields of ethylphenols in H_2O_2 than in CH_3CO_3H may be due to the lower acidity of H_2O_2 solution which stabilizes the HO-aromatic adduct,[6] because peracetic acid solution contains acetic acid which increases acidity.

On the other hand, the photolysis of acetyl peroxide in ethylbenzene gave isopropylbenzene, ethyltoluene, and 2,3-diphenylbutane in a ratio of 13.4:2.6:84.0 with 2537-Å light and a ratio of 34.9:6.2:58.9 with >2900-Å (1 kW) light. With acetyl peroxide, the yields of ethyltoluenes are lower than those of other products in both photolyses. Hence, the extent of addition of CH_3· radical to the ring is smaller than that of H-atom abstraction and this is also true for the photolysis of peracetic acid.

In conclusion, the yields in photolysis of peracetic acid in ethylbenzene depend on the wavelength but not the intensity of the light; i.e., the yields at 2537 Å are propylbenzenes > phenethyl alcohols, while the yields at >2900 Å are phenethyl alcohols > propylbenzenes, where the distribution of these products at >2900 Å does not change when a 300-W lamp is changed to a 1-kW lamp. α-Phenethyl alcohol was formed by coupling (eq 11), induced reaction (eq 13), and a peroxide mechanism (eq 14). The formation of isopropylbenzene at 2537 Å may involve "exciplex" (eq 7 and 8) besides coupling (eq 10).

Experimental Section

Apparatus. GLC analyses were performed on a Yanagimoto gas chromatograph with FID and TCD, Model G 180. A Shimadzu GC/MS 7000 gas chromatograph/mass spectrometer was used to determine and identify the photolysis products. NMR spectra were recorded on a Hitachi R-24B spectrometer, using Me_4Si as an internal standard. IR spectra were recorded on a Perkin-Elmer 337 spectrophotometer. A Halos low-pressure 30-W Hg lamp, a Halos high-pressure 300-W Hg lamp, and a Halos high-pressure 1-kW Hg lamp were used as light sources. All experiments were carried out in a cylindrical quartz vessel (2 × 12 cm) or a cylindrical Pyrex vessel (2 × 12 cm).

Materials. Peracetic acid was prepared by the reaction of acetic anhydride (205 g) with 90% aqueous H_2O_2 (35 g) added with concentrated H_2SO_4 (0.5 mL) at 35–40 °C.[7] **Ethylbenzene** (bp 136–136.5 °C (760 mm)) was purified by distillation over P_2O_5. A water-free peracetic acid–ethylbenzene solution was prepared by the method of Hormer[8] and was immediately irradiated after the estimation of peracid concentration. ***o*-Ethyltoluene** was prepared by aldol condensation of crotonaldehyde giving 5,6-dihydro-*o*-tolualdehyde which was condensed with MeMgI and then dehydrated:[9] yield 42%; mp 161–162 °C (760 mm); NMR (CCl_4) δ 1.27 (t, 3 H, Me), 2.24 (s, 3 H, Me), 2.57 (q, 2 H, CH_2), 6.92 (s, 4 H, aromatic). ***m*-Ethyltoluene** was prepared by Clemmensen reduction of *m*-methylacetophenone prepared by the Grignard reaction of *m*-bromotoluene with acetaldehyde followed by chromic acid oxidation:[10,11] yield 53%; mp 160–161 °C (760 mm); NMR (CCl_4) δ 1.20 (t, 3 H, Me), 2.25 (s, 3 H, Me), 2.65 (q, 2 H, CH_2), 7.12 (s, 4 H, aromatic). ***p*-Ethyltoluene** was prepared by Wolff–Kishner reduction of *p*-methylacetophenone obtained by Friedel–Crafts acylation of toluene:[12,13] yield 68%; mp 161–163 °C (760 mm); NMR (CCl_4) δ 1.18 (t, 3 H, Me), 2.23 (s, 3 H, Me), 2.52 (q, 2 H, CH_2), 6.86 (s, 4 H, aromatic). **2,3-Diphenylbutane** was prepared by the reaction of α-phenethyl chloride with Mg in ether.[14] Meso isomer: yield 32%; mp 125.5 °C (white plates); NMR (CCl_4) δ 1.00 (d, 6 H, Me), 2.75 (m, 2 H, CH), 7.16 (s, 10 H, Ph). *dl* isomer: yield 43%; mp 155–157 °C (15 mm). Commercial α- and β-phenethyl alcohols and *o*-, *m*-, and *p*-ethylphenols, etc., of guaranteed reagent grade were used.

Photolysis of a Mixture of Peracetic Acid and Ethylbenzene. A mixture of peracetic acid and ethylbenzene was photolyzed in a quartz vessel with a 30-W low-pressure Hg lamp or in a Pyrex vessel with a 300-W high-pressure Hg lamp or with a 1-kW high-pressure Hg lamp through a water jacket. After estimation of peracid remaining in the solution, a constant amount of Me_2SO–benzene was added to the photolysate to avoid the contamination in GLC thermolysis of peracid. Gaseous products were analyzed by the method previously described[1,2] and the products in the solutions were analyzed by GLC with FID and TCD (Porapak QS, Bentone 34-DIDP, and PEG 20M-Silicon DC 550).

Photolysis of a Mixture of Hydrogen Peroxide and Ethylbenzene. A 1:30 mixture of 90% aqueous H_2O_2 and MeOH was dried over anhydrous Na_2SO_4; the solution was mixed with ethylbenzene (ca. 0.3–0.05 M) and photolyzed. The photolysate was treated and analyzed in a similar manner to the photolysis of peracetic acid solution. Methanol was used as a phase-transfer agent to dissolve H_2O_2 in ethylbenzene. Therefore, the yields of products from ethylbenzene are relative amounts.

Photolysis of a Mixture of Acetyl Peroxide and Ethylbenzene. Ethylbenzene was added to the ethereal solution of acetyl peroxide which was prepared by the reaction of acetic anhydride with sodium peroxide.[15] Solvent ether was removed from the solution under vacuum and the mixture was photolyzed. The photolysate was treated and analyzed in a similar manner to that above.[16]

Registry No. 1, 79-21-0; acetic anhydride, 108-24-7; ethylbenzene, 100-41-4; *o*-ethyltoluene, 611-14-3; crotonaldehyde, 4170-30-3; 5,6-dihydro-*o*-tolualdehyde, 60468-96-4; methyl iodide, 74-88-4; *m*-ethyltoluene, 620-14-4; *m*-methylacetophenone, 585-74-0; *m*-bromotoluene, 591-17-3; acetaldehyde, 75-07-0; *p*-ethyltoluene, 622-96-8; *p*-methylacetophenone, 122-00-9; toluene, 108-88-3; *meso*-2,3-diphenylbutane, 4613-11-0; *dl*-2,3-diphenylbutane, 2726-21-8; α-phenethyl chloride, 672-65-1; carbon dioxide, 124-38-9; oxygen, 7782-44-7; water, 7732-18-5; methane, 74-82-8; ethane, 74-84-0; methanol, 67-56-1; propylbenzene, 103-65-1; isopropylbenzene, 98-82-8; α-phenethyl alcohol, 98-85-1; β-phenethyl alcohol, 1321-27-3; *o*-ethylphenol, 90-00-6; *m*-ethylphenol, 620-17-7; *p*-ethylphenol, 123-07-9.

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