room temperature the adduct decomposed. Upon addition of more TCNE the formation of yet another adduct (presumably 2:1) was observed (also at −40 °C) suggesting the presence of a vinylcyclopropane moiety in the initially formed adduct **25.** Because of the encountered difficulties in workup no adduct was isolated.

Registry No.—**1**, 50590-86-8; **3**, 65103-68-6; **4**, 65103-69-7; **5**, 65103-70-0; **6**, 65103-71-1; **7**, 65103-72-2; **8**, 65103-73-3; **9**, 65103-74-4; **10**, 65103-75-5; **11**, 65103-76-6; **12**, 65103-77-7; **13**, 65103-78-8; **14**, 65103-79-9; **15**, 65103-80-2; **16**, 65103-81-3; **17**, 19063-11-7; **18**, 56745-77-8; **19**, 65103-82-4; **20**, 65103-83-5; **21**, 65103-84-6; **23**, 65103-85-7; **24**, 65103-86-8; **25**, 65103-87-9; chloroform, 67-66-3; bromoform, 75-25-2; diazomethane, 334-88-3.

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Photoinduced Decomposition of Peracetic Acid in Benzene

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The decomposition of peracetic acid in benzene, which was initiated by two light sources (at 2537 Å or over 2900 Å), showed preferential reaction of methyl radical with benzene, affording toluene, rather than reaction of hydroxyl radical, affording phenols. Analysis of simple products including methane, ethane and water showed that induced decomposition of peracid by methyl and hydroxyl radicals is the major pathway rather than aromatic radical substitution. The formation of biphenyl by phenyl radical coupling or addition of phenyl radical to benzene is not important.

The interaction between radicals and aromatic hydrocarbons may involve two reactions, i.e., radical addition and hydrogen atom abstraction, and radical addition is said to predominate in solution.[1,2] The reaction of methyl radical with benzene affords mainly toluene via addition and dehydrogenation,[1,2] while hydroxyl radical gives phenols and coupling products.[3–5]

The thermal decomposition of peracetic acid in benzene has been studied kinetically[6] but is only limited information on the decomposition mechanism and products. The photolysis of peracetic acid in cyclohexane was reported to give mainly cyclohexanol which suggests induced decomposition of peracid by cyclohexyl radical.[7]

Our previous study[8] suggested that the photolysis of peracetic acid in toluene involved the induced decomposition of peracid by $CH_3\cdot$, $HO\cdot$, and $PhCH_2\cdot$ radicals and the extent of the induced decomposition varied with wavelength of light.

The present paper discloses the mechanism of photoinduced decomposition of peracetic acid in benzene, where more induced decomposition occurs than in toluene.

Results

The photolysis of peracetic acid in benzene with 2537 Å or >2900 Å light afforded carbon dioxide, oxygen, methane, ethane, water, methanol, methyl acetate, toluene, phenol, and biphenyl (trace). The yield of phenol with 2537 Å light increases with a decrease in peracid concentration, while only a trace of phenol is formed at >2900 Å independent of the peracid concentration. Trace amounts of xylenes and methylbiphenyls (M^+ 168, *m/e* 152, 153, 165, 167, 168 and no peak of *m/e* 91 corresponding to $PhCH_2$)[9] were obtained in both photolyses.

Estimation of CO_2 and O_2. CO_2 (1 mol) was evolved from 1 mol of peracid decomposed with 2537 Å light, but the yield of CO_2 was 5–10% lower at >2900 Å (Tables I and II). The yield of O_2 was 5–15% of peracid decomposed at 2537 Å and >2900 Å.

Products. The time dependence of yields was studied in order to know primary products and the possibility of further reaction. These results are shown in Tables I (2537 Å) and II (>2900 Å). As is apparent from the tables, the yield of H_2O, methane, and toluene increases as the photolysis proceeds, i.e., the concentration of peracid decreases. The yield of phenol is relatively high at 2537 Å, while only a trace was detected at >2900 Å.

Analogously to toluene,[8] the yield of MeOH decreases as the photolysis proceeds. The MeOH initially formed being esterified to methyl acetate with acetic acid.

The effects of the concentrations of peracid and radicals on the yields were studied to estimate the reactivity of methyl and hydroxyl radicals, and the results are shown in Tables III (2537 Å) and IV (>2900 Å).

The effects of peracid concentration on the yields (Tables III and IV) were similar as observed in the time dependence (Tables I and II). The remarkable difference between 2537 Å and >2900 Å was observed in the yields of H_2O, CH_4, C_2H_6, and PhOH. That is, at 2537 Å, the yield of H_2O is high (relative to >2900 Å) and the yield of CH_4 is less than that of C_2H_6. Whereas at >2900 Å, the yield of H_2O is low and the yield of CH_4 is greater than that of C_2H_6. In addition, the yield of

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Table I. Time Dependence of Product Yields on Irradiation (2537 Å) Time in Photolysis of Peracetic Acid[c] in Benzene

Time, h	[CH_3CO_3H decomposed] × 10^4 mol (%)	Products × 10^4 mol (%)										
		CO_2[a]	O_2[b]	H_2O[a]	CH_4[a]	C_2H_6[b]	MeOH[a]	MeOAc[a]	PhMe[a]	Xylene[b]	PhOH[a]	PhPh[b]
0.5	3.135	3.079	Trace	0.429	0.509	0.690	0.640	0.014	0.210	0.016	0.017	0.011
	(8.5)	(98.2)		(13.7)	(16.2)	(44.0)	(20.4)	(0.4)	(6.7)	(1.0)	(0.2)	(0.7)
1.0	5.141	5.017	0.084	0.952	0.866	1.089	0.897	0.037	0.562	0.044	0.105	0.015
	(13.9)	(97.6)	(3.3)	(18.5)	(16.9)	(42.4)	(17.5)	(0.7)	(10.9)	(1.7)	(2.0)	(0.6)
3.0	13.79	14.10	0.396	3.092	2.372	2.835	2.045	0.142	1.808	0.139	0.441	0.026
	(37.3)	(102.3)	(5.7)	(22.4)	(17.2)	(41.1)	(14.8)	(1.0)	(13.1)	(2.0)	(3.2)	(0.4)
4.5	18.18	17.89	0.658	4.861	3.240	3.748	2.227	0.340	2.800	0.193	0.791	0.028
	(49.2)	(98.4)	(7.2)	(26.7)	(17.8)	(40.6)	(12.3)	(1.9)	(15.4)	(2.1)	(4.4)	(0.3)
7.0	24.45	23.94	0.949	6.936	4.460	4.831	2.245	0.645	3.888	0.308	1.208	0.088
	(66.1)	(97.9)	(7.8)	(28.4)	(18.2)	(39.5)	(9.2)	(2.6)	(15.9)	(2.5)	(4.9)	(0.3)

[a] % = [yield]/[peracid decomposed] × 100. [b] % = 2 × [yield]/[peracid decomposed] × 100. Experimental error was within ±5% by GLC analysis. [c] Initial concentration of peracid = 3.699 mmol/25 mL (0.148 M).

Table II. Time Dependence of Product Yields on Irradiation (>2900 Å) Time in Photolysis of Peracetic Acid[c] in Benzene

Time, h	[CH_3CO_3H decomposed] × 10^4 mol (%)	Products × 10^4 mol (%)										
		CO_2[a]	O_2[b]	H_2O[a]	CH_4[a]	C_2H_6[b]	MeOH[a]	MeOAc[a]	PhMe[a]	Xylene[b]	PhOH[a]	PhPh[b]
1.0	2.608	2.283	0.009	0.146	1.149	0.239	0.491	0.003	0.118	0.009		
	(7.1)	(87.5)	(0.7)	(5.6)	(44.1)	(18.4)	(18.8)	(0.1)	(4.5)	(0.7)		
2.0	4.931	4.455	0.041	0.518	2.239	0.422	0.908	0.018	0.333	0.018	0.002	0.001
	(13.3)	(90.3)	(1.7)	(10.5)	(45.4)	(17.1)	(18.4)	(0.4)	(6.8)	(0.7)	(0.1)	(0.1)
4.0	9.575	8.546	0.148	1.631	4.493	0.813	1.540	0.056	0.831	0.027	0.006	0.005
	(25.9)	(89.3)	(3.1)	(17.0)	(46.9)	(17.0)	(16.1)	(0.6)	(8.7)	(0.6)	(0.1)	(0.1)
6.0	13.27	12.26	0.380	2.696	6.108	1.083	2.006	0.122	1.084	0.033	0.024	0.008
	(35.9)	(92.4)	(5.7)	(20.3)	(46.0)	(16.3)	(15.1)	(0.9)	(8.2)	(0.5)	(0.2)	(0.1)
9.0	17.98	16.46	0.788	3.848	8.553	1.424	2.411	0.223	1.881	0.058	0.047	0.013
	(48.6)	(91.6)	(8.8)	(21.4)	(47.6)	(15.8)	(13.4)	(1.2)	(10.5)	(0.6)	(0.3)	(0.2)
12.0	21.71	20.46	1.220	4.928	10.56	1.811	2.872	0.239	2.338	0.078	0.080	0.022
	(58.7)	(94.3)	(11.2)	(22.7)	(43.6)	(16.7)	(13.2)	(1.1)	(10.8)	(0.7)	(0.4)	(0.2)

[a] % = [yield]/[peracid decomposed] × 100. [b] % = 2 × [yield]/[peracid decomposed] × 100. Experimental error was within ±5% by GLC analysis. [c] Initial concentration of peracid = 3.699 mmol/25 mL (0.148 M).

PhOH increases with decreasing peracid concentration at 2537 Å, while only a trace of PhOH is observed at >2900 Å. The difference may be due to the concentration of produced radicals.

Discussion

Initial Process. As reported previously with toluene,[8] in view of the extinction coefficient of benzene ($\epsilon_{2537Å} = 90$ and $\epsilon_{>2900Å} \approx 0$)[10] and peracetic acid ($\epsilon_{<2537Å} < 25$,[11] $\epsilon_{2900Å} = 2.4$, $\epsilon_{3000Å} = 1.23$, and $\epsilon_{3600Å} = 0.046$),[8] the 2537 Å light should be absorbed predominantly by benzene, since the extinction coefficient of benzene is ca. 5 times as large as that of peracid and benzene is in a large excess. Then excited benzene must transfer energy to peracid as toluene does,[8] producing two radicals (eq 1–3). On the other hand, the >2900 Å irradiation excites mainly peracetic acid resulting in the O–O cleavage (eq 4), because the extinction coefficient of peracid is much higher than that of benzene at >2900 Å.

$$\mathrm{PhH} \xrightarrow{h\nu\ (2537\ Å)} [\mathrm{PhH}]^* \tag{1}$$

$$[\mathrm{PhH}]^* + CH_3CO_3H \rightarrow \mathrm{PhH} + [CH_3CO_3H]^* \tag{2}$$

$$[CH_3CO_3H]^* \rightarrow CH_3CO_2\cdot + HO\cdot \rightarrow CH_3\cdot + CO_2 + HO\cdot \tag{3}$$

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

The rate of radical production by eq 1–3 with 2537 Å may be greater than that by eq 4 with >2900 Å, since half-time of decomposition is ca. 4.2 h with 2537 Å and ca. 9.5 h with >2900 Å. This is due to the higher extinction coefficient of benzene than that of peracetic acid and also to a large excess of benzene. Therefore, this high relative absorbance at 2537 Å (where total light would be absorbed within a pathlength of 2 cm) indicates the possibility of producing high local concentrations of the radicals relative to the >2900 Å photolysis. This would certainly have an effect on yields of radical–radical coupling products.

Induced Decomposition of Peracid by Radicals. As reported previously with toluene,[8] $CH_3\cdot$ and HO· radicals formed in eq 3 and 4 may induce the following reactions.

$$\mathrm{PhH} + R\cdot \rightarrow \mathrm{Ph}\cdot + RH \tag{5}$$

$$CH_3CO_3\mathbf{H} + R\cdot \rightarrow CH_3CO_3\cdot + RH \tag{6}$$

$$CH_3CO_2\mathbf{OH} + CH_3\cdot \rightarrow CH_3CO_2\cdot + CH_3OH \tag{7}$$

$$R = CH_3 \text{ and } HO$$

The direct H-atom abstraction by radicals (eq 5) may occur.[12] However, this reaction is not important since the yield of the coupling product (e.g., biphenyl) is very low even at high concentrations of peracid (Tables III and IV).

In the 2537 Å photolysis, the total yields of CH_4 and H_2O are ca. 46–60% per peracid decomposed and the total yields of products bearing phenyl group are 11–27% as shown in Table III. The total yields of CH_4 and H_2O in the >2900 Å photolysis are ca. 58–73% and the total yields of products bearing phenyl group are ca. 4–16% (Table IV). Therefore,

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

$[CH_3CO_3H]^a$ × 10 M	$[CH_3CO_3H$ decomposed] × 10^4 mol (%)	Products × 10^4 mol (%)									
		O_2^b	H_2O^c	CH_4^c	$C_2H_6^b$	MeOH^c	MeOAc^c	PhMe^c	Xylene^b	PhOH^c	PhPh^b
4.372	84.91	2.428	25.65	14.29	17.90	18.99	2.700	7.727	0.403	0.403	0.055
	(77.7)	(5.7)	(30.2)	(16.8)	(42.2)	(22.4)	(3.2)	(9.1)	(1.0)	(0.6)	(0.1)
3.240	54.65	1.465	15.65	10.16	11.41	10.25	1.459	5.771	0.281	0.312	0.082
	(67.5)	(5.4)	(28.6)	(18.6)	(41.8)	(18.8)	(2.7)	(10.6)	(1.0)	(0.6)	(0.3)
2.665	57.51	2.088	19.13	10.46	11.58	10.93	1.984	6.688	0.316	0.719	0.101
	(86.3)	(7.3)	(33.3)	(18.2)	(40.3)	(19.8)	(3.5)	(11.6)	(1.1)	(1.3)	(0.4)
1.874	36.96	1.464	11.30	7.266	7.000	6.180	1.005	5.463	0.224	1.087	0.052
	(78.9)	(7.9)	(30.6)	(19.7)	(37.9)	(16.7)	(2.7)	(14.8)	(1.2)	(2.9)	(0.3)
1.197	23.94	0.903	8.216	5.214	4.715	3.347	0.491	3.871	0.138	1.183	0.037
	(80.0)	(7.5)	(34.3)	(21.8)	(39.4)	(14.0)	(2.1)	(16.2)	(1.2)	(4.9)	(0.3)
0.942	19.34	0.838	6.303	4.094	3.695	2.798	0.414	3.050	0.120	1.400	0.017
	(82.1)	(8.7)	(32.6)	(21.2)	(38.2)	(14.5)	(2.1)	(15.8)	(1.2)	(7.2)	(0.2)
0.391	7.354	0.346	2.519	1.624	1.359	1.174	0.134	1.025	0.044	0.480	0.012
	(75.2)	(9.4)	(34.3)	(22.1)	(37.0)	(16.0)	(1.8)	(13.9)	(1.2)	(6.5)	(0.3)
0.176	3.535	0.201	1.320	0.787	0.667	0.427	0.067	0.663	0.024	0.241	0.008
	(80.3)	(11.4)	(37.4)	(22.3)	(37.7)	(12.1)	(1.9)	(18.8)	(1.4)	(6.8)	(0.4)

[a] Initial concentration. [b] % = 2 × [yield]/[peracid decomposed] × 100. [c] % = [yield]/[peracid decomposed] × 100. Experimental error was within ±5% by GLC analysis.

Table IV. Effect of Peracetic Acid Concentration on Product Yields in Irradiation (>2900 Å) of Peracetic Acid in Benzene

$[CH_3CO_3H]^a$ × 10 M	$[CH_3CO_3H$ decomposed] × 10^4 mol (%)	Products × 10^4 mol (%)									
		O_2^b	H_2O^c	CH_4^c	$C_2H_6^b$	MeOH^c	MeOAc^c	PhMe^c	Xylene^b	PhOH^c	PhPh^b
4.372	65.39	3.845	11.92	26.18	6.461	12.15	2.256	2.138	0.016	0.098	0.134
	(59.8)	(11.8)	(18.2)	(40.0)	(19.8)	(18.6)	(3.5)	(3.3)	(0.1)	(0.2)	(0.4)
3.240	44.30	2.997	8.258	18.79	4.191	7.194	1.444	1.741	0.053	0.089	0.071
	(54.7)	(13.5)	(18.6)	(42.4)	(18.9)	(16.2)	(3.3)	(3.3)	(0.2)	(0.2)	(0.3)
2.665	44.20	3.346	10.40	18.72	3.803	7.850	1.114	2.475	0.066	0.141	0.066
	(66.3)	(15.1)	(23.5)	(42.4)	(17.2)	(17.8)	(2.5)	(5.6)	(0.3)	(0.3)	(0.3)
1.874	26.68	1.717	5.963	11.85	2.180	3.975	0.758	2.644	0.111	0.125	0.017
	(57.0)	(12.9)	(22.4)	(44.4)	(16.3)	(14.9)	(2.8)	(9.9)	(0.8)	(0.5)	(0.1)
1.197	17.54	1.058	4.257	8.088	1.243	2.703	0.217	1.775	0.080	0.074	0.021
	(58.6)	(12.1)	(24.3)	(46.1)	(14.2)	(15.4)	(1.2)	(10.1)	(0.9)	(0.4)	(0.2)
0.942	13.01	0.727	2.970	5.989	0.920	1.941	0.215	1.443	0.082	0.047	0.012
	(55.2)	(11.2)	(22.8)	(46.0)	(14.2)	(14.9)	(1.7)	(11.1)	(1.3)	(0.4)	(0.2)
0.391	6.720	0.439	1.696	3.156	0.452	0.816	0.088	0.892	0.035	0.028	0.008
	(68.7)	(13.1)	(25.2)	(47.0)	(13.4)	(12.2)	(1.3)	(13.3)	(1.0)	(0.4)	(0.3)
0.176	2.781	0.168	0.719	1.299	0.184	0.345	0.031	0.394	0.017	0.008	0.003
	(63.1)	(12.1)	(25.9)	(46.7)	(13.3)	(12.4)	(1.1)	(14.2)	(1.2)	(0.3)	(0.2)

[a] Initial concentration. [b] % = 2 × [yield]/[peracid decomposed] × 100. [c] % = [yield]/[peracid decomposed] × 100. Experimental error was within ±5% by GLC analysis.

$CH_3\cdot$ and $HO\cdot$ must abstract H atom from peracid, because the quantities of H atoms available from benzene are insufficient for the CH_4 and H_2O produced.

Furthermore, as shown in Tables I and II, the yield of H_2O increases with decomposing peracid. The yield of CH_4 at 2537 Å is lower than that of H_2O after 1-h irradiation, while the yield of CH_4 at >2900 Å is much higher than that of H_2O at any reaction time. These results suggest that radicals $CH_3\cdot$ and $HO\cdot$, which were directly formed by eq 3 and 4, couple to give C_2H_6, H_2O_2, and CH_3OH, and alternatively they decompose CH_3CO_3H (eq 6 and 7) to give CH_4, H_2O, CH_3OH, and (H_2O_2). Thus induced decompositions (eq 6 and 7) reduce the concentration of $HO\cdot$ compared with that of $CH_3\cdot$ because $CH_3CO_3\cdot$ and $CH_3CO_2\cdot$ (eq 6 and 7) give $CH_3\cdot$ alone. Therefore, the yield of H_2O will be lower than that of CH_4 although the H-atom abstraction by $HO\cdot$ is preferred to that by $CH_3\cdot$.[13]

Acetylperoxy radical ($CH_3CO_3\cdot$) by eq 6 should decompose to give $CH_3\cdot$, CO_2, and O_2 as reported previously;[14] $CH_3\cdot$ thus formed may repeatedly be used in the induced reaction, since $CH_3\cdot$ will again be produced by a radical attack on peracetic acid.

Coupling of Radicals. Ethane may be formed by radical coupling ($2CH_3\cdot \rightarrow C_2H_6$). Table V shows that the ratio $[C_2H_6]/[CO_2]$ (≈0.19 with 2537 Å and ≈0.075 with >2900 Å) is greater than that with toluene (≈0.16 with 2537 Å and ≈0.065 with >2900 Å). This fact reveals that coupling of $CH_3\cdot$ is favored in benzene, because ring H atoms are difficult to abstract compared with the methyl H atoms of toluene.

As stated above, the induced decomposition (eq 6) and thus radical concentration are related to the wavelength used, e.g., the higher absorbance at 2537 Å may give higher (local) concentrations of radicals relative to the >2900 Å photolysis. As shown in Table V, the ratio $[C_2H_6]/[CO_2]$ is higher at 2537 Å. This is due to the high concentration of $CH_3\cdot$ radical at 2537 Å, which again accelerates the formation of $CH_3\cdot$ by induced

Table V. Decomposition of Peracetic Acid in Benzene vs. Toluene

Temp, °C	$[CH_3CO_3H]$[a] × 10^2 M	CO_2/ $[CH_3CO_3H$ decomposed]	CH_4/CO_2	C_2H_6/CO_2	$(CH_4 + C_2H_6)/CO_2$
rt[b]	9.42	0.98	0.216	0.195	0.606
rt[b]	3.91	0.97	0.228	0.191	0.610
rt[b]	1.76	1.01	0.220	0.189	0.598
rt[c]	9.42	0.89	0.517	0.080	0.677
rt[c]	3.91	0.93	0.505	0.072	0.649
rt[c]	1.76	0.91	0.513	0.073	0.659
rt[d]	6.50	1.01	0.40	0.16	0.72
rt[d]	3.70	1.02	0.44	0.16	0.76
rt[e]	10.6	0.89	0.70	0.064	0.83
rt[e]	6.8	0.91	0.65	0.057	0.76
85.0[f]	2.30	0.07	0.72		
65.0[g]	7.60		0.293	0.024	0.340

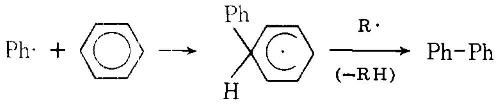
[a] Initial concentration. [b] With 2537 Å light irradiation. [c] With >2900 Å light irradiation. [d] Data summarized for photolysis of peracetic acid in toluene with 2537 Å light by Y. Ogata and K. Tomizawa, *J. Org. Chem.* **43**, 261 (1978). [e] Data summarized for photolysis of peracetic acid in toluene with >2900 Å light by Y. Ogata and K. Tomizawa, *J. Org. Chem.*, **43**, 261 (1978). [f] Data reported for thermal decomposition of peracetic acid in toluene by F. W. Evans and A. H. Sehon, *Can. J. Chem.*, **41**, 1826 (1963). [g] Data reported for thermal decomposition of diacetyl peroxide in benzene by M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 5981 (1954).

decomposition of peracid (eq 6) and eventually leads to the high ratio.

This is apparent from the formation of methanol. The total yields of methanol and methyl acetate were 14–25% at 2537 Å and 13–22% at >2900 Å with benzene, while those yields were 2.4–10.7% at 2537 Å and 5.6–8.5% at >2900 Å with toluene. The increase of total yields in benzene compared with that in toluene may be due to the decrease of the reactivity of radical on benzene, i.e., the acceleration of coupling of $CH_3\cdot$ and HO· radicals and an induced reaction (eq 7).

In contrast, there is obtained only a trace of biphenyl which is formed by coupling (eq 8) and/or addition (eq 9).

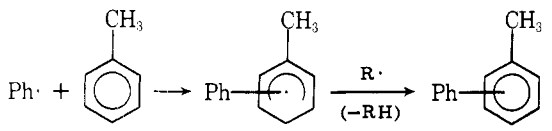
$$2\mathrm{Ph}\cdot \longrightarrow \mathrm{Ph{-}Ph} \qquad (8)$$



(9)

Coupling (eq 8) is less probable than the addition (eq 9) in view of the low concentration of phenyl radical which is formed by the ring H atom abstraction.

Methylbiphenyls detected by GC–MS may also be formed similarly (eq 10).

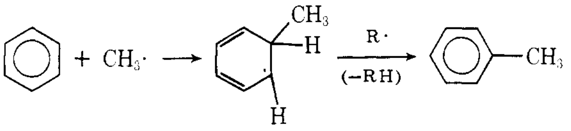


(10)

Addition and Abstraction by Radicals. The formation of CH_4 or H_2O) via abstraction of ring H atoms by $CH_3\cdot$ and HO· radicals is unlikely, so that toluene, xylene, and phenol may be formed by addition of the appropriate radical to benzene (eq 11–13).

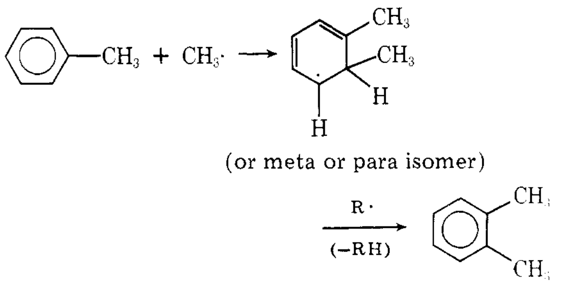
As to the formation of xylenes, eq 12a is preferred to eq 12b, since intermediate 1 is converted readily to toluene in the presence of radicals, xylenes formed in this photolysis include *o*-, *m*- and *p*-xylenes, and there is no evidence for the presence of dimethyldihydrobenzene (**2**) by means of GC–MS.

The photolysis of methylmercuric iodide in benzene with 3130 Å light gave toluene (ca. 40%) and xylenes (ca. 1%).[15] The lower yield in our photolysis (Tables III and IV) is attributed to the variety of reactants for attack of $CH_3\cdot$, i.e., peracetic acid (induced reaction shown in eq 6 and 7), $CH_3\cdot$ and HO· (coupling), and benzene (addition), in contrast to the simple reactant (benzene alone) in methylmercuric iodide photolysis.



(11)

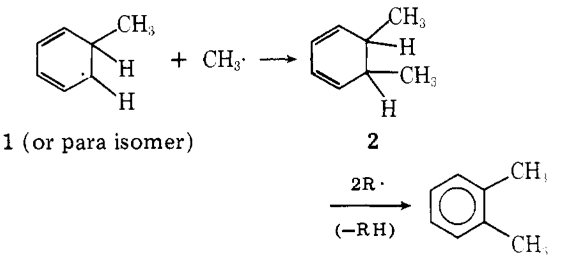
1 (or para isomer)



(or meta or para isomer)

(12a)

(or meta or para isomer)

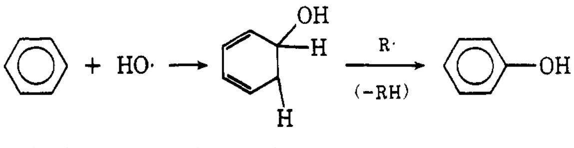


1 (or para isomer)

2

(12b)

(or para isomer)



(13)

An increase of the yield of toluene was observed at lower peracid concentration (Tables III and IV). With increasing peracid concentration, the concentration of radicals generated by photolysis (eq 1–4) and also by induced decomposition (eq 6 and 7) increases, hence coupling is more important than addition, whereas with lowering peracid concentration, the extent of coupling decreases and hence the extent of addition increases.

The yield of phenol at 2537 Å is less than that of toluene and the yield increases with a decrease of peracid concentration. The concentration of HO· is lower than that of $CH_3\cdot$ because of the occurrence of eq 6 and 7 and hence the yield of phenol is lower than that of toluene. The proportionality of the yield of phenol and 1/[CH_3CO_3H] may be due to a similar reason as that given for toluene as stated above.

The very low yield of phenol at >2900 Å (Table IV) is attributable to the facile reaction of HO· with peracid (eq 6) and/or its reaction with benzene to abstract H atom forming stable H_2O rather than addition to benzene. On the other hand, the high relative yield of phenol at 2537 Å compared with the >2900 Å photolysis may be due to higher concentration of HO· (directly formed) on account of the higher absorbance at 2537 Å. The increase of the yield of phenol with decreasing peracid concentration may be due to the increasing ratio of addition vs coupling.

As stated above, the yields of aromatic products, i.e., toluene, xylenes, phenol, and biphenyl, are low on the basis of peracetic acid decomposed. This is due to the low reactivity of benzene to radicals (CH_3· and HO·) which attacks preferentially peracid by abstracting atoms, as reported in the reaction of peracetic acid with *tert*-butoxy radical,[14] thus CH_3· and HO· abstract H atom of CH_3CO_3-**H** to give CH_4 and H_2O, respectively, and CH_3· abstracts HO· of CH_3CO_2-OH to form methanol.

For the formation of O_2 there are two conceivable mechanisms, i.e., dark disproportionation of peracid (eq 14) and decomposition of peroxyacetyl radical (eq 15).[14]

$$2CH_3CO_3H \rightarrow 2CH_3CO_2H + O_2 \quad (14)$$

$$2CH_3CO_3\cdot \rightarrow 2CH_3\cdot + 2CO_2 + O_2 \quad (15)$$

Equation 14 does not evolve CO_2, so that is not in accord with our results (Tables I and II); hence the formation of O_2 may be due to eq 15. O_2 evolved by eq 15 may react rapidly with alkyl radical (CH_3·) to give peroxy radical (CH_3OO·) and/or may escape out of the solution. When the concentration of CH_3· is high, the reaction of CH_3· with O_2 is probable and thus methylperoxy radicals formed may react with themselves and peroxyacetyl radicals to form CH_3OH, CH_3CO_2H, O_2 etc., as reported previously.[14] In fact, an increase of concentrations of peracid at 2537 Å in our photolysis increased the yield of CH_3OH by the reaction of CH_3· with O_2 and/or coupling of CH_3· with HO· and/or induced decomposition (eq 7). On the other hand, the higher yield of O_2 at lower concentration of peracid may be due to the evolution of O_2 from the solution without reacting with CH_3·.

The concentration of radicals formed by eq 4 is low at >2900 Å compared with that at 2537 Å; therefore, the possibility of reaction of O_2 with CH_3· is lower than that at 2537 Å and hence the yield of O_2 evolved is higher than that at 2537 Å. Tables III and IV show that this is the case.

Conclusions

(i) The decomposition of peracid by excited energy transfer (eq 1–3) is more effective at 2537 Å than that by the direct decomposition (eq 4) at >2900 Å, so that the contribution of induced decomposition (eq 6) at 2537 Å may be less than that at >2900 Å. This less contribution of induced decomposition (eq 6) may be due to the increased coupling at 2537 Å caused by the higher concentrations of radicals. Therefore, the evolution of O_2 at >2900 Å is greater than that at 2537 Å.

(ii) The reaction of radicals with peracid, i.e., induced decomposition, is preferred to the reaction with benzene.

(iii) The yield of toluene, a product via addition of CH_3· to benzene, is ca. 9–18% (2537 Å) and 3–14% (>2900 Å), while the yield of xylenes from toluene[8] is 10–14% (2537 Å) and 5–7% (>2900 Å).

Experimental Section

Materials. Peracetic acid was prepared by the reaction of acetic anhydride (205 g) with 60% aqueous H_2O_2 added with concentrated H_2SO_4 (0.5 mL) at 35–40 °C.[16] Benzene was purified by distillation over P_2O_5. A water-free peracetic acid–benzene solution was prepared by the method of Hormer[17] and was immediately irradiated after the estimation of peracid concentration.

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 gaseous products and identify the photolysis products. A Halos low-pressure 30 W Hg lamp and a Halos high-pressure 300 W 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).

Analyses of Gaseous Products. The gaseous products evolved by photolysis were collected in a gas buret (300 mL) connected with a capillary tube to the photolysis system. Analysis of gaseous products was carried out by two methods: (A) Analysis of CO_2 was carried out by the measurement of the gas volume absorbed in 33% aqueous KOH and then analysis of O_2 was done by absorption with aqueous alkaline pyrogallol.[18] Gaseous products remaining in the gas buret were analyzed by GC–MS and GLC with columns packed with Porapak T (80–100 mesh, 2.5 mm × 2 m) and Porapak QS (80–100 mesh, 2.5 mm × 2 m); the mass analysis of CH_4 and C_2H_6 was done by the comparison of peaks with those of authentic samples.[19] (B) Analyses of O_2 and CH_4 were carried out by GLC with a column packed with Molecular Sieve 5A (80–100 mesh, 2.5 mm × 2 m) with thermal conductivity detector (TCD) using He as a carrier gas. Analyses of CO_2,CH_4, and C_2H_6 were performed by GLC with a column packed with Porapak QS with TCD.

Another estimation of CO_2 was done also by acidimetry with 10^{-2} N $Ba(OH)_2$ in which the gas had been bubbled with N_2 as a carrier.

Photolysis of a Mixture of Peracetic Acid and Benzene. A mixture of peracetic acid and benzene was photolyzed in a quartz cell with a 30 W low-pressure Hg lamp or in a Pyrex cell with a 300 W high-pressure Hg lamp through a water jacket (18–20 °C). After estimation of peracid remaining in the solution, a constant amount of Me_2SO–benzene was added to the photolyzate to avoid contamination by GLC thermolysis products of peracid.[20] Gaseous products evolved were analyzed by the above method and the products in the solutions were analyzed by GLC with TCD and FID (Porapak QS, Bentone 34-DIDP, PEG 20M Chamelite CS, and Apiezon Grease L). The same mixtures of peracetic acid–benzene as used in photolysis were kept standing under the same conditions (in the dark) without irradiation. After the same treatments as used in the photolysis, the solutions were analyzed by GLC. The yields of photolysis products were corrected by the observed yields (trace) of the dark reaction.

Registry No.—Peracetic acid, 79-21-0; benzene, 71-43-7; toluene, 108-88-3.

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