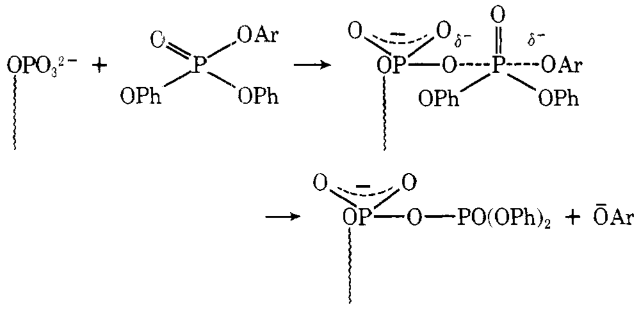
Scheme II



Ar = p-O$_2$NC$_6$H$_4$

The situation is different for deacylation in a micellized amine.[10] Reactions with nonmicellized amines are general base catalyzed, and both water- and amine-catalyzed reactions have been identified in reactions of micellized n-alkylamines with carboxylic esters, suggesting that a proton is transferred from nitrogen in the transition state and a micellized alkylamine could function very effectively as the base.

These observations suggest that micellar catalysis of bimolceular reactions depends on the bringing together of the reactants at the micellar surface prior to reaction, but that unfavorable coulombic interactions between the head groups and the transition state can prevent reaction, even though the reactants are taken up by the micelle. This conclusion should apply to reactions in both chemically inert and functional micelles, and it is consistent with the treatment of micelles as if they behave as a separate phase with their own solvent properties. We also note that micellar effects upon unimolecular reactions are wholly due to free-energy differences between initial and transition states.[20]

Registry No.—I, 10359-36-1; n-BuOPO$_3$Na$_2$, 64114-42-7; NaDodP, 7423-32-7; NaF, 7681-49-4; 2,4-dinitrophenyl-3-phenylpropionate, 23522-80-7; CTABr, 57-09-0; DodTABr, 1119-94-4.

References and Notes

(1) Support of this work by the National Science Foundation and the Institute of Arthritis, Metabolic, and Digestive Diseases of the U.S. Public Health Service is gratefully acknowledged.
(2) On leave from the Faculty of Physical and Mathematical Sciences, University of Chile, Santiago, Chile, under the University of Chile–University of California Cooperative Program.
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Photoinduced Decomposition of Peracetic Acid in Toluene

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Received February 28, 1977

A mixture of peracetic acid and toluene has been photolyzed at room temperature. The main products with 2537-Å light were carbon dioxide, methane, ethane, methanol, ethylbenzene, o-, m-, and p-xylenes, and bibenzyl together with smaller amounts of benzyl alcohol and o-, m-, and p-cresols. On the other hand, with light over 2900 Å, different yields of benzyl alcohol (a main product) and cresols (undetectably small) were observed. The effects of concentration of peracid on yields were studied, and the mechanism and reactivities of methyl and hydroxyl radicals were discussed.

The photolysis of a mixture of peracetic acid and toluene is of particular interest because of the possibility of reaction both with aliphatic and aromatic parts of the toluene molecule. The vapor-phase pyrolysis of peracetic acid in a stream of toluene was reported to involve both radical and wall reactions,[1b] while the thermolysis in liquid phase involves the two simultaneous reactions.[2] The photolysis of peracetic acid in cyclohexane gives cyclohexanol.[3]

As to the reaction of methyl radical with toluene both in the liquid and gas phases, evidences were presented for both addition to the ring and abstraction of hydrogen atom to form methane.[4–7] But there is little information on the yields of the other products besides gaseous products. The reaction of a hydroxyl radical with toluene gives cresols and bibenzyl.[8]

The present paper reports on the photolysis of peracetic acid in toluene. The mechanism of decomposition and the behavior of the produced radicals, i.e., $CH_3\cdot$ and $HO\cdot$ were discussed on the basis of the products analysis.

Results

The photolysis products from peracetic acid in toluene were carbon dioxide, methane, ethane, methanol, methyl acetate, ethylbenzene, xylenes, benzyl alochol, benzaldehyde, cresols, bibenzyl, and a trace of benzoic acid with quartz filter (2537-Å light). An almost similar distribution of products was also obtained with Pyrex-filtered light (>2900 Å), except for a marked decrease in the yield of cresols and an increase of the yield of benzyl alcohol.

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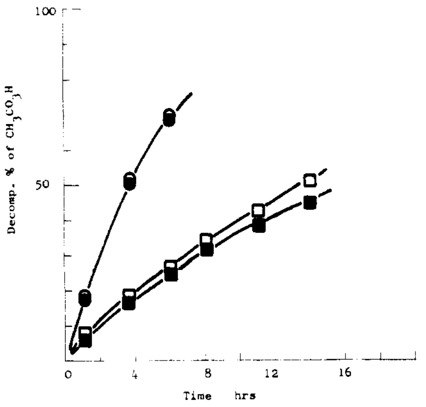


Figure 1. Time dependence of decomposition % estimated by evolved CO_2: (○) measured by iodometry with 2537-Å light, (●) by CO_2 evolution with 2537-Å light, (□) by iodometry with >2900-Å light, and (■) by CO_2 evolution with >2900-Å light. Initial concentration of peracid = 5.00 mmol/25 mL.

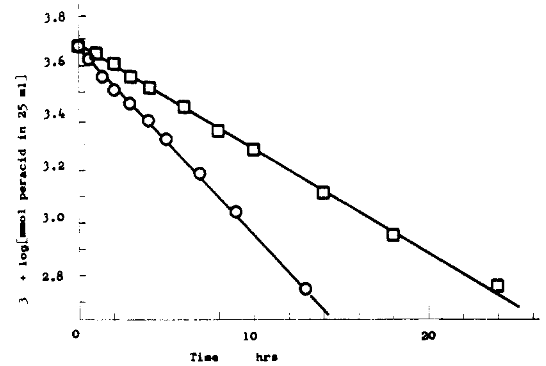


Figure 2. Kinetics of the overall decomposition of peracetic acid: (○) 2537-Å light irradiation, (□) >2900-Å light irradiation. Initial concentration of peracid = 4.58 mmol/25 mL.

Relation between Peracetic Acid Decomposition and CO_2 Evolution. The yield of CO_2 from peracetic acid was measured to see the mode of photolysis. As shown in Figure 1, the photolysis with 2537-Å light is only a radical decomposition giving CO_2, $CH_3\cdot$, and $HO\cdot$, while with >2900-Å light the photolysis proceeds 90% via the radical but 10% via the other mode of decomposition.

The rate of the overall decomposition was first order in peracetic acid (Figure 2), and, hence, [CH_3CO_3H decomposed] = [CO_2 formed] with 2537-Å light, while [CH_3CO_3H decomposed] = [CO_2 formed] + [CH_3CO_2H formed] with >2900-Å light, where [ ] means the molar amount of each compound.

Time Dependence of the Product Yields. The time dependence of product yield and the possibility of further reactions were studied and the yields which vary little with time except for methanol and benzyl alcohol are shown in Figures 3 (2537 Å) and 4 (>2900 Å). Methanol initially formed is partially esterified to methyl acetate with acetic acid originally present, while benzyl alcohol is partially oxidized to benzaldehyde.

The 2537-Å photolysis products with a methyl radical, i.e., ethylbenzene and xylenes, have a higher yield than the products with a hydroxyl radical, i.e., benzyl alcohol and cresols. A remarkable difference between 2537- and >2900-Å light photolysates is the higher yields of benzyl alcohol and bibenzyl and the lower yields of cresols with >2900-Å light.

Effect of Initial Concentration of Peracetic Acid on Product Yield. The effects of the concentrations of peracetic acid and produced radicals on the yield were measured to study the reactivities of methyl and hydroxyl radicals and are shown in Tables I (2537 Å) and II (>2900 Å). Table I leads to eq 1, where [CO_2 evolved] ≈ [methyl radical], i.e.

$$[CH_4 + 2C_2H_6 + CH_3OH + CH_3CO_2CH_3 + PhEt + xylenes] \approx [CO_2] \text{ or } [CH_3\cdot] \quad (1)$$

The yield of methane is 35–45% and that of ethane is ca. 32% per methyl radical, and the yields of methanol and methyl acetate increase with an increase of initial concentration of

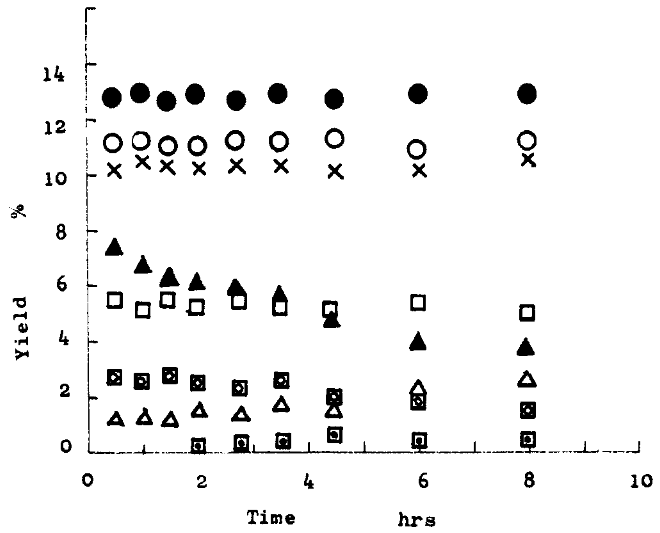


Figure 3. Time dependence of product yields with 2537-Å light decomposition. The yield means the value of the mole of formed compound vs. the mole of decomposed peracid. Initial concentration of peracid = 5.13 mmol/25 mL, decomposition (8 h) = 80%: (▲) methanol, (△) methyl acetate, (○) ethylbenzene, (●) xylenes, (×) bibenzyl, (□) benzyl alcohol, (⊡) benzaldehyde, (□) cresols.

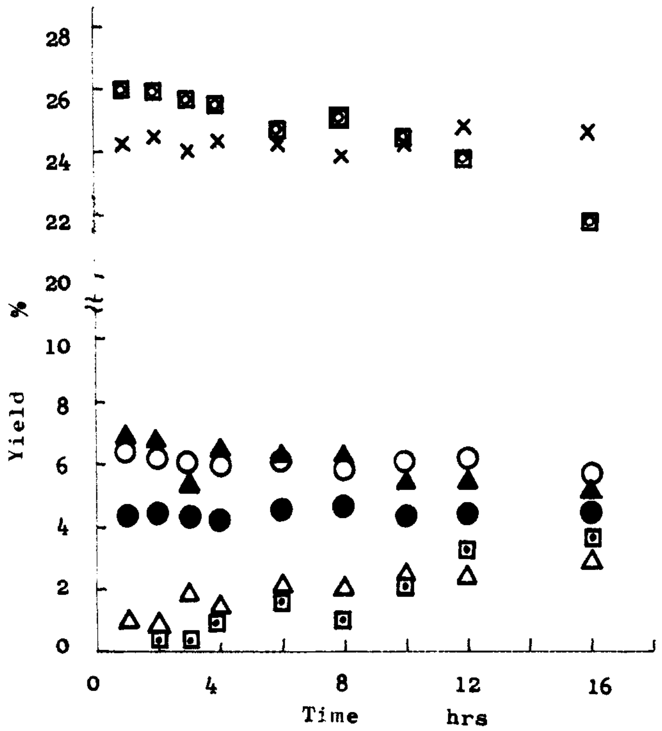


Figure 4. Time dependence of product yields with 2900-Å light decomposition. The yield means the value of the mole of formed compound vs. the mole of decomposed peracid. Initial concentration of peracid = 4.69 mmol/25 mL, decomposition (16 h) = 72%: (▲) methanol, (△) methyl acetate, (○) ethylbenzene, (●) xylenes, (×) bibenzyl, (□) benzyl alcohol, (⊡) benzaldehyde.

Table I. Effect of Peracetic Acid Concentration on the Yield of Products with 2537-Å Light

$[CH_3CO_3H]$[a] × 10 M	$[CH_3CO_3H$ decomposed] × 10^4 mol	Product × 10^4 mol (%)[b]									
		CH_4	C_2H_6	CH_3OH	$CH_3CO_2CH_3$	PhEt	Xylene[c]	$PhCH_2OH$	PhCHO	Cresol[c]	$(PhCH_2)_2$
3.51	54.4	18.5 (34.5)	8.61 (31.6)	3.16 (5.8)	2.65 (4.9)	7.04 (12.9)	7.49 (13.7)	1.77 (3.3)	0.39 (0.7)	1.64 (3.0)	1.90 (7.0)
2.00	43.7	16.0 (36.0)	7.31 (33.5)	1.69 (3.9)	1.57 (3.6)	4.69 (10.7)	5.99 (13.7)	0.75 (1.7)	0.24 (0.5)	2.10 (4.8)	2.37 (10.8)
1.81	30.5	11.3 (37.0)	5.00 (32.3)	1.03 (3.8)	0.76 (2.1)	3.31 (10.9)	3.70 (12.1)	0.44 (1.4)	0.09 (0.3)	1.47 (4.8)	1.64 (10.7)
0.65	13.8	5.62 (40.8)	2.20 (31.9)	0.34 (2.5)	0.20 (1.4)	1.23 (8.9)	1.71 (12.5)	0.31 (2.2)	0.04 (0.3)	0.76 (5.5)	1.11 (16.0)
0.37	7.23	3.25 (45.0)	1.19 (33.0)	0.13 (1.8)	0.06 (0.8)	0.63 (8.9)	0.75 (10.8)	0.16 (2.2)	trace (trace)	0.45 (6.1)	0.53 (14.6)

[a] Amount of sample is 25 mL. [b] (Moles of product/moles of decomposed peroxide) × 100, except for ethane and bibenzyl where this number is doubled. [c] The total amounts of ortho, meta, and para isomers.

Table II. Effect of Peracetic Acid Concentration on the Yields of Products with >2900-Å Light

$[CH_3CO_3H]$[a] × 10 M	$[CH_3CO_3H$ decomposed] × 10^4 mol	Product × 10^4 mol (%)[b]									
		CH_4	C_2H_6	CH_3OH	$CH_3CO_2CH_3$	PhEt	Xylene[c]	$PhCH_2OH$	PhCHO	Cresol	$(PhCH_2)_2$
4.71	51.3	30.4 (59.3)	3.27 (12.8)	2.74 (5.3)	1.64 (3.2)	2.06 (4.0)	2.39 (4.7)	11.3 (22.9)	1.93 (3.8)		2.76 (10.8)
3.77	45.0	29.0 (64.5)	2.27 (10.0)	2.45 (5.4)	1.90 (4.2)	1.75 (3.9)	1.66 (4.2)	10.1 (22.4)	1.70 (3.8)		2.75 (12.2)
2.74	34.2	21.2 (62.1)	2.24 (13.0)	0.97 (2.8)	0.67 (2.0)	1.63 (4.8)	1.40 (4.6)	7.60 (22.2)	2.02 (5.9)		2.97 (17.4)
1.87	23.2	14.0 (59.9)	1.30 (11.6)	1.06 (4.5)	0.43 (1.9)	1.38 (5.9)	1.02 (4.4)	5.83 (24.9)	1.40 (6.0)		2.82 (24.1)
1.06	11.6	7.19 (61.7)	0.66 (11.4)	0.44 (3.8)	0.10 (0.9)	0.92 (7.9)	0.70 (6.0)	2.77 (23.7)	0.53 (4.6)		1.60 (28.7)
0.68	8.90	5.26 (59.4)	0.46 (10.4)	0.39 (4.4)	0.11 (1.2)	0.65 (6.7)	0.65 (6.7)	1.82 (20.5)	0.29 (3.3)		1.17 (26.4)

[a] Amount of sample is 25 mL. [b] (Moles of product/moles of decomposed peroxide) × 100, except for ethane and bibenzyl where this number is doubled. [c] The total amounts of ortho, meta, and para isomers.

Table III. Effect of Peracetic Acid Concentration on the Yield

	2537-Å light		>2900-Å light	
$[CH_3CO_3H]$[a] × 10 M	$[CH_3CO_3H$ decomposed] × 10^4 mol	H_2O × 10^4 mol (%)	$[CH_3CO_3H$ decomposed] × 10^4 mol	H_2O × 10^4 mol (%)
5.08	85.9	25.5 (29.7)	73.1	9.14 (12.5)
2.86	59.0	16.3 (27.6)	48.1	7.94 (16.5)
2.13	45.4	13.8 (30.3)	36.3	6.82 (18.8)
0.94	20.4	5.00 (24.5)	16.5	2.57 (15.6)
0.39	7.80	2.06 (26.4)	7.10	1.58 (22.2)

[a] Initial concentration.

peracid, where methyl acetate is derived from direct photolysis and/or esterification of methanol, whereas the yields of ethylbenzene and xylenes are almost constant and isomer composition of xylenes decreases in the order: meta > ortho > para. In contrast, the yields of hydroxylation products are lower than those of methylation, the isomer composition of cresols being in the order: ortho > para > meta.

Equation 1 is valid with >2900-Å light, but, based on the amount of decomposed peracid, eq 2 is more appropriate.

$$[CH_4 + 2C_2H_6 + CH_3OH + CH_3CO_2CH_3 + PhEt + xylenes] \approx 0.9[CH_3CO_3H \text{ decomposed}] \quad (2)$$

The yields of methane and ethane per decomposed peracid are ca. 60 and 11%, respectively; the yields of ethylbenzene and xylenes decrease only by ca. 2–3% with increasing concentration of peracid. The isomer distribution of xylenes decreases in the order ortho > meta > para at a higher concentration of peracid. The yield of benzyl alcohol based on the decomposed peracid is 20–25% and that of benzaldehyde is 3–6%; the yields of cresols are very low.

A similar effect of peracid concentration on the yield of bibenzyl was observed; i.e., an increase of peracid concentration caused a decrease in the yield, especially with >2900-Å light.

Analysis of Water Produced by Photolysis. A hydroxyl radical formed by direct photolysis of peracid may also abstract a H atom from both toluene and peracetic acid to give water and it may couple with each other to H_2O_2 which then decomposes thermally to H_2O and O_2.

The analysis of water was done by means of GLC with a thermal-conductivity detector (TCD) under similar experimental conditions, and the results are shown in Table III, although the analysis by TCD is less accurate than that by FID. The yields of water per decomposed peracid were 25–30% at 2537 Å and 15–20% at >2900 Å. The observed difference of yields at 2537 and >2900 Å may be due to the difference of HO· radical concentration.

Discussion

Initial Process of Decomposition. In view of the extinction coefficients of toluene and peracetic acid shown in Table IV, the 2537-Å light should be absorbed predominantly by

Table IV. Extinction Coefficient at Various Wavelengths

Compd	ϵ_{240}, nm	ϵ_{254}, nm	ϵ_{290}, nm	ϵ_{300}, nm	ϵ_{360}, nm
$PhCH_3$		170	0.025		
CH_3CO_3H	25[a]		2.40[b]	1.23[b]	0.046[b]

[a] Data by O. H. Wheeler and L. A. Kaplan, "Organic Electron Spectral Data", Vol. 3, Interscience, New York, N.Y., 1966. [b] The value obtained in CH_3OH containing a small amount of acetic acid whose extinction coefficient is negligible at over 290 nm.

toluene, since its extinction coefficient is ca. ten times as large as that of peracid and toluene is in large excess. Then excited toluene transfers energy to peracid, producing two radicals (eq 3–5).

$$PhCH_3 \xrightarrow{h\nu\ (2537\ \text{Å})} [PhCH_3]^* \tag{3}$$

$$[PhCH_3]^* + CH_3CO_3H \rightarrow PhCH_3 + [CH_3CO_3H]^* \tag{4}$$

$$[CH_3CO_3H]^* \rightarrow CH_3CO_2\cdot + \cdot OH \rightarrow CH_3\cdot + CO_2 + \cdot OH \tag{5}$$

$$CH_3CO_3H \xrightarrow{h\nu\ (>2900\ \text{Å})} CH_3CO_2\cdot + \cdot OH \rightarrow CH_3\cdot + CO_2 + \cdot OH \tag{6}$$

In fact, Stern–Volmer plots in quenching fluorescence of toluene by peracetic acid are shown in Figure 5, in which a fairly good linearity was observed. The rate constant for quenching (k_q) was $1.71 \times 10^{10}\ M^{-1}\ s^{-1}$. Therefore, the excited (singlet) toluene may transfer energy to peracid at the diffusion-controlled rate.

On the other hand, the >2900-Å irradiation excites mainly peracetic acid, resulting in the O–O cleavage (eq 6) because the extinction coefficient of peracid is much higher than that of toluene at >2900 Å.

The radical concentration of eq 3–5 may be greater than that of eq 6, since the O–O cleavage via eq 3–5 should be faster, because the decomposition rate by eq 3–5 is much faster than that by eq 6, as shown in Figure 2. This faster rate is due to the higher extinction coefficient of toluene than that of peracetic acid and is also due to the presence of a large excess of toluene.

Induced Decomposition of Peracid by Radicals. Two sorts of radicals ($CH_3\cdot$ and $HO\cdot$) formed initially in eq 5 and 6 may induce following propagation (eq 7–9):

$$PhCH_3 + R\cdot \rightarrow PhCH_2\cdot + RH \tag{7}$$

$$CH_3CO_3\text{-}H + R\cdot \rightarrow CH_3CO_3\cdot + RH \tag{8}$$

$$CH_3CO_2\text{-}OH + CH_3\cdot \rightarrow CH_3CO_2\cdot + CH_3OH \tag{9}$$

$$(R\cdot = CH_3\cdot \text{ and } HO\cdot)$$

The benzyl radical formed in eq 7 may take part in eq 8 and 9. When $R\cdot$ is $CH_3\cdot$, eq 7 and 8 give methane and eq 9 gives methanol. When $R\cdot$ is $HO\cdot$, water is produced by eq 7 and 8; H_2O_2 may also be formed by coupling of $HO\cdot$ (eq 10). The H_2O_2 formed may decompose to water and oxygen (eq 11).

$$2HO\cdot \rightarrow H_2O_2 \tag{10}$$

$$H_2O_2 \rightarrow H_2O + 0.5O_2 \tag{11}$$

Therefore, water may be produced from one or two $HO\cdot$ radicals, and hence the total moles of $HO\cdot$ radicals yielding water is larger than the total moles of produced water.

In the 2537-Å photolysis, total yields of methane and water (from Tables I and III) are 60–70% per decomposed peracid, and total yields of products from toluene are ca. 40%. The results suggest that $CH_3\cdot$ and $HO\cdot$ radicals must abstract a H atom from peracid as *tert*-butoxy radical does,[9] because the quantity of H atoms from toluene is insufficient for total yields of methane and water.

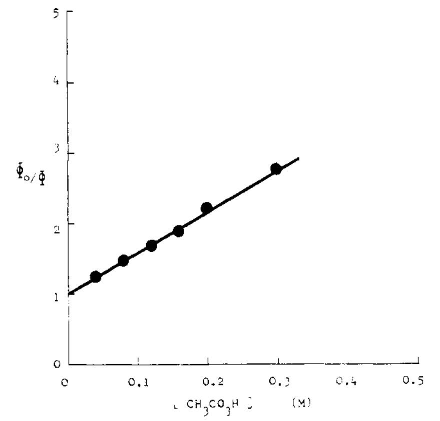


Figure 5. Stern–Volmer plot for quenching of the singlet state of toluene by peracetic acid. Slope ($k_q\tau$) = 5.83, $k_q = 1.71 \times 10^{10}\ M^{-1}\ s^{-1}$, where k_q is the quenching rate constant and τ is the lifetime of lowest singlet state. The value of τ (3.4×10^{10} s) was quoted from S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, N.Y., 1973.

This assumption is further confirmed in the >2900-Å photolysis; i.e., even the yield of methane alone (ca. 60%) is greater than total yields of products from toluene (45–60%). In view of the yields of water (ca. 15%), eq 8 must contribute to the extent of 15–30% for decomposition of peracid. Therefore, assuming an occurence of a dark reaction of ca. 10% and a benzyl radical-induced reaction (eq 9) of ca. 20% (see below), the contribution of eq 6 for total decomposition of peracid may be below 50% at >2900 Å.

Acetylperoxy radical ($CH_3CO_3\cdot$) in eq 8 should decompose to give $CH_3\cdot$, CO_2, and O_2, and also reacts with $CH_3OO\cdot$ to give CH_3CO_2H and HCHO via various known termination steps.[9] Unfortunately, we have no estimation of formed O_2 and CH_3CO_2H yet, since the original solution contains CH_3CO_2H in a large excess (see Experimental Section).

Formation of Methane and Ethane. Ethane may be formed by radical coupling shown in eq 12 and 13. In view of the faster decomposition rate of acetoxy radical ($1.6 \times 10^{-9}\ s^{-1}$ at 60 °C),[10] ethane may mainly be formed via eq 12.

$$2CH_3\cdot \rightarrow C_2H_6 \tag{12}$$

$$2CH_3CO_2\cdot \rightarrow C_2H_6 + 2CO_2 \tag{13}$$

Table V reveals that $[C_2H_6]/[CO_2]$ ($\approx$0.16 with 2537 Å and $\approx$0.065 with >2900 Å light) is little affected by peracid concentration, which indicates that the rate of radical formation is in a steady state. The higher yield at 2537 Å may be due to the higher radical concentration. The thermolysis of peracetic acid in toluene gave no ethane, since the reaction gives acetic acid preferentially, and thus methyl radical concentration is lower.[2] The photolysis proceeds via radical reactions because $[CO_2]$/[decomposed peracid] is close to unity. This decomposition is similar to thermolysis of diacetyl peroxide in toluene[6] with $[CH_4]/[CO_2]$ = 0.65–0.78 and $[C_2H_6]/[CO_2]$ = 0.02–0.047 on the basis of a comparable value of $[CH_4]/[CO_2]$ = 0.65–0.74 and $[C_2H_6]/[CO_2]$ = 0.057–0.072 for our reaction at >2900 Å. But the values at 2537 Å are different, which is attributed to either a higher concentration of methyl radical or the effect of an energy transfer from excited toluene.

Hydrogen Abstraction and Addition of Methyl Radical. A methyl radical in the gas phase does not add to the ring, but the addition to the ring is more important in the liquid

Table V. Decomposition of Peracetic Acid in Toluene

Temp °C	$[CH_3CO_3H]$[a] × 10 M	$\frac{CO_2}{[CH_3CO_3H \text{ decomposed}]}$	$\frac{CH_4}{CO_2}$	$\frac{C_2H_6}{CO_2}$	$\frac{CH_4 + C_2H_6}{CO_2}$
Rt[b]	3.51	1.02	0.33	0.16	0.65
Rt[b]	2.00	0.98	0.37	0.17	0.71
Rt[b]	1.81	0.98	0.38	0.17	0.72
Rt[b]	0.65	1.01	0.40	0.16	0.72
Rt[b]	0.37	1.02	0.44	0.16	0.76
Rt[c]	4.71	0.89	0.66	0.072	0.80
Rt[c]	3.77	0.87	0.74	0.058	0.86
Rt[c]	2.74	0.92	0.67	0.071	0.81
Rt[c]	1.87	0.86	0.70	0.068	0.84
Rt[c]	1.06	0.89	0.70	0.064	0.83
Rt[c]	0.68	0.91	0.65	0.057	0.76
74.9[d]	0.14		0.88		
85.0[d]	0.23	0.07	0.72		
94.8[d]	0.14		0.76		
64.9[e]	0.068	0.86	0.78	0.047	0.87
64.9[e]	0.081	0.87	0.66	0.040	0.74
64.9[e]	0.663	1.01	0.67	0.020	0.71
64.9[e]	0.675	0.93	0.65	0.034	0.72

[a] Initial concentration. [b] At room temperature, with 2537-Å light irradiation. [c] At room temperature, with >2900-Å light irradiation. [d] Data summarized for thermal decomposition of peracetic acid by F. W. Evans and A. H. Sehon, *Can. J. Chem.*, 41, 1826 (1963). [e] Data summarized for thermal decomposition of diacetyl peroxide in toluene by M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 5981 (1954).

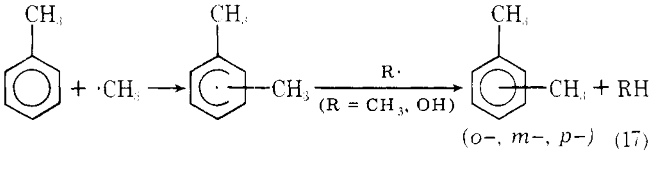
phase.[11] The yields of xylenes (10–14%) increase slightly with an increase of peracid concentration (Table I). The formation of methane is suppressed as the peracid concentration increases; hence, the addition of a methyl radical to the ring and the coupling of a methyl radical with other radicals become important. The yield of $CH_3\cdot$ radical addition at >2900 Å is smaller than that at 2537 Å, and the yields of H abstraction are the reverse order. This difference may be due to the difference in rate of $CH_3\cdot$ radical formation.

A probable mechanism for the formation of methane, ethylbenzene, and xylene is shown in eq 14–17.

$$PhCH_3 + \cdot CH_3 \rightarrow PhCH_2\cdot + CH_4 \quad (14)$$

$$CH_3CO_3\text{-}H + \cdot CH_3 \rightarrow CH_3CO_3\cdot + CH_4 \quad (15)$$

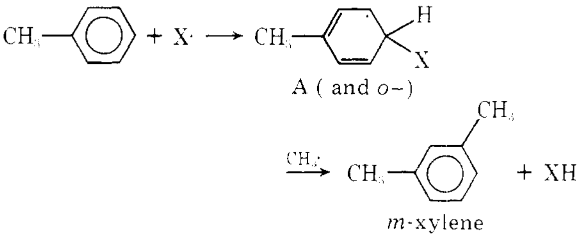
$$CH_3\cdot + PhCH_2\cdot \rightarrow PhCH_2CH_3 \quad (16)$$



(17)

In view of the strong aromatic C–H bond as compared to a benzylic C–H bond, the formation of methane via direct abstraction of a ring H atom by a $CH_3\cdot$ radical is unlikely. As stated above, the total yields of methane and water are larger than those of products obtained from toluene. Hence, H abstraction of peracid by $CH_3\cdot$ may occur considerably (eq 15). Ethylbenzene is obtained in yields of 9–13 and 4–8% at 2537 and >2900 Å, respectively, though the photolysis of azomethane in toluene is reported to give enthybenzene in a lower yield than that of *o*-xylene.[11] The observed high yield of ethylbenzene in the liquid phase is explained by the longer life of the benzyl radical and the higher concentration of the $CH_3\cdot$ radical in comparison with the above report.[11]

The formation of xylene may involve addition of a $CH_3\cdot$ radical to the ring followed by H abstraction by other radicals ($CH_3\cdot$ and $HO\cdot$) (eq 17). The isomer content of xylenes is in the order: meta > ortho > para at 2537 Å and ortho > meta > para at >2900 Å (Table VI). The electrophilic addition to the ground-state toluene (>2900 Å) predicts the order ortho > meta, para, and the order agrees at least with the higher yield of ortho isomer at >2900 Å, which is also in accord with the result of the photolysis of azomethane in toluene[11] and of the thermolysis of diacetyl peroxide[12] with the order ortho > meta > para. On the other hand, the frontier electron density in the excited toluene calculated by the CI method predicts the order meta > para,[13] which is in accord with our observation at 2537 Å. Another explanation of *m*-xylene formation is shown in eq 18.



(18)

$(X = CH_3CO_2, HO, \text{and/or } PhCH_2)$

The release of a radical by the attack of another radical in the transition state (A) is reported when the attacking radical is a benzoyloxy radical.[14–16] But no evidence for the presence of A and its derivatives was obtained now in these photolyses.

The Reaction of Hydroxyl Radical with Toluene. There are four possible mechanisms for the formation of benzyl alcohol, i.e., coupling (eq 19), the "induced reaction" (eq 20), a toluene–peracid complex decomposition (eq 21), and a toluene–molecular oxygen complex (eq 22).

$$PhCH_2\cdot + \cdot OH \rightarrow PhCH_2OH \quad (19)$$

$$PhCH_2\cdot + CH_3CO_2\text{-}OH \rightarrow PhCH_2OH + CH_3CO_2\cdot \quad (20)$$

$$[PhCH_3 \cdot CH_3CO_3H]^*_{complex} \rightarrow PhCH_2OH + CH_3CO_2H \quad (21)$$

$$[PhCH_3 \cdot O_2]^*_{complex} \rightarrow PhCH_2OH + PhCHO + PhCH_2OOH^{17} \quad (22)$$

Equation 22 is negligible because neither PhCHO nor $PhCH_2OH$ is detectable in the absence of peracid and the ratio $[PhCH_2OH]/[PhCHO]$ is over 3; in contrast to the literature value (below 1),[17] the yield of PhCHO increases with time. Equation 21 can also be eliminated, because eq 21 evolves no CO_2.

In spite of the lower concentration of $HO\cdot$, the yield of $PhCH_2OH$ at >2900 Å is considerably larger than that at 2537 Å. Hence, the major process for formation of $PhCH_2OH$ at >2900 Å may be a reaction induced by $PhCH_2\cdot$ (eq 20), as exemplified by the photolysis of peracetic acid in cyclohexane leading to cyclohexanol,[3] where the participation of eq 19 is small. The yield of $PhCH_2OH$ is only a few percent, though the concentration of $HO\cdot$ is high at 2537 Å. Therefore, at low radical concentration, the longer-lived $PhCH_2\cdot$ compared with $CH_3\cdot$ and $HO\cdot$ plays an important role for the formation of $PhCH_2OH$.

In the 2537-Å photolysis, eq 19 becomes more important in comparison with >2900-Å photolysis, since $[HO\cdot]$ is higher at 2537 Å.

Cresols, which may be produced via an attack of $HO\cdot$ on toluene (eq 23), were favored at 2537 Å. The trace formation of cresols at >2900 Å is attributable to low $HO\cdot$ concentration (eq 6) on account of the consumption of peracid in eq 7–9 and 20 as stated above. The less formation of hydroxyl compounds ($PhCH_2OH$ and cresols) compared with methyl compounds

Table VI. The Isomer Distribution of Xylene

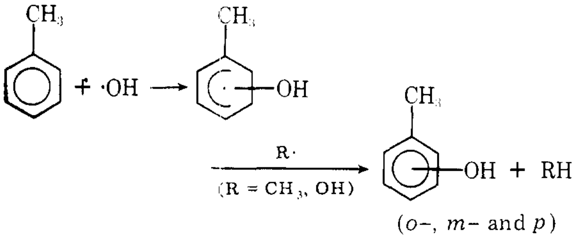
$[CH_3CO_3H]$[a] × 10 M	$[CH_3CO_3H$ decomposed] × 10^4 mol	Xylene × 10^4 mol (orientation %)			$[CH_3CO_3H]$[b] × 10 M	$[CH_3CO_3H$ decomposed] × 10^4 mol	Xylene × 10^4 mol (orientation %)		
		o-	m-	p-			o-	m-	p-
3.51	54.4	2.64	4.19	0.66	4.71	51.3	1.36	0.78	0.25
		(35)	(56)	(9)			(57)	(32)	(11)
2.00	43.7	1.95	3.34	0.70	3.77	45.0	0.95	0.53	0.18
		(33)	(56)	(11)			(57)	(32)	(11)
1.81	30.5	1.15	2.08	0.47	2.74	34.2	0.84	0.38	0.18
		(31)	(56)	(13)			(60)	(27)	(13)
0.65	13.8	0.53	0.94	0.24	1.87	23.4	0.56	0.32	0.14
		(31)	(55)	(14)			(55)	(31)	(14)
0.37	7.23	0.27	0.40	0.08	1.06	11.6	0.34	0.24	0.12
		(36)	(53)	(11)			(49)	(34)	(17)

[a] Irradiation with 2537-Å light. [b] Irradiation with >2900-Å light.

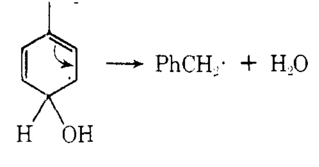
Table VII. The Isomer Distribution of Cresols in the Photolysis with 2537-Å Light

$[CH_3CO_3H]$ × 10 M	$[CH_3CO_3H$ decomposed] × 10^4 mol	Cresol × 10^4 mol (orientation %)		
		o-	m-	p-
3.54	54.4	0.97	0.17	0.50
		(59)	(10)	(31)
2.00	43.7	1.23	0.12	0.75
		(59)	(6)	(35)
1.81	30.5	0.85	0.09	0.53
		(58)	(6)	(36)
0.65	13.8	0.45	0.05	0.26
		(59)	(7)	(34)
0.37	7.23	0.30	trace	0.15
		(67)		(33)

(PhEt and xylenes) at 2537 Å is attributable to its more effective radical abstraction from peracetic acid (eq 8 and 9) and from toluene by HO· than by CH_3· leading to the lower concentration of HO· than CH_3·. Further, cresols may give a benzyl radical (eq 24)[8] by acid-catalyzed elimination of water.



(23)



(24)

The yields of cresols were low (ca. 3–6%) with 2537 Å light, though a high concentration of HO· is expected. Their isomer distribution (o- > p- > m-) (Table VII) is consistent with the electrophilic nature of the HO· radical.[18] The observed difference between xylenes and cresols in their isomer distributions is attributable to the more random attack of the reactive HO· radical, which favors ortho and meta attack in a factor of 2. In fact, the photolysis of H_2O_2 in toluene affords also cresols in the similar distribution of ortho > para > meta.[8]

The Small Cage Reaction of the Formation of Methanol. Methanol may be formed by coupling in or out of a cage (eq 25 and 26, respectively) and/or by the reaction of a CH_3· radical with peracid (eq 27).

$$[CH_3\cdot + CO_2 + \cdot OH]_{cage} \rightarrow CH_3OH + CO_2 \quad (25)$$

$$CH_3\cdot + \cdot OH\ (\text{free}) \rightarrow CH_3OH \quad (26)$$

$$CH_3\cdot + CH_3CO_2\text{-}OH \rightarrow CH_3OH + CH_3CO_2\cdot \quad (27)$$

The fact that yield increases with increasing peracid concentration indicates that eq 26 and 27 may be major pathways, though the cage reaction (eq 25) is not eliminated. Equation 26 is less important at >2900 Å because of the low [HO·].

Methyl acetate may be formed by eq 28, 29, and/or 30, but actually reaction 28 and 29 are negligible at 2537 Å because $[CO_2]$/[decomposed peracid] is almost at unity; hence,

$$CH_3CO_2\cdot + \cdot CH_3 \rightarrow CH_3CO_2CH_3 \quad (28)$$

$$CH_3CO_2\text{-}OH + \cdot CH_3 \rightarrow CH_3CO_2CH_3 + \cdot OH \quad (29)$$

$$CH_3OH + CH_3CO_2H \rightarrow CH_3CO_2CH_3 + H_2O \quad (30)$$

esterification with acetic acid present in the starting material (eq 30) is the most probable pathway for methyl acetate. The ratio $[CO_2]$/[decomposed peracid] for >2900 Å is ca. 0.9 and, therefore, ca. 10% of peracid decomposition proceeds via no evolution of CO_2. But a CH_3CO_2· radical should decompose rapidly to form a CH_3· radical and CO_2 rather than eq 28. A similar yield of methanol at >2900 and 2537 Å (Table I and II) may be due to the participation of eq 29 and 30 which also afford methyl acetate.

Finally, an increase of bibenzyl formation with a decrease of peracid concentration may be due to the stability of a $PhCH_2$· radical relative to CH_3· and HO· radicals. Thus, coupling between $PhCH_2$· radicals is preferred to coupling of a $PhCH_2$· radical with the other radicals at lower peracid concentration.

Our results on peracetic acid photolysis show that both CH_3· and HO· may abstract both H of RCO_3-H and HO of RCO_2-OH and that their abstraction reactions compete with toluene-induced photolysis or direct photolysis (eq 3–5 and 6). The induced decomposition of peracid by CH_3· or HO· becomes predominant at >2900 Å, and the direct photolysis is suppressed to below 50% per decomposed peracid.

Experimental Section

Materials. Peracetic acid was prepared by the reaction of $(CH_3CO)_2O$ (205 g) with 60% aqueous H_2O_2 added with concentrated H_2SO_4 (0.5 mL) at 35–40 °C.[19] Toluene was purified by distillation over P_2O_5. A water-free peracetic acid–toluene solution was prepared by the method of Hormer;[20] i.e., 40–50 g of P_2O_5 was suspended in 200 mL of dried toluene and 20–50 mL of 3.0–3.5 M peracetic acid was added slowly under cooling and stirring. After 10–15 min, the solution was filtered and then the mixture of a water-free peracetic acid and toluene was immediately irradiated after the estimation of peracid concentration.

Apparatus. UV spectra were measured by a Hitachi 124 spectrophotometer. GLC analyses were performed on a Yanagimoto gas chromatograph with FID, Model GCG-550F, and on a Yanagimoto gas chromatograph with FID and TCD, Model G 180. A Hitachi RMS-4 gas chromatograph–mass spectrometer was used to determine gaseous 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 burette (300 mL volume) connected with a capillary tube to the photolysis system. Analysis of CO_2 in the gas, carried out by the measurement of the volume absorbed in 33% aqueous KOH, and then analysis of O_2 were done by measurement with an alkaline pyrogallol solution[21] or a Fieser's solution,[22] in which a little of O_2 was evolved with both 2537- (quartz vessel) and >2900-Å light (Pyrex vessel), but the reproducibility of the analysis of O_2 was poor because of insufficient exclusion of the present O_2 in the initial solution and/or considerable solubility of O_2 in this solution. Gaseous products which remained in the gas burette were analyzed by GC–MS and GLC with two sorts of columns packed with Porapak Type T (80–100 mesh, 2.5 mm × 2 m) and Porapak Type QS (80–100 mesh, 2.5 mm × 2 m), and analyses of mass peaks of CH_4 and C_2H_6 were carried out by the comparison of standard samples.[23] The other CO_2 estimation was carried out by acidimetry of aqueous $Ba(OH)_2$ which had been bubbled by the gas together with N_2 as a carrier gas.

Photolysis of a Mixture of Peracetic Acid and Toluene. A mixture of peracetic acid and toluene 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-cooling jacket. Gaseous products evolved were analyzed by the above method and the products in the solutions were analyzed by GLC with four sorts of columns (Porapak Type QS, Bentone 34-DIDP, PEG 20M Chamelite CS, and Apiezon Grease L). All peracid which remained in photolyzed solutions were decomposed with $Na_2S_2O_3$ or Na_2SO_3 under cooling (−15 to −20 °C) to remove peracid and then analyzed by GLC. This method gave always reproducible data within experimental error.

Analysis of water was carried out alternatively. After estimation of peracid remained in the solution, a constant amount of Me_2SO–toluene was added to the photolysate to avoid the formation of water by GLC thermolysis, and this solution was analyzed by GLC with TCD (Porapak QS column) in triplicate runs.

Quenching of the Singlet State of Toluene. A toluene–peracetic acid solution diluted with isopentane 100-fold was used because of the strong self-quenching ability of toluene. Fluorescence spectra of toluene were measured with a Hitachi fluorescence spectrophotometer, Model MPF-2A, at room temperature and appeared at λ_{max} 284 nm, the optimum excitation wavelength was 240 nm, and the red shift was observed by an increase of peracetic acid concentration. No fluorescence of peracetic acid was observed, and no quenching fluorescence of toluene by acetic acid was observed. Stern–Volmer plots for quenching of excited toluene showed a good linearity within 0–0.3 M peracetic acid concentration.

Registry No.—peracetic acid, 79-21-0; toluene, 108-88-3; methyl radical, 2229-07-4; hydroxyl radical, 3352-57-6.

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