

Photoinduced Decomposition of Peracetic Acid in Isopropylbenzene¹⁾

Yoshiro OGATA* and Kohtaro TOMIZAWA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464

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Synopsis. Irradiation of peracetic acid in isopropylbenzene with 254 nm and over 290 nm lights gave as aromatic products mainly *t*-butylbenzene, 2-phenyl-2-propanol, and 2,3-dimethyl-2,3-diphenylbutane. The yield of *t*-butylbenzene was higher in 254 nm photolysis than that with >290 nm, while the yield of hydroxylated aromatics, *i. e.*, 2-phenyl-2-propanol, was much higher with >290 nm than that with 254 nm. The distribution of products was little affected by the intensity of light. These results are discussed by a mechanism involving radicals of different reactivity derived from peracetic acid decomposition.

As reported by us previously, the photolysis of peracetic acid in aromatic hydrocarbons gives fairly stable radicals (*e.g.*, benzyl radical), which in >290 nm photolysis react with peracetic acid through an induced reaction to give hydroxylated product (*e.g.*, benzyl alcohol), but in 254 nm photolysis the contribution of this induced decomposition was less than that at >290 nm.²⁻⁴⁾

The change of decomposition rate of peracid with changing light intensity affects the rate of radical formation but affects little the distribution of products.⁴⁾ Therefore, the marked difference in yields in 254 nm and >290 nm photolyses may depend on the wavelength.⁴⁾

In this paper, we selected isopropylbenzene because α -H-atom of isopropylbenzene is easily abstracted to give a stable radical, $\text{PhMe}_2\dot{\text{C}}$; this solvent is suitable for examination of the possibility of exciplex formation.

Results and Discussion

The photolysis of peracetic acid (**1**) in isopropylbenzene was carried out with three sorts of light sources, *i.e.*, a 30 W low-pressure Hg lamp (254 nm light), a 300 W (>290 nm light), and a 1 kW high-pressure Hg lamp (>290 nm light). Table 1 shows the product yields which are average of six runs at $1.2\text{--}30.9 \times 10^{-2}$ M peracid concentration. These products were identified by GLC and GC-MS in comparison with their authentic samples.

Formed butylbenzenes (side chain methylation products) are consisted of *s*- and *t*-butylbenzene, the ratio of yields for *s*:*t* being 1:5—7. The low ratio is due to the easier abstraction of tertiary H-atom of the side chain than that of primary H-atom. Isopropyltoluenes (cymenes), which were formed by an attack of methyl radical on the ring, gave yields of three isomers in the order; ortho>meta \approx para at both 254 nm and >290 nm.

2-Phenylpropanols were formed by side chain hydroxylation. The yield of 2-propanol was much higher than 1-propanol. Isopropylphenols were obtained by hydroxylation of the ring in the order of yield: ortho \geq para>meta. 2,3-Dimethyl-2,3-diphenylbutane was formed by the coupling of radical $\text{PhMe}_2\dot{\text{C}}$; furthermore, an adduct of radical $\text{PhMe}_2\dot{\text{C}}$ to the ring,

TABLE 1. PRODUCTS AND YIELDS IN PHOTOLYSIS OF PERACETIC ACID (**1**) IN ISOPROPYLBENZENE (**2**)^{a)}

Products (%) ^{b)}	Light (nm)		
	254	>290(1 kW)	>290 (300 W)
Oxygen	6.4	4.2	5.7
Water	38.6	19.7	18.0
Methane	40.6	68.3	74.2
Ethane	5.9	2.8	1.6
Methanol	8.6	9.9	4.6
Butylbenzenes ^{c)}	21.2	7.0	5.0
Isopropyltoluenes ^{d)}	6.0	2.5	2.7
2-Phenylpropanols ^{e)}	14.1	46.6	42.5
Isopropylphenols ^{f)}	3.9	3.5	1.4
2,3-Dimethyl-2,3-diphenylbutane	24.6	31.1	28.1

a) The average of six runs. b) (Mol of product/mol of decomposed **1**) $\times 100$, except with oxygen, ethane, and 2,3-dimethyl-2,3-diphenylbutane, for which this figure is doubled. c) Total amounts of *s* and *t*-isomers. d) Total amounts of ortho, meta, and para-isomers. e) Total amounts of 2-phenyl-1-propanol and -2-propanol. f) This value contains that of $\text{PhMe}_2\text{C}-\text{C}_6\text{H}_4-\text{CHMe}_2$.

$\text{PhMe}_2\text{C}-\text{C}_6\text{H}_4-\text{CHMe}_2$, was detected by GC-MS (see Experimental).

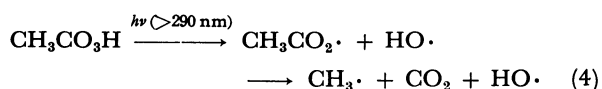
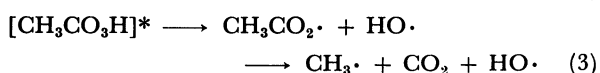
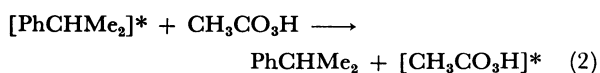
In this photolysis, there were little time dependence within 80% conversion of **1** and little effect of the peroxy acid concentration on the product yields, except for 2,3-dimethyl-2,3-diphenylbutane, a dimerization product of $\text{PhMe}_2\dot{\text{C}}$, yield of which increased ($\approx 10\%$) with decreasing peroxy acid concentration. This decrease of peracid concentration favors the fraction of addition of $\text{PhMe}_2\dot{\text{C}}$ to isopropylbenzene to form $\text{PhMe}_2\text{C}-\text{C}_6\text{H}_4-\text{CHMe}_2$ rather than coupling of $\text{PhMe}_2\dot{\text{C}}$ with other radicals.

The half-times for decomposition of peracetic acid depend on the lamp in the order: 1 kW (>290 nm) < 30 W (254 nm) < 300 W (>290 nm); *e.g.*, *ca.* 2 h with a 1 kW lamp (>290 nm), *ca.* 4 h with a 30 W lamp (254 nm), and *ca.* 8 h with a 300 W (>290 nm) at 2.19×10^{-1} M peracid. The highest concentration of radicals is expected with a 1 kW lamp.

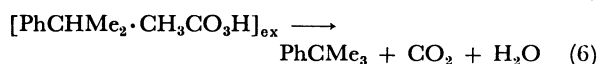
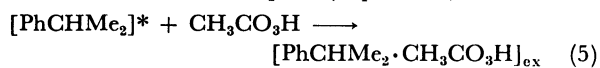
As apparent from Table 1, the product distribution with >290 nm (1 kW) is similar to that with >290 nm (300 W), but different from that with 254 nm; these results are inconsistent with the rate of peroxy acid decomposition, *e.g.*, the yields of butylbenzenes were higher at 254 nm than those at >290 nm, but the yields of 2-phenylpropanols were reversed. Therefore, this discrepancy between the yields and the rate of peracid decomposition suggests that, even in isopropylbenzene, the product distribution depends on the wavelength rather than the light intensity.

This is explicable by the difference of excited species, *i.e.*, aromatic solvent which is in large excess is mainly excited with 254 nm light, transferring the excited energy to peroxy acid (Eqs. 1—3), but peracetic acid is excited directly by >290 nm light (Eq. 4), in view of no absorbance of >290 nm light by aromatics.



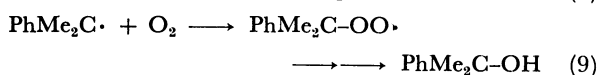
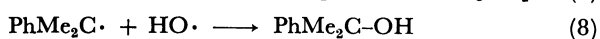
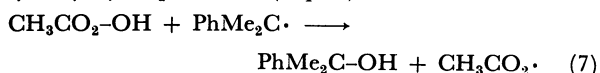


Active species generated *via* Eqs. 1–3 with 254 nm light are identical with those *via* Eq. 4 with >290 nm light. Therefore, assuming that all products are formed *via* these species, the product distribution should be similar in 254 nm and >290 nm photolyses, but this is not the case (Table 1). The higher yield of methylated aromatics with 254 nm may be explained by the formation of a sort of exciplex (Eqs. 5–6).⁴⁾



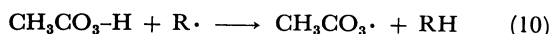
On the other hand, a main path for *t*-butylbenzene at >290 nm may be radical coupling between $\text{PhMe}_2\text{C}\cdot$ and $\text{Me}\cdot$.

The reactivity of radical $\text{HO}\cdot$ is higher than that of $\text{Me}\cdot$; *i.e.*, both the H-abstraction by $\text{HO}\cdot$ and the addition of $\text{HO}\cdot$ to the ring are faster than those of $\text{Me}\cdot$,⁵⁾ but in spite of the higher decomposition rate of peracetic acid with >290 nm (1 kW), the yields of water and isopropylphenols at >290 nm (1 kW) are lower than the yields at 254 nm. Therefore, the preferential formation of 2-phenylpropanol at >290 nm is attributable to the effective reaction of HO-group of peracetic acid; *i.e.*, to the induced decomposition of peracetic acid by $\text{PhMe}_2\text{C}\cdot$ (Eq. 7) beside radical coupling (Eq. 8) and the pathway *via* 1-methyl-1-phenylethylhydroperoxide (Eq. 9).



The pathway *via* Eq. 9 is possible, because the reaction of radical $\text{R}\cdot$ with O_2 gives $\text{ROO}\cdot$, followed by the formation of hydroxylated compound.⁶⁾

Oxygen evolved in this system may be formed *via* dark disproportionation of peroxy acid and/or decomposition of acetylperoxyl radical.⁷⁾ Therefore, the induced decomposition (Eq. 10) was confirmed by the evolution of O_2 and by the higher yields of methane and water than the total yields of aromatic products. Hence, peracetic acid is one of H-atom sources.



These results have been observed with toluene and ethylbenzene. In conclusion, (i) the yields of methylated aromatics are higher at 254 nm than those at >290 nm. (ii) Hydroxylation of side chain occurs probably *via* Eqs. 7, 8, and 9. The higher yields of hydroxylated products at >290 nm than at 254 nm may be due to the Eq. 7, which needs $\text{CH}_3\text{CO}_3\text{H}$ and hence favored

at >290 nm than at 254 nm. Therefore, hydroxylation of side chain is a preferential pathway at >290 nm.

Experimental

Materials. The syntheses of peracetic acid (1) and a water-free peracetic acid-isopropylbenzene solution were described in our previous paper.^{2–4)} Samples of commercial guaranteed reagent grade were used as authentic samples of GLC.

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. 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) and were repeated in triplicate.

Photolysis of Peracetic Acid in Isopropylbenzene. Peracetic acid in isopropylbenzene 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 remained in the solution, a given amount of Me_2SO -benzene was added to the photolytate to avoid the contamination caused by the peracid thermolysis during GLC. Gaseous products were analyzed by the method previously described^{2,3)} and the products in the solutions were identified and estimated by GLC with FID and TCD (Porapak QS, Bentone 34-DIDP and PEG 20M-Silicone DC 550) in comparison with authentic samples.

GC-MS Analysis of Aromatic Products. Photolysis products were characterized by means of GC-MS employing a column packed with Bentone 34-DIDP for aromatic hydrocarbons as follows: *t*-butylbenzene, *m/e* 134 (M^+), 119 (base peak), 41, and 39; *s*-butylbenzene, *m/e* 134 (M^+), 106, 105 (base peak), and 91; isopropyltoluene, *m/e* 134 (M^+), 119 (base peak), and 91, the elution order of isopropyltoluenes by GLC was para, meta, and ortho-isomer. Other aromatic products were characterized by a column packed with PEG 20M-Silicone DC 550; 2-phenyl-1-propanol, *m/e* 136 (M^+), 106, 105 (base peak), 103, 92, and 91; 2-phenyl-2-propanol, *m/e* 136 (M^+), 121, 118, 117, 115, 108, 91, and 43 (base peak); isopropylphenols, *m/e* 136 (M^+) and 121 (base peak); coupling product, 2,3-dimethyl-2,3-diphenylbutane, *m/e* 238 (M^+) and 119 (base peak); $\text{PhMe}_2\text{-C}_6\text{H}_4\text{-CHMe}_2$, *m/e* 238 (M^+) and 223 (base peak).

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