PHOTOCHEMICAL REACTION OF DIACYL PEROXIDES WITH AROMATIC COMPOUNDS. EFFECTS OF TEMPERATURE AND WAVELENGTH ON THE ORIENTATION OF RADICAL SUBSTITUTION[1]

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Abstract

The orientation in aromatic substitution of methyl and phenyl radicals generated in the decomposition of acyl peroxide under u. v. irradiation has been studied. Methyl radical, generated from acetyl peroxide, reacts with toluene to give xylenes, where their isomer distribution depends on both wavelength and temperature and is in the order of ortho > meta > para with 254nm light at 30°C, but the meta fraction increases with decreasing temperature leading to meta > ortho > para below −50°C. On the other hand, the orientation with > 290nm light is the same as that for thermal dark reaction, and is almost independent of the temperature. The analogous photochemical methylation of anisole with acetyl peroxide and phenylation of toluene with benzoyl peroxide show little dependence on temperature and wavelength. Conceivable mechanisms for these reactions are discussed.

Introduction

In our previous paper,[2] the photochemical reactions of acetyl and benzoyl peroxides with toluene at room temperature were reported.

Phenyl radical, generated by the photolysis of benzoyl peroxide, reacts with toluene to give methylbiphenyls, whose isomer distribution is the same as that of thermal reaction: $o/2>p>m/2$, irrespective of the wavelength. On the other hand, the isomer distribution of xylenes from the reaction of acetyl peroxide with toluene shows a wavelength dependence; *i. e.*, the orientation with 254nm light is $o/2>m/2>p$, while the orientation with >290nm light is $o/2>p>m/2$, which is the same order as that in thermolysis.

We wish to report here the further experiments on the effect of temperature concerning the orientation for photochemical methylation and phenylation of toluene and anisole by the corresponding radicals generated from diacyl peroxides.

Results and Discussion

Reaction of Acetyl Peroxide with Toluene

Photolyses of acetyl peroxide in excess toluene were conducted at $-70°C \sim +70°C$, giving isomeric xylenes with distribution listed in Table 1.

Table 1. Isomer distributions of xylenes produced in photolysis of acetyl peroxide in toluene at various temperatures[a]

Wavelength (nm)	Temp. (°C)	Xylene composition		
		ortho (%)	meta (%)	para (%)
>290	30	57	27	16
>290	20	56	26	18
>290	−40	47	32	21
>290	−50	48	34	18
254	70	57	27	16
254	30	51	35	14
254	10	50	40	10
254	−20	39	41	20
254	−50	40	45	15
254	−70	37	51	12
[b]	70	57	27	16

[a] 300W and 1kW high-press. Hg lamps with a Pyrex cell were used for >290nm irradiation and a 30W low-press. Hg lamp with a quartz cell was used for 254nm irradiation.
[b] Thermal reaction.

The reaction with >290nm light at $-50°C \sim +30°C$ affords orientation at all temperatures: ortho>meta>para or $o/2>p>m/2$ taking the statistical factor 2 for o and m positions. In contrast, the reaction at 254nm shows a marked temperature dependence of orientation, i. e., the order $o/2>p>m/2$ at 70°C is the same with that in the thermal reaction, while the order: $m/2>o/2<p$ at $-50°C \sim -70°C$ is quite different from the order in the thermolysis.

The above data may be explained as follows. Toluene does not absorb>290nm light,[2] while acetyl peroxide absorbs both 254 and >290nm lights. The photolysis of acetyl peroxide to methyl radical at >290nm occurs by its direct absorption. Xylenes are formed by substitution of methyl radical on ground-state toluene, giving the orientation governed by the electronic density. In this case, $CH_3COO\cdot$ radical may rapidly decompose to $CH_3\cdot + CO_2$ ($k=1.6\times10^9 s^{-1}$ at 60°C),[3] and will react with ground-state toluene.

On the other hand, the photolysis of acetyl peroxide at 254nm occurs via an

energy transfer from toluene.   The fluorescence of toluene was quenched by addition of acetyl peroxide with the diffusion controlled rate; $i. e.$, the Stern-Volmer plot[4] of fluorescence intensity vs. Peroxide concentration[5] gave a very large second-order rate constant for energy transfer (3.2×10^9 $M^{-1}s^{-1}$) in spite of lower singlet excitation energy of toluene ($E_s = 105$kcal/mol)[6] than that of acetyl peroxide ($E_s =$ ca. 120kcal/mol) estimated by MINDO/3 method using the reported configuration.[7]   Further, the rate constant for the quench of fluorescence of anisole, which was measured by the same method as that of toluene, was a value of 1.1×10^{10} $M^{-1}s^{-1}$.   This value for anisole is higher than that of toluene in spite of the lower singlet energy of aromatic sensitizer ($E_s = 102$ kcal/mol for anisole).[6]   Hence the energy may be transferred via an exciplex formation as in the photolysis of benzoyl peroxide.[8]   The exciplex, in which excited toluene may have an electron distribution different from that of ground state, would result in the observed abnormal orientation, especially at low temperature probably because of decreasing contribution of the thermal radical reaction.

An alternative mechanism is conceivable, which involves a simultaneous addition of acetoxy and methyl radicals to form **1a** or **1b** in a solvent cage, followed by elimination of acetic acid to give m-xylene.[9]

$$\text{(1)}$$
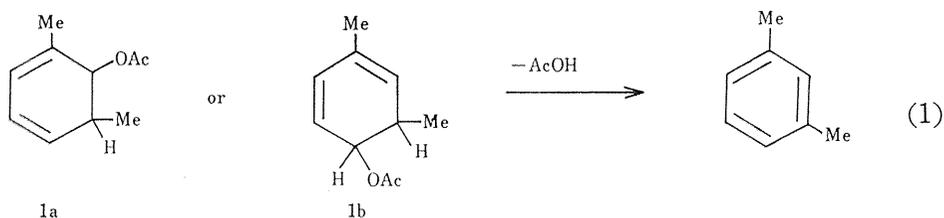
A trace of acetic acid was detected, which may be formed in equation 1, but not in outside of the solvent cage.   Since the stability of AcO· radical increases with decreasing temperature,[10] the contribution of this mechanism would increase with lowering temperature.   In contrast, the photolysis of acetyl peroxide at >290 nm does not occur via excited toluene; hence AcO· and Me· radicals may not be in proximity and in suitable positions for an attack on benzene carbon, thus resulting in the same orientation as that in thermolysis.

Table 2. Isomer distributions of methylbiphenyls in photolysis of
benzoyl peroxide in toluene

Wavelength (nm)	Temp. (°C)	Methylbiphenyl composition		
		ortho (%)	meta (%)	para (%)
>290	30	68	18	14
>290	−45	68	20	12
254	30	64	21	15
254	5	62	24	14
254	−50	64	23	13
a	80	65	21	14

a Thermal reaction.

Reaction of Benzoyl Peroxide with Toluene

Photolyses of benzoyl peroxide in toluene giving isomeric methylbiphenyls were conducted at $-50°C \sim +30°C$ and summerized in Table 2.

The isomer distribution is analogous to that of thermolysis and varies little with wavelength and temperature. This can be explained by the faster and less selective nature of reaction of phenyl radical than methyl radical.

Reaction of Acetyl Peroxide with Anisole

Acetyl peroxide dissolved in excess anisole was photolyzed at $-60°C \sim +20°C$ to give methylanisoles as summarized in Table 3, which shows smaller but similar effects of temperature and wavelength on the orientation than those for toluene.

Table 3. Isomer distributions of methylanisoles in photolysis of acetyl peroxide in anisole

Wavelength (nm)	Temp. (°C)	Methylanisole composition		
		ortho (%)	meta (%)	para (%)
>290	20	75	15	10
>290	−50	66	20	14
254	20	68	21	11
254	−20	56	28	16
254	−60	54	32	14

Experimental

Materials

Authentic *o*-, *m*-, and *p*-methylbiphenyls were prepared by the Gomberg reaction of diazotized toluidines with benzene,[11] and *o*-, *m*-, and *p*-methylanisoles were prepared by the methylation of cresols with dimethyl sulfate.[12] All these materials were characterized by i. r. and n. m. r., and they had single g. l. c. peaks.

Analysis

The peroxide content was determined iodometrically as follows. A peroxide solution (1m*l*) was added to aq. $4N-H_2SO_4$ (30m*l*) and saturated aq. KI (1m*l*) was added. For benzoyl peroxide, the mixture was titrated directly with 1/100 N $Na_2S_2O_3$ after 30min standing at room temperature. For acetyl peroxide, the mixture was titrated after heating to 80°C for a few minutes.

Products were analyzed by g. l. c. using a Yanagimoto G–180 gas chromatograph and by g. l. c.–mass using a Shimadzu GCMS–7000 mass spectrometer. A Bentone 34 column (2m) for benzoyl peroxide and Bentone 34+DIDP (5+5%) column (2m) for acetyl peroxide were used. The identification was done by g. l. c.–mass as well as by comparison of g. l. c. peaks with those of the authentic samples. The yields were estimated by g. l. c. using anisole as an internal standard for benzoyl peroxide and mesitylene for acetyl peroxide. Gaseous products, methane and ethane, were analyzed by g. l. c. using a Porapak QS column (2m).

Photoreaction of Acetyl Peroxide with Toluene

A toluene solution of 0.1~0.2M acetyl peroxide was irradiated with a 30W low-press. Hg lamp in a cylindrical 10×200mm quartz cell and a 1 kW or 300W high-press. Hg lamp in a Pyrex cell. Low temperature (−70°C ~ −20°C) experiments were done by cooling a reaction cell with a Yamato Neocool DIP Model BD-21 cooling apparatus. Decomposition percent of peroxide and yields of products were listed in Table 4.

Table 4. Yields of some products in photolysis of diacyl peroxides in toluene and anisole

Wavelength (nm)	Temp. (°C)	Irrad. time (h)	[Peroxide]$_0$ (M)	Solvent	Decomp. (%)	Yield of Me substn product (%)[a]	Yield of other product (%)[b]
>290	20	39	0.16[c]	toluene	99	3.5	3.4
>290	−40	42	0.17[c]	toluene	47	2.7	6.8
254	70	6	0.19[c]	toluene	96	4.3	9.5
254	30	10.5	0.10[c]	toluene	76	1.8	15
254	−20	52	0.10[c]	toluene	99	1.6	7.3
254	−50	25.5	0.15[c]	toluene	77	1.5	4.0
>290	30	3	0.10[d]	toluene	87	11	64
>290	−45	46.5	0.10[d]	toluene	83	5.1	24
254	30	9	0.10[d]	toluene	82	14.5	24
254	−50	33	0.10[d]	toluene	74	8.0	38
>290	−50	40	0.11[e]	anisole	66	6.5	3.2
254	−20	24	0.11[e]	anisole	92	5.4	2.2
254	−60	41	0.11[e]	anisole	90	5.4	1.3

[a] Products: xylenes from toluene–Ac$_2$O$_2$, methylbiphenyls from toluene–(PhCOO–)$_2$ and methylanisoles from anisole–Ac$_2$O$_2$. Yields are based on peroxides decomposed.

[b] Ethylbenzene from toluene–Ac$_2$O$_2$, benzene and biphenyl from (PhCOO·)$_2$ and phenetol from anisole–Ac$_2$O$_2$. Yields are based on peroxide decomposed.

[c] Acetyl peroxide.

[d] Benzoyl peroxide.

[e] 1kW high-press. Hg lamp.

Photoreaction of Benzoyl Peroxide with Toluene

A solution of 0.1M benzoyl peroxide was irradiated and worked up similarly as in the case of acetyl peroxide. The decomposition and yield percentages were also listed in Table 4. Identified products were methylbiphenyls, biphenyl, benzene, phenyl benzoate, tolyl benzoate, benzyl benzoate and dimethylbiphenyl. The total yield of substitution products was higher than those from acetyl peroxide.

Photoreaction of Acetyl Peroxide with Anisole

An anisole solution of 0.1M acetyl peroxide was irradiated and worked up similarly as in the case of toluene. The results are summarized in Table 4. The yields of methylanisoles were 2 ~ 3 fold higher than those of xylenes from toluene.

Fluorescence

Fluorescence of 7.56×10^{-2}M toluene together with $1.2 \sim 7.2 \times 10^{-3}$M acetyl peroxide and that of 7.36×10^{-2}M anisole together with $1.23 \sim 7.38 \times 10^{-3}$M acetyl peroxide in methanol were measured by a Hitachi 565-10S fluorescence spectrophotometer with 254nm light at room temperature. The Stern-Volmer plots were followed at λ_{max} 288nm for toluene and 300nm for anisole.

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