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PHOTOCHEMICAL DECOMPOSITION OF BENZOYL PEROXIDE IN AROMATIC SOLVENTS AND AROMATIC BENZOYLOXYLATION INDUCED BY OXYGEN

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In spite of the wide interest at present shown in photochemical organic reactions, there have been very few investigations of the photolysis of benzoyl peroxide, and all of them deal with this subject chiefly from the kinetic point of view (1,2,3). We now report our study, based on product analysis, of the photochemical decomposition of benzoyl peroxide in aromatic solvents and describe the behaviour of the benzoyloxy radical in the presence of oxygen.

Irradiation of benzoyl peroxide in benzene with a high pressure mercury lamp under an atmosphere of nitrogen at room temperature was found, as shown in Table 1, to give phenyl benzoate in an amount (about 10 mole% of the peroxide), which is definitely greater than found in the usual thermal decomposition, in addition to the well-established products from the homolytic decomposition of this peroxide (4), viz., carbon dioxide, benzoic acid, biphenyl, 1,4-dihydrobiphenyl and quaterphenyl. Passage of oxygen through reaction mixtures under irradiation caused a remarkable increase in the yield of phenyl benzoate (50-60 mole%), and at the same time phenol was produced at the expense of biphenyl (5).

Irradiation of benzoyl peroxide in several aromatic solvents, whether under nitrogen or under oxygen, invariably afforded about 10 mole% of phenyl benzoate, as shown in Table 2. This finding together with the observation that nearly the same amount of this ester was formed in the photolysis even in the presence of iodine, an efficient radical scavenger, evidently indicates that phenyl benzoate arises from a molecule of the peroxide, to an extent of about 10 mole%, within a solvent-cage as formulated below,

$$(PhCO_2)_2 \longrightarrow (PhCO_2\cdot + PhCO_2\cdot)_{cage} \longrightarrow$$
$$(PhCO_2\cdot + Ph\cdot + CO_2)_{cage} \longrightarrow$$
$$(PhCO_2Ph + CO_2)_{cage} \longrightarrow PhCO_2Ph + CO_2$$

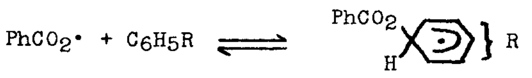
The fact that, in the presence of oxygen, the benzoyloxylation of substituted benzenes takes place to give aryl benzoates (Table 2), which are scarcely produced under nitrogen, clearly indicates that the increased formation of phenyl benzoate in benzene in the presence of oxygen (Expt. No. 2 in Table 1) is due to benzoyloxylation of benzene by the benzoyloxy radical. We propose a mechanism for the aromatic benzoyloxylation, in which a benzoyloxy radical adds to an aromatic molecule reversibly to give a benzoyloxycyclohexadienyl radical (reaction 1) (6), which is then oxidized by oxygen to afford aryl benzoate (reaction 2), the latter process being analogous to the oxidation of phenylcyclohexadienyl radicals by oxygen (7).

TABLE 1

Yields[b)] of Products from Irradiation of Benzoyl Peroxide in Benzene[a)]

Expt. No.	1	2	3[e)]	4[e)]
Atmosphere	N_2	O_2	N_2	O_2
CO_2[c)]	135	40	58	23
Ph_2	33	22	32	33
PhCOOH[d)]	30	7	51	5
PhCOOPh	13	58	3	54
PhOH	0	17	0	8

a) Benzoyl peroxide (3.2 g.) in benzene (600 ml.) was irradiated with a 100-w. high pressure mercury lamp in a Pyrex reaction vessel until the peroxide had completely decomposed; it usually took fifty to sixty hours except Expt. No. 3. b) In mole% of the peroxide, determined by v.p.c. unless otherwise stated. c) Determined by gravimetry. d) Isolated and weighed. e) With benzophenone (0.002 M).



···(1)

···(2)

The finding that, in the irradiation of benzoyl peroxide in benzene (Expt. Nos. 1 and 2 in Table 1), oxygen increases the yield of phenyl benzoate at the expense of both carbon dioxide and benzoic acid can be understood in terms of this mechanism, since reaction 2 will shift equilibrium 1 to the right-hand side of the equation with consumption of the benzoyloxy radical resulting in the diminished production of carbon dioxide and benzoic acid.

This mechanism is further supported by the results of photolyses of benzoyl peroxide in mixtures of benzene and cyclohexane (5:1 and 1:1 by volume), in which, under oxygen, almost the same yields of phenyl benzoate (35 and 33 mole%, respectively) were obtained together with a little benzoic acid (6 and 7 mole%), whereas the photolyses under nitrogen under otherwise the same conditions gave phenyl benzoate in much lower yields (7 and 2 mole%) and benzoic acid in higher yields (30 and 39 mole%). These findings show that, in spite of the presence of cyclohexane, a reactive hydrogen-donor, oxygen causes an efficient benzoyloxylation through reactions 1 and 2, the benzoyloxy radical being diverted from abstraction of hydrogen from cyclohexane.

TABLE 2

Yields[a)] of Aryl Benzoates in Photochemical (at room temperature) and Thermal (at 79°C) Decomposition of Benzoyl Peroxide in Aromatic Solvents

Solvent		Toluene			p-Xylene			Chlorobenzene			Anisole	Nitrobenzene
Conditions[b)]		P	P	T	P	P	T	P	P	T	T	T
		N_2	O_2	O_2	N_2	O_2	O_2	N_2	O_2	O_2	O_2	O_2
$PhCO_2Ph$		12	11	tr	7	11	tr	9	11	tr	3	2
$PhCO_2Ar$	o-	tr	26	7	tr	34	18	0	4	tr	11	0
	m+p-	tr	30	12[c)]				0	18	tr	22	0

a) In mole% of the peroxide. b) P and T stand for the photochemical and the thermal decomposition, respectively. c) The proportions of o-, m- and p-tolyl benzoate formed were found to be 47, 35 and 18% respectively in the photolysis and 39, 41 and 20% respectively in the thermal decomposition. d) tr stands for trace.

The homolytic benzoyloxylation caused by oxygen was found to take place also in the thermal decomposition of benzoyl peroxide in substituted benzenes, giving substituted phenyl benzoates (except the case of chlorobenzene and nitrobenzene) together with less than 3 mole% of phenyl benzoate, a cage-product (Table 2). In benzene under oxygen the yield of phenyl benzoate increased with lowering of the reaction temperature, being 6 and 18 mole% at 80° and 62°C, respectively, whereas its yield under nitrogen was lower and did not change (4 mole%) with the reaction temperature, probably because of its formation as a cage-product. The formation of the substituted phenyl benzoates in relatively lower yields in the thermal decomposition than in the corresponding photolyses and also the enhanced benzoyloxylation of benzene with lowering of the reaction temperature are certainly due to both the decrease in the rate of decomposition of the benzoyloxy radical and the increase in the concentration of dissolved oxygen with decrease in the reaction temperature.

TABLE 3

Yields[a)] of Aryl Benzoates in Thermal Decomposition of Benzoyl Peroxide in a Mixture of Two Aromatic Compounds (ArH and Ar'H) under Oxygen (at 75°)

ArH	Benzene	Benzene	Benzene	Benzene	Toluene	
Ar'H	Toluene	Chloro-benzene	p-Xylene	Anisole	Anisole	
Molar ratio, ArH/Ar'H	0.98	1.14	1.07	1.07	0.99	
$PhCO_2Ph$	3.7	5.1	3	6	2.4	
Ar:					Tolyl	Anisyl
$PhCO_2Ar$ o-	4	trace	14	8	3	8
m+p-	7	trace		16	4	17

a) In mole% of the peroxide.

The results of thermal decomposition of benzoyl peroxide in mixtures of two aromatic compounds at 75°C under oxygen, in which the aryl benzoates competitively formed were determined (Table 3), enable us to conclude that the relative reactivities of the aromatic compounds towards benzoyloxylation decrease in the following order: anisole, p-xylene, toluene, benzene, chlorobenzene, nitrobenzene, the last being not benzoyloxylated at all. This sequence shows that the homolytic benzoyloxylation takes place readily with the nucleus activated with an electron-releasing group and contrasts with the case of the homolytic aromatic arylation (8). The reactivity sequence thus determined, however, is an apparent one, since the mechanism of benzoyloxylation postulated here comprises two reaction steps 1 and 2 and the effects of substituents are not readily compared. The present result suggests either that the benzoyloxy radical behaves as an electrophilic radical and the polar effect is important in reaction 1 or that reaction 2, an oxidation step, which should be facilitated by electron-releasing substituents, is important in the substituent effect, even if the conjugative effect, e. g., of the nitro-group, exceeds the polar effect in reaction 1 reversing partly the sequence expected from the latter effect.

The mechanism of the photochemical excitation of benzoyl peroxide is not certain, but we infer that the decomposition of the peroxide in benzene without any added sensitizers is caused by energy transfer from benzene in an excited singlet state to the peroxide, followed by its homolytic decomposition, since, in the first place, the photolysis of benzoyl peroxide is found to proceed very slowly in cyclohexane, whereas addition of benzene accelerates the decomposition, and secondly, oxygen, an effective quencher of the triplet state excitation, did not cause any retardation of the decomposition of the peroxide. The present conclusion is in keeping with the result by Vasil'ev and Krongaus who conclude that toluene causes photosensitized decomposition of benzoyl peroxide, on the basis of measurements of the quantum yield of disappearance of the peroxide (2).

The above mechanism of excitation is supported by experiments using benzophenone as a photosensitizer. The photolysis in benzene under oxygen, whether in the presence or in the absence of benzophenone, gave almost the same results, especially phenyl benzoate being produced in the same yield (Expt. Nos. 2 and 4 in Table 1). Walling and Gibian (3) have shown that triplet energy transfer occurs from benzophenone to benzoyl peroxide, but in the present experiments, oxygen will quench the triplet state of benzophenone leaving excited singlet benzene as the only species that is capable of causing the homolysis of the peroxide by energy transfer, giving the same results as without benzophenone. In the photolysis under nitrogen, however, there is a distinct difference between the benzene-sensitized and the benzophenone-sensitized decomposition, the former giving 13 mole% of phenyl benzoate, while the latter only 3 mole% of it. A possible explanation of this fact is that the sensitization by singlet benzene may excite the peroxide to a higher energy level than by triplet benzophenone, and it may therefore possess enough energy to decompose in rapid succession or simultaneously into a benzoyloxy radical, a phenyl radical and a molecule of carbon dioxide, so that the two resulting radicals undergo immediate recombination within a solvent cage to afford phenyl benzoate. With benzophenone as a sensitizer, benzoyloxy radicals may be produced in a more stable state and therefore be able to diffuse apart from each other before they proceed to form phenyl benzoate in the original solvent cage.

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