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Naphthalene-sensitized Photolysis of Dibenzoyl Peroxide

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Synopsis. Naphthyl benzoates and phenylnaphthalenes were produced, on naphthalene-sensitized photolysis of dibenzoyl peroxide, in different distribution of their isomers from its thermolysis in the presence of naphthalene, suggesting that naphthalene as sensitizer interacts with dibenzoyl peroxide in a specific orientation in the sensitization process.

Aromatic hydrocarbon-sensitized photolysis of dibenzoyl peroxide (BPO) has previously been shown to proceed by way of a singlet exciplex.[1,2] Although most photosensitized reactions are supposed to take place without any chemical change of sensitizers, the present work is concerned with the products from naphthalene-sensitized photolysis of BPO, particularly with the fate of the sensitizer.

Thus, in the sensitization process, the excited sensitizer molecule will take a favourable orientation with respect to the peroxide molecule to form efficiently an exciplex, which will subsequently undergo cleavage of the peroxide moiety into free radicals. Therefore, immediately after the cleavage, the resulting free radicals will attack the sensitizer molecule, still located in a close proximity of the radicals in a specific orientation, to give reaction products in a different distribution from random encounters of the free radicals with the sensitizer molecules. The investigation of these reaction products will give insight into the favourable orientation of the sensitizer and peroxide molecules in the exciplex, and this attempt is described below.

Results and Discussion

A solution of BPO (0.03 M) and naphthalene (0.04 M) in benzene was irradiated under nitrogen atmosphere at room temperature with a 400-W high pressure mercury lamp through a Pyrex wall. For comparison, BPO (0.03 M) was allowed to decompose thermally in the presence of naphthalene (0.04 M) in benzene at 80 °C. The products were quantitatively analyzed by GLPC. The results are summarized in Table 1.

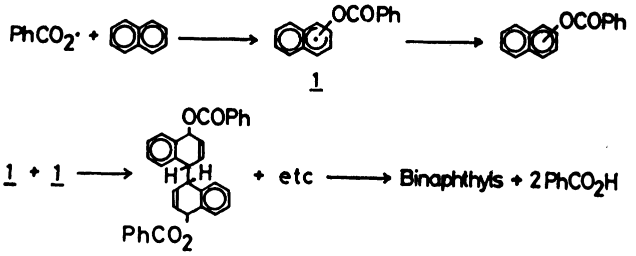
Table 1. Yield of products in photolysis and thermolysis of dibenzoyl peroxide in the presence of naphthalene in benzene

Product	Yield[a)]	
	Photolysis	Thermolysis
Biphenyl	0.28	0.40
Phenyl benzoate	0.23	0.029
1-Phenylnaphthalene	0.036	0.006
2-Phenylnaphthalene	0.011	0.004
1-Naphthyl benzoate	0.036	0.013
2-Naphthyl benzoate	0.007	0.013
Benzoic acid	0.15[c)]	
Naphthalene[b)]	0.77	0.70
1,1′-Binaphthyl[b)]	0.014	0.003
1,2′-Binaphthyl[b)]	0.009	0.003
2,2′-Binaphthyl[b)]	0.016	0.008

a) Yields in mol/mol peroxide unless otherwise noted. Average values of data obtained by duplicate runs. b) Yields in mol/mol naphthalene. c) Determined by isolation.

Production of biphenyl, phenyl benzoate, and benzoic acid is reasonably understood by a mechanism previously postulated.[3] Thus, the peroxide moiety decomposes through simultaneous two-bond cleavage into a benzoyloxyl radical and a phenyl radical, which subsequently undergo geminate recombination into phenyl benzoate or diffusion out of the solvent cage to react with benzene finally affording biphenyl and benzoic acid.

As Table 1 shows, it is remarkable that the photolysis produced larger amounts of naphthyl benzoates (1-naphthyl and 2-naphthyl benzoate) and phenylnaphthalenes (1-phenyl- and 2-phenylnaphthalene) than the thermolysis. Moreover, among the above compounds 1-naphthyl derivatives were produced in several times higher yields than their corresponding 2-naphthyl derivatives in the photolysis, in contrast with the thermolysis which gave nearly equal amounts of 1-naphthyl and 2-naphthyl derivatives. A possibility that this fact would be due to more rapid change of the resulting 2-naphthyl benzoate and 2-phenylnaphthalene than their respective 1-naphthyl derivatives under the photolytic conditions was eliminated by control experiments.



It is certain that naphthyl benzoates result from addition of benzoyloxyl radicals to naphthalene followed by loss of a hydrogen atom from the resulting cyclohexadienyl radicals (**1**).[4] Phenylnaphthalene must be similarly formed through addition of phenyl radicals to naphthalene. Production of 1,1′-, 1,2′-, and 2,2′-binaphthyl is presumably through recombination of the cyclohexadienyl radicals (**1**) followed by elimination of two moles of benzoic acid for each mole of binaphthyls formed.[4]

As mentioned above, it is reasonably supposed that when the two-bond cleavage of the peroxide moiety in the exciplex generates simultaneously benzoyloxyl and phenyl radicals in the proximity of the naphthalene molecule, which has worked as sensitizer, these radicals will be captured by the naphthalene molecule in competing with their diffusion out of the solvent cage into the bulk of the solvent benzene. This reasoning can explain the formation of higher yields of phenylnaphthalenes and naphthyl benzoates from the photolysis than from the thermolysis, in which these compounds would result from random encounters of the radicals and naphthalene. Furthermore, the aforementioned finding that the production of higher yields of 1-phenylnaphthalene and 1-naphthyl benzoate than their respective 2-naphthyl derivatives from the photolysis might suggest that, immediately after the cleavage of the peroxide moiety, the radical centres of benzoyloxyl and phenyl radicals would be located closer to the C-1 carbon of naphthalene than to the C-2 carbon. This orientation can be taken as reflecting the conformation of the exciplex, as supposed by the construction of the molecular model, where the aromatic nucleus of the peroxide would overlap with the naphthalene molecule and the C-1 ring carbon of the peroxide would be close to the C-1 carbon of the naphthalene.

Experimental

Photolysis and Thermolysis of Dibenzoyl Peroxide with Naphthalene in Benzene. A solution of dibenzoyl peroxide (3.00 g, 0.012 mol) and naphthalene (2.00 g, 0.016 mol) in benzene (400 ml) was irradiated under nitrogen atmosphere for 2.3 h (five times half-life periods determined by iodometry) by a 400-W high pressure mercury lamp immersed in a Pyrex cooling well. Thermolysis was carried out at a half scale of photolysis at 80 °C in an oil bath for 21.7 h (five times half-life periods) under nitrogen gas bubbling. After the reaction was completed, the solution was concentrated to one-tenth of its original volume. Naphthalene, biphenyl, phenylnaphthalenes, naphthyl benzoates, and binaphthyls were determined quantitatively by GLPC. Benzoic acid was isolated by extraction with aqueous sodium hydrogencarbonate solutions and determined by gravimetry.

Irradiation of Naphthyl Benzoates in Benzene. A solution of 1-naphthyl benzoate (35.7 mg, 0.14 mmol) and 2-naphthyl benzoate (77.4 mg, 0.31 mmol) in benzene (40 ml) was similarly irradiated by a 400-W high pressure mercury lamp for 2.4 h. GLPC analysis of the irradiation mixture revealed the ratio of remaining 1-naphthyl benzoate/2-naphthyl benzoate to be 0.25.

References

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