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THE EFFECT OF THE SPIN MULTIPLICITY OF SENSITIZERS ON THE FORMATION OF FREE RADICAL CAGE REACTION PRODUCT IN THE IRRADIATION OF DIBENZOYL PEROXIDE

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Decomposition of dibenzoyl peroxide with singlet sensitization gives phenyl benzoate resulting from the cage recombination between a benzoxyl and a phenyl radical as noticeably as with the direct photolysis; on the contrary, the triplet sensitization gives only low yield of phenyl benzoate.

Dibenzoyl peroxide, on thermal decomposition in solution under nitrogen, gives only a small amount of phenyl benzoate resulting from recombination of a benzoxyl radical and a phenyl radical formed from a molecule of dibenzoyl peroxide in a solvent cage,[1,2,3] but the direct irradiation with ultraviolet light affords phenyl benzoate in a noticeable yield.[4,5,6] We now wish to report that the use of aromatic hydrocarbons as sensitizers acting in their excited singlet states gives phenyl benzoate as noticeably as from the direct irradiation, but the use of aromatic ketones as sensitizers acting in their triplet states affords only low yield of phenyl benzoate. To our knowledge, this seems the first observation of the dependence of the formation of a radical cage reaction product on the spin multiplicity of the sensitizers employed.

Dibenzoyl peroxide (0.02 M) in benzene or toluene in the presence or in the absence of sensitizers was irradiated under nitrogen with a high pressure mercury lamp through Pyrex wall until the peroxide was completely decomposed and the resulting phenyl benzoate was determined as summarized in the table.[7,8]

Regardless of whether the irradiation was carried out at room temperature or at higher temperatures, as shown in the table (Nos. 1-4), phenyl benzoate was produced in more than 10% yield in direct irradiation or in chrysene sensitization. These results indicate that the noticeable formation of phenyl benzoate from the irradiation compared with thermolysis is evidently characteristic of a photochemical pathway and does not owe to the employment of lower temperature, at which the radical cage reaction would be facilitated,[9] for the irradiation than for the thermolysis.

As the table indicates, sensitization by aromatic hydrocarbons (Nos. 3, 4, and 6-13) gave phenyl benzoate in nearly or more than 10% yield; on the other hand, sensitization by aromatic ketone (Nos. 14, 16 and 18) afforded it in nearly 3% yield. A result of control experiment that phenyl benzoate was nearly

Table The Yield of Phenyl Benzoate Produced from the Irradiation of Dibenzoyl Peroxide (0.02 M).

Solvent: benzene except Nos. 5 and 6; concentration of sensitizers: 0.02 M in most runs; in Nos. 15 and 17 ketones in 0.05 M and naphthalene in 0.01 M; temperature: room temperature except Nos. 2 and 4.

No.	Sensitizer	Yield(%)	No.	Sensitizer	Yield(%)
1	None	13	10	Triphenylene	11
2	None(56°C)	12	11	Phenanthrene	15
3	Chrysene	17	12	Anthracene	8
4	Chrysene(70°C)	13	13	9,10-Diphenylanthracene	8
5	None(in toluene)	12	14	Acetophenone	3
6	Chrysene(in toluene)	12	15	Acetophenone-Naphthalene	3
7	Fluorene	9	16	Benzophenone	3
8	Naphthalene	11	17	Benzophenone-Naphthalene	3
9	p-Terphenyl	10	18	2-Acetonaphthone	3

quantitatively recovered after the irradiation in benzene in the presence of acetophenone eliminates the possibility that the low yield of phenyl benzoate from the triplet sensitization would be due to the further sensitizing action of the triplet ketone to result in the disappearance of the once formed benzoate. Previously, it was shown that aromatic hydrocarbons act in their excited singlet states[10,11,12] and aromatic ketones act in their triplet states[5,11-14] to sensitize the decomposition of dibenzoyl peroxide. Among the aromatic ketones, benzophenone was reported to cause the decomposition of the peroxide through both energy transfer and induced decomposition by 1-hydroxy-1-phenylbenzyl radicals, $Ph_2\dot{C}OH$, which arise from triplet benzophenone($^3n,\pi^*$) by way of abstraction of hydrogen atoms from solvent,[14] so the occurrence of the induced decomposition would reduce the yield of phenyl benzoate. However, a finding that the use of 2-acetonaphthone whose lowest triplet is abundant in π,π^* character and unreactive towards hydrogen atom abstraction[15] also gave nearly 3% yield of phenyl benzoate indicates that aromatic ketones, if they act as sensitizers, irrespective of the electronic configuration of their lowest triplet states or their ability to abstract hydrogen atoms, do not appreciably yield the radical cage reaction product.

In the sensitization by the aromatic hydrocarbons, it was previously shown that their excited singlet states are responsible for the decomposition of the peroxide to produce phenyl benzoate on the ground of no appreciable effect of 1,3-pentadiene to reduce the quantum yield for the decomposition, quenching of fluorescence of the hydrocarbons by the peroxide, analysis of the quantum yields for the decomposition of varying concentrations of the peroxide[10] together with CIDNP results.[11,12] In the presence of the peroxide, the excited singlet hydrocarbons, though to small extent, will cross over to the triplet state. So, it would still remain possible that the triplet state of the hydrocarbons would contribute, if any, though to much less extent than the excited singlet state, to the sensitization of the decomposition of the peroxide to give phenyl benzoate.

In order to examine the above possibility, double sensitization experiments were carried out. Thus (Nos. 15 and 17), the peroxide was irradiated with 366 nm light in the presence of both aromatic ketone and naphthalene in benzene, in which the concentrations of the substances were adjusted so that only the ketone(0.05 M) would absorb the light to be excited to the singlet state, the triplet ketone produced by rapid intersystem crossing would predominantly transfer the triplet excitation to naphthalene(0.01 M) rather than interact with the peroxide(0.02 M), and the resulting triplet state of naphthalene would act on the peroxide.16) The above double sensitization gave as low yield of phenyl benzoate as the sensitization solely by the aromatic ketone. This result clearly demonstrates that the triplet state of the hydrocarbons can sensitize the decomposition of the peroxide but, contrary to their singlet state, is not effective to produce phenyl benzoate.

Therefore, it is clear that the direct irradiation and the singlet sensitization of dibenzoyl peroxide noticeably produce phenyl benzoate in contrast with the triplet sensitization. This fact can be understood on the ground that the singlet pair of a benzoxyl radical and a phenyl radical in a solvent cage arising from the direct irradiation or the singlet sensitization of the peroxide would more facilely recombine into phenyl benzoate than the radicals in the triplet pair resulting from the triplet sensitization, which would readily diffuse out of the solvent cage before undergoing spin inversion into the singlet pair followed by the recombination.18) The detailed mechanism will be discussed in a full paper.

Finally, we would like to arouse attention to a fact that in the direct irradiation with a high pressure mercury lamp through Pyrex wall 313 nm light is effective to cause the decomposition of dibenzoyl peroxide to yield phenyl benzoate but 366 nm light is not effective because it is scarcely absorbed by the peroxide; with sensitization by aromatic hydrocarbons such as chrysene, 9,10-diphenylanthracene, etc. 366 nm light is as effective to produce phenyl benzoate as 313 nm light in the direct irradiation. On the contrary, with sensitization by aromatic ketones, 366 nm light or 313 nm light, though it causes the sensitized decomposition of the peroxide, is not effective to give phenyl benzoate. It is noteworthy that light of 313 nm from a high pressure mercury lamp in the direct irradiation can be replaced in the presence of aromatic hydrocarbon sensitizers by light with lower energy, 366 nm, to produce phenyl benzoate from dibenzoyl peroxide. From the sunlight arriving at the earth surface 366 nm light is available but 313 nm light is not available. So, when a suitable aromatic hydrocarbon is employed as a sensitizer, the sunlight becomes utilizable to result in the same reaction products as from the direct photolysis by light of higher energy from a mercury lamp. We believe that this type of sensitization to be called as "sunlight-utilizable sensitization" would be valuable for the efficient utilization of the solar energy.

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8) The yields indicated are not optimal. The quantum yield for production of phenyl benzoate is, for example, 0.085 for sensitization by chrysene at the extrapolated infinite concentration of dibenzoyl peroxide in benzene with 366 nm irradiation.

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