The Singlet Sensitized Decomposition of Benzoyl Peroxide

Toshio NAKATA and Katsumi TOKUMARU

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

(Received July 17, 1970)

In spite of recent investigations by several groups of workers,[1–5] the mechanism of the photochemical decomposition of benzoyl peroxide remains puzzling. We wish to present clear evidence that irradiation of benzoyl peroxide in benzene in the presence of aromatic hydrocarbons such as chrysene, anthracene, pyrene, naphthalene or phenanthrene, under nitrogen with light of 366 nm or over 300 nm at room temperature leads to the sensitized decomposition of the peroxide (denoted by P) by the added hydrocarbons (denoted by S) in their excited singlet states through the following mechanism.

$$S^*(S_1) + P(S_0) \xrightarrow{k_t} X \tag{1}$$

$$X \xrightarrow{k_r} S(S_0) + \text{Decomposition Fragments} \tag{2}$$

$$X \xrightarrow{k_d'} S(S_0) + P(S_0) \tag{3}$$

Thus, the excited singlet sensitizer, on interaction with the peroxide, forms an exciplex (process 1), which subsequently undergoes either decomposition leading to products (process 2) or deactivation (process 3).

The above mechanism for the singlet sensitization is supported by the following findings. First, the quantum yield of the decomposition of the peroxide (0.02M) in the presence of chrysene or phenanthrene was scarcely reduced by the addition of 1,3-pentadiene. For example, the quantum yield observed with added chrysene (0.0064M) was 0.38 and 0.37 in the absence and in the presence (0.08M) of 1,3-pentadiene, respectively. Secondly, fluorescence of the aforementioned hydrocarbons in benzene was effectively quenched by benzoyl peroxide,[*1] obeying the following Stern-Volmer equation: $I_0/I = 1 + k_t\tau_0[P]$, with $k_t\tau_0$ 105, 39, 171 and 160 mol^{-1} l for chrysene, anthracene, pyrene and naphthalene respectively, where I_0 and I represent the intensities of the fluorescence of the hydrocarbons in the absence and in the presence of the peroxide in the concentration [P], respectively, and τ_0 denotes the average life time of the excited singlet state in the absence of the peroxide. Thirdly, plots of the reciprocals of the quantum yields for the decomposition of the peroxide (Φ) measured in the presence of a constant concentration (0.007M) of chrysene irradiated with 366 nm light were shown to be linear with the reciprocals of varying concentrations of the peroxide, and were analyzed according to the following Stern-Volmer equation, which is derived from the aforementioned mechanism: $1/\Phi = (1 + k_d'/k_r)\cdot(1 + 1/k_t\tau_0[P])$. The value for k_d'/k_r was shown to be 0.98 and that for $k_t\tau_0$ to be 1.87×10^2 mol^{-1}l. The latter value agrees satisfactorily with the aforementioned value for $k_t\tau_0$, 1.05×10^2 mol^{-1}l, obtained from the quenching of the fluorescence of chrysene. Fourthly, the experimental values for $k_t\tau_0$ for the hydrocarbons examined, on being divided by the reported values for τ_0,[6] give the values for k_t in the range of 10^9–10^{10} mol^{-1}l sec^{-1} (for example, 9.8×10^9 mol^{-1}l sec^{-1} for anthracene, with τ_0 reported to be 4×10^{-9} sec[6]), nearly equal to the magnitude of the diffusion-controlled rate constant. The fluorescence spectra of the above hydrocarbons do not overlap with the absorption spectrum of the peroxide, the former being in longer wave length region than the latter. These facts rule out the possibility that the excited singlet hydrocarbon undergoes energy transfer to the peroxide by resonance mechanism[7] or by simple collisional mechanism,[7] therefore supporting the mechanism shown in the above scheme in which the energy transfer takes place through the formation of the exciplex.[7]

The present conclusion together with previous results[1–5] clearly demonstrates that, among sensitizers, aromatic hydrocarbons act in their excited singlet states, and aromatic ketones (if they act at all) in their excited triplet states to sensitize the decomposition of benzoyl peroxide.

[*1] Fluorescence was measured without exclusion of atmospheric oxygen, with exciting light of 366 nm except for naphthalene which was excited with 300 nm.

1) T. Nakata, K. Tokumaru and O. Simamura, *Tetrahedron Lett.*, **1967**, 3303.

2) J. C. Bevington and T. D. Lewis, *Trans. Faraday Soc.*, **54**, 1340 (1958).

3) I. N. Vasil'ev and V. A. Krongauz, *Kinet. Katal.* **4**, 204 (1963).

4) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3413 (1965).

5) W. F. Smith, Jr., *Tetrahedron*, **25**, 2071 (1969); W. F. Smith, Jr., and B. W. Rossiter, *ibid.*, **25**, 2059 (1969).

6) The average life times in the aerated condition are taken from I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York (1965).

7) For general features of the energy transfer process, see, for example, A. A. Lamola, "Technique of Organic Chemistry," Vol. 14, ed. by P. A. Leermakers and A. Weissberger, Interscience Publishers, New York (1969), p. 17.