Energy Transfer in the Radiolysis of Benzoyl Peroxide Solutions

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When ionizing radiation acts on organic solutions, the energy initially absorbed may be transferred from one component to another, which leads to a violation of the "averaging rule" ($^{1-5}$). To elucidate the influence of the nature of the solvent on energy transfer, we studied the radiolysis of benzoyl peroxide solutions in benzene, cyclohexane, and ethyl acetate. The radiolysis was carried out under the action of γ-rays from Co^{60} in the absence of air. The differential dose was $1.74 \cdot 10^{15}$ eV/ml·sec. The initial rate of peroxide decomposition was determined iodometrically, and the amount of peroxide decomposed did not exceed 10-20% of its initial concentration.

Figure 1 shows the dependence of the initial rate of radiolysis of benzoyl peroxide in benzene on its initial concentration. Of all the energy absorbed by the solution, a portion proportional to the electronic fraction of the peroxide in the solution is absorbed by the benzoyl peroxide. Calculation of the number of peroxide molecules decomposing when 100 eV of energy is absorbed by the peroxide itself, for a concentration of 0.01 mol/l, gives a value of 1760. This value is 20 times greater than the number of peroxide molecules that would decompose if all 100 eV of energy absorbed by the peroxide were used to rupture the bond –O–O–.

To determine the causes responsible for the high radiation yield of benzoyl peroxide decomposition, we carried out experiments with diphenylpicrylhydrazyl (DPPH) to determine the yield of free radicals both from pure benzene and from benzoyl peroxide solutions in it. The change in DPPH concentration was determined spectrophotometrically. The critical DPPH concentration, i.e., the concentration required to capture all radicals formed during radiolysis (^{6}), was determined beforehand. This value proved to be $1 \cdot 10^{-4}$ mol/l. The yield of free radicals established by us for the radiolysis of pure benzene, equal to 0.75 per 100 eV, agrees well with the data of other authors (^{5,7}).

In Fig. 1, point B on the ordinate axis corresponds to the rate of formation of free radicals in pure benzene. Since this rate is considerably lower than the rate of peroxide decomposition, the high radiation yield of peroxide decomposition cannot be explained by the interaction of the peroxide with these radicals.

Figure 2 shows the dependence, obtained with DPPH (curve I), of the rate

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

of formation of primary free radicals upon irradiation of peroxide solutions in benzene on the peroxide concentration. For comparison, curve II is given, corresponding to the initial segment OA of the curve in Fig. 1, but constructed from the calculation that each decomposed peroxide molecule gives two radicals. The two curves practically coincide. It follows from this that the radiolysis of peroxide in benzene does not proceed by a chain mechanism. In chain decomposition, the rate of bleaching of DPPH would be less than the rate

decomposition of the peroxide under the same conditions, since DPPH would "trap" the free radicals leading the chain. The absence of chain decomposition is also indicated by the fact that the rate of radiolysis of the peroxide in the presence of methyl methacrylate, which is a strong inhibitor of chain decomposition of peroxides (8), proved to be equal to the rate of radiolysis without it (Fig. 1).

Fig. 1. Dependence of the rate of radiolysis of benzoyl peroxide on the initial concentration of peroxide in benzene. The cross denotes the rate of radiolysis of the peroxide in the presence of 0.02 mol/l methyl methacrylate

It may be assumed that the high radiation yield of the radiolytic decomposition of the peroxide is due to energy transfer from initially excited benzene molecules to peroxide molecules. To confirm this supposition, the radiolysis of peroxide solutions in benzene was studied in the presence of condensed aromatic hydrocarbons—anthracene and phenanthrene. It is known that dilute solutions of these compounds fluoresce under the action of ionizing radiation. This is associated with energy transfer from the solvent to the dissolved substance (9,10). It may be expected that introducing fluors into a peroxide solution will lead to a decrease in the rate of peroxide radiolysis, since some of the excited benzene molecules will transfer their energy to fluor molecules.

It is seen from Fig. 3 that phenanthrene and anthracene exert a protective action with respect to the peroxide. Benzoic anhydride also protects the peroxide from decomposition.

Fig. 2

Fig. 3

Fig. 3

Figure 3: Fig. 3

Fig. 4. Dependence of the rate of peroxide radiolysis on its initial concentration in solutions of cyclohexane (a), ethyl acetate (b), ethyl acetate in the presence of methyl methacrylate 0.02 mole/liter (c), phenanthrene 0.1 mole/liter (d), and benzene 0.4 mole/liter (e).

Figure 4: Fig. 4. Dependence of the rate of peroxide radiolysis on its initial concentration in solutions of cyclohexane (a), ethyl acetate (b), ethyl acetate in the presence of methyl methacrylate 0.02 mole/liter (c), phenanthrene 0.1 mole/liter (d), and benzene 0.4 mole/liter (e).

Fig. 2. Dependence of the rate of formation of free radicals on the concentration of peroxide in benzene: I—rate of consumption of DPPH; II—twice the rate of peroxide decomposition.
Fig. 3. Dependence of the rate of radiolysis of the peroxide on the concentration of additions of phenanthrene (a), anthracene (b), and benzoic anhydride (c). Benzoyl peroxide concentration $= 4.5 \cdot 10^{-3}$ mol/l

However, as is evident from the figure, the rate of radiolysis of the peroxide, having reached a limiting value, does not decrease further with increasing concentration of the protective additives. This can be explained by the fact that fluor molecules that have received energy from excited benzene molecules are deactivated not only by emission of fluorescence light, but also

transferring energy to the peroxide molecules. It is not difficult to show that this leads to the attainment of a limiting value of the peroxide decomposition rate at sufficiently high concentrations of fluorenes.

Figure 4, I shows the dependence of the rate of radiolysis of peroxide in cyclohexane and ethyl acetate on its initial concentration. Since the solubility of the peroxide in cyclohexane at room temperature does not exceed 0.03 mole/liter, it was not possible to follow the change in the rate of radiolysis of the peroxide in cyclohexane above this concentration. However, as is seen from the figure, the rate of radiolysis of the peroxide in both solvents coincides.

The introduction into a solution of the peroxide in cyclohexane or in ethyl acetate of 0.02 mole/liter methyl methacrylate sharply decreases the rate of peroxide decomposition (Fig. 4, II), which indicates chain decomposition of the peroxide during radiolysis in these solvents. Determination by means of DPPH (critical concentration 10^{-3} mole/liter) of the yield of free radicals from pure solvents and from solutions of the peroxide in them shows that, in the presence of peroxide, the rate of formation of free radicals is practically equal to the rate of their formation from the pure solvents. Consequently, no transfer of energy from the solvents to the peroxide occurs, since otherwise, in addition to radicals formed from the solvent, radicals would be formed as a result of peroxide decomposition caused by energy transfer (as was observed in benzene solutions).

Fig. 4. Dependence of the rate of peroxide radiolysis on its initial concentration

in solutions of cyclohexane (*a*), ethyl acetate (*b*), ethyl acetate in the presence of methyl methacrylate 0.02 mole/liter (*c*), phenanthrene 0.1 mole/liter (*d*), and benzene 0.4 mole/liter (*e*).

Obviously, the chain decomposition of the peroxide is initiated by radicals formed during the radiolytic decomposition of the solvent. Using the steady-state principle, the following expression can be obtained for the rate of chain decomposition of the peroxide V:

$$V = k_p \left(v_{\text{in}}/k_{\text{ob}}\right)^{1/2} [\text{PB}] + v_{\text{in}},$$

where k_p and k_{ob} are the constants of chain propagation and termination, and v_{in} is the initiation rate. The value of v_{in} can be determined by extrapolating the rectilinear section of curve *I* (Fig. 4) to its intersection with the ordinate axis. The failure of a linear dependence to hold for the decomposition rate at peroxide concentrations greater than 0.1 mole/liter is associated with the inhibiting action of aromatic products of peroxide decomposition ([11]). As is seen from Fig. 4, in the presence of small amounts of benzene and phenanthrene the rate of peroxide decomposition is substantially decreased. From the slope of line *II* (chain decomposition does not occur in the presence of methyl methacrylate) it is possible to calculate the radiation yield of peroxide decomposition due to absorption of energy by the peroxide itself. This value is 40 molecules per 100 eV.

From a comparison of the data on the radiolysis of benzoyl peroxide in different solvents, it is evident that the transfer of energy from the solvent to the dissolved substance depends substantially on the nature of the solvent.

Let us consider the following processes occurring during the radiolysis of peroxide solutions in benzene: 1) formation of excited benzene molecules upon absorption of radiation energy; 2) spontaneous deactivation of excited benzene molecules; 3) transfer of energy from excited benzene molecules to the peroxide and decomposition of the latter; 4) decomposition of the peroxide due to absorption of γ-radiation energy by the peroxide itself.

On the basis of the proposed scheme, proceeding from the steady-state principle, the following expression can be obtained for the rate of radiolysis of benzoyl peroxide in benzene:

$$V = \frac{I_{\text{abs}} k_1 k_3 [\text{PB}]}{k_2 + k_3 [\text{PB}]} + k_4 I_{\text{abs}} [\text{PB}], \tag{1}$$

where I_{abs} is the energy absorbed by the solution; k_1, k_2, k_3, and k_4 are the rate constants of reactions 1, 2, 3, and 4.

At low peroxide concentrations, the absorption of energy by the peroxide itself is small, and the second term in equation (1) may be neglected (section *OA*,

Fig. 1). In this case $1/V$ depends linearly on 1/[PB], which makes it possible to determine graphically k_2/k_3 ($4 \cdot 10^{-6}$ mol/l). Knowing this quantity, one can estimate the average lifetime of excited benzene molecules, using the usual theory of fluorescence quenching (^{12}). Assuming that deactivation of excited benzene molecules occurs at every collision with peroxide molecules, we obtain a lifetime of excited molecules of $\sim 10^{-7}$ sec.

It may be assumed that when the peroxide concentration is increased above 0.01 mol/l (the rectilinear section of the curve in Fig. 1), all excited benzene molecules capable of transferring energy to the peroxide are deactivated only by reaction 3, and the further increase in the rate with concentration is due to absorption of energy by the peroxide itself. However, a more detailed analysis of the course of the curve at high concentrations compels one to admit the existence of excited benzene molecules with a shorter lifetime in the excited state, which begin to play a substantial role as the peroxide concentration is increased.

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