THE RADIATION-CHEMICAL EFFECT OF EXCITATION-ENERGY TRANSFER IN THREE-COMPONENT SOLUTIONS

1957

SovietRxiv

Fig. 1. Dependence of the rate of radiolytic decomposition of benzoyl peroxide in $(\mathrm{mol/l \cdot h}) \cdot 10^{-3}$ on phenanthrene concentration. 1—peroxide concentration in solution 0.0125 mol/l; 2—0.0083 mol/l; 3—0.0042 mol/l

Figure 1: Fig. 1. Dependence of the rate of radiolytic decomposition of benzoyl peroxide in $(\mathrm{mol/l \cdot h}) \cdot 10^{-3}$ on phenanthrene concentration. 1—peroxide concentration in solution 0.0125 mol/l; 2—0.0083 mol/l; 3—0.0042 mol/l

Abstract

Full Text

PHYSICAL CHEMISTRY

V. A. KRONGAUZ and Kh. S. BAGDASAR' YAN

THE RADIATION-CHEMICAL EFFECT OF EXCITATION-ENERGY TRANSFER IN THREE-COMPONENT SOLUTIONS

(Presented by Academician N. N. Semenov, 25 IV 1957)

Previously we showed that, during the radiolysis by γ-rays of solutions of benzoyl peroxide in benzene, there occurs a transfer of the primarily absorbed energy from excited benzene molecules to benzoyl peroxide molecules (1,2). As a result, the amount of peroxide decomposed is many times greater than would be expected on the assumption of nonselective absorption of energy by each component of the mixture. At the same time it was established that the addition to a solution of benzoyl peroxide in benzene of small amounts of condensed aromatic hydrocarbons—anthracene and phenanthrene—reduces the rate of radiolytic decomposition of the peroxide.

As is known, dilute solutions of anthracene and phenanthrene fluoresce under the action of ionizing radiation, which is associated with transfer of energy from the solvent to the dissolved substance (3). Evidently, the protective action of these luminophores with respect to benzoyl peroxide is due to the fact that a portion of the excited benzene molecules transfers energy to the luminophore molecules.

Fig. 1. Dependence of the rate of radiolytic decomposition of benzoyl peroxide in $(\mathrm{mol/l \cdot h}) \cdot 10^{-3}$ on the concentration of phenanthrene.
1—peroxide concentration in solution 0.0125 mol/l; 2—0.0083 mol/l; 3—0.0042 mol/l.

It is characteristic that, as the concentration of the luminophores is increased, the rate of peroxide decomposition, after reaching a certain limiting value, no longer decreases. Apparently, this is explained by the fact that at sufficiently high concentrations of luminophores the decrease in the probability of energy transfer in the direction

$$\text{benzene} \rightarrow \text{benzoyl peroxide}$$

is compensated by energy transfer according to the scheme

$$\text{benzene} \rightarrow \text{phenanthrene} \rightarrow \text{benzoyl peroxide}.$$

In order to study in greater detail the mechanism of energy transfer during the radiolysis of three-component mixtures benzene + phenanthrene + benzoyl peroxide, in the present work we investigated the kinetics of the radiolytic decomposition of benzoyl peroxide in these mixtures over a wide range of phenanthrene concentrations (0—1 mol/l) at three different concentrations of benzoyl peroxide (0.0125; 0.0083; 0.0042 mol/l).

The radiolysis of the solutions was carried out under the action of γ-rays from Co^{60} in the absence of air. The differential dose was $1.5 \cdot 10^{15}$ eV/ml $\cdot$ s. The amount decomposed—

the peroxide formed was determined iodometrically and did not exceed 10–20% of its initial concentration.

Figure 1 shows the dependence of the initial rate of radiolysis of benzoyl peroxide on the phenanthrene concentration for three peroxide concentrations. As can be seen from the figure, with increasing phenanthrene concentration the rate of radiolysis of the peroxide first decreases and then, after passing through a minimum, increases linearly.

In accordance with the assumptions stated above, let us consider the following elementary processes occurring during radiolysis of the solutions under study:

$$\begin{array}{rll}
\text{I.} & \mathrm{C_6H_6} \underset{\sim\sim\sim}{\xrightarrow{k_1}} \mathrm{C_6H_6^*}, & v_1 = k_0 I_0 k_1 [\mathrm{C_6H_6}] \varepsilon_{\mathrm{C_6H_6}}, \\
\text{II.} & \mathrm{C_6H_6^*} \xrightarrow{k_2} \mathrm{C_6H_6}, & v_2 = k_2 [\mathrm{C_6H_6^*}], \\
\text{III.} & \mathrm{C_6H_6^*} + \mathrm{PB} \xrightarrow{k_3} \mathrm{C_6H_6} + \mathrm{PB}^* \rightarrow \mathrm{C_6H_6} + 2\mathrm{R}^{\cdot}, & v_3 = k_3 [\mathrm{C_6H_6^*}][\mathrm{PB}], \\
\text{IV.} & \mathrm{C_6H_6^*} + \Phi \xrightarrow{k_4} \mathrm{C_6H_6} + \Phi^*, & v_4 = k_4 [\mathrm{C_6H_6^*}][\Phi], \\
\text{V.} & \Phi \underset{\sim\sim\sim}{\xrightarrow{k_5}} \Phi^*, & v_5 = k_0 I_0 k_5 [\Phi] \varepsilon_{\Phi}, \\
\text{VI.} & \Phi^* \xrightarrow{k_6} \Phi + h\nu, & v_6 = k_6 [\Phi^*], \\
\text{VII.} & \Phi^* + \mathrm{PB} \xrightarrow{k_7} \Phi + \mathrm{PB}^* \rightarrow \Phi + 2\mathrm{R}^{\cdot}, & v_7 = k_7 [\Phi^*][\mathrm{PB}],
\end{array}$$

Fig. 2. Dependence of $1/B$ on $1/[\mathrm{PB}]$

Figure 2: Fig. 2. Dependence of $1/B$ on $1/[\mathrm{PB}]$

where I_0 is the intensity of the incident radiation; $[\mathrm{C_6H_6}]$, [PB], and $[\Phi]$ are the concentrations of benzene, peroxide, and phenanthrene; $\varepsilon_{\mathrm{C_6H_6}}$ and ε_{Φ} are the numbers of electrons in the molecules of benzene and phenanthrene; k_0 is the proportionality constant; $R^{\cdot}$ denotes radicals formed during decomposition of the peroxide.

Fig. 2. Dependence of $1/B$ on $1/[\mathrm{PB}]$

In the proposed scheme the following simplifying assumptions have been made: (a) since the concentrations of benzoyl peroxide in the solution are small, decomposition of the peroxide due to direct action of the radiation may be neglected; (b) decomposition of excited benzene and phenanthrene molecules into radicals is not considered, owing to the small radiation yield of radicals from these hydrocarbons; (c) the excited phenanthrene molecules obtained by reactions IV and V are kinetically identical.

In the stationary state,

$$k_0 I_0 k_1 [\mathrm{C_6H_6}]\varepsilon_{\mathrm{C_6H_6}} = k_2[\mathrm{C_6H_6^*}] + k_3[\mathrm{C_6H_6^*}][\mathrm{PB}] + k_4[\mathrm{C_6H_6^*}][\Phi]; \tag{1}$$

$$k_0 I_0 k_5 [\Phi]\varepsilon_{\Phi} + k_4[\mathrm{C_6H_6^*}][\Phi] = k_6[\Phi^*] + k_7[\Phi^*][\mathrm{PB}]. \tag{2}$$

Since the rate of radiolytic decomposition of benzoyl peroxide is

$$V = -\frac{d[\mathrm{PB}]}{dt} = k_3[\mathrm{C_6H_6^*}][\mathrm{PB}] + k_7[\Phi^*][\mathrm{PB}], \tag{3}$$

then, substituting into (3) the values of $[\mathrm{C_6H_6^*}]$ and $[\Phi^*]$ determined from (1) and (2), one readily obtains an equation for the rate of peroxide decomposition.

At sufficiently high phenanthrene concentrations, processes II and III may be neglected in comparison with process IV. Since under these conditions

$$V = k_7[\Phi^*][\mathrm{PB}],$$

then we obtain

$$V = \frac{k_0 I_0 k_5 \varepsilon_{\Phi} k_7 [\mathrm{PB}]}{k_6 + k_7[\mathrm{PB}]}[\Phi] + \frac{k_7 k_0 I_0 k_1 [\mathrm{C_6H_6}]\varepsilon_{\mathrm{C6H_6}}[\mathrm{PB}]}{k_6 + k_7[\mathrm{PB}]}. \tag{4}$$

At [PB] = const, the second term in equation (4) is a constant quantity and, consequently, the rate of decomposition of benzoyl peroxide increases linearly with increasing phenanthrene concentration.

By extrapolating the linear portions of the curves in Fig. 1 to their intersection with the ordinate axis, one can determine the intercept B in equation (4) for each of the three peroxide concentrations (see Table 1).

Table 1

$[\mathrm{PB}] \cdot 10^3$, mol/l	12.5	8.3	4.2
$B \cdot 10^3$, mol/l • h	0.125	0.110	0.095

Introducing the notation $I_{\mathrm{C6H_6}} = k_0 I_0 [\mathrm{C_6H_6}] \varepsilon_{\mathrm{C6H_6}}$, we obtain

$$\frac{1}{B} = \frac{1}{I_{\mathrm{C6H_6}}} + \frac{k_6}{k_7 I_{\mathrm{C6H_6}}} \frac{1}{[\mathrm{PB}]},$$

i.e., $1/B$ is a linear function of $1/[\mathrm{PB}]$ (see Fig. 2). Hence $k_6/k_7 = 2 \cdot 10^{-3}$ mol/l.

It is of interest to estimate the mean lifetime of excited phenanthrene molecules that transfer energy to benzoyl peroxide. If it is assumed that energy transfer occurs upon collision of excited phenanthrene molecules with peroxide molecules and that each collision is effective, then the mean lifetime of phenanthrene molecules in the excited state can be calculated from the formula

$$k_6/k_7 = 1/4\pi D R \tau, \tag{5}$$

where R is the half-sum of the effective radii of the phenanthrene and benzoyl peroxide molecules ($\sim$ 5 Å); D is the diffusion coefficient in benzene ($\sim 10^{-5}$ cm^2/sec); τ is the mean lifetime of the excited phenanthrene molecules. The calculation gives $\tau \simeq 10^{-7}$ sec.

It should be noted that for excited benzene molecules, which determine the decomposition of benzoyl peroxide at concentrations of the latter below 0.01 mol/l, τ, as was shown earlier ([1,2]), is also equal to $\sim 10^{-7}$ sec.

Recently, in a number of studies on the fluorescence of solutions of organic substances ([4–6]), it has been shown that in many cases resonance energy transfer occurs from excited solvent molecules to luminophore molecules.

Bowen and Brocklehurst ([7]) believe that in solutions of organic substances resonance energy transfer occurs over a distance of $\sim$ 50 Å.

If it is assumed that, for resonance energy transfer, relation (5) remains valid ([5]), then, taking $R = 50$ Å, we obtain for resonance energy transfer for excited molecules of both benzene and phenanthrene a mean lifetime $\tau \simeq 10^{-8}$ sec.

The authors express their gratitude to Prof. S. S. Medvedev for his interest in the present work.

Physicochemical Institute
named after L. Ya. Karpov

Received
25 IV 1957

CITED LITERATURE

1. V. A. Krongauz, Kh. S. Bagdasar' yan, DAN, **114**, No. 4, 829 (1957).
2. V. A. Krongauz, Kh. S. Bagdasar' yan, Collection of works on radiation chemistry, 1957 (in press).
3. H. Kallmann, M. Furst, Phys. Rev., **79**, 857 (1950).
4. E. Bowen, R. Livingston, J. Am. Chem. Soc., **76**, 6300 (1954).
5. T. P. Belikova, M. D. Galanin, Z. A. Chizhikova, Izv. AN SSSR, ser. fiz., **20**, 384 (1956).
6. R. Hardwick, J. Chem. Phys., **26**, 323 (1957).
7. E. Bowen, B. Brocklehurst, Trans. Farad. Soc., **49**, 1131 (1953).

Note: Figure translations are in progress. See original paper for figures.