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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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TRANSFER OF EXCITATION ENERGY AND SENSITIZATION OF CHEMICAL REACTIONS DURING THE RADIOLYSIS OF SOLUTIONS OF ORGANIC DISULFIDES

(Presented by Academician S. S. Medvedev on February 6, 1960)

In papers ([1,2]), the radiolysis of dilute solutions of organic peroxides and azo compounds in benzene was studied. It was established that certain aromatic substances that readily decompose into radicals (benzoyl peroxide, phenylazotriphenylmethane) decompose in solutions with yields that are considerably greater than the yields corresponding to the direct action of radiation. This is connected with a very effective transfer of excitation energy from benzene to the dissolved substances.

Fig. 1. Dependence of the decomposition yield of disulfides on their concentration in solutions:
a –DPhD; *b* –DBD; *v* –DBDS. The points on the curves correspond to mean values from several independent measurements.

In the present work, the study was continued of the influence of the chemical nature of the acceptor on the efficiency of energy transfer and on the degree of utilization of this energy in the decomposition reaction of the acceptor. The radiolysis of dilute solutions of organic disulfides in benzene was studied. Disulfides containing aromatic and aliphatic substituents were investigated.

Thiyl radicals formed upon dissociation of disulfides are comparatively inactive and, upon recombination with one another, form the original molecules. Therefore, the rate of radiolytic decomposition of disulfides in benzene cannot be determined directly from the decrease in the concentration of disulfides, as was established by specially designed experiments.

Fig. 2. Dependences of $1/G^0(-D)$ on $1/[D]$ (designations as in Fig. 1)

Figure 2: Fig. 2. Dependences of $1/G^0(-D)$ on $1/[D]$ (designations as in Fig. 1)

In order to prevent the reverse reaction, diphenylpicrylhydrazyl (DPPH) was added to the disulfide solutions. DPPH radicals interact with the radicals formed during radiolysis and thus prevent recombination of thiyl radicals with one another.

Radiolysis of solutions carefully freed from air was carried out under the action of Co^{60} γ-rays. The yield of radicals per 100 eV of energy absorbed by the solution was determined from the decrease in the concentration of DPPH. Since two radicals are formed upon decomposition of one disulfide molecule, the radiation yield of disulfide decomposition was determined as one half of the difference between the radical yields from the solution and from the pure solvent. The concentration of DPPH was measured on an SF-4 spectrophotometer at $\lambda = 520$ mμ.

For determining, with the aid of DPPH, the yield of radicals from solutions, we first established the critical concentrations of DPPH, i.e., the minimum concentrations at which all radicals formed during radiolysis interact with DPPH ([3]). DPPH concentrations of $5 \cdot 10^{-4}$–$2 \cdot 10^{-3}$ M were used, which in all cases exceeded the critical concentrations.

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Figure 1 shows curves for the dependence of the radiation yield of decomposition of diphenyl disulfide (DPD), dibenzyl disulfide (DBD), and dibenzoyl disulfide (DBDS) on the concentration of these substances in solution.

The radiation yields of decomposition of the disulfides per 100 eV of energy absorbed by the disulfides themselves, calculated from the slope of the initial portions of the curves, are approximately 1000 for DPD and DBD, and approximately 400 molecules for DBDS. The dissociation energy of DPD and DBDS apparently does not exceed 30 kcal/mol, while that of DBD is 70 kcal/mol (4, 5). This means that the decomposition yields of these disulfides at low solution concentrations exceed, by at least an order of magnitude, the maximum yields that can be expected if it is assumed that the energy absorbed by the dissolved substances is spent entirely on their dissociation. It is probable that in solutions of disulfides, energy transfer occurs from the solvent to the dissolved substances.

Fig. 2. Dependences of $1/G^0(-D)$ on $1/[D]$ (designations as in Fig. 1)

Starting from the assumption of energy transfer and the steady-state condition, we arrive at the following dependence (1) of the yield of disulfide decomposition $G^0(-D)$ on their concentration in solution $[D]$:

$$G^0(-D) = \frac{100k_1k'_3k'_5[D]}{(k_2 + k'_3[D])(k'_4 + k'_5)}, \quad (1)$$

where k_1 is the rate constant for the formation of excited benzene molecules, expressed in molecules per 1 eV; k_2 is the rate constant of their spontaneous deactivation; k'_3 is the rate constant of energy transfer from benzene to the disulfides; k'_4 and k'_5 are the rate constants of deactivation and dissociation of excited disulfide molecules. Equation (1) is applicable for acceptor concentrations not higher than approximately $0.01\,M$, when its decomposition due to energy transfer considerably exceeds decomposition as a result of the direct action of radiation.

Table 1

Disulfide	$\frac{k'_3}{k_2}$	$\frac{k_1k'_5}{k'_4 + k'_5}$
DPD	250 ± 15	0.02 ± 0.002
DBD	200 ± 15	0.02 ± 0.002
DBDS	100 ± 15	0.02 ± 0.002

Figure 2 shows the dependences of $1/G^0(-D)$ on $1/[D]$, which, in accordance with equation (1), are linear. The point of intersection of these straight lines with the ordinate axis corresponds to the values $(k'_4 + k'_5)/100k_1k'_5$ for the indicated disulfides, and from the slopes of these straight lines one can calculate k'_3/k_2 (Table 1). The ratios k'_3/k_2 characterize the efficiency of energy transfer from benzene to the disulfides, while the quantities $k_1k'_5/(k'_4 + k'_5)$ are the probability of decomposition of excited disulfide molecules into radicals, multiplied by the constant k_1 characteristic of the given solvent.

As can be seen from Table 1, DPD and DBD are equally active energy acceptors, while DBDS accepts excitation energy with approximately half the efficiency. At the same time, decomposition of the excited molecules occurs in these three disulfides with approximately equal probability.

Since $k'_5/(k'_4 + k'_5) \leqslant 1$, the minimum value of k_1 is 0.02 molecule per 1 eV. Thus, per 100 eV of radiation energy absorbed by the solution, at least 2 excited benzene molecules are formed that are capable of efficiently transferring energy to disulfides.

It may be assumed that, in the radiolysis of solutions of aromatic disulfides, the excitation energy of benzene is initially accepted by the phenyl rings of the acceptor and is then transferred to other parts of the molecule. In this case, comparison of the data for diphenyl and dibenzyl disulfide indicates that the presence of aliphatic CH_2 groups between the phenyl rings and the disulfide group apparently does not hinder energy migration from the phenyl rings to the S—S group.

Fig. 3. Dependence of $G(-\mathrm{PB})$ on $[D]$ for DBD (a) and DBDS (b)

Figure 3: Fig. 3. Dependence of $G(-\mathrm{PB})$ on $[D]$ for DBD (a) and DBDS (b)

The radiation yields of decomposition of 0.01 M solutions of all the disulfides we studied are compared below.

DPD	DBD	DBDS	Methoxybenzyl disulfide	Diallyl disulfide	Diethyl disulfide	Dioctyl disulfide
1.5	1.4	0.9	0.8	0.7	0.3	0.3

The fact that the decomposition yields of diethyl and dioctyl disulfide are identical makes it possible to conclude that lengthening the hydrocarbon chain does not lead to a noticeable decrease in the probability of decomposition of excited disulfide molecules. One may think that the excitation energy can migrate, without appreciable losses, along the aliphatic chain to the S—S bond. The lower radiolytic decomposition yields of aliphatic disulfides compared with aromatic ones are possibly associated with the considerably lower efficiency of intermolecular energy transfer (1). Since the dissociation energy of DBD and of aliphatic disulfides is about 70 kcal/mol, it is natural to assume that energy quanta of at least 3 eV are transferred from benzene to the acceptors.

Fig. 3. Dependence of $G(-\mathrm{PB})$ on $[D]$ for DBD (**a**) and DBDS (**b**)

It was shown earlier that, when energy acceptors such as anthracene, phenanthrene, benzoic anhydride, phenylazotriphenylmethane, and diazoaminobenzene are added to benzene solutions of benzoyl peroxide, the yield of radiolytic decomposition of benzoyl peroxide decreases substantially[1,2,6]. This is evidently associated with competition among acceptors in the process of energy transfer from excited benzene molecules.

Figure 3 shows the dependences of the decomposition yield of a 0.005 M solution of benzoyl peroxide on the concentrations of DBD and DBDS. (It was established in separate experiments that the effect of DBD and DPD on the radiolysis of the peroxide is practically identical, while diethyl disulfide at concentrations < 0.02 M does not exert a noticeable protective action.)

It is seen from the figure that DBDS exerts a considerably greater protective action than DBD. As the concentration of disulfides is increased, the peroxide decomposition yield approaches a limiting value. If it is assumed that energy transfer occurs only from excited benzene molecules to competing acceptors, it is not difficult to obtain:

Fig. 4. Dependence of $\frac{G^0(-\mathrm{PB})}{G(-\mathrm{PB})} - 1$ on $[D]$ for DBD (a) and DBDS (b)

Figure 4: Fig. 4. Dependence of $\frac{G^0(-\mathrm{PB})}{G(-\mathrm{PB})} - 1$ on $[D]$ for DBD (a) and DBDS (b)

$$\frac{G^0(-\mathrm{PB})}{G(-\mathrm{PB})} - 1 = \frac{\frac{k_3'}{k_2}[D]}{1 + \frac{k_3}{k_2}[\mathrm{PB}]}, \tag{2}$$

where $G^0(-\mathrm{PB})$ and $G(-\mathrm{PB})$ are the radiation yields of decomposition of benzoyl peroxide in the absence and presence of protective additives, and k_3 is the rate constant for transfer of excitation energy from benzene to the peroxide.

At $[\mathrm{PB}] = \mathrm{const}$, the value of the left-hand side of equation (2) should be proportional to $[D]$. It is seen from Fig. 4 that, for the disulfides we investigated, the proportional dependence is not obeyed. As before[6], we assumed that energy can be transferred from excited disulfide molecules to benzoyl peroxide. Proceeding from the condition of stationarity of the processes, we have*:

$$\frac{G(-\mathrm{PB})}{G^0(-\mathrm{PB})} = \left(1 + \frac{k_3'}{k_3}\frac{[D]}{[\mathrm{PB}]}\alpha\right) \times \left(1 + \frac{\frac{k_3'}{k_3}\frac{[D]}{[\mathrm{PB}]}}{\frac{k_2}{k_3}\frac{1}{[\mathrm{PB}]} + 1}\right)^{-1}, \tag{3}$$

where

$$\alpha = \frac{k_6[\mathrm{PB}]}{k_4' + k_5' + k_6[\mathrm{PB}]};$$

k_6 is the rate constant for transfer of energy from the disulfide to the peroxide. α may be regarded as the probability of energy transfer from the disulfide to the peroxide.

Fig. 4. Dependence of $\frac{G^0(-\mathrm{PB})}{G(-\mathrm{PB})} - 1$ on $[D]$ for DBD (a) and DBDS (b)

The decomposition of benzoyl peroxide in the presence of DBD and DBDS agrees with equation (3), which, after certain transformations, makes it possible to determine α and k_3'/k_2 graphically. For DBD and DBDS, k_3'/k_2, determined from their protective action, is $\sim$ 150 and 400. The agreement between the values of k_3'/k_2 for DBD obtained from the data on the rate of decomposition of DBD and from its protective action is satisfactory. For DBDS there is no such agreement: from the protective action, DBDS is an approximately four times more efficient energy acceptor than can be concluded from the rate of its radiolytic decomposition. The reason for this discrepancy is at present still unclear to us.

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* A detailed kinetic analysis of the results obtained in the present and previously published works will be presented in another article.

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