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Abstract

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STUDY OF THE MECHANISM OF THE INTERACTION OF BENZOYL PEROXIDE WITH DIMETHYLANILINE BY SPECTRAL METHODS

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Recently, a considerable number of works have been devoted to the study of the interaction between peroxides and amines, most of which concern tertiary amines. Interest in studying the reactions of peroxides with tertiary amines is explained by the fact that these systems are used as an effective initiator in the polymerization of vinyl compounds in bulk and in emulsions.

A number of authors ([1–5]) have studied the mechanism of the interaction of benzoyl peroxide with tertiary amines. In the schemes they proposed for the interaction of benzoyl peroxide with tertiary amines (mainly with dimethylaniline), the formation of an amine ion-radical is assumed at an intermediate stage of the reaction.

According to Horner ([1]), an indirect proof of the formation of the dimethylaniline ion-radical may be the coloration of a mixture of peroxide with amine in chloroform in the presence of chloride ion. However, in none of the cited works was there direct proof of the formation of the amine ion-radical.

In a number of cases, assumptions about the occurrence of ion-radicals under photochemical and radiation action on certain amines were confirmed by spectrophotometric methods of investigation ([6–8]). Similar observations were also made in other cases, for example, in the oxidation of tritolylamine: by the method of potentiometric titration ([9]) and by the method of paramagnetic resonance ([10]).

To prove the formation of an amine ion-radical in the interaction of benzoyl peroxide with dimethylaniline, in the present work the mechanism of this reaction was investigated with the aid of UV and IR absorption spectra.

The electronic absorption spectra of solutions of the substances under investigation were studied on a Hitachi EPS-2U recording spectrophotometer (with a crystalline-quartz prism) at room temperature and at the temperature of liquid nitrogen (−196°). As solvent, an EPA mixture was used (ether : isopentane : ethanol = 5 : 5 : 2 by volume), since at low temperatures it gave a transparent

Fig. 1. Absorption spectra of a 0.05 M DMA solution in EPA. 1 –solution at room temperature before irradiation; 2 –solution at −196° after irradiation (irradiation time 1 h); 3 –solution 2 upon warming to room temperature

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glassy matrix. The components comprising the EPA were carefully purified and dried.

A quartz cuvette 0.6 cm thick was placed in a quartz Dewar with flat windows, which was inserted into the cuvette compartment of the spectrophotometer.

The IR absorption spectra were studied on a Unicam SP-100 self-recording vacuum spectrophotometer in the region from 400 to 3600 cm^{-1} and on an IKS-14 instrument. Cuvettes of NaCl, KBr, and LiF with thicknesses of 0.01, 0.05, and 0.1 mm were used. The investigations were carried out at room temperature. In all experiments, atmospheric oxygen was excluded from the reaction system.

To check the adopted procedure, experiments were carried out to detect the ion-radicals of amines studied in works ([7,8,11]). For this purpose, 0.05 M solutions of aniline, dimethylaniline, β-naphthylamine, and diphenylamine in EPA were prepared. These solutions, freed from dissolved

air in them, cooled to the temperature of liquid nitrogen, and irradiated with a low-pressure mercury lamp, the emission maximum of which lay in the region of 2537 Å. The irradiation time was varied from 15 min to 2 h. In this case, coloration of the frozen solution was observed; at low temperature it persisted for a long time. When the solutions were warmed to room temperature, the coloration rapidly and irreversibly disappeared. According to the data of works ([7], [8], [11]), the appearance of coloration in frozen solutions of amines indicates the presence of the corresponding ion-radicals. The change in coloration with increasing temperature means the disappearance of the ion-radicals. (The coloration of the solutions observed by us upon their irradiation is in good agreement with the literature data.) At the same time, the UV absorption spectra of amine solutions before and after irradiation were studied. Figure 1 shows the absorption spectra of dimethylaniline. As can be seen from this figure, after irradiation a broad absorption band appears in the spectrum of dimethylaniline (DMA), with a maximum at $\lambda_{\max}$4600 Å, which was absent before irradiation. According to the literature data ([11], [12]), this band should be assigned to the dimethylaniline ion-radical. Thus, the use of an EPA solvent matrix under the experimental conditions makes it possible to detect the amine ion-radical.

Fig. 1. Absorption spectra of a 0.05 *M* DMA solution in EPA. 1 –solution at room temperature before irradiation; 2 –solution at −196° after irradiation (irradiation time 1 h); 3 –solution 2 upon warming to room temperature.

Fig. 2

Figure 2: Fig. 2

In studying the spectra of a solution of a mixture of benzoyl peroxide (BP) with dimethylaniline in EPA at room temperature, the appearance of a broad absorption band with $\lambda_{\text{max}} \approx 4600–4700$ Å was also observed (see Fig. 2). The magnitude of the absorption-band maximum decreases with time, and after approximately 45 min the band disappears completely.

The appearance of a maximum at $\lambda_{\text{max}} \approx 4600–4700$ Å in the spectra of a solution of a mixture of BP and DMA in EPA may serve as direct proof of the existence of the DMA ion-radical formed in the reaction of interaction of benzoyl peroxide with dimethylaniline (see Figs. 1 and 2). Consequently, even at room temperature the concentration of amine ion-radicals arising upon interaction of BP with DMA is quite sufficient for their detection.

In parallel with the study of the UV absorption spectra of the solution of the mixture of BP with DMA in EPA, the IR absorption spectra of the same solution were studied. Figure 2B presents spectra in the region 1650–1850 cm^{-1}. In this region there are characteristic bands of $C = O$ stretching vibrations corresponding to benzoyl peroxide (1794 and 1772 cm^{-1}) and benzoic acid (1720 cm^{-1}). As can be seen from Fig. 2B, the intensity of the bands at 1794 and 1772 cm^{-1} decreases with time, whereas the intensity of the band ···

1720 cm^{-1} increases. The change in the intensity of these bands is in good agreement with data on the decomposition of benzoyl peroxide in the presence of dimethylaniline, obtained by chemical methods of investigation ([1,5]).

Comparison of Figs. 2A and 2B shows that the time of consumption of benzoyl peroxide from the reaction system (disappearance of the bands 1794 and

Fig. 2. Absorption spectra of a solution of a mixture of BP and DMA in EPA (equimolecular concentrations 0.05 mol/l) at room temperature. A –ultraviolet, B –infrared; cell thickness 0.1 mm. 1 –initial mixture, 2 –after 8 min., 3 –after 20 min., 4 –after 45 min., 5 –after 60 min.

1772 cm^{-1}) approximately coincides with the time of disappearance of the band with a maximum at $\lambda_{\text{max}} \approx 4600–4700$ Å, characterizing the presence of the dimethylaniline ion-radical. Thus, this is a direct confirmation of the principal scheme of the interaction of benzoyl peroxide with dimethylaniline, in which, as an intermediate stage of the reaction, the formation of a complex including the amine ion-radical is envisaged, followed by its decomposition to benzoic acid ([1]).

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