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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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OXIDATION AND REDUCTION BY RADICAL PRODUCTS OF THE RADIOLYSIS OF ORGANIC COMPOUNDS

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The occurrence of oxidation reactions under the action of ionizing radiation, without the participation of molecular oxygen, owing to the products of radiolysis of an organic solvent, was established by us for solutions of leuco bases of certain triphenylmethane dyes in ketones ([1]). This study was then extended to other organic solvents; the reversible redox pair methylene blue (MB)—leucomethylene blue (LMB), whose radiation behavior has repeatedly been studied in aqueous solutions ([2]-[4]), was used as an indicator of oxidation-reduction processes. The present communication gives results showing that, depending on the nature of the organic solvent, irradiation may bring about either oxidation of LMB or reduction of MB.

Fig. 1. Dependence of the yield of radiation oxidation of LMB to MB on concentration:
1 —acetone, 2 —nitromethane, 3 —methanol, 4 —ethanol

The effect of radiation was studied on solutions of LMB and MB from $10^{-6}M$ to $10^{-1}M$ in acetone, nitromethane, methanol, ethanol, *n*-propanol, *n*-butanol, formamide, pyridine, N-methylformamide, and N,N-dimethylformamide. All solvents were carefully purified; MB was recrystallized several times from water and ethyl alcohol. Colorless LMB solutions were prepared by reducing MB with hydrogen in the presence of Pd black directly in the solvent under investigation, followed by displacement of the hydrogen with nitrogen and separation of the LMB solution from the catalyst without contact with air. In all the solvents studied, appreciable reduction of MB to LMB takes place under these conditions. Solutions sealed in a nitrogen atmosphere were exposed to x-ray and gamma

Fig. 2

Figure 2: Fig. 2

radiation at a dose rate from $2.8 \cdot 10^{12}$ to $5 \cdot 10^{15}$ eV/cm^3 per sec and were spectrophotometered in the same ampoule. Details of the procedure are given elsewhere.

Oxidation of LMB. Upon irradiation, colorless LMB solutions in acetone, nitromethane, and methanol become colored. Comparison of the absorption spectrum of the product of the radiation reaction with the spectrum of MB in the corresponding solvent shows that, under the action of radiation, oxidation of LMB to MB occurs. The linear increase in MB concentration with dose observed in all the cases studied in the region up to 5000–7000 rad makes it possible to calculate the radiation yield of the reaction.

Figure 1 presents the dependence of the radiation yield of oxidation of LMB to MB on the LMB concentration for four solvents. In nitromethane and methanol, an initial increase of the yield with concentration is observed, followed by a region in which the yield is independent of concentration between $\sim 10^{-5} M$

and $\sim 10^{-2}\ M$, and, finally, a new increase in yield; in the case of acetone the yield is considerably higher and reaches constancy only at $C \sim 10^{-2}\ M$. In the ethanol given for comparison, oxidation is practically absent at concentrations below $\sim 10^{-1}\ M$.

Fig. 2. Reversibility of the radiation decolorization of MG. **1** –formamide, **2** – N-methylformamide, **3** –N,N-dimethylformamide. Solid lines –irradiation in a nitrogen atmosphere; dashed lines –holding without irradiation after admission of air (horizontal scale 0.5 cm = 10 min.)

Reduction of MG. Nitrogen-saturated solutions of MG in organic solvents are always decolorized upon irradiation with a greater or lesser yield, but not in all cases is the decolorization determined only by reduction of MG to LMG. The criterion for the latter is complete restoration of the initial color intensity when oxygen is admitted into the solution.

The curves presented in Fig. 2, corresponding to irradiation in a nitrogen atmosphere and holding without irradiation after admission of oxygen, illustrate three possible cases: completely reversible reduction to LMG in formamide, partial reduction to LMG and partially irreversible decolorization in N-methylformamide, and completely irreversible decolorization in N,N-dimethylformamide. The initial sections of the curves are linear, and their slope, corresponding to the radiation yield of the reaction, depends on the initial concentration of the dye. Fig. 3 presents the yield of reversible reduction as a function of the concentration of MG in a series of solvents. The character of the dependence is analogous to that observed in the reactions of oxidation of LMG to MG, but the curves break off earlier, since in more concentrated solutions the possibility of measurements is

Fig. 3

Figure 3: Fig. 3

limited by the high optical density.

Fig. 3. Dependence of the yield of radiation reduction of MG to LMG. **1** –methanol, **2** –ethanol, **3** –*n*-propanol, **4** –butanol, **5** –formamide, **6** –N-methylformamide, **7** –pyridine.

Figs. 1 and 3 demonstrate the influence of functional groups in the molecules of organic solvents on the reactions considered: in nitromethane only oxidation of LMG occurs, in methanol oxidation of LMG and reduction of MG occur to an equal extent, while in aliphatic normal alcohols, begin-

in ethanol, in formamide, and in pyridine only reversible reduction of MG to LMG. Up to concentrations of $\sim 10^{-2} M$, the direct action of radiation on the dissolved substance may be neglected, and all processes are determined by the interaction of the acceptor with the radiolysis products of the solvent.

In the organic liquids studied, various molecular products are formed under the action of radiation. Special experiments established that, although in a number of cases these products are oxidizing agents or reducing agents for the acceptor (HNO_2, HCHO, CH_3CHO, etc.), their role during irradiation in our experiments is negligibly small, and the observed processes occur only at the expense of short-lived radiolysis products.

The general form of the dependence of the yield on the acceptor concentration, represented in Figs. 1 and 3 by curves with a characteristic plateau in the concentration region $\sim 10^{-4}$–$10^{-2} M$, is well known in the radiation chemistry of aqueous solutions, where it is interpreted on the basis of competition between different reactions of water radiolysis products with one another and with acceptors. The plateau corresponds to complete trapping by the acceptor of radicals available for the given reaction, while the subsequent increase in yield corresponds to the appearance of a new process. This suggests that in organic solvents as well, oxidation and reduction reactions in dilute solutions are carried out by the primary radical products of solvent radiolysis, the direction and efficiency of the processes depending on the nature of the radicals and on their yield.

The redox pair used, MG–LMG, corresponds to a two-step transition. In radiation transformations, the participation of primary radicals in successive stages of a multistep transition is unlikely. It may therefore be considered that, in the system under consideration, the primary radicals provide only a one-step transition from LMG or MG to an intermediate semiquinone, while the final products are formed as a result of disproportionation according to the scheme

$$A \rightsquigarrow \dot{R}, \quad \dot{R} + (\text{L or M}) \rightarrow \dot{S} \text{ and } 2\dot{S} \rightarrow M + L,$$

where A is the solvent, $\dot{S}$ is the semiquinone, M is the dye, and L is the leuco form, as occurs in nonradiation oxidation and reduction reactions of this type (5).

The yields of primary radicals exhibiting oxidizing and reducing properties with respect to the pair used can be estimated from the yields of formation of MG and LMG in the region where they are independent of the acceptor concentration. The corresponding values obtained in the radiolysis of the solvents studied are given below.

Table 1

Solvent	$G(\dot{R}_{\text{ox}})$	$G(\dot{R}_{\text{red}})$	Solvent	$G(\dot{R}_{\text{ox}})$	$G(\dot{R}_{\text{red}})$
Nitromethane	4.0 ± 0.3	0	*n*-Butanol	0	4.4 ± 0.2
Methanol	3.6 ± 0.2	2.8 ± 0.2	Formamide	0	6.0 ± 0.4
Ethanol	0	7.0 ± 0.2	N-methylformamide	0	4.8 ± 0.2
n-Propanol	0	6.4 ± 0.4	Pyridine	0	1.2 ± 0.2

Table 1 does not include the results obtained with acetone. The very high values of the limiting yield of MG ($G \sim 13$) and the concentration at which it is reached ($C \sim 10^{-2} M$) make a purely radical mechanism of oxidation unlikely. It is possible that the reaction is partially due to excited acetone molecules. This question requires further investigation. In all other cases, the yields remain within the limits expected for radicals of ionization origin.

The radicals formed during the radiolysis of a given solvent may perform different functions with respect to different acceptors.

Thus, for example, in the case of methanol we obtained, for radicals reducing MG and oxidizing LMG, respectively, $G(\dot{R}_{\text{red}}) = 2.8$ and $G(\dot{R}_{\text{ox}}) = 3.6$. At the same time, the yield of reduction of Fe^{III} in the radiolysis of its neutral methanolic solutions is, according to Adams and Baxendale [6], $G(\mathrm{Fe}^{II}) = G(\dot{R}_{\text{red}}) = 6.1$, i.e., close to the sum of the yields of reducing radicals and oxidizing radicals with respect to the MG–LMG system. Evidently, the same organic radicals, according to the authors mentioned, mainly $\dot{\mathrm{C}}\mathrm{H}_2\mathrm{OH}$ and $\dot{\mathrm{C}}\mathrm{H}_3$, are capable of reducing Fe^{III} and oxidizing LMG. The study of reactions in which free radicals arising during the radiolysis of organic compounds enter into reaction with various acceptors is thus a source of information about their tendency to add or donate electrons under different conditions. To obtain such characteristics, it is necessary to identify the radicals active in each particular case, which can be achieved by combining conclusions drawn on the basis of kinetic studies with data obtained by the method of electron paramagnetic resonance.

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