PHYSICAL CHEMISTRY

1962

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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STUDY OF THE MECHANISM OF RADIATION OXIDATION AND REDUCTION BY THE METHOD OF ELECTRON PARAMAGNETIC RESONANCE

(Presented by Academician A. N. Frumkin, 27 IX 1961)

As we established earlier (^{1} ^{2}), in various organic liquids, under the action of ionizing radiation, oxidation–reduction transformations occur in the pair methylene blue (MB)—leuco base (LMB). The nature of the dependence of the radiation yield on the concentration of the acceptor was interpreted, by analogy with aqueous solutions, as corresponding to reactions of the acceptor with radical products of radiolysis of the solvent. The correctness of this assumption can be established directly if, simultaneously with the formation and disappearance of the dye, the nature and concentration of free radicals in the irradiated system are determined by a direct method.

In the present communication we give the results of work carried out for this purpose, in which, in frozen methanolic, acetone, and nitromethane solutions, the radiation transformations of the LMB—MB pair were studied spectrophotometrically, and free radicals by the method of electron paramagnetic resonance. The solutions were prepared as described in (^{1}). Special devices made it possible to carry out measurements on SF4 and SF2M spectrophotometers at specified temperatures from 77° K to 293° K. In the work γ-radiation from Co^{60} of 1.25 MeV and Cs^{137} of 0.60 MeV was used, as well as X-radiation of 0.08 MeV at dose rates from $3.2 \cdot 10^{14}$ to $5.5 \cdot 10^{15}$ eV/g • sec and integral doses from 10^{17} to 10^{19} eV/g. The EPR spectra were recorded with an EPR-2 IKhF radiospectrometer (^{3}) in the form of differential curves of resonance absorption both after and during irradiation. In the latter case the beam of X-rays was introduced directly into the resonator (^{4}). The concentration of free radicals in samples containing 0.08–0.10 cm^3 of the solution under study was determined from the area under the integral resonance-absorption curve, calibrated with the aid of a standard carefully evacuated benzene solution of DPPH. For the study of EPR spectra in irradiated samples, ampoules of special glass that gave no signals in this region of the spectrum were used (^{4}). Irradiation of the samples and measurement of the EPR spectra were carried out in the temperature interval 77–153° K.

On irradiation of oxygen-free 10^{-6}–10^{-2} M frozen solutions of LMB in methanol,

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

acetone, and nitromethane in the indicated temperature interval, the formation of the MB dye is observed (as also at room temperature in the liquid phase), its concentration increasing linearly with dose up to $\sim 10^{19}$ eV/g. Figure 1 gives the values of the radiation yield of the dye as a function of the concentration of LMB and of temperature. The yield of MB increases with increasing LMB concentration and with rising temperature, but the curves, in contrast to those obtained at ordinary temperature, do not have characteristic plateaus corresponding to complete capture by the acceptor of the available radicals. As can be seen, radiation oxidation practically does not occur at 77° K, but it already proceeds with a noticeable yield at temperatures considerably below the melting points.

Oxygen-free 10^{-6}–10^{-4} M frozen solutions of MG in methanol are decolorized under the action of irradiation. The rapid restoration of the initial coloration at room temperature after admission of air indicates reversible reduction of MG to LMG. Figure 2 presents the dependence of the radiation yield of LMG on the concentration of MG in methanol at temperatures from 77° to 293° K. In contrast to the oxidation of LMG, the yield of reduction of MG does not depend on temperature.

Fig. 1. Radiation oxidation of LMG at low temperatures: in methanol: 1 –190°K, 2–168°K, 3–77°K; in nitromethane: 4–253°K, 5–219°K, 6–77°K; in acetone: 7–190°K, 8–168°K, 9–77°K

Fig. 2. Radiation reduction of MG in methanol at various temperatures: 1–293°K; 2–190°K; 3–168°K; 4–77°K

The EPR spectrum of methanol irradiated at 77° K is shown in Fig. 3A. It consists of three lines with an intensity ratio of $1:4:1$; the mean hyperfine splitting between the lines is 17.5 ± 0.5 oersted. Similar three-line spectra, but with different intensity ratios, have been reported by a number of authors (5–8). The form of the spectrum and the intensity ratio remain unchanged throughout the entire range of doses and temperatures investigated by us, and also upon storage for 1–2 weeks at 77° K. The radical accumulation curve reaches saturation at doses of $\sim 10^{19}$ eV/g.

Investigation of the products of liquid-phase radiolysis of methanol (9–11) leads to the conclusion that the principal primary radicals are $\dot{C}H_2OH$, $CH_3\dot{O}$, $\dot{C}H_3$, $\dot{O}H$; H atoms are usually also included among them, although in (11) a reaction scheme without their participation was proposed. From consideration of the spectra obtained by us it follows that they contain no lines corresponding to CH_3 radicals, H radicals, or OH radicals. On the basis of the data given for methane in (6), it may be expected that $\dot{C}H_3$ radicals disappear very rapidly in methanol at 77° K. The same applies to the H radical, which is observed in irradiated methane at 20° K, but not at 77° K (6). The absence of H signals in methanol is also mentioned in (8). Thus, it may be considered that at 77° the EPR spectrum of irradiated methanol represents a superposition of the spectra of the radicals $\dot{C}H_2OH$ and $CH_3\dot{O}$, the first of which

gives a triplet 1 : 2 : 1; to the second we assign a singlet line with

$$\frac{\Delta H}{2} = 14 \pm 0.5 \text{ Oe},$$

by analogy with the interpretation given in (6) for the spectrum of irradiated trioxane. From the observed ratio 1 : 4 : 1 it follows that under these conditions there are twice as many $\dot{C}H_2OH$ radicals as $CH_3\dot{O}$ radicals.

Fig. 3. EPR spectra of irradiated systems: *A*—methanol at −77°K; *B*—methanolic solution of MG at 77°K; *V*—methanolic solution of LMG at 153°K. Dependence of radical yield on temperature: 1—methanol; 2—methanolic solution of MG; 3—methanolic solution of LMG; 4—acetone; 5—acetone solution of IMG; 6—nitromethane; 7—nitromethane solution of LMG

Fig. 4. Change in radical concentration as a function of storage time at 153°K in methanol irradiated at 77°K in the presence and absence of LMG. 1—sum of radicals in methanol; 2—$\dot{C}H_2OH$ in methanol; 3—$CH_3\dot{O}$ in methanol; 4—$\dot{C}H_2OH$ in the presence of LMG; 5—$CH_3\dot{O}$ in the presence of LMG

Comparison of the EPR spectra of irradiated solutions and of the pure solvent makes it possible to judge the nature of the radicals carrying out oxidation or reduction reactions. Figure 3 shows spectra obtained with solutions of MG (spectrum *B*) and LMG (spectrum *V*) in methanol. Solutions of concentration 10^{-4} *M* were irradiated at 77° and 153°K, respectively, i.e., under conditions in which the yields of MG reduction and LMG oxidation reached $G = 0.38$ and $G = 0.03$. As can be seen, neither in the character of the spectrum nor in the yields of radicals at different temperatures (Fig. 3, 2) does the MG solution differ in any way from pure methanol. From this it may be concluded that the radiation reduction reaction of MG is not carried out by any of the radicals registered at 77°K. A different picture is observed in irradiated LMG solutions. The EPR spectrum differs sharply from the spectrum of methanol, representing a triplet 1 : 2 : 1, and the yield of radicals registered at different temperatures is substantially lower than in methanol (Fig. 3, 3). Figure 4 shows the kinetics of disappearance at 153°K of the sum of radicals, as well as of the $\dot{C}H_2OH$ and $CH_3\dot{O}$ radicals separately, in pure methanol and in an LMG solution irradiated at 77°K. As can be seen, in an LMG solution the $CH_3\dot{O}$ radicals are completely absent from the very beginning of observation, whereas in pure methanol they constitute 30% of the total amount and disappear only after 7-8 min, simultaneously with the $\dot{C}H_2OH$ radicals. In the presence of LMG the latter are consumed faster than in pure methanol.

The results obtained unambiguously prove that the radiation oxidation of LMG in methanolic solutions is carried out by radical products of the radiolysis of the solvent, and make it possible to ascribe it primarily to $CH_3\dot{O}$ radicals, and also, but to a lesser extent, to $\dot{C}H_2OH$ radicals. At 168°K, i.e., 7° below the melting point of CH_3OH, their mobility

is already sufficient for the reaction to proceed with a yield of $G = 0.05$ molecules/100 eV. The two-step reaction apparently proceeds by a double action of the oxidizing radical, since in the solid phase disproportionation of the bulky semiquinone is impossible. As for the reduction of MG, the data obtained are insufficient for considering a specific mechanism. The independence of the yield from temperature shows that the reaction is carried out by very mobile agents, possibly hot H atoms or thermalized electrons. The question requires further investigation, first of all experiments at lower temperatures.

Figure 3 also gives the total yields of radicals in acetone and nitromethane solutions of LMG irradiated at different temperatures, and in pure solvents. As in the case of methanol, the observed oxidation corresponds to a definite consumption of free radicals; however, the EPR spectra were not interpreted, and the oxidation reactions cannot be assigned to particular radicals.

Table 1

G (R)	methanol	ethanol	*n*-propanol	*n*-butanol	acetone	methyl ethyl ketone	methyl butyl ketone	nitromethane	formamide	N-methylformamide	N,N-dimethylformamide	pyridine
EPR	5.5	9.0	8.8	7.5	1.4	5.6	6.0	4.1	9.5	6.4	3.1	1.1
Oxid. LMG	3.6	0	0	0	26	6.2	6.0	4.0	0	0	0	0
Red. MG	2.8	7.0	6.4	4.4	0.8	0	0	0	6.0	4.8	1.2	1.2

Table 1 gives, for a number of organic solvents, the radiation yields of radicals determined by the EPR method at 77° K after irradiation at the same temperature, and the yields calculated from data on the radiation oxidation of LMG and reduction of MG at ordinary temperature in the region of concentration independence, on the basis of two radicals per one transformed molecule.

As should be expected for a radical mechanism of the reactions and the independence of the radiation yield of radicals from temperature, in most cases $G(R)_{\mathrm{EPR}} \geq G(R)_{\mathrm{act}}$. The exception is acetone, for which $G(R)_{\mathrm{EPR}} \ll G(R)_{\mathrm{act}}$. This confirms the supposition expressed earlier (2) that the very high reaction yields observed in the case of acetone cannot be determined only by radical processes.

The authors express their gratitude to Yu. B. Yakovlev and G. A. Semenov for carrying out part of the EPR measurements.

Institute of Electrochemistry
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Received
23 IX 1961

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