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Abstract

Full Text

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RADIATION OXIDATION OF LEUCO BASES IN KETONES IN THE ABSENCE OF OXYGEN

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Reactions of radiation oxidation in organic systems at the expense of molecular oxygen are widely known. One may, however, expect by analogy with aqueous solutions that, in organic liquids, dissolved substances are capable of being oxidized under the action of radiation even in the absence of molecular oxygen, at the expense of radical and molecular products of radiolysis of the solvent. In organic compounds these products are substantially more varied than in water, but not in all cases do they possess sufficiently sharply expressed oxidizing properties.

Daynton and co-workers (1) described and used, for the accounting of free radicals formed, the reduction of trivalent iron in various organic liquids under the action of radiation. Data relating to analogous oxidation reactions are not encountered in the literature. Their appearance is most probable in cases where the solvent contains functional groups with readily reducible oxygen, such as, for example, carbonyl groups, nitro groups, etc.

Fig. 1. Absorption spectra of crystal violet and of the product of radiation transformation of its leuco base: 1 –$5 \cdot 10^{-3}\,M$ solution of LCV in acetone; 2–7 –irradiated solutions of LCV ($5 \cdot 10^{-3}\,M$); doses: 2 –$2.5 \cdot 10^{16}$; 3 –$5 \cdot 10^{16}$; 4 –$7.9 \cdot 10^{16}$; 5 –$1.2 \cdot 10^{17}$; 6 –$1.5 \cdot 10^{17}$; 7 –$2.1 \cdot 10^{17}$ eV/cm^3; K and K' –$1 \cdot 10^{-6}$ and $1.2 \cdot 10^{-6}\,M$ solutions of CV.

The investigation we carried out of the action of ionizing radiations on nitrogen-saturated solutions of the leuco bases of crystal violet (LCV) in acetone and methyl ethyl ketone showed that in these systems oxidation of the leuco bases does indeed take place.

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

In Fig. 1 are presented the spectra of the product of the radiation transformation of LCV at increasing doses (curves 2-7) and, for comparison, the spectrum of CV in the same solvent (curve K). The intense coloration of solutions of triphenylmethane dyes ($\varepsilon \sim 10^5$) makes it possible to follow easily the initial stages of the process; throughout the concentration range used, up to $10^{-4}\ M$ of the dyes formed, the Lambert—Beer law is obeyed.

Solutions of leuco bases in carefully purified ketone were sealed, after displacement of the air by nitrogen, in tubes 18-20 mm in diameter and of length

100-120 mm, which made it possible to carry out irradiation and the subsequent determination of the optical density with an SF-2M recording spectrophotometer without bringing the solution into contact with air. The solutions were exposed to Co^{60} γ-rays, 80 kV_{max} X-rays, and polonium α-particles. In the first two cases the dose rate was determined by ferrous sulfate dosimetry, with the appropriate recalculation for the ketone; for α-particles it was calculated from the amount of polonium perchlorate introduced.

Fig. 2. Effect of X-radiation, γ-radiation, and α-particles on solutions of LCV at different dose rates:
1—α-particles, 2—0.05 r/sec, 3—0.4, 4—5.6, 5—0.1, 6—1.0, 7—1.6 r/sec; 2—4—γ-Co^{60}, 5—7—X-radiation.

Figure 2 shows, for all three types of radiation, the increase in the concentration of the dye formed as energy is absorbed in $5 \cdot 10^{-3}\ M$ LCV irradiated at 25°C.

As can be seen, the amount of dye increases in direct proportion to the dose. The yield $G = 2.06 \pm 0.03$ molecules/100 eV is the same for acetone and methylethyl ketone and depends neither on the nature of the radiation nor on the dose rate. A study carried out under the action of X-radiation in the interval from -85° to $+50^\circ$ showed that the yield likewise does not change with temperature, remaining equal to 2.0 ± 0.1. The dependence of the yield on the LCV concentration is shown in Fig. 3 for acetone and methyl butyl ketone.

Fig. 3. Dependence of the yield of the dye formed on the concentration of leuco crystal violet for acetone (1) and butyl methyl ketone (2).

Figure 4

Figure 4: Figure 4

Fig. 4. Change in optical density of a $5{\cdot}10^{-3}$ M LCV solution during irradiation and after irradiation. 1—irradiation; 2—after irradiation.

At the concentrations considered, 10^{-3}–10^{-2} M, the radiation transformations of the dissolved substance are entirely caused by its reactions with products of radiolysis of the solvent, and not by the direct action of the radiation. Under ordinary experimental conditions, the observed chemical actions of short-lived radical products cease together with the action of the radiation, whereas stable molecular products can react even after the end of irradiation.

Figure 4 shows the change in optical density of the solution during the absorption of different doses and after irradiation has been stopped. As can be seen, a solution that has absorbed no more than $\sim 10^{17}$ eV/cm^3 remains unchanged for a long time. This makes it possible to conclude that the radiation oxidation of LCV is effected by radical products of radiolysis of ketones. The radical mechanism is also supported by the dependence of the yield on concentration (Fig. 3), which is distinguished by the presence of a characteristic plateau at 10^{-3}–10^{-2} M, corresponding to complete capture of the available radicals. From the absence of a dependence of the oxidation yield on the nature of the radiation (ionization density) it follows that, in contrast to

of water; in organic liquids, intratrack interactions of radicals do not play a substantial role. This is also indicated by the independence of the yield of gaseous products of hydrocarbon radiolysis from the ionization density (2). At doses exceeding $3 \cdot 10^{17}$ eV/cm^3, the yield of CV formation begins to decrease, and after irradiation is stopped the solution gradually becomes decolorized.

A study of the action of γ-radiation on acetone and deuterioacetone (3) permits the conclusion that among the primary products of radiolysis the principal role is played by the radicals $CH_3\dot{C}O$, $\dot{C}H_3$, and $\dot{C}H_2COCH_3$; of these, the radical $CH_3\dot{C}O$ should readily carry out an oxidation reaction of the type $CH_3\dot{C}O + RH \longrightarrow CH_3CHO + \dot{R}$.

The conversion of the colorless leuco base into the dye

$$[\ \text{(structural formula)}\ ] \longrightarrow [\ \text{(structural formula)}\ ]^{+} + \text{anion}^{-} \qquad (1)$$

is a two-stage oxidative process. Owing to the low probability of repeated action on one and the same particle, it may be assumed that, at the comparatively high yield $G \sim 2$–2.5, only the first step—i.e., abstraction of a hydrogen atom from the central carbon atom of the LCV—is radiational, and that it is effected by the radical $CH_3\dot{C}O$ according to

$$[(CH_3)_2NC_6H_4]_3CH + CH_3\dot{C}O \rightarrow [(CH_3)_2NC_6H_4]_3\dot{C} + CH_3CHO. \qquad (2)$$

By the analogous reaction

$$CH_3\dot{C}O + CH_3COCH_3 \rightarrow CH_3CHO + \dot{C}H_2COCH_3 \qquad (3)$$

one can explain the formation of acetaldehyde, whose yield upon irradiation of pure acetone in the absence of oxygen is $G = 2.5 \pm 0.2$ molecules/100 eV. The aftereffect corresponding to doses above $\sim 3 \cdot 10^{17}$ eV/cm^3 is due to accumulated molecular products of radiolysis. Separate experiments showed that acetone irradiated in the absence of oxygen acquires the ability to decolorize CV. On the other hand, it was established that the molecular products of acetone radiolysis—acetaldehyde and acetylacetone—decolorize a dye solution in unirradiated acetone.

Since acid is absent in the irradiated LCV solution, the observed formation of the cation must occur by transfer of an electron from the aminotriphenylmethyl radical to the solvent or to some polar impurity, for example to water, with formation of the corresponding anion (4).

Analogous oxidation reactions with different yields occur under the action of radiation on solutions of leuco bases of other triphenylmethane dyes (malachite green, brilliant green, ethyl violet). Radiation oxidation in ketones in the absence of oxygen is determined by the presence of the carbonyl group. In solvents with other functional groups, substantially different processes are possible. Thus, for example, in ethyl alcohol oxidation of LCV almost does not occur: at an LCV concentration of 10^{-3} M, $G(\mathrm{CV}) = 0.066$ instead of $G(\mathrm{CV}) = 1.2$ in acetone. At the same time, in alcohol, upon irradiation, there occurs the forma-

recovery of methylene blue to the leuco base, which does not take place in acetone.

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Institute of Electrochemistry
Academy of Sciences of the USSR

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