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Anomalous radiothermoluminescence at temperatures above the region of decay of primary products of radiolysis

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Radiothermoluminescence (RTL) of frozen solutions normally consists of one or more maxima located at temperatures higher than the temperature of irradiation; each of these maxima coincides with the temperature range of recombination of one or another primary products of radiolysis.[1] Previously it has been assumed that at the temperature at which RTL ceases, recombination processes also stop. Hence, if irradiation is carried out at exactly the temperature of completion of RTL, subsequent heating should not lead to any luminescence, since all of the primary radiolysis species have characteristic intervals of existence, located at lower temperatures.

We found anomalous behavior of tetramethylene sulfoxide (TMSO). When it is irradiated at 77 K, the RTL is completed already at 180 K (Fig. 1, *a*). However, irradiation of TMSO at an even higher temperature (194.5 K, solid CO_2), to which the primary products of radiolysis should not have survived (Fig. 1, *b*), unexpectedly gave a new RTL curve recorded during heating.

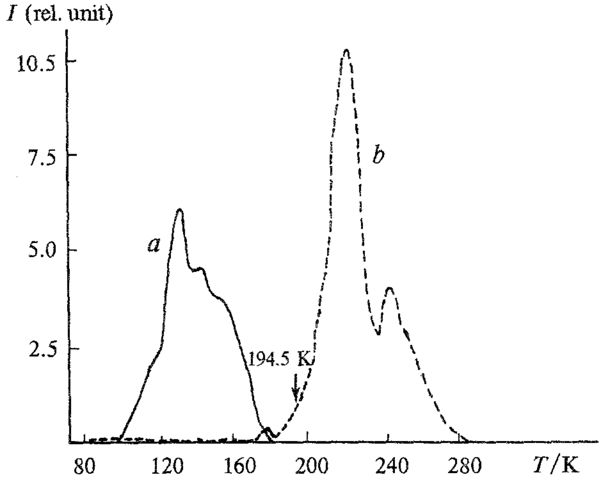

Fig. 1. Radiothermoluminescence of TMSO after γ-irradiation (with a dose of 10^4 Gy) at 77 K (*a*) and 194.5 K (*b*) (after irradiation, the specimen was cooled to 77 K).

Previously[2] we reported that $SO_4^{\cdot -}$ radical ions may be stabilized in solutions of sulfuric acid at 194.5 K (the temperature of irradiation) or at higher temperatures. These radicals, generated by irradiation at 77 K, normally decay even below 180 K. Their anomalous stability was explained by the conditions of cooling that ensured the formation of a particular phase composition during freezing of the solution of sulfuric acid. Another possible reason is anomalous stability of the products of radiolysis of TMSO at temperatures above 194.5 K. However, it may also be significant that irradiation temperature can accidentally fall within an interval between phase transitions in a frozen solution of TMSO, when the rates of chemical transformations dramatically decrease and this would enable accumulation of unstable primary products. While studying low-temperature chemiluminescence of the reaction of XeF_2 with uranium(IV) in solutions of sulfuric acid, we observed several luminescence maxima. Although the reaction itself remained the same, its rate increased at temperatures of phase and relaxation transitions and dramatically decreased in the intervals between them.[3] It is this effect, named the "Hadwall effect," that possibly[4] accounts for the anomalous RTL observed.

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Aerobic photochemical oxygenation of alkanes sensitized by pyrazine derivatives

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Photochemical transformations of saturated and alkylaromatic compounds under the action of molecular oxygen to give oxygen-containing products usually occur in the presence of sensitizers. The key step of these reactions is abstraction of a hydrogen atom from a substrate by a photoexcited species of the sensitizer or an electron transfer to this species with subsequent or synchronous abstraction of a proton (see, for example, Refs. 1—3).

When we continued our studies dealing with photooxygenation of alkanes sensitized by organic compounds,[4,5] we unexpectedly found that pyrazine-2-carboxylic acid (which we previously used as a cocatalyst of a dark reaction[6]) is an efficient photosensitizer. In fact, irradiation of a solution containing cyclohexane (0.46 mol L^{-1}) and pyrazine-2-carboxylic acid (**1**; $4 \cdot 10^{-4}$ mol L^{-1}) in MeCN for 4 h afforded cyclohexanol (**2**), cyclohexanone (**3**), and cyclohexyl hydroperoxide (**4**) (their total concentration was $2.2 \cdot 10^{-3}$ mol L^{-1}; the **2** : **3** : **4** ratio was 1 : 1 : 1.5). In all experiments, a MeCN solution, placed in a glass vessel cooled to ~15 °C with running water was irradiated in air with the full light of a 125 Wt luminescence lamp, $\lambda > 300$ nm. Methyl pyrazine-2-carboxylate (**5**) exhibits much higher activity ($3.7 \cdot 10^{-4}$ mol L^{-1} of products was obtained after irradiation for 4 h; **2** : **3** : **4** = 1 :1 : 1.5), and unsubstituted pyrazine is less active ($1.8 \cdot 10^{-4}$ mol L^{-1}; a glass vessel, **2** : **3** : **4** = 1 :1 : 2.2). It is significant that the activity of pyrimidine is substantially lower ($0.5 \cdot 10^{-4}$ mol L^{-1}, **2** : **3** : **4** = 1 : 1 : 4.6); some other heterocyclic compounds (imidazole, picolinic acid, phenanthroline) or anthranilic acid do not sensitize oxygenation at all. The dependence of the initial rate of the reaction (defined as the concentration (*C*) of products after irradiation for 1 h) on the concentration of ester **5** is characterized by the following values:

$[5] \cdot 10^{-3}$/mol L^{-1}	0	0.4	0.8	3.9
$[C] \cdot 10^{-3}$/mol L^{-1}	0	1.0	1.5	4.8

Oxidation of *n*-hexane in the presence of compound **1** gives products resulting from oxidation at the C(1), C(2), or C(3) atom in a ratio of 1 : 35 : 32. In the case of 2-methylhexane, primary, secondary, and tertiary C—H bonds are oxidized at relative rates of 1, 16, and 100, respectively. These data indicate that oxidation in the presence of the sensitizer found is much more selective than aerobic photooxidation through the action of hydroxyl radicals. In fact, when oxidation is carried out by hydrogen peroxide in MeCN, the corresponding values are 1 : 10 : 7 for *n*-hexane and 1 : 6 : 30 for 3-methylhexane (see Ref. 7). However, the observed selectivity parameters are lower than those for anthraquinone-sensitized oxygenation (1 : 55 : 57 in oxidation of *n*-hexane and 1 : 43 : 55 for 3-methylhexane).[8] It is likely that the process of oxygenation in the presence of pyrazine begins with abstraction of a hydrogen atom of alkane by photosensitized heterocyclic species and

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