Effect of the structure of frozen solutions of H_2SO_4 on radiothermoluminescence

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A pronounced effect of structural heterogeneity (cracks) of glass-like solutions of 4.9 *M* H_2SO_4 on their radiothermoluminescence (RTL) was found. In "perfect" glasses one RTL peak was observed at 115 K. Additional luminescence peaks appeared at 165, 195, and 240 K in glasses having cracks. The effect observed was explained by elevated thermal stability of the $SO_4^{\cdot -}$ radical stabilized on the surface of sulfuric acid crystal hydrates: $H_2SO_4 \cdot 4H_2O$ and $H_2SO_4 \cdot 6.5H_2O$.

Key words: radiolysis, radiothermoluminescence; differential thermal analysis; glass, $SO_4^{\cdot -}$ radical.

When studying the radiothermoluminescence (RTL) of frozen solutions, difficulties often emerge, due to the necessity of obtaining samples identical in their physical properties. In particular, glasses obtained by fast cooling solutions to 77 K in metallic cups have cracks whose number and dimensions can vary within a wide range. The destruction of samples is caused by the great difference between the coefficients of thermal expansion for metal and glass. Metallic cups are used because most other materials (glass, pyrex, quartz, and teflon) possess their own RTL. We found significant differences in the shapes of the temperature dependences of RTL intensity ("RTL curves") for 4.9 *M* H_2SO_4 glasses obtained in two ways. In the first method a sample was prepared by submerging a platinum cup (d = 12 mm) containing 0.2 mL of the solution into liquid nitrogen (cooling rate was 15—20 deg s^{-1}). In the second method the solution was frozen at the same rate in a thin teflon film having a boat-like shape that is easily separated from glass, and not having visible defects. The RTL curve of the sample of more "perfect" glass exhibits only one peak at 115 K, while the RTL curve of the cracked sample shows, in addition, a series of maxima at 165, 195, 205—210, and 240 K (Fig. 1).

The temperature dependence of RTL, similar to curve *2* (see Fig. 1) and characteristic of cracked 5 *M* H_2SO_4 glass, was obtained for the first time in Refs. 1 and 2, where it was shown that low-temperature luminescence in the 115—120 K range was not connected with recombination of the hydrogen atoms and the relation of the RTL peak at 160—180 K to the destruction of $SO_4^{\cdot -}$ radicals was possible. It is known that $H^{\cdot}$ atoms and $OH^{\cdot}$ radicals, the products of low-temperature (77 K) radiolysis of aqueous solutions of sulfuric

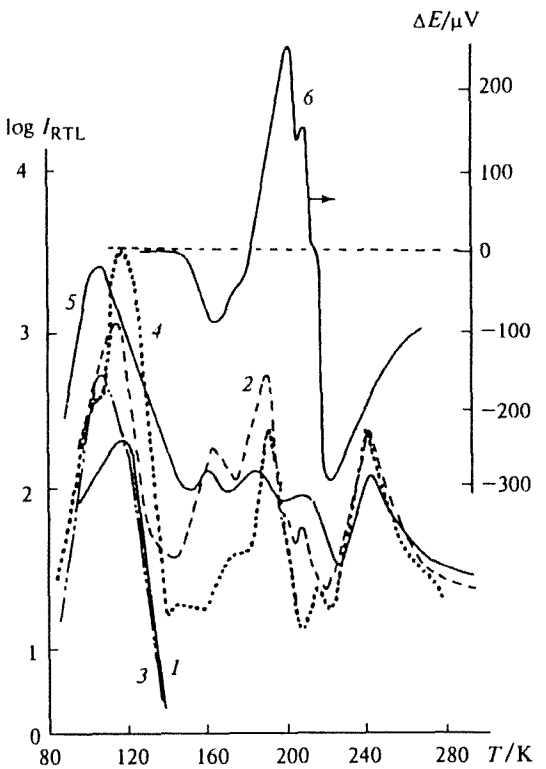

Fig. 1. Temperature dependences of RTL intensity, obtained by heating (77 K) frozen 4.9 *M* H_2SO_4 solutions exposed to X-irradiation (*1*, structurally homogeneous glass; *2*, glass-like solution with cracks irradiated with the light (λ = 400 nm); *3*, glass without macrodefects; *4*, cracked glass; *5*, polycrystalline sample; *6*, curve of differential thermal analysis of 4.9 *M* H_2SO_4 (cracked glass)). Heating rate was 3 deg min^{-1}, X-radiation energy E = 40 KeV, absorbed dose was 300 Gr.

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acid, disappear rapidly when the irradiated samples are heated to 120 K,[3] and the recombination process for the $SO_4^{\cdot -}$ radicals in 5—10 *M* H_2SO_4 starts, according to EPR data, at 160 K.[4] Photowhitening of "perfect" glass by light with $\lambda \geq 400$ nm causes the low-temperature RTL peak to increase several times (see Fig. 1, curve *3*). A similar effect is observed for photowhitened glass with cracks as well (curve *4*). We believe that the RTL maximum at 105—115 K in glasses and in polycrystalline samples of 4.9 *M* H_2SO_4 is due to the recombination of the $OH^{\cdot}$ radicals:

$$OH^{\cdot} + OH^{\cdot} \longrightarrow H_2O_2 + A_1^*; \quad A_1^* \longrightarrow A_1 + h\nu_1, \quad (1)$$

where A_1 is an acceptor of energy released in the course of the reaction. This assumption is based on the known reaction of the photoinduced disappearance of the $SO_4^{\cdot -}$ radical.[4]

$$SO_4^{\cdot -} \cdot H_2O \overset{h\nu}{\rightleftharpoons} (SO_4^{\cdot -} \cdot H_2O)^* \longrightarrow HSO_4^- + OH^{\cdot} \quad (2)$$

Photowhitening of X- or γ-irradiated sulfate glasses at 77 K leads not only to the disappearance of the amber color caused by the presence of $SO_4^{\cdot -}$ radicals in the samples, but also to an increase in the concentration of $OH^{\cdot}$ radicals. The fact that the RTL peak at 115 K is more intense in the cracked glasses and in the polycrystalline samples (see Fig. 1, curve *5*) than in "perfect" glasses is probably connected with a higher concentration of RTL emitters. The structural defects on the surface of the amorphous or crystalline phase can act as RTL emitters. In the course of heating a glass-like solution exposed to ionizing irradiation, its viscosity decreases considerably as it goes to the subcooled liquid state, and recombination of $SO_4^{\cdot -}$ radicals is made possible. As can be seen from the curve of differential thermal analysis (DTA) obtained when 4.9 *M* H_2SO_4 glass is heated (from 77 K), the indicated phase transition begins at 145—150 K (see Fig. 1, curve *6*). It can be assumed that there is no appropriate acceptor of energy for the reaction of radical recombination in intact glass, and the $SO_4^{\cdot -}$ particles disappear in the subcooled solution in the range of 150—160 K without light radiation.

The situation changes in defective glasses. When comparing curves *2* and *6* in Fig. 1, it can be seen that devitrification of the sample at 145—150 K causes an increase in RTL intensity. Visual observations of the 4.9 *M* H_2SO_4 glass during its heating show that the ends of the cracks contract, as viscosity decreases, but the cracks themselves, growing darker in the transmitted light, remain visible even when the subcooled solution can be stirred with effort using a glass capillary with a sealed-in thermocouple. The dark formations appearing in place of the cracks and keeping their steric shapes seem to be areas in which the sulfuric acid solution crystallized on the surfaces of cracks. We believe that at low temperatures, a part of $SO_4^{\cdot -}$ radicals near to the crystallization front of the subcooled solution can be captured on freshly the formed surface of the sulfuric acid crystal hydrate. The energy of recombination reaction of $SO_4^{\cdot -}$ radicals:

$$SO_4^{\cdot -} + SO_4^{\cdot -} \longrightarrow S_2O_8^{2-} + A_2^*; \quad A_2^* \longrightarrow A_2 + h\nu_2 \quad (3)$$

is transmitted to appropriate acceptors (A_2), which may be adsorption centers or other defects on the surface of the crystalline phase. High viscosity of the solution causes the existence of local crystalline areas with $SO_4^{\cdot -}$ radicals (up to 175—180 K) when crystallization begins in the bulk of the sample and proceeds with considerable heat release. The mobility of the $SO_4^{\cdot -}$ radicals stabilized on the surface of sulfuric acid crystal hydrates increases during the phase transition, which causes a synchronous increase in RTL intensity, caused by reaction (3), and in the heat release rate (see Fig. 1, curves *2* and *6*).

A satisfactory correlation between the RTL and DTA curves is therefore observed. Even the RTL peak at 205—210 K is resolved, because of the two-stage character of the crystallization of the subcooled 4.9 *M* H_2SO_4 solution: initially, a metastable eutectic $H_2SO_4 \cdot 4H_2O$ + ice with m.p. 200 K is formed, which is further transformed into a stable eutectic $H_2SO_4 \cdot 6.5\ H_2O$ + ice with m.p. 211 K.[5—7]

The assumption that the surface of the sulfuric acid crystal hydrates on which the $SO_4^{\cdot -}$ radicals are stabilized, plays a significant role in RTL radiation within a 140—220 K range is confirmed by the results of an RTL investigation of polycrystalline samples of 4.9 *M* H_2SO_4. The latter were obtained by heating a glass-like 4.9 *M* H_2SO_4 solution from 77 to 195—200 K, keeping the sample at this temperature, and then recooling it to 77 K. A definite similarity between the RTL curves of polycrystalline samples (see Fig. 1, curve *5*) and glass-like cracked samples was observed. The slightly resolved structure on curve *5* in the 160—220 K range is due to the presence of a small amount of glass-like phase in the polycrystalline sample.

The considerable decrease in total RTL in the 140—200 K range in the case of the sample in which the concentration of $SO_4^{\cdot -}$ radicals is decreased as a result of photowhitening at 77 K (see Fig. 1, curve *4*) may also be interpreted within the framework of the concept that assumes the participation of the $SO_4^{\cdot -}$ radical in processes responsible for RTL emission. The existence of $SO_4^{\cdot -}$ radicals at $T > 200$ K was detected in polycrystalline samples of concentrated H_2SO_4 by EPR.[8] Although polycrystalline 18.3 *M* H_2SO_4 differs from the corresponding samples of 4.9 *M* H_2SO_4 in composition (ice and sulfuric acid monohydride crystals), the stabilization mechanism of the $SO_4^{\cdot -}$ radicals can be similar in the both cases. Clarification of the nature of the emission with a maximum at 240 K, is the subject of further investigations.

Thus, the character of the changes in the temperature dependences of RTL intensity in passing from "perfect" glasses to glasses with cracks or to polycrystalline samples can be explained by assuming that RTL in the 140—220 K range is connected with the recombination of the $SO_4^{\cdot -}$ radicals stabilized on the surface of sulfuric acid crystals.

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Dinitramide and its salts

11. Synthesis of dinitramide by nitration of nitramide with nitryl salts

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Nitration of nitramide to dinitramide with nitryl salts is described.

Key words: nitration, nitryl salts, nitramide, dinitramide.

In previous reports,[1—3] we have described "organic" methods of synthesis of some inorganic compounds, *viz.*, dinitramide salts (DNA). In the present paper, DNA was synthesized by methods of inorganic chemistry: the nitration of nitramide (NA). NA is a rather labile compound, which is decomposed to N_2O and H_2O under the action of acids and particularly bases,[4] which rules out the possibility of "alkaline" nitration. The nitration of NA with nitric acid or sulfuric-nitric mixtures is difficult due to the instability of NA and DNA in these media. Also, it is necessary to assume that NA has low nucleophilicity. For the these reasons, our attempts to nitrate NA to DNA with a mixture of HNO_3 with Ac_2O or N_2O_5 were unsuccessful. The treatment of NA with a mixture of HNO_3 and trifluoroacetic anhydride afforded only a trace amount of DNA. However, it appeared that the quantitative transformation of NA to DNA is possible in nitration with nitryl salts.*

$$H_2N{-}NO_2 + NO_2^+X^- \longrightarrow HN(NO_2)_2 + HX$$

$$X = BF_4,\ SO_3F,\ S_2O_7H,\ S_2O_7NO_2$$

A thorough study of this reaction showed that the yield of DNA depends substantially on the type of nitryl salt, solvent used, temperature, and reaction time (Table 1). Nitryl tetrafluoroborate (NTFB), nitryl fluorosulfonate (NFS), nitryl hydrogen pyrosulfate (NHP), and nitryl pyrosulfate (NP) were studied as the salts.

The easiest nitration proceeds for NTFB and NFS. Under their action in MeCN at −20—0 °C, NA transforms to DNA in a quantitative yield after only 5 min. Increasing the reaction time results in a decrease in the yield of DNA. MeCN, CH_2Cl_2, EtOAc, and hexane were studied as solvents. It appeared that for the nitration of NA with NTFB or NFS, the best yields of DNA were achieved in MeCN. When CH_2Cl_2 or EtOAc were used, the yield of DNA decreased by several times, and in hexane, DNA was not formed at all. Apparently, this result may be substantially explained by the different solubility of the starting materials in these solvents. In

* For Part 10, see Ref. 3.
* See also Ref. 5.

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