Letters to the Editor

The destruction of sulfuric acid induced by ultrasonic vibrations

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Previously^{1,2} sonochemical destruction of $HClO_4$ and H_3PO_4 to chlorine and phosphorus compounds with lower degrees of oxidation than those of the initial products has been found. The purpose of this work is to study the behavior of aqueous H_2SO_4 solutions under ultrasonication.

Argon or helium were bubbled through 0.1-18 M H₂SO₄ solutions which were subjected to ultrasonic vibrations (44 kHz) using a UZDN-2T dispergator. Using the test with the titanyl ion it was shown that hydrogen peroxide is accumulated during ultrasonication under an Ar atmosphere at [H₂SO₄]<0.6 M. In highly concentrated (>9 M) solutions of H₂SO₄ marked destruction of H_2SO_4 takes place to give sulfur, SO_2 , and the traces of H₂S. The rates of sonochemical destruction determined by the alkaline titration of periodically taken aliquots of the acid are ~0.18 mol $L^{-1} h^{-1}$ for $[H_2SO_4] = 18 M$ and 0.05 mol L^{-1} h⁻¹ for $[H_2SO_4] = 9 M$. No visible changes were observed in the ultrasonicated system for the 0.6 to 9.0 M range of $[H_2SO_4]$. Neither the accumulation of H_2O_2 , nor the decomposition of H_2SO_4 were observed in the whole range of $[H_2SO_4]$ under the atmosphere of He.

 H_2O_2 is formed via the following reactions³

It may be speculated that the decomposition of H_2SO_4 occurs because of the transfer of energy from the excited species formed in the ultrasonically generated cavity³ to the H_2SO_4 molecules and HSO_4^- ions on its wall. In concentrated H₂SO₄, evaporation of H₂SO₄ molecules into a cavitation bubble is possible at the stage of its dilation. This is followed by their interaction with the electrons present in the gas phase due to electric discharge in the cavitation bubble. In more dilute solutions the penetration of H_2SO_4 into the cavity becomes more difficult, which results in a decrease in the yield of decomposition products. In the intermediate range of $[H_2SO_4]$, both H_2O_2 and the products of the reductive decomposition of H₂SO₄ are formed. Once formed, they annihilate one another at a rather high rate (cf. Ref. 4). The reductive decomposition of H_2SO_4 by its interaction with atomic hydrogen in the solution is rather unlikely due to the slow rate of this reaction.⁵

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Degradation of the holmium—barium—copper oxide superconductor, HoBa₂Cu₃O_{6.92}, under the action of H₂O and D₂O: a study by the radiothermoluminescence method

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Information about the existence of impurities and defects on the surfaces of high- T_c superconductors (HTSC) can be obtained by radiothermoluminescence (RTL).^{1,2} The degradation of HTSC materials results from their interaction with water and CO₂:

$$2RBa_{2}Cu_{3}O_{7-x} + 3H_{2}O \rightarrow R_{2}BaCuO_{5} + 3Ba(OH)_{2} + 5CuO + (0.5-x)O_{2}, Ba(OH)_{2} + CO_{2} \rightarrow BaCO_{3} + H_{2}O,$$

where R is yttrium or a rare earth element.

It has been established that the intensity of RTL is very insignificant for freshly prepared HTSC or for samples stored in a dry atmosphere. However, a large increase in RTL intensity occurs if specimens are in contact with water.³ Barium hydroxide, carbonate, and oxides make the largest contribution to RTL of superconducting ceramics with degraded surfaces. The RTL curves for Ba(OH)₂ and BaCO₃ differ slightly from each other,³ which makes it difficult to estimate the contribution of each of them to the luminescence observed.

An isotope effect, manifested by the difference in the shapes of the RTL curves for specimens of HoBa₂Cu₃O_{6.92} treated with hot H₂O or D₂O (Fig. 1, curves *1* and *2*, respectively) was observed in this work. In the latter case, there is a peak at 155-160 K on the log I_{RTL} vs. T(K) curve. This peak is absent in the case of the ceramics in contact with H₂O. The isotope effect is more pronounced in the RTL curves of the model systems Ba(OH)₂ and Ba(OD)₂ (curves *3* and *4*, respectively). A well resolved peak is observed in the RTL curve of Ba(OH)₂ at 155-160 K, whereas in the case of



Fig. 1. Temperature dependence of the RTL of HoBa₂Cu₃O_{6.92} in contact with H₂O (*I*) and D₂O (*2*), and the same for the RTL of Ba(OH)₂ (*3*) and Ba(OD)₂ (*4*) after their exposure to X-radiation (T = 77 K, E = 40 keV, absorbed dose 150 Gr, dose power 300 Gr h⁻¹).