Effect of Oxygen on the Determination of Hydrogen Atom Yields in Irradiated Ice Matrices

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The formation of hydrogen atoms in γ-irradiated sulphuric, phosphoric and perchloric acid ices at 77 °K was first observed by Livingston, Zeldes and Taylor1. Subsequently, it was suggested that hydrogen atoms are formed by radiation-produced electrons in ice at 77 °K by reacting with hydrogen ions and/or acid anions2. The hydrogen atoms which are trapped by the oxyanions present in the ice matrix are characterized by the ESR doublet (splitting 506 G) with g = 2.00197. The yields depend largely on the nature and concentration of the oxyanions but are virtually independent of the cation and to some extent of pH. All these experiments provide good evidence for the formation of radiation-produced mobile electron hole-pairs2 which react with acids anions or hydrogen ions to give hydrogen atoms while the hole reacts with the corresponding oxyanions to give a free radical species. More recently it has been found that the relaxation time of the trapped hydrogen atoms decreases with radiation dose and it has been suggested that this is due to the increased spin-spin interaction3.

We have carried out ESR studies on the power saturation of hydrogen atoms in acid ices and we have found that under comparable conditions there is a very marked effect of oxygen on the magnitude of the ESR signal of the hydrogen atoms. Experiments were carried out with 1 M H2SO4 where the hydrogen atom signal increases because there is evidently cross relaxation through nearby oxygen molecules. Thus, the hydrogen atoms intensities from irradiated acidic ices cannot be compared unless the microwave power is below the power-saturation value.

In oxygen saturated acidic ices at powers up to 1.0 mW the signal intensity of the trapped hydrogen atoms increases because there is evidently cross relaxation through nearby oxygen molecules. Thus, the hydrogen atoms intensities from irradiated acidic ices cannot be compared unless the microwave power is below the power-saturation value.

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