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 TAYLOR[1]. 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 anions[2]. 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-pairs[3] 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 interaction[4].

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 H_2SO_4. Samples were prepared by the method described previously[2]. When the acid solutions before freezing are saturated with oxygen (1 atm) there is an increase in the hydrogen atom signal. We have been led to the conclusion that this is due to an effect on the relaxation time of the hydrogen atom in the ice matrix.

Although there is presumably also a reaction between hydrogen atoms and the molecular oxygen in the ice, this appears to be relatively small compared with the effect of the oxygen on the ESR signal as such so that the net result appears as an increase in the yields.

Studies of microwave power-saturation from about 0.05 to 5 mW indicate that the hydrogen atom yields in the nitrogen saturated acidic ices apparently increase as the power is decreased but the signal is still saturated at 1 mW. The hydrogen atom signal intensities in both systems converge to nearly the same value at microwave powers of about 0.1 mW. The nitrogen flushed acidic ices show power saturation above 0.1 mW.

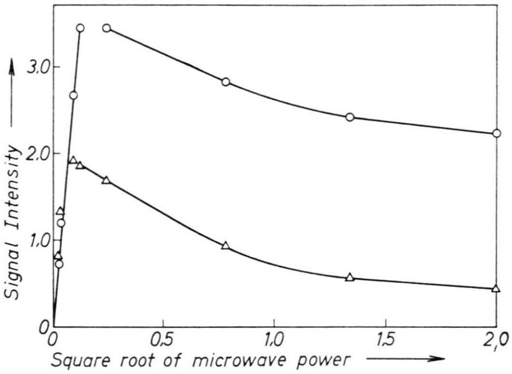

Fig. 1. Plots of signal intensity vs. Square root of microwave power for trapped hydrogen atoms in 1 M H_2SO_4 ice: ○ O_2 saturated; △ N_2 saturated.

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.

In the experiments of ZIMBRICK and KEVAN[4] it is not clear to which extent such an oxygen effect may be present as they do not state whether they work in air free systems and if molecular oxygen which may be present after large doses of radiation influences the relaxation time.

An effect of molecular oxygen on the spin-lattice relaxation has been observed previously[5, 6] and this may be due, in general, to a cross relaxation mechanism by the paramagnetic oxygen molecules.

We have also investigated the effect of oxygen on the relaxation time of electrons in alkaline ice. There, however, the result was negative: this is probably due to cross relaxation with the 0^- ions which are formed in irradiated alkaline ice simultaneously with the electrons.

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