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Received February 20, 1976.

On the Photochemical Behaviour of Radiation Produced Trapped Electrons in an Alcohol/Water Glass

JOHAN MOAN

Norsk Hydro's Institute for Cancer Research, The Radium Hospital, Montebello, Oslo 3, Norway

Radiation produced electrons are stabilized at low temperatures in a variety of solvents among which alcohols and alcohol/water mixtures are the most frequently studied cases. The processes following an ionization event in an alcohol glass are:[1–4]

$$RCH_2OH \xrightarrow{\gamma,\ X} RCH_2OH^+ + e^- \quad (1)$$

$$e^- \longrightarrow e_t^- \text{ (electron trapping)} \quad (2)$$

$$RCH_2OH^+ + RCH_2OH \longrightarrow RCH_2OH_2^+ + RC{\cdot}HOH \quad (3)$$

($R = H, CH_3, C_2H_5$ *etc.*)

The trapped electron, e_t^-, has an absorption spectrum in the visible part of the spectrum and is easily bleached during exposure to visible light, giving rise to alcohol radicals.[5] The nature of this process is somewhat unclear. One possibility is that the photomobilized electrons (e_m^-) react with $RCH_2OH_2^+$ ions [2,5,6] which probably are trapped within a few Ångströms of the electrons, the reactions being:

$$RCH_2OH_2^+ + e_m^- \longrightarrow RCH_2OH + H \quad (4)$$

followed by

$$RCH_2OH + H \longrightarrow RC{\cdot}HOH + H_2 \quad (5)$$

Another possibility would be that mobilized electrons react with neutral alcohol molecules according to the scheme:[7]

$$RCH_2OH + e_m^- \longrightarrow RCH_2O^- + H \quad (6)$$

followed by (5).

To distinguish between the two processes we studied the dependence of the photobleaching efficiency on the dose of ionizing radiation delivered to the sample. We have carried out such an experiment in the case of an ethylene glycol/water glass (1:1 by volume) at 77 K. The results are, as shown below, definitely in favour of the second hypothesis.

We exposed an ethylene glycol/water glass at 77 K to the radiation from a 4 MeV modified AEI-linear accelerator. The samples were prepared by allowing 20 μl drops of sample solution to fall into liquid N_2. The irradiated samples were analyzed by ESR methods. Fig. 1 shows how the yield of trapped electrons and ethylene glycol radicals varies with the dose. It can be seen that while the yield of ethylene glycol radicals increases practically linearly with the dose, the electron yield reaches a plateau.

A similar dose dependence of the electron yield has been reported for a variety of solvents. Thus, the yields are generally reaching a maximum and then decreasing (see review article in Ref. 8). A number of explanations of this behaviour has been proposed: (1) only a limited number of electron traps exist,[9] (2) reactions of the electrons with radicals in the sample[10] and (3) reactions of mobile electrons with positive ions produced by the radiation, or reactions of mobile positive ions with trapped electrons.[11] The maximum concentration of trapped electrons was found to be of the order of 5×10^{-3} M, which is in correspondence with the findings of others for alcohol matrices (see review in Ref. 8).

The samples could be optically bleached by exposing them to the light of a 200 W high pressure mercury lamp fitted to a Bausch & Lomb grating monochromator. Except for the lowest dose (500 krad) the ESR signals from trapped electrons decreased practically linearly with the exposure time during bleaching. This shows that with exception of the first case the samples are total absorbing thus explaining the apparent low quantum efficiency of bleaching at this dose (Fig. 1). For doses exceeding 2 Mrad, Fig. 1 shows that the quantum efficiency of electron bleaching is practically constant. This is true both for bleaching at 366 nm (3.4 eV) and at 625 nm (2.0 eV). The photomobilization threshold for electrons in the present matrix is 2.2 eV.[12] Hence irradiation at 366 nm causes photomobilization of the trapped electrons, while irradiation at 625 nm causes excitation. Since the quantum efficiency of bleaching is dose independent, and since the concentrations of $RCH_2OH_2^+$ as well as

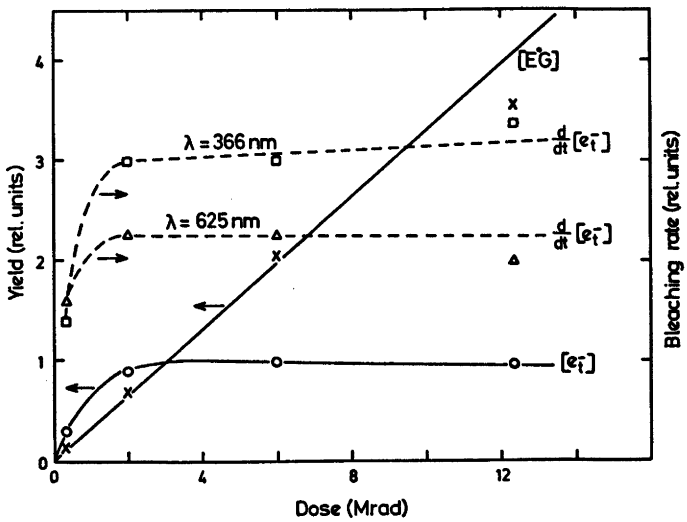

Fig. 1. Ethylene glycol/water mixtures irradiated at 77 K with different doses from a 4 MeV electron accelerator. ○, concentration of trapped electrons; ×, concentration of ethylene glycol radicals; △, quantum efficiency of bleaching at 625 nm; □, quantum efficiency of bleaching at 366 nm.

of RC˙HOH is supposed to increase nearly linearly with the dose, the present data strongly suggest that the mechanism of optical bleaching of e_t^- is described by eqn. (6) rather than by eqn. (4). Thus, the electrons probably react mainly with neutral alcohol molecules when being excited. This is what one would expect for excitation with quantum energies below the photomobilization threshold (*i.e.* for excitation at 625 nm). It is a somewhat surprising result that the same mechanism seems to be operative also at 366 nm where the trapped electrons are mobilized and should have the possibility of encountering $RCH_2OH_2^+$ ions.

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Received February 24, 1976.