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Effect of Irradiation Temperature on the Yield of UV-induced Trapped Electrons in Ethyleneglycol/Water Glass

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Trapped electrons were produced by irradiation of tryptophan in an ethyleneglycol/water glass with 250 nm UV-light. The yield of trapped electrons as measured by optical absorption spectroscopy and ESR spectroscopy increased by a factor of approximately 1.6 when the irradiation temperature was raised from 77 to 120 K. The yield of thermoluminescence emitted above 120 K increased with a factor of approximately 2.3 in the same temperature range. Comparison of optical absorption and thermoluminescence measurements suggests that the electrons become trapped closer to their mother ions when the irradiation temperature increases. This conclusion is also in accordance with the fact that electron scavengers act less efficiently at 123 K than at 77 K. The increase in the yield of trapped electrons with irradiation temperature is accompanied by a decrease in the probability of spontaneous recombination and may probably be explained by increasing mobility of molecular dipoles or polar groups like the $-OH$ and $-CH_3$ groups of the alcohol with increasing temperature.

During the last decade a great number of experiments have been carried out in various laboratories to elucidate the nature of the trapped electron. In spite of this, many problems still remain unsolved. Among these is the role of molecular rotation in trapping of electrons in polar substances. It is frequently supposed that the molecular dipoles are completely "frozen in" in the glassy state at 77 K.[1] However, the experiments of several investigators seem to show that polar molecules or polar groups like the $-OH$ and $-CH_3$ groups of the alcohols may relax in the field of charge carriers.[2,3] Several authors report an increase in the yield of trapped radicals with increasing irradiation temperature.[3–5] Higashimura *et al.*[3] suppose that molecular relaxation is responsible for a higher yield of trapped electrons in a water-ethyleneglycol glass at 77 K compared to 4 K. Their work does not, however, quantitatively show the temperature dependence of the yield.

In the present paper we report quantitative measurements of the dependence of the yield of trapped electrons in a water/ethyleneglycol glass on the irradiation temperature in the range 77 – 140 K. Trapped electrons were produced by photoionization of tryptophan,[6] and the yields were measured by recording (a) the absorption spectra, (b) the ESR-spectra, and (c) the thermoluminescence glow curves.

EXPERIMENTAL

Materials and irradiation. L-Tryptophan of analytical grade from Sigma was dissolved to a concentration of 5×10^{-4} mol/l in a mixture of ethyleneglycol and water, 1 : 1 by volume (EG/H_2O). The ethyleneglycol was "chromatoquality" from Matheson, Coleman & Bell, and the water was triple distilled.

The UV-source was a 200 W high pressure mercury lamp fitted to a Bausch & Lomb grating monochromator operated at 254 nm thus utilizing an intense line in the spectrum of the lamp. The light intensity was about 10^{-8} Einstein/cm^2 sec at the sample and the exposure time was 40 sec in the absorption and ESR experiments and 10 sec in the luminescence experiments.

Optical absorption and luminescence measurements. The samples, contained in 1 mm deep vessels of 0.1 mm thick aluminium foil, were degassed by controlled evacuation and cooled to the appropriate temperature. Immediately after irradiation, the temperature was lowered to 77 K. In the temperature range 77 – 160 K the samples were completely transparent without cracks or bubbles. The optical density of the samples at different wavelengths were measured by passing a narrow monochromatic light beam vertically down on the samples. The light beam was reflected from the bottom of the sample holders and its intensity was measured by a photomultiplier tube. Measurements of the luminescence intensity of the irradiated samples could be carried out in the same apparatus. The apparatus is described in more detail elsewhere.[7]

ESR-measurements. 100 µl of the sample solution was irradiated in a quartz tube of inner diameter 3.5 mm. During irradiation the sample was kept at the appropriate temperature by placing it in a stream of cold N_2-gas, the temperature of which could be kept constant anywhere between 80 and 160 K. The temperature was measured outside the quartz tube by a thermocouple. Immediately after irradiation the temperature was lowered to 77 K by plunging the quartz tube into liquid N_2 and the recording of the ESR-spectra took place at this temperature within 5 min. The ESR-spectrometer was an X-band transmission type with a 110 kc/sec field modulation and was operated at a frequency of 9100 Mc/sec.

RESULTS

(a) Optical absorption. Fig. 1 shows how the absorption spectrum varies with the irradiation temperature. According to Hase *et al.*[8] this absorption spectrum is caused almost entirely by trapped electrons. There is a small blueshift of the spectrum when the irradiation temperature increases, and the yield of trapped electrons, as measured by the optical density at the absorption maximum, increases with the irradiation temperature up to about 130 K where the decay of trapped electrons during irradiation becomes important (Fig. 2). Addition of electron scavengers such as H^+ and NO_3^- reduced the yield of trapped electrons. It was found that the scavengers were less efficient at 123 K than at 77 K (Table 1).

(b) ESR-spectrum. The ESR-spectrum is a triplet spectrum superimposed on a singlet spectrum as shown by Steen.[9] The triplet spectrum, which probably stems from an ethyl radical [9] produced by the reaction of ethyleneglycol with

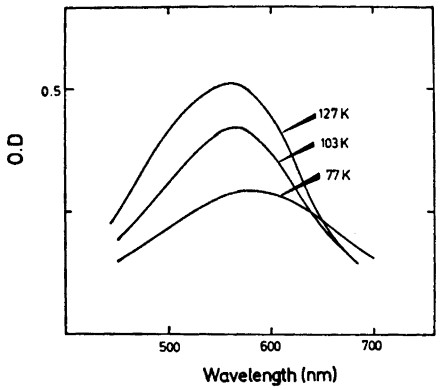

Fig. 1. Absorption spectra of UV-induced trapped electrons in EG/H_2O-glass irradiated at different temperatures. The temperature was lowered to 77 K immediately after irradiation.

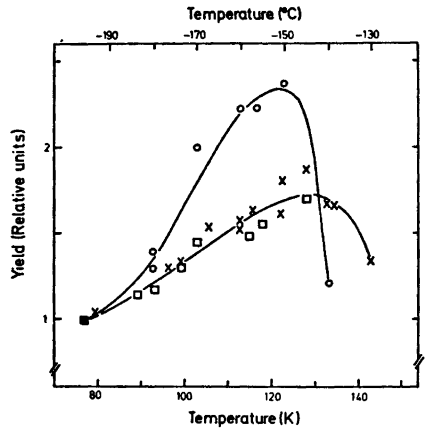

Fig. 2. Yields of thermoluminescence emitted above 120 K (TL_2) (○), trapped electrons as measured by optical absorption spectroscopy (□), and electron spin resonance spectroscopy (×), plotted as a function of the irradiation temperature.

either electrons or positive tryptophan ions, may be subtracted from the total spectrum, and in accordance with Steen's conclusion,[9] it will be supposed that the difference is the singlet spectrum of the trapped electron. However, it cannot be excluded that tryptophan radical ions also contribute to this spectrum.[10] The variation of the intensity of the singlet spectrum with irradiation temperature as measured by the peak to peak value is shown in Fig. 2. The ratio of the intensity of the triplet spectrum to that of the singlet spectrum increased slightly with the irradiation temperature. Thus, the total amount of trapped radicals were, by a factor of about 1.8, larger at 120 K than at 77 K, while the intensity of the singlet spectrum increased by a factor of about 1.6 in the same temperature range.

Table 1. The table shows how the yield of trapped electrons depends on the concentration of the electron scavenger NO_3^- at 77 K and at 123 K. The yields are not corrected for the reduction in the intensity of the irradiation light caused by absorption from NO_3^-, and the bleaching effect of the irradiation light on the trapped electrons.

Concentration of NO_3^-	0	0.02 M	0.04 M
Yield of trapped electrons at 77 K (rel. units)	1	0.49	0.32
Yield of trapped electrons at 123 K (rel. units)	1	0.58	0.42

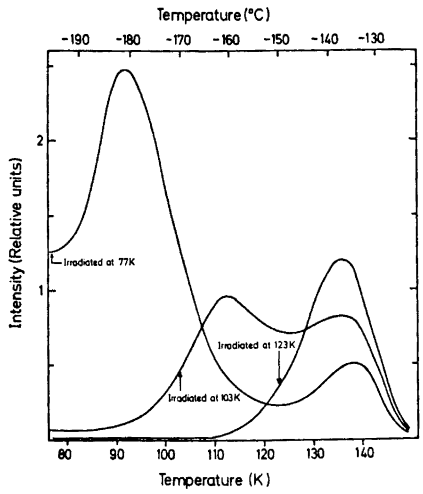

Fig. 3. Glow curves of tryptophan in EG/H_2O-glass irradiated with UV-light at different temperatures.

(c) Thermoluminescence. The thermoluminescence glow curve of tryptophan in EG/H_2O-glass irradiated at 77 K consists of two peaks, as shown in Fig. 3, and is attributed to the recombination of trapped electrons with tryptophan ions.[6] The glow peak at 135 K (TL_2) seems to be associated with a glass transition of the solvent and the great majority of trapped electrons – as seen from ESR and optical absorption measurements – disappear at this temperature.[6] Thus, the low temperature glow peak (TL_1) is accompanied by a decrease in optical density only at wavelengths above 650 nm, and after warming to 110 K, less than 5 % of the total number of trapped electrons have disappeared. Addition of electron scavengers reduces the yield of thermoluminescence and alters the shape of the glow curve. Thus, the H^+-concentration needed to halve the TL_1-yield (*i.e.* the emission observed between 77 K and 120 K) is about 0.25 mol/l, while the H^+-concentration needed to halve the TL_2-yield (*i.e.* the emission observed above 120 K) is only 0.02 mol/l.

If the irradiation temperature is changed, the form of the glow curve changes as shown in Fig. 3. Thus, with increasing irradiation temperature the TL_1-glow peak is reduced and shifted towards higher temperatures and the TL_2-glow peak increases. This increase is qualitatively depicted in Fig. 2. In this figure the integrated yield of thermoluminescence emitted above 120 K is plotted as a function of the irradiation temperature.

DISCUSSION

The reported increase in the yield of trapped electrons with irradiation temperature may be explained in at least two ways.

(1) The kinetic energy of thermal electrons increases with temperature. Thus, if the electrons are trapped mainly outside the critical radius r_c (*i.e.* the radius where the thermal energy of the electron equals the Coulomb

interaction with the positive ion), the probability of escape from recombination should increase with temperature according to Onsager's theory.[11]

(2) The mobility of molecular dipoles or polar groups like the $-OH$ and $-CH_3$ groups of the alcohols may increase with temperature whereby the trapping process is facilitated.

Let us first discuss alternative (1) and suppose that no molecular relaxation takes place. Consequently, we must use the infrared dielectric constant ε_∞ in the calculation of the critical radius r_c. This gives

$$r_c = \frac{e^2}{6\pi\varepsilon_0\varepsilon_\infty kT} = 300 \text{ Å}$$

if we insert $\varepsilon_\infty = 4.5$, which is the infrared dielectric constant of H_2O [12] and $T = 77$ K. ε_0 is the dielectric constant of vacuum. However, scavenger experiments [6,13] and paramagnetic relaxation studies [14–16] seem to show that the electrons are on the average trapped at distances of about 30 – 60 Å from their mother ions in rigid polar solutions. This is well within the calculated critical radius of 300 Å, and it seems that the increase in trapping probability cannot be explained by the fact that the critical radius diminishes when the temperature increases. Using a higher dielectric constant will reduce r_c, but as soon as we use a higher dielectric constant than the infrared one, we imply that the dipoles may rotate. We therefore find alternative (2) above a more plausible explanation of the temperature effect than alternative (1).

When a polar liquid freezes, the dielectric relaxation time increases by many orders of magnitude. Water at room temperature has a dielectric relaxation time of 10^{-11} sec, while the corresponding value for ice at -10.8°C is 6×10^{-5} sec.[1] A thermal electron at 77 K travels a distance of 60 Å in a time shorter than 10^{-11} sec. This will probably be too short a time for the orientation of the dipoles even if the strong electric field from the electron and the positive ion is taken into account. However, the temperature dependence of the yield may be explained in terms of variation in the dipolar relaxation time if we suppose that the electrons are captured by pre-existing traps and that a fraction of the traps are so shallow that the electrons may readily be released from them and recombine with positive ions. Some of the shallow traps may relax more or less in the field of the electrons whereby they become deeper. The mechanism of the relaxation is thought to be a rotation of molecular dipoles or polar groups. The formation of relaxed traps from unrelaxed ones by dipole orientation is facilitated when the temperature increases. This explanation is supported by the experiments of Higashimura *et al.*[3] which show that in an EG/H_2O-glass at 4 K about one half of the trapped electrons are captured in deep, relaxed traps, while the second half are captured in shallow, unrelaxed traps. Upon warming the glass from 4 K to 77 K, the unrelaxed traps are transformed into relaxed ones. Our explanation is also in line with the findings of Richards and Thomas [17] who report that the absorption spectrum of the electron in pulse radiolysed ethanol at 77 K changes with time in the μsec region. The change was attributed to a reorganization of the trapping site.

Fig. 4 shows the yields plotted on a logarithmic scale *vs.* the inverse of the temperature. From this figure an activation energy of 0.2 – 0.3 kcal/mol is

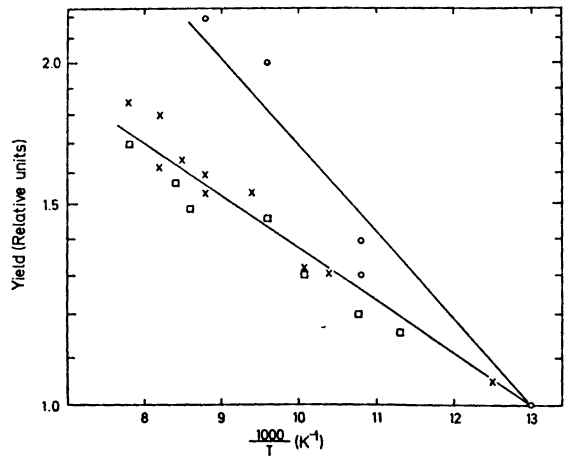

Fig. 4. Yields of trapped electrons plotted on a logarithmic scale as a function of the inverse of the irradiation temperature (see Fig. 2).

found. This is much less than 13.3 kcal/mol which is the energy needed for the rotation of H_2O in ice.[12] Therefore we feel that only polar groups of the molecules may be rotated or slightly distorted in the field of the electron. However, no firm conclusion can be drawn since 0.2 kcal/mol is a lower limit of the energy associated with the relaxation because (1) the yield of electrons primarily captured in deep traps is probably independent of the irradiation temperature, and (2) the probability of thermally stimulated recombination of shallowly trapped electrons increases with temperature.

Fig. 2 shows that the increase in the yield of TL_2 is approximately a factor 1.5 larger than that of trapped electrons as measured by optical absorption and ESR. This is in accordance with the above model if we assume that the electrons which recombine to give TL_2 are trapped closer to their mother ions than are the bulk of the electrons. Such an assumption is in line with previous findings [6] which show that the thermoluminescence glow curve may be interpreted in terms of the distance between the trapped electrons and the positive tryptophan ions. This distance increases with the temperature at which the two ions recombine. Furthermore, Fig. 2 shows that the electrons which cause TL_2 are more susceptible to recombination during irradiation at temperatures above 125 K than are the bulk of the electrons. The probability of spontaneous recombination of electrons captured in unrelaxed traps should increase with decreasing distance from their mother ions. Hence, if there is a competition for these electrons between deeper trapping and recombination, the yield of electrons permanently trapped close to their mother ions should be more temperature dependent than that of electrons trapped further away from their mother ions. Accordingly the mean distance travelled by the electrons before trapping should decrease with increasing temperature. This is in accordance with the fact that electron scavengers are less efficient at 123 K than at 77 K (Table 1).

We have regarded trapping and recombination as competing processes. An increase in trapping probability should then be accompanied by a decrease in recombination probability. Indeed, Steen[18] has found – in the same system as used in this work – that the G-value for spontaneous recombination following X-ray induced ionization of tryptophan decreases from 4.2 at 77 K to 3.2 at 120 K, *i.e.* by a factor of 0.76. Our results suggest that there is an increase in the escape probability by a factor of about 1.8 in the same temperature range. If we call the recombination probability P_R and suppose that P_R varies with the temperature in the same way for X-ray and UV-induced ionization we have:

$$P_R^{120\,K} = 0.76\, P_R^{77\,K}$$

$$1 - P_R^{120\,K} = 1.8(1 - P_R^{77\,K})$$

This gives $P_R^{77\,K} = 0.8 \quad P_R^{120\,K} = 0.6$

Therefore it seems that at 77 K recombination is more probable than escape.

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