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The Effect of Electron Scavengers on Photo-produced Electrons in Ethyleneglycol/Water Glass

JOHAN MOAN

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

Several studies of electron scavenging in glassy media by means of optical absorption- and ESR-spectroscopy have been reported.¹⁻³ Trapped electrons may also be studied by thermoluminescence measurements since their recombination with positive ions upon heating may give rise to luminescence. It is therefore possible to carry out scavenging studies by means of thermoluminescence measurements. A problem that may be solved by this method is whether the recombining electrons have the same relative reactivity as the mobile electrons prior to trapping. In the present communication we report measurements of the effect of various electron scavengers on the yield of UV-induced trapped electrons as measured by optical absorption-spectroscopy and the effect of the same scavengers on the yield of UV-induced thermoluminescence.

Trapped electrons were produced by photoionization of tryptophan which was dissolved to a concentration of 5×10^{-4} mol/l in a mixture of ethyleneglycol and

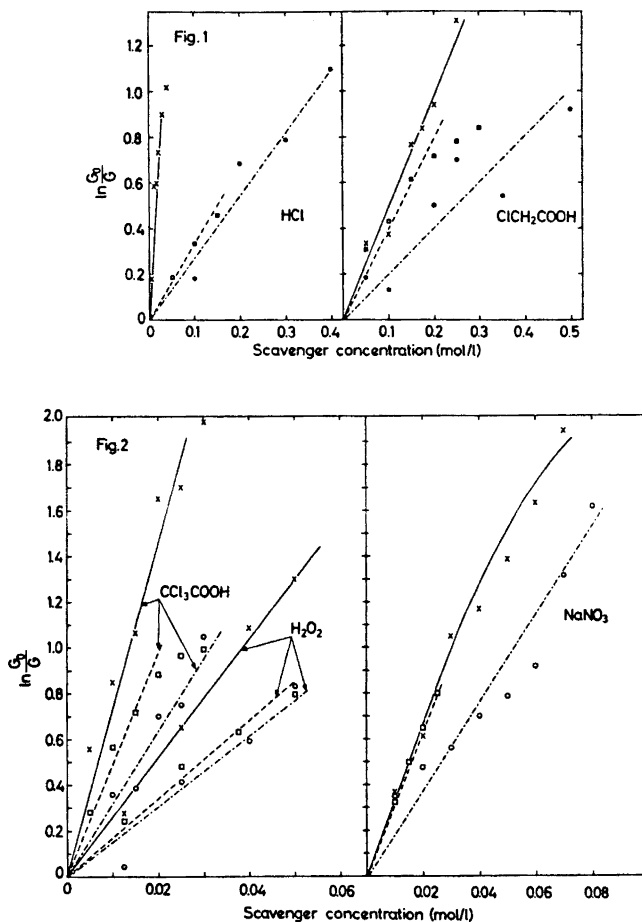
water (EG/H₂O) 1:1 by volume.⁴ The samples were irradiated by 250 nm UV-light at 77 K and their optical densities and thermoluminescence glow curves observed upon heating were recorded by an apparatus described elsewhere.⁵

When an electron scavenger is present in the samples the electrons may be captured by it both on their way out from the positive ion prior to trapping and after being released from their traps. We will first look at the scavenging of the mobile electrons prior to trapping. Let r be the mean distance travelled by the electrons prior to trapping. We will suppose that a scavenger molecule which is within the distance r of a ionization reacts with the ejected electron with a probability k_m . If the scavenger molecules are distributed in the volumes $V = \frac{4}{3}\pi r^3$ according to Poisson's formula, this leads to the following equation for the yield G of trapped electrons:^{10,11}

$$G_0/G = \exp(k_m V[S]) \quad (1)$$

where G_0 is the yield when no scavenger is present and $[S]$ is the scavenger concentration. As may be seen from the stippled curves on Figs. 1 and 2 this equation seems to be in accordance with the experiments to a first approximation. However, in the case of CCl₃COOH and ClCH₂COOH the experimental points for the highest scavenger concentrations lie distinctly below the theoretical curves. The reason for this is not understood. The relative values for k_m and the scavenger concentrations $[S]_{1/2}$ needed to halve the yield of trapped electrons can be found from the figures. The values are given in Table 1. The values of $[S]_{1/2}$ are about a factor 1.5 smaller than those reported by Steen *et al.*³ in the case of X-ray induced ionization of EG/H₂O. This is in qualitative accordance with the findings of Hase and Kevan.⁶ They attributed the difference in the values of $[S]_{1/2}$ for X-ray and UV-induced mobile electrons to spur formation in the case of X-rays. Thus the electrons produced in the spurs do not travel far enough to randomize before they become trapped.

The quenching of the thermoluminescence by scavengers include both the scavenging of mobile electrons prior to trapping and the scavenging of released, recombining electrons. The glow curve of tryptophan in EG/H₂O-glass irradiated at 77 K consists of two peaks.⁴ Only a small part of the trapped electrons (less than 2 %) disappear in the temperature region



Figs. 1 and 2. Effect of scavenger concentration on the UV-induced yield of a) trapped electrons as measured by optical absorption spectroscopy $-\square-$ b) TL₂ $-\times-$ and c) TL₁ $-\circ-$. TL₁ is the thermoluminescence emitted between 77 and 110 K and TL₂ is the thermoluminescence emitted above 110 K. (The data are not corrected for the bleaching effect of the UV-light on the trapped electrons. This effect will be dealt with in a subsequent paper.) Scavenger concentrations are given in mol/l (M).

of the low temperature glow peak (TL₁). These electrons mainly absorb in the long wavelength side of the absorption spectrum. The glow peak at the higher temperature (TL₂), however, is accompanied by disappearance of all the trapped electrons. As may be seen from Figs. 1 and 2 and Table 1, TL₁ is less susceptible to quenching by the present scavengers than is TL₂. This is in agreement with our earlier conclusion⁴ that

the glow curve may be interpreted in terms of the distribution of ion-electron distances (trapping distances). Thus the electrons which cause TL₁ are stabilized nearer their mother-ions and in shallower traps than are the electrons which cause TL₂. It seems that the electrons which cause TL₂ are trapped nearer their mother-ions than are the bulk of the electrons.⁷ In correspondence with our earlier assumption the

Table 1. Scavenging of UV-induced trapped electrons and thermoluminescence.

					k_m/k_R		$\frac{k_{TL_2}V_2}{k_{TL_1}V_1}$
	$[S]_{1/2}(M)$	k_mV rel. units	$k_{TL_2}V_2$ rel. units	$k_{TL_1}V_1$ rel. units	$V_2/V=1$	$V_2/V=0.5$	
CCl ₃ COOH	0.013	50	75	32	2.0	0.50	2.3
H ₂ O ₂	0.041	17	26	15.5	1.9	0.49	1.7
NaNO ₃	0.022	31	32.5	18	~20	0.91	1.8
ClCH ₂ COOH	0.175	4.0	4.8	2.0	5.0	0.71	2.4
HCl	~0.2	~3.3	32	2.7	~0.1	~0.055	12.0

yield of TL₂ should depend on the scavenger concentration according to the following equation:

$$G_0/G = \exp\{(k_m + k_R)V_2[S]\} \quad (2)$$

$V_2 = \frac{3}{4}\pi r_2^3$, r_2 is the mean distance travelled by the electrons which cause TL₂. Hence, $V_2 < V$. k_R is the probability that a scavenger molecule within V_2 will react with a recombining electron. It may be seen from the figures that the experimental results seem to be in accordance with the model. However, the scatter of the experimental points is so large that no firm conclusion can be drawn about the kinetics of the scavenging. (The bad reproducibility of the experiments was caused by variation of the intensity of the UV-lamp and difficulties in making equal samples.) In Table 1 we have calculated k_m/k_R for two values of V_2/V . From these results it seems that the reactivity of the scavengers with mobile electrons prior to trapping is not proportional to the corresponding reactivity with the recombining electrons. Especially H⁺ behaves differently from the other scavengers. (It has previously been shown that the scavenging effect of Cl⁻ is negligible.³) While H⁺ is rather inefficient in scavenging the mobile electrons prior to trapping, it is very efficient in scavenging the electrons that cause TL₂ on recombination. The fact that H⁺ is an inefficient scavenger of mobile electrons is in accordance with the findings of Wolff *et al.*⁸ and Steen *et al.*³ It is also well known that H⁺ is an efficient scavenger of solvated electrons.⁹ Our results therefore indicate that the recombining electrons resemble solvated electrons rather than mobile ones. This is reasonable, since the thermal energy of the electrons at 140 K is hardly as high as the trapping energy (the trap depth). Thus the recombining

electrons are probably moving with less energy than mobile free electrons, *i.e.* they are perhaps moving by tunnelling from trap to trap. From Table 1 it is also evident that the ratio $k_{TL_2}V_2/k_{TL_1}V_1$ is much larger for H⁺ than for the other scavengers. ($V_1 = \frac{3}{4}\pi r_1^3$ where r_1 is the mean distance travelled by the electrons which cause TL₁ on recombination.) This seems to indicate that the electrons which cause TL₁ react with scavengers only before trapping, *i.e.* as mobile ones. The distance travelled by these electrons is perhaps so short that scavenger molecules within this distance react with them with a probability close to unity, and trapping within this distance occurs only when no scavenger molecule is present.

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