Localization of $\leqslant 2$ eV Electrons in a 3-Methylpentane Glass

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The mean-square diffusion distance of electrons photoliberated from traps depends on the photon energy: the limit value (solvation length) in 3-methylpentane is $\simeq 63$ Å.

The participation of 'hot' electrons, $e^-_{\rm hot}$ (with excess energy above thermal energy, $k_{\rm B}T$) in reactions in liquid and rigid non-polar media has been the subject of a long-standing discussion (see, for example, ref. 1). The simplest process for creating such electrons is photoliberation from traps:

$$e^-_{\rm tr} + h\nu \;\rightarrow\; e^-_{\rm hot}$$

(excess energy is $h\nu - E_{\rm i}$, where $E_{\rm i}$ is the ionization threshold of a trapped electron, $e^-_{\rm tr}$). Whether the thermalization process for an electron photoliberated from a trap precedes the electron trapping process,

$$e^-_{\rm hot} \;\rightarrow\; e^-_0 \;\xrightarrow{\tau_0^{-1}}\; e^-_{\rm tr}$$

(here e^-_0 denotes a thermalized electron) or whether an electron is trapped in a non-thermalized state (thermalization during the localization process) is still an open question. However, we notice the following.

(1) In some papers, there are indications that $e^-_{\rm hot}$ takes part in capture reactions by acceptor molecules and radicals in non-polar hydrocarbon glasses.[2–7] In addition, the influence of 'bleaching' of $e^-_{\rm tr}$ by IR on the radiation yield of free ions, $G_{\rm fi}$ (escaping recombination with 'parent' ions), detected in the same media[8] provides direct evidence for the participation of non-thermalized electrons in the reaction of geminate[1] electron-ion recombination.

(2) The most direct data on electron reactions in rigid media were obtained by electric methods. However, the analysis of these data was carried out almost without exception under the assumption[9,10] that the drift displacement of a 'hot' electron is negligibly small in comparison with the displacement of a thermalized electron, *i.e.*, $\Delta_{h\nu} \simeq \Delta_{\rm th}$, where $\Delta_{h\nu} = \mu_0\tau_0|_{h\nu}$ is the drift displacement of a photoliberated electron in unit electric field and $\Delta_{\rm th} = \mu_0\tau_0$ is the drift displacement of a thermalized electron, μ_0 and τ_0 being the mobility and the lifetime, respectively.

Point (2) is very pertinent. In essence, under this assumption the independence of the lifetime of the photoliberated electron on the excess energy is postulated beforehand. This is done even in the most modern form of the Onsager model,[11] the 'two state electron model'.[10] It is likely for this reason that the model in ref. 10, as with other models suggested earlier, is faced with the difficulties of interpreting the dependence of $G_{\rm fi}$ on the strength of the external electric field, E, in γ-irradiated rigid non-polar hydrocarbons [*e.g.* in 3-methylpentane (3MP)[8]]. The difficulties emerge when we try to describe the electron migration under light exposure and its migration in the dark simultaneously, *i.e.*, with the same space distribution function of the trapped electrons, $f_{\rm tr}(r)$ (r is the initial distance between a trapped electron and a parent ion). In fact, the probability for a geminate pair to be separated into free ions, ϕ, in the low field limit depends linearly on E:

$$\phi(E) \approx \left(1 + \frac{eEr_{\rm c}}{2k_{\rm B}T} + \ldots\right) \int 4\pi r^2 f_0(r) \exp\left(-\frac{r_{\rm c}}{r}\right) {\rm d}r \qquad (1)$$

where $f_0(r)$ is the initial distribution function of the pairs, $r_{\rm c} = e^2/\varepsilon_0 k_{\rm B}T$ is the Onsager's radius and ε_0 is the relative permittivity). The quantity ϕ is controlled only by the ratio of the diffusion coefficient of an electron to its mobility, *i.e.*, by the temperature of the medium:

$$D_0/\mu_0 = (k_{\rm B}/e)T \qquad (2)$$

It follows from equation (1) that the slope of $\phi(E)$ in the low-field limit is practically independent of the form of the initial distribution function $f_0(r)$. If we also ascribe to a photoliberated electron the 'effective' temperature, determined by the 'generalized' Einstein relation,

$$T_{\rm eff} = \frac{1}{\alpha}(e/k_{\rm B})\frac{D_{\rm eff}}{\mu_{\rm eff}} \qquad (3)$$

[where $D_{\rm eff}$ is the mean diffusion coefficient, $\mu_{\rm eff}$ is the mean mobility of the electron and $\alpha = \alpha(h\nu)$ is the 'correlation' coefficient], the increase in $G_{\rm fi}$ under light irradiation can be associated with $T_{\rm eff} > T$: for $G_{\rm fi} = \phi G_{\rm tr}$ it follows from equations (1)–(3) that:

$$G^{h\nu}_{\rm fi}(E) \approx 4\pi G_{\rm tr}\left(1 + \frac{e^3}{2\varepsilon_0 k_{\rm B}^2 \alpha^2 T_{\rm eff}^2}E\right) \int r^2 f_{\rm tr}(r) \exp\left(-\frac{e^2}{\varepsilon_0 k_{\rm B}\alpha T_{\rm eff}} \cdot \frac{1}{r}\right) {\rm d}r \qquad (4)$$

where $G_{\rm tr}$ is the initial radiation yield of $e^-_{\rm tr}$. The initial slope of $G_{\rm fi}(E)$,

$$s^{h\nu} = G^{h\nu}_{\rm fi}(0)^{-1}\frac{\rm d}{{\rm d}E}G^{h\nu}_{\rm fi}(E) \simeq \frac{e^3}{2\varepsilon_0 k_{\rm B}^2 \alpha^2 T_{\rm eff}^2} \qquad (5)$$

is practically independent of $f_{\rm tr}$ as in equation (1). Unfortunately, among non-polar hydrocarbon glasses only for 3MP are sufficient experimental data available with which to test problems in the models of geminate pair separation. According to data in ref. 8, the initial slope of $G^{h\nu}_{\rm fi}(E)$ dependence in 3MP is $s^{h\nu} \simeq 1.7 \times 10^{-4}$ cm V^{-1} for $0 \leqslant E \leqslant 6 \times 10^3$ V cm^{-1} and $h\nu = 1.2$ eV; the slope differs a little from that in the dark, $s \simeq 2.3 \times 10^{-4}$. These data are consistent neither with the model in refs. 8, 11 nor with the model in ref. 10: the predicted slope of $G_{\rm fi}(E)$ dependence in the dark is four times greater than that in the light, and the quantity $G_{\rm fi}(E = 0)$ is 2.5 times less than experimentally observed, $\simeq 5 \times 10^{-3}$ (per 100 eV of absorbed energy).

There could be two reasons for the discrepancy between the model in ref. 10 and the data in ref. 8: i, the assumption (2) is not true; ii, there is an additional neglected yield of free ions caused by an ion separation process that depends only slightly on temperature. For example, this neglected yield could be caused by: iia, conversion of pairs into free ions during irradiation; iib, tunneling[12] of electrons from trap to trap. The latter assumption (iib) does not contradict estimations of the 'critical' temperature, T^*,[13] at which the efficiencies of under-barrier and over-barrier transfers in geminate recombination are equal: $T^* \sim 70$–100 K for hydrocarbon glasses.

With the conditions i and ii, the consideration of the dynamics of conversion of geminate pairs into free ions is a complicated problem which is still not solved. In this paper, we show only a fundamental possibility of improving the model and make some simplifications for this purpose. If we are not aiming at determining the thermalization length of e_{hot} in 3MP (that was done in ref. 10) but restrict ourselves to obtaining the localization length of e_{hot}, then we need not use the condition i. In addition, we do not consider the possibility iia. We take into account the condition iib using coefficient α in equation (5). For example, it is not difficult to deduce in the simplest case of separation of a pair having initial size r at $E = 0$:

$$\phi(r, E = 0) = \exp\left(-\frac{r_c}{\alpha r}\right) \tag{6}$$

Summing the diffusion and drift flows for under-barrier and over-barrier transfers of electrons, it can be shown that $\alpha \simeq 1$ for $T > T^*$ and $\alpha \simeq T^*/T > 1$ for $T < T^*$, approximately. According to equation (6), this can result in an increase in the yield of ions escaping geminate recombination in the dark as compared with the yield predicted for over-barrier transfers.

Assuming that the contribution of under-barrier transfers to pair separation is negligibly small under photoliberation of electrons ($T_{\text{eff}} > T^*$), its contribution to G_{fi} in the dark can be estimated by successive approximations. Let $\alpha = 1$ at first. It then follows from equation (5) that the slope $s^{h\nu}$ obtained experimentally for 3MP in ref. 8 gives $T_{\text{eff}} \simeq 175$ K. A numerical calculation[†] using the original Onsager relation instead of equation (4) results in a slightly different value: $T_{\text{eff}} \simeq 160$ K. The value of G_{fi} and the dependence of G_{fi} on temperature depend strongly on the parameters used for $f_{\text{tr}}(r)$. However, numerical calculations with trial functions of different sites (see types of function in ref. 1) show that the gauss function with $b = 72$ A fits the experimental data[8] for $G_{\text{fi}}^{h\nu}(E = 6 \times 10^3\ \text{V cm}^{-1})$ dependence at $0 \leqslant h\nu \leqslant 2$ eV [where $h\nu = 0$ corresponds to $G_{\text{fi}} = 1.2 \times 10^{-2}$ (per 100 eV of radiation energy absorbed) at 80–85 K in the dark]. Comparing the calculated value of $G_{\text{fi}}(E = 0)$ with data for the dark, the contribution of under-barrier transfers can be eliminated. In the first approximation the yield is $\simeq 60\%$. This value results in an estimation for $\alpha \simeq 1.2$ and $T^* \simeq 95$–100 K and for $s \simeq 5 \times 10^{-4}$ cm V^{-1} in the dark. The last value is in much better agreement with experiment than that in the model in ref. 10. Furthermore, a second approximation can be made and so on. The agreement between G_{fi} and experiment[8] at $0 \leqslant E \leqslant 4 \times 10^4$ V cm^{-1} is 30%. Unfortunately, the fundamental problem is not resolved at present, *i.e.* the influence of external electric field on the probability of conversion of a geminate pair into free ions for under-barrier transfer of an electron from trap to trap. The data[8] could be better explained if there was no such influence at low electric fields (in contrast to geminate recombination). In this case both G_{fi} and $s \simeq 3 \times 10^{-4}$ cm V^{-1} fit well with the experiment.

The calculated dependence of the ratio of effective values $D_{\text{eff}}/\mu_{\text{eff}}$ on $h\nu$ for 3MP is shown in Figure 1. It can be seen that the ratio increases sharply at photon energy $h\nu \simeq 0.6 - 0.8$ eV, and reaches the limit at $h\nu \simeq 1.0$–2.5 eV which is close to the quantity determined from the slope of the dependence of $G_{\text{fi}}^{h\nu}(E)$.

By multiplying the numerator and the denominator of the ratio $D_{\text{eff}}/\mu_{\text{eff}}$ by the effective lifetime of electron capture, τ_{eff}, the ratio can be related to the mean square, l^2, of the diffusion distance of the electron for the time of transfer from trap to trap $D_{\text{eff}}\tau_{\text{eff}}/(\mu_{\text{eff}}\tau_{\text{eff}}) = l^2/6$ ($= \mu_{\text{eff}}\tau_{\text{eff}}$ is the drift displacement in unit electric field). The experimental data of most authors testify that for free electrons does not depend on $h\nu$ at $h\nu > 0.7$ eV ($= 5 \times 10^{12}$ cm^2 V^{-1}).[10] If we accept this fact, the dependence of $D_{\text{eff}}/\mu_{\text{eff}}$ on $h\nu$ (Figure 1) can be represented as the dependence of mean square of the diffusion distance of an electron for the transfer time from trap to trap, $l^2(h\nu) = 6D_{\text{eff}}\tau_{\text{eff}} = 6(k_B/e)\alpha T_{\text{eff}}$. The limit of $l^2(h\nu)$ dependence is $l_s \simeq 63$ A.

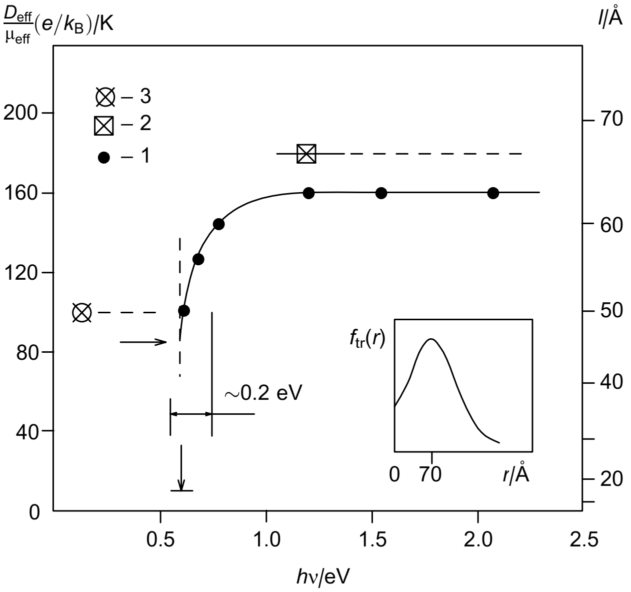

Figure 1 The dependence of the ratio of diffusion coefficient to mobility and the mean square of diffusion displacement of a photoliberated electron on photon energy in 3MP, calculated from the data in ref. 8: 1, based on the dependence of G_{fi} on the wavelength of bleaching illumination at $E = 6 \times 10^3$ V cm^{-1}; the function $f_{\text{tr}}(r)$ is shown in the inset; 2, based on the slope of the dependence of G_{fi} on the external electric field strength at $h\nu = 1.2$ eV; 3, based on the quantity of $G_{\text{fi}}(E = 0)$ and on the slope of $G_{\text{fi}}(E)$ dependence in the dark. The arrows show the ionization energy threshold of e_{tr}^- and the result of extrapolation.

The limit value l_s is in agreement with the values of the trap concentrations estimated by several authors in spite of different, non-reproducible methods of preparation of the glasses. In fact, compare: $l_s^{-3} \simeq 4 \times 10^{18}$ cm^{-3}, and, for example, the mean concentration of traps in 3MP is $\simeq 6 \times 10^{18}$ cm^{-3},[15] $\simeq 1 \times 10^{18}$ cm^{-3}.[16] Based on this fact, the limit value l_s can be referred to as the mean-square solvation length of a photoliberated electron. The quantity l_s is also in accordance with the result $\simeq 66$ A,[10] although obtained under the other assumptions. In addition, the value l_s is very similar to the mean-square thermalization length of photoliberated electrons, l_{th}, obtained in the study of electron injection into 3MP at 77 K: $l_{\text{th}} \simeq 80$ A.[17]

The $l^2(h\nu)$ dependence flattens out sharply (see Figure 1) at photon energy near $h\nu \sim 0.8$ eV, when the excess electron energy exceeds the photoionization threshold by ~ 0.2 eV.[‡] The capture of electrons with excess energy $\simeq 0.1$–0.2 eV from the ‘hot’ state is likely to be more preferable in 3MP. The suggested interpretation does not contradict the model of electron thermalization[19] since the ‘sensitivity’ range of the value of l^2 with respect to $h\nu$ is limited by the excess energy of electrons $\simeq 0.3$–0.4 eV (Figure 1). The extrapolation of $l^2(h\nu)$ dependence to the ionization energy threshold of e_{tr}^- (Figure 1) shows that the mean-square diffusion distance during the trapping-time of a ‘thermalized’ electron is less than l_s: $\simeq 45$ A. This result corresponds to a decrease in the e_{tr}^- photobleaching quantum yield for the long wavelength band of the absorption spectrum that has been observed already in previous studies[1,15] of electrons in 3MP.

[†] The Gaussian distribution function $f_{\text{tr}}(r)\alpha\exp\{-[(r-b)/b]^2\}$ with parameter $b = 72$ A and $G_{\text{tr}} = 0.8$ (per 100 eV of absorbed radiation energy) were used for numerical calculation. This quantity of parameter b is consistent with results for liquid 3MP.[14]

[‡] This differs from the case of H_2O[18] where the $l_{\text{th}}(h\nu)$ dependence does not approach a plateau, but maintains a shallow, positive gradient to beyond $h\nu > 2.5$ eV.

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