On the Isothermal Decay of Trapped Electrons Formed in a Rigid γ-Irradiated Medium

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(Received September 29, 1965)

The study of trapped electrons formed by the γ-irradiation of organic glasses is of great significance in the elucidation of the primary processes in radiation chemistry. The isothermal decay of trapped electrons in 2-methyltetrahydrofuran (MTHF)[1] and in 3-methylpentane[2] at low temperatures has recently been observed by spectroscopic methods. It does not appear, however, that the mechanism for the isothermal decay of trapped electrons has been established.

As a theoretical approach to this problem, we have made a calculation of the tunneling of an electron from an electron-trapping center to a positive hole in MTHF. In the calculation the following formula has been used; it is similar to that used in the calculation of the tunneling of F-center electrons in alkali halides[3]:

$$\lambda(R)=-\frac{E_0}{\hbar}\exp\left[-\frac{4\pi}{\hbar}\int_{r_0}^{r^*}\sqrt{2m\{U(r)-E_0\}}\,dr\right]$$

where λ is the decay constant; R, the distance between a trapping center and a positive hole; E_0, the ground-state energy of the trapped electron; m, the electron mass, and $\hbar$, the Planck constant. $U(r)$, the potential function, is given by;

$$U(r)=-\frac{e^2}{\varepsilon(R-r)}, \qquad R>r\geq r_0$$

where r is the distance from the trapping center; r_0, the radius of the trapping center[4]; r^*, the distance at which the kinetic energy of the trapped electron becomes negative and equal to $R-(e^2/\varepsilon E_0)$, and ε, the dielectric constant of the medium. In the numerical computation we have used the values of $E_0=-1$ eV.[5] and $\varepsilon=4.6$ for MTHF.

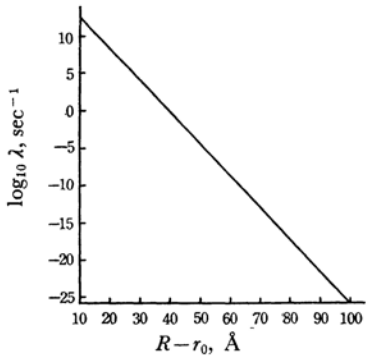

Fig. 1. Decay constant of trapped electrons in MTHF as a function of the ion-pair separation distance.

Figure 1 shows the decay constant of trapped electrons in MTHF, calculated as a function of the ion-pair separation distance. The decay constants of trapped electrons measured by Smith and Pieroni[1] are of the order of 10^{-4}—10^{-5} sec^{-1} in this system. From Fig. 1 the corresponding ion-pair separation distance is obtained as $\sim$50 Å, in good agreement with the average distance ascertained experimentally.[1] Thus the tunneling of electrons is a possible mechanism for the isothermal decay of trapped electrons formed in rigid γ-irradiated media.

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1) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **43**, 876 (1965).
2) M. Burton, M. Dillon and R. Rein, *J. Chem. Phys.*, **41**, 2228 (1964).
3) D. L. Dexter, *Phys. Rev.*, **93**, 985 (1954).
4) The radius of the trapping center, r_0, would be about 3Å. It should be noted that the value of r_0 is not explicitly required for the present purpose.
5) This value corresponds to the electronic transition energy at the absorption maximum, which is believed to be close to the binding energy of the trapped electron in the ground state. W. H. Hamill, J. P. Guarino, M. R. Ronayne and J. A. Ward, *Discussions Faraday Soc.*, **36**, 169 (1963).