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The Temperature Dependence of the Localization and Scavenging of Electrons in a Glassy 2-Methyltetrahydrofuran Matrix

Masato Yoshizaki, Masaaki Ogasawara,* and Hiroshi Yoshida
Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo 060

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The nature and behavior of localized electrons in a γ-irradiated 2-methyltetrahydrofuran matrix were studied at 4 and 77 K by optical absorption measurements. Electrons localized in shallow traps generated at 4 K in a neat matrix showed one broad peak with ε_{max} of 1.2×10^4 mol^{-1} dm^3 cm^{-1} at 1490 nm. The yield was 1.9 (for 100 eV energy absorbed). This yield is less than the yield of electrons localized in deep traps at 77 K, 2.6. With an increasing concentration of biphenyl added to the matrix, the localized electrons were completely transformed into biphenyl anions. The scavenging efficiency was twice as high at 4 K as at 77 K. These results indicated that the electron scavenging took place by tunneling of the once localized electrons.

Glassy 2-methyltetrahydrofuran (MTHF) is a rigid organic matrix in which the nature and behavior of radiation-generated localized electrons at 77 K have been extensively studied by means of optical absorption and electron spin resonance (ESR) measurements.$^{1)}$ The temperature dependence of an electron scavenging reaction in this glassy matrix was first studied by Higashimura and two of the present authors (M. O. and H. Y.). They used the 4 K γ-irradiation technique combined with the ESR method. From the observed temperature dependence it was inferred that the scavenging efficiency of biphenyl was higher by about a factor of four at 4 K than at 77 K. This was attributed to a temperature-dependent competition among localization, charge recombination, and scavenging of electrons.$^{2)}$ In this early study, however, the ESR measurements were made after warming of the samples to 77 K, so that ambiguity caused by the effect of warming could not be avoided. Hase *et al.* have tried to study the relaxation of electrons localized in the MTHF matrix by a 4 K irradiation-optical absorption method, but the spectrum of localized electrons obtained prior to their relaxation was not clear enough, mainly because of the efficient electron-scavenging at 4 K by impurities contained in the sample.$^{3)}$ Hager and Willard have studied the relaxation of localized electrons in this matrix by generating them photolytically in the temperature range 10—97 K.$^{4)}$

Owing to the recent progress in pulse radiolysis studies at low temperatures, electron tunneling from localized states to scavenger molecules has become the prevailing interpretation of the mechanism for electron scavenging reactions in rigid matrices.$^{5)}$ In this respect, we thought it was necessary to re-examine the temperature dependence of the electron scavenging in the MTHF matrix in a more quantitative way and also to examine the absorption spectrum of the localized electrons before their relaxation.

Experimental

MTHF was washed with an aqueous NaOH solution, distilled over Na metal, and dried with a Na–K alloy. Solutions of zone-refined biphenyl in MTHF were degassed with freeze-pump-thaw cycles, sealed in Suprasil quartz cells (0.2 cm optical path) under a vacuum of 10^{-5} Torr,† frozen in liquid nitrogen into the glassy state, and transferred into a liquid helium cryostat. In order to avoid breakage of the cells in liquid helium, the glass in the cells was usually made moderately cracked by introducing a tiny piece of quartz.

The samples were irradiated with ^{60}Co γ-rays at a dose rate of 6.24×10^{18} eV g^{-1} h^{-1} at 77 K (in the cryostat filled with liquid nitrogen) or at 4 K, and subjected to optical absorption measurements at the irradiation temperatures with a Shimadzu MPS-5000 spectrophotometer. Post-irradiation annealing of the samples irradiated at 4 K was carried out by transferring them into liquid nitrogen, keeping them there for ten minutes, and transferring them back into the liquid helium cryostat again. All measurements and the handling of the samples were carried out in complete darkness. The absorption spectra were corrected for the background absorption recorded before the irradiation.

Results and Discussion

Spectra of Localized Electrons. The absorption spectrum due to localized electrons in neat MTHF irradiated at 4 K initially showed a broad single peak at 1490 nm and a long absorption tail to the high energy side as shown in Fig. 1. Annealing at 77 K changed the spectral shape; it became red-shifted and double-peaked at 1150 and 1300 nm. Such a spectral change has been observed previously and was attributed to the rearrangement of MTHF molecules around electron

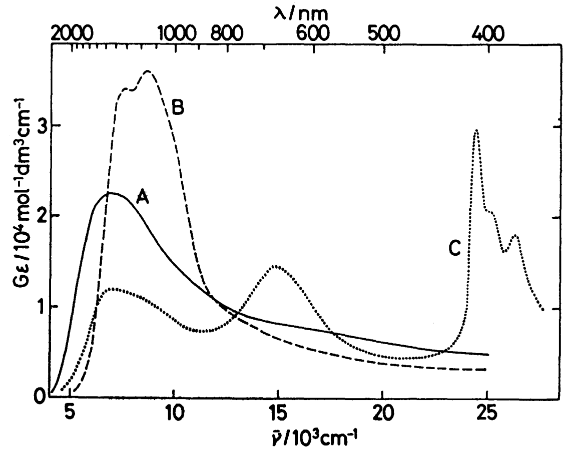

Fig. 1. Absorption spectra obtained from γ-irradiated MTHF at 4 K (A) in the absence and (C) presence of biphenyl. The spectrum B was obtained from γ-irradiated neat MTHF at 4 K after annealing the sample at 77 K for 10 min.

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† 1 Torr≈133. 322 Pa.

traps.[3,4,6] The possibility that the spectral change is due to a redistribution of the electrons into deeper traps, as is the case for aqueous glasses[7] and (partly) for alcoholic glasses,[8] cannot yet be discarded however. Irrespective of the mechanism responsible for the spectral change, the localization of the electrons becomes deeper when the samples are annealed at 77 K. The spectral shape after the annealing is almost the same as that recorded from MTHF irradiated at 77 K.

The intensity increase at the absorption maximum during annealing seems to be complemented by a disappearance of the low-energy part of the absorption and an intensity decrease of the high-energy absorption tail. This kind of spectral change is theoretically expected from an effective deepening of electron traps on the basis of the cavity model.[9] Assuming no loss of electrons during annealing, the molar absorptivity at the absorption maximum, $\varepsilon_{\mathrm{max}}$, of the electrons localized in shallow traps at 4 K is calculated to be 1.2×10^4 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ at 1490 nm, based on the reported $\varepsilon_{\mathrm{max}}$ value, $1.9\times10^4\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ for the electrons localized in deep traps generated at 77 K.[10] It turns out that the yield (for 100 eV energy absorbed, *G*-value) of the localized electrons at 4 K is 1.9, which is significantly lower than the *G*-value at 77 K, 2.6.[11] This result is consistent with the previous finding[2] that the *G*-value at 4 K is 75% of that at 77 K in MTHF and is similar to the temperature-dependence of the *G*-values observed in glassy alkanes by steady-state measurements.[12] Klassen *et al.*,[13] however, have claimed, based on their pulse radiolysis study, that the apparent difference in the *G*-value is due to rapid decay of a fraction of localized electrons immediately after their formation. This is more significant at 4 K than at 77 K.

In the presence of a small amount of biphenyl in MTHF, the optical absorption signal recorded after the irradiation at 4 K is comprised of the spectrum due to localized electrons and that due to biphenyl molecular anions as is shown in Fig. 1C. Although the high-energy absorption tail of the electron spectrum could not be examined in detail because it was overlapped by the anion spectrum peaks at 395, 408, and 650 nm, the low-energy side of the electron spectrum is efficiently depleted. This depletion can probably be attributed to the selective scavenging by biphenyl of the localized electrons. In contrast, the electron spectrum at 77 K is depleted homogeneously by the addition of biphenyl. The heterogeneous depletion of electron spectra at 4 K has also been demonstrated for glassy ethanol.[14,15]

Electron Scavenging of Biphenyl. The yields of localized electrons and biphenyl anions were determined for 4 K and 77 K-irradiations as a function of the biphenyl concentration by graphically decomposing the recorded absorption curves into their component spectra. They are shown in Fig. 2. The electron yield at 77 K was determined from the absorption peak height at 1150 nm, while that at 4 K was estimated from the spectral intensity integrated down to 400 nm (below this wavelength, free radicals from MTHF contribute to the optical absorption[16]) to minimize the effect of the heterogeneous spectral depletion. The anion yield at 4 and 77 K was determined by using the $\varepsilon_{\mathrm{max}}$ at 408 nm measured at 77 K, $3.9\times10^4\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$, reported by Shida,[10] as the present study has shown $\varepsilon_{\mathrm{max}}$ to be independent of the temperature.

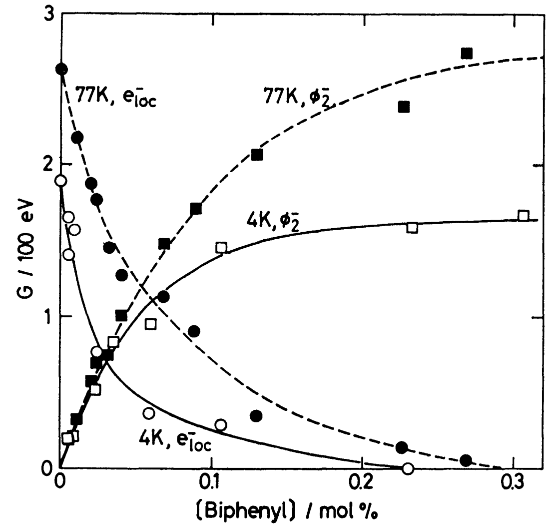

Fig. 2. Effect of biphenyl concentration on the yield of the localized electron, e^-_{loc}, and biphenyl anion, ϕ_2^-, in γ-irradiated MTHF at 4 and 77 K.

The plateau value of the anion yield at 77 K for high biphenyl concentrations agrees with the electron yield in the absence of the scavenger at the same temperature. The plateau value at 4 K is 1.7, which appears to be a little lower than the initial electron yield of 1.9. However, this small difference may be the result of the uncertainty in the $\varepsilon_{\mathrm{max}}$ value for the localized electrons at 4 K. If one assumes a partial disappearance of 10% of the localized electrons in the MTHF during annealing, then the $\varepsilon_{\mathrm{max}}$ value will be $1.1\times10^4\ \mathrm{mol^{-1}}$ $\mathrm{dm^3\,cm^{-1}}$ instead of $1.2\times10^4\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$, and agreement at 4 K will be attained between the yields of the localized electrons and the anions. Within the uncertainty of the present experiments, it can be concluded that the yield of scavengeable electrons is equal to the yield of stably localized electrons in the absence of the scavenger. The yield of such electrons is appreciably lower at 4 K than at 77 K.

Figure 2 also indicates the temperature dependence of the electron scavenging efficiency. The efficiency can be estimated from the reciprocal of that biphenyl concentration at which the electron yield is halved or from that where the anion yield is half of its plateau value. Biphenyl is about twice as efficient at 4 K as at 77 K in scavenging electrons. This temperature dependence is less significant but qualitatively consistent with the previous result obtained by ESR for the biphenyl–MTHF system.[2] When the concentration of added biphenyl exceeded 1 mol%, the *G*-value of the anion was found to decrease slowly at both 4 and 77 K. The reason for this is probably complicated.

Localization and Tunneling of Electrons. The temperature dependence of the electron yield combined with the complete conversion into biphenyl anions at a high enough biphenyl concentration naturally leads to the conclusion that at first the electrons are localized in traps in the matrix; subsequently they are transferred to the scavenger molecules. If one assumes that the electrons are scavenged before localization, the observed temperature dependence of the electron yield can only be interpreted by the rather improbable hypothesis that the *G*-value of ionization is lower at 4 K than at 77 K, *i.e.*, that the *W*-value in the MTHF matrix is dependent on temperature. Otherwise, the plateau *G*-value of the anion should have been independent of temperature, as the electrons must be scavenged completely by biphenyl at sufficiently high concentrations.

The low *G*-value of localized electrons at 4 K is interpreted as a competition between electron localization and charge recombination. The former process will become less dominating at a lower temperature because of weaker interactions between the excess electron and the motions of the matrix molecules, so that the electron has a greater chance of encountering positive ions as its migration path is longer before being localized. An alternative interpretation is that a large fraction of the localized electrons have disappeared at low temperature before the steady-state measurements took place. This is the result of charge recombination by electron tunneling which competes with the slow relaxation of the localized electrons. This interpretation, however, seems unlikely as it predicts that the *G*-value of scavengeable electrons (the plateau *G*-value of the anions) is independent of temperature.

The transfer of the localized electrons to scavenger molecules has generally been explained by a tunneling mechanism.[5] The observed dependence of the electron and anion yields on the scavenger concentration is replotted in Fig. 3; this shows the survival probability of the localized electrons to decrease exponentially, consistent with the tunneling mechanism. The tunneling transfer of electrons in the MTHF matrix is also suggested by the previous observation that the rate of decay of the localized electrons by charge recombination deviates from an Arrhenius-type dependence in the low temperature region and is almost independent of temperature below 77 K.[17]

The slopes of the straight lines in Fig. 3 again indicate that the efficiency of scavenging of the localized electrons is about twice as high at 4 K as at 77 K. This temperature dependence can be understood qualitatively by taking into account that the height of the potential barrier to tunnel through is effectively lower for the electrons localized in shallow traps at 4 K than the ones in deep traps at 77 K. Unfortunately direct calculation of the tunneling probability is difficult or even impossible for the present case. The discrete electron energy pectrum of the chemical product of the scavenging reaction is unknown, so that the energy difference between electron-donating levels and electron-accepting levels can not be properly expressed in the calculation of the tunneling probability. Efficient scavenging of electrons localized in shallow traps has been reported also in glassy ethanol by using benzyl chloride[14] and toluene[15] as scavengers.

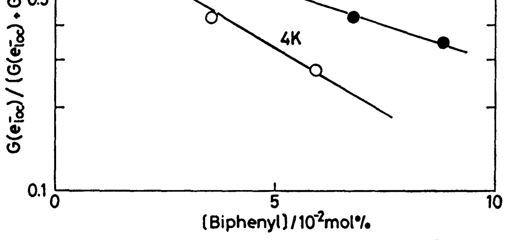

Fig. 3. Survival probability of the localized electron as a function of biphenyl concentration at 4 and 77 K.

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