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Positive-Charge Scavenging by Amines in Pulse-Irradiated sec-Butyl Chloride Glasses at 77 K. Dependence of Rate on the Ionization Potential of Amines

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sec-Butyl chloride glasses containing amines were pulse radiolyzed at 77 K and the time change of matrix holes was monitored over the time range of 3 μs to 1.7 s. Similar observation was made for glasses containing both amine and excess biphenyl, where biphenyl cations were monitored. The survival fraction of either matrix holes or biphenyl cations continued to decrease over several orders of magnitude of time. The rate of positive-charge transfer to amines increased with decreasing ionization potential of amine but did not differ for two positive-charge donors, matrix holes and biphenyl cations. The net process of the observed positive-charge transfer can be regarded as long-range electron transfer from amines. The dependence of the rate on the ionization potential of amines was explained by estimating the electronic interaction matrix element for long distance on the basis of electron tunneling between two Coulombic traps.

Introduction

The formation of solute cations in glassy solutions exposed to ionizing radiations was being explained in terms of mobile-hole capture for more than a decade.[1-4] Recently it has been revealed that the cation formation proceeds over a wide range of time[5-7] and that not only matrix holes but also solute cations can be a positive-charge donor.[6,7] Phenomenologically, these results are quite similar to those observed for electron transfer from trapped electrons or solute anions to electron scavengers.[8,9] Positive-charge transfer can be regarded as a phenomenological appearance of electron transfer; therefore, it is of interest to compare its experimental results with theories of electron transfer which have recently been developed.[8-16]

This paper deals with the decay of cationic species in the presence of a positive-charge scavenger in pulse-irradiated sec-butyl chloride (s-BuCl) glasses at 77 K in the time region of 3 μs to 1.7 s. Our previous results for solutes of aromatic hydrocarbons[6] were rather qualitative because of difficulties in correction for overlapping strong bands of aromatic cations produced on positive-charge transfer. In the present study, quantitative measurements were carried out by using aliphatic amines and aniline derivatives for which corrections for absorption overlap are trivial or small. Emphasis was placed on the dependence of the positive-charge transfer rate on the ionization potential of the amines, namely, the dependence of the electron transfer rate on the trap depth of electron donors. No systematic studies have ever been made on this type of dependence, though a trap depth has been adjusted to fit the experimental data of electron scavenging.

Experimental Section

Samples mounted in a cryostat described elsewhere[6] were irradiated with 2-μs electron pulses from a Van de Graaff accelerator operating on 2.5 MV and 120–160 mA (pulse peak current). Analyzing light was detected by a Hamamatsu-TV R-374 photomultiplier, whose output was fed through a preamplifier to a Riken Denshi TCH-4000S transient converter (digital recorder) consisting of 4000 words of 8-bit memories. Writing of the memories was actuated by external clock pulses whose time interval varies quasi-logarithmically.

Figure 1 shows examples of records after re-conversion to analog signals. The clock operates as follows. After the end of an electron pulse where $t = t_p$, it feeds 128 pulses of 0.1-μs interval, then 64 0.2-μs interval pulses, then 64 0.4-μs interval ones and so on, and the time for every 64th pulse measured from t_p is given by

$$t_n = 2^n \times 6.4 \times 10^{-6} \text{ s} \qquad (1)$$

where the n values are 0, 1, 2, ..., and these values are put on the abscissa in Figure 1 in place of t_n. If the memories are read out with a constant time interval, the position on the recording chart, x_n, is a logarithmic function of t_n

$$x_n - x_0 \propto t_n - \log t_0 \qquad (2)$$

In the region between x_n and x_{n+1} the length does not change logarithmically but linearly in time; however, a maximum deviation in the linearly changing region from the logarithmic change is 0.3% of the total length for measurement over five orders of magnitude of time. The measurements were terminated when n reached 18 (1.678 s).

sec-Butyl chloride glasses were rather opaque except for those containing such solutes as happen to make the glass transparent. In order to minimize possible errors caused by the scattering of analyzing light in a sample, apertures of a 3-mm diameter are set at both entrance and exit of a sample cell on the analyzing light axis. Fast decaying emission from a sample was often observed during ca. 10 μs after an electron pulse; accordingly, the data for time after 3 μs were used. For instance, the initial slow growth of curve A in Figure 1 is due to the emission; this was confirmed by measurement without use of the analyzing light. At 100 μs after the pulse, the absorbances of the same sample were reproducible within ±5%. The data will be presented in the form of a ratio of the absorbances of two samples, and the experimental errors in this ratio can be ca. ±10%.

The samples were aerated. Wako Junyaku's s-BuCl was treated with sulfuric acid and then fractionally distilled. Aliphatic amines of Tokyo Kasei (TK) were distilled over sodium metal. Biphenyl was a TK zone-refined reagent. Other chemicals (TK) were used as received.

Results

First, the results of preliminary γ-irradiation experiments concerning the spectral change will be mentioned briefly. Figure 2 exhibits the absorption spectra in γ-irradiated s-BuCl glasses with and without triethylamine. The spectra after irradiation, 1 and 2, are composed of a
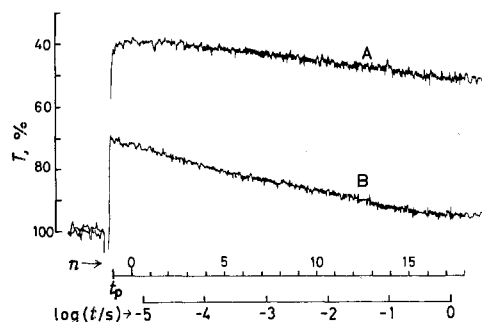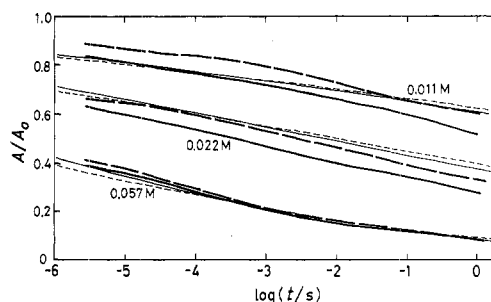
Figure 1. Records of time changes in biphenyl cation absorption at 700 nm: t_p, the end of the electron pulse; see eq 1 concerning n. (A) 0.26 M biphenyl; (B) 0.26 M biphenyl + 0.06 M triethylamine, both in s-BuCl at 77 K.
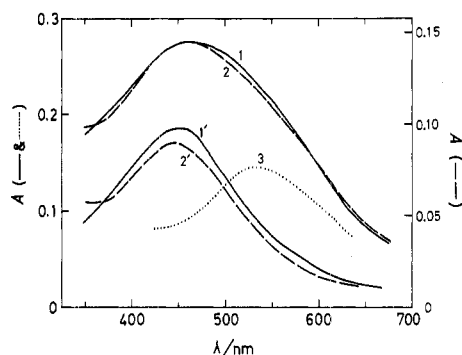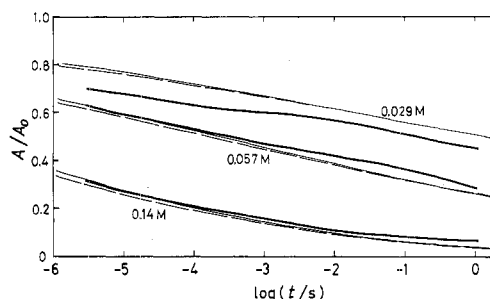

Figure 2. Absorption spectra of s-BuCl glasses γ-irradiated at 77 K (1, 2) and after subsequent photobleaching (1', 2'): 1 and 1', no solutes; 2 and 2', 0.01 M triethylamine; 3, a difference between curves 1 and 2; dose, 3.6 × 10^{18} eV/cm^3; optical path length, 1.5 mm.

Figure 3. Survival curves of matrix holes in the presence of triethylamine at the concentrations indicated, measured at 480 nm (bold dashed line) and 560 nm (bold solid line). Simulations based on eq 9 and 4 ($\nu_0 F$ = 1 × 10^{15} s^{-1}): fine solid line for ϵ = 2.0 and B_0 = 4.4 eV; fine dotted line for ϵ = 1.0 and B_0 = 6.2 eV.
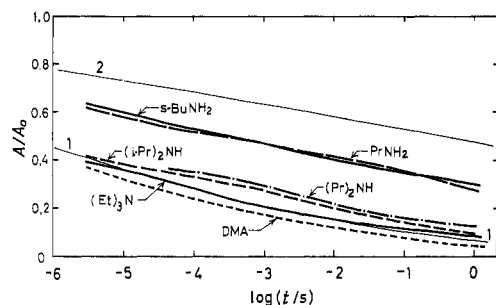

Figure 4. Survival curves of matrix holes measured at 560 nm in the presence of propylamine at the concentrations indicated (bold line). Simulations based on eq 9 and 4 (ϵ = 2.0): fine solid line for B_0 = 5.7 eV and $\nu_0 F$ = 1 × 10^{14} s^{-1}; fine dashed line for B_0 = 6.2 eV and $\nu_0 F$ = 1 × 10^{15} s^{-1}.

photobleachable band with a peak near 540 nm and a photopersisting band with a peak at 450 nm[2b,3] which have been assigned by Aria et al.[3] to trapped s-BuCl holes and 2-butene cations, respectively. In the present paper, the terms bleachable and unbleachable holes, or matrix holes inclusively, will be used for the species characterized by these bands. The similar shape of spectra 1 and 2 indicates that triethylamine removes both bleachable and unbleachable holes with the same efficiency. Spectra 1' and 2' were taken after subsequent exposure to the light from a tungsten lamp for 2 min. This exposure seemed to be sufficient, for an additional 1-min exposure hardly caused further change in the absorption. Curve 3, a difference for curve 1 minus curve 2, provides a rough sketch for the bleachable band. If spectra 1' and 2' are compared with 1 and 2, it is obvious that the ratio of the yield of the bleachable hole to that of the unbleachable hole is hardly affected by the addition of triethylamine. A new band whose tail was seen on curves 2 and 2' was observed in the near-UV region in the presence of triethylamine, but no detailed measurements were made.

The data of time change will be presented in the form of A/A_0 as a function of the logarithm of time, where A and A_0 denote the absorbances of a positive-charge donor in the presence and absence of a scavenger, respectively. This ratio represents a survival fraction of the donor in the presence of the scavenger. Figure 3 shows the survival curves of matrix holes in the presence of triethylamine. The measurements were made at 480 nm where the unbleachable band predominates and at 560 nm where the bleachable band prevails. The curve at 480 nm resembles the corresponding one at 560 nm, though the former appears to lie slightly above the latter. The same tendency also occurred for 480-nm and 560-nm curves for scavenging by sec-butylamine (data not illustrated). In both cases, however, the differences between the two curves are com-

parable to conceivable experimental errors; i.e., the accuracy of the experiments is not sufficient to discriminate between the reactivities of bleachable and unbleachable holes. Figure 4 shows the survival curves measured at 560 nm for scavenging by propylamine where the scavenging efficiency is lower than in scavenging by triethylamine.

The absorption band near 350 nm in a neat s-BuCl glass, which decays accompanying the partial growth of the bleachable and unbleachable bands, has been assigned tentatively to a precursor such as a shallowly trapped s-BuCl hole.[6] Under the present experimental conditions, the absorbance at 350 nm decayed by 20% during the period from 20 μs to 1 s after the pulse. If the 350-nm absorbing species is really the precursor, reactions of this with scavengers will reduce the yield of the bleachable and/or unbleachable holes; therefore, A_0 at 480 and 560 nm should be replaced by A_0' ($<A_0$), an absorbance for a hypothetical case where the precursor reacts with scavengers but the matrix hole does not. The value of A_0' cannot be determined experimentally. Preliminary measurements at 350 nm provided a survival curve for scavenging by 0.022 M triethylamine which decreased from 0.76 at 10 μs to 0.36 at 1 s. This curve can be regarded as the same as the curves at 480 and 560 nm for the same scavenging conditions in Figure 3, considering inaccuracy due to the poor transparency and intense emission of the sample at 350 nm. The decay of the precursor leads to the decrease in A_0'/A_0 at 480 and 560 nm with increasing time. The true survival fraction A/A_0' at 480 and 560 nm may be larger than A/A_0 by factors which increase with time. No reasonable estimation can be made at present, but we believe that the factor does not exceed 1.2.

In Figure 5 the survival curves measured at 560 nm for scavenging by various amines at a concentration of 0.057 M are compared. The curve shifts upward; i.e., the scavenging efficiency decreases as the ionization potential of the amine increases. The gas-phase ionization potentials

Figure 5. Survival curves of matrix holes measured at 560 nm for scavenging by various amines at a concentration of 0.057 M. Fine line: simulations based on eq 7 for $B = 2.2$ eV (1) and 6.5 eV (2).
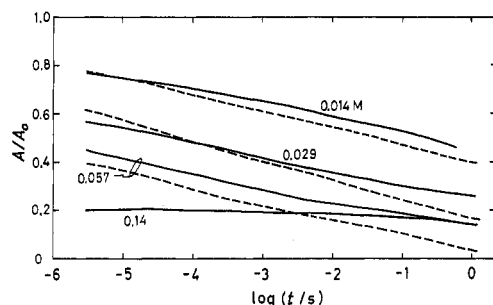

Figure 6. Survival curves of matrix holes (solid line, 560 nm) and biphenyl cations (dashed line, 700 nm) for scavenging by DMA at the concentrations indicated. Biphenyl concentration in the biphenyl cation scavenging: 0.26 M. In this figure, A for matrix holes was not corrected for the overlap of the DMA cation absorption.

(in eV) are[17] 7.10 for N,N-dimethylaniline (DMA), 7.50 for triethylamine, 7.73 for dipropylamine, 7.84 for diisopropylamine, 8.70 for sec-butylamine, and 8.78 for propylamine. The curve for DMA in Figure 5 is corrected for the overlapping absorption of DMA cations.

Figure 6 shows comparatively the survival curves of matrix holes and of biphenyl cations for scavenging by DMA. The curves of biphenyl cations were measured in the presence of excess biphenyl, where positive charges have transferred effectively, within microseconds, to biphenyl before the start of measurement. The absorbances of biphenyl cations were measured at 700 nm where the relative intensity of DMA cations was negligibly weak. The A_0 of biphenyl cations decays considerably as shown in curve A in Figure 1. The decay of A_0 of biphenyl cations is seemingly faster than that of the matrix holes, but this may be superficial, since the decay of A_0 of the matrix holes could be compensated by the growth due to their production from the precursor. In Figure 6 the decay curves of the hole were not corrected for the overlapping absorption of DMA cations. The flat survival curve of the hole for scavenging by 0.14 M DMA is interpreted as that the growth of the DMA cation absorption[18] cancels the decay of the hole absorption at 560 nm. Considering this correction, the net curves of the hole appear to agree with the curves of biphenyl cations. Similar results were obtained for scavenging by N,N-diethylaniline (data not illustrated). The survival curve of biphenyl cations for scavenging by 0.06 M triethylamine shown in Figure 7 agrees with that for 0.057 M in Figure 3. Thus, scavenging efficiencies of amines of low ionization potential are practically the same between scavenging of matrix holes and of biphenyl cations.

As also shown in Figure 7, biphenyl cations are removed in the presence of sec-butylamine and propylamine, both of which possess higher ionization potentials than biphenyl (8.27 eV). This behavior looks as if positive charges could transfer to a site whose ionization potential is 0.4 eV
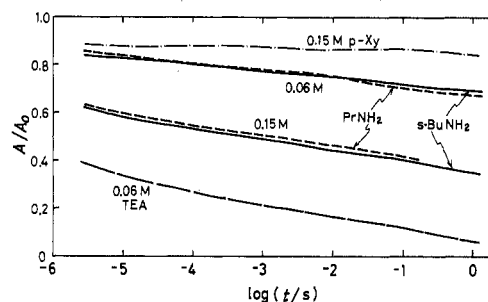
Figure 7. Survival curves of biphenyl cations measured at 700 nm for scavenging by triethylamine, propylamine, sec-butylamine, and p-xylene. Biphenyl concentration: 0.26 M.

higher. However, a very small scavenging efficiency was observed for p-xylene as shown in Figure 7, though its gas-phase ionization potential is 8.44 eV. This difference in reactivity between the two amines and p-xylene suggests that in s-BuCl glass the ionization potentials of these amines are very close to or slightly lower than the ionization potential of biphenyl.

Discussion

The observed survival curves for positive-charge scavenging resemble the curves reported previously for electron scavenging in inorganic and organic glasses.[8,9,19] Current theories of the electron transfer in glass are classified into two categories: long-range electron transfer due to electron and phonon interactions[9-15] and electron hopping by non-Gaussian diffusion.[16] If electron transfer is the net process of the observed positive-charge transfer, the former theory is applicable to the present results. It appears difficult for the latter to explain intermolecular electron transfer between solutes, as has been pointed out by Zamaraev et al.[19] The results shown in Figures 6 and 7 indicate that positive charges transfer from biphenyl cations to amine molecules, though the diffusion of solute molecules is negligible. Holes or electrons that may hop are not produced unless a few electron volts of energy is supplied for detrapping of these entities from deep traps, viz. solute cations or molecules. The similarity between the curves for hole-to-solute transfer and for intersolute transfer suggests that both of these two types of processes had better be explained in terms of a common mechanism. Consequently, the theories of long-range electron transfer seem to apply smoothly to the present results, though the hopping of holes or electrons is not completely ruled out. Henceforth the phenomena will be described as electron transfer whenever it is convenient, and positive-charge donors and acceptors will be referred to as electron acceptors and donors, respectively.

In a simple theory based on Fermi's golden rule, a rate constant of the electron transfer, k, is given by[9-11]

$$k = 2\pi|V(R)|^2\rho F/\hbar = \nu(R)F \qquad (3)$$

where $V(R)$ denotes a perturbation matrix element between the initial and final electronic state at a donor–acceptor distance of R, F is the Franck–Condon factor, and ρ is the density of states. A frequency $\nu(R)$ is associated with $|V(R)|^2$ and will be called the electronic interaction frequency hereafter. In the positive-charge scavenging as observed in this study, a small amount of electron acceptors is produced by irradiation in a glass containing a large amount of electron donors. If the donors are randomly distributed, the probability that the electron acceptors fail to receive the electrons to survive is given by[20]

$$P_A(t) = \exp\left[-C_d\int_0^\infty \{1 - \exp(-\nu(R)Ft)\}4\pi R^2 \, dR\right] \quad (4)$$

where C_d denotes an electron-donor concentration.

Equation 4 can be solved analytically provided that [20,21]

$$\nu(R) = \nu_0 \exp(-R/\alpha) \qquad (5)$$

where ν_0 and α are constants. The relation of eq 5 is believed to be a good approximation for electron exchange interaction at long distance,[10-13,22,23] but α cannot be evaluated on the molecular theoretical basis because of poor knowledge on the far tail of molecular wave functions.[10-13,22] A method so far used for estimation of α is to equate the exponential in eq 5 to the probability of electron tunneling through a square potential barrier.[9-11] This procedure leads to the equation[8-11]

$$\nu(R) = \nu_0 \exp[-2(2mB)^{1/2}R/\hbar] \qquad (6)$$

where m denotes the electron mass and B is a binding energy of an electron in the donor trap, which equals the barrier height in this model. A simplified expression for $P_A(t)$ derived on the assumption of eq 6 is

$$P_A(t) = \exp[(-0.00251C_d)\{a_0 + 2.26(\log \nu_0 Ft)^3/B^{1/2}\}] \quad (7)$$

where a_0 (in Å) is a correction relating to radii of donor and acceptor traps; C_d and B are in the units of M and eV, respectively. Equation 7 is a version of Miller's equation[8,9] into positive-charge scavenging. Miller's equation fits the data of trapped-electron scavenging by some efficient scavengers, provided that reasonable values are assigned to the parameters $\nu_0 = 10^{15}$ s^{-1}, $F = 1$, $a_0 = 4$ Å, and $B = 1$-2 eV.

A survival curve calculated in terms of eq 7 for the same $\nu_0 F$ and a_0 values as the above fits the data of positive-charge scavenging by, namely, electron transfer from triethylamine, if B is set at 2.2 eV, as shown in Figure 5. This value of B, however, is not considered to be reasonable in this case, as mentioned below. In the square-barrier model, the barrier height B is regarded as equal to the ionization potential of an electron donor molecule in a glass, I_s, which is estimated by using a relation[24]

$$I_s = I_g + U_0 + P_+ \qquad (8)$$

where I_g is the gas-phase ionization potential of the molecule, U_0 is the ground-state energy of an excess electron in the glass, and P_+ is the polarization energy of the glass due to a cation. Experimental values of $I_g - I_s$ for TMPD (tetramethyl-p-phenylenediamine) range from 0.86 in alkane glasses to 1.86 in a methanol glass.[25] Although no experimental values have been reported for $I_g - I_s$ of TMPD in a s-BuCl glass, the above data enable us to estimate it roughly at 1.0-1.5 eV. The $I_g - I_s$ is also a function of P_+ whose negative value is inversely proportional to the radius of a charge center.[25] The radius is considered to be smaller in aliphatic amines where the positive charge is localized on a nitrogen atom and larger in aromatic compounds such as biphenyl and TMPD where the charge is delocalized. The relatively low values of I_s for propylamine and sec-butylamine, which have been mentioned in relation to the results in Figure 7, can be ascribed to the small charge-center radius of these amines. If the I_s of these amines are the same as that of biphenyl, as the experimental results suggest, then the value for P_+ of these amines must be ca. 0.4 eV smaller than that of biphenyl. Taking this difference in P_+ into account, one can estimate the $I_g - I_s$ of aliphatic amines in s-BuCl at 1.4-1.9 eV, which lead to values of 5.6-6.1 eV for the I_s of triethylamine. The last values are obviously much larger than the above value of B used for the simulation based on eq 7.

The curve calculated in terms of eq 7 for $B = 6.5$ eV lies far above the experimental curves, as shown in Figure 5.
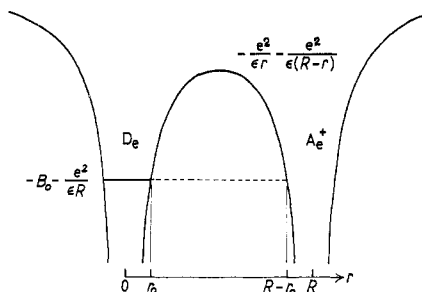

Figure 8. An energy barrier diagram for electron tunneling from D_e to A_e^+.

For this curve to fit the data for triethylamine, F must be ca. 10^5 or a_0 must be more than 10 Å, both of which are unreasonable. In our previous work on positive-charge scavenging by aromatic hydrocarbons, a value of 10^5 for F was required when eq 7 was fitted to the data on the assumption that $B = 4.0$ eV. Miller and Beitz[7] have recently reported a value of 1.8 eV for B for pyrene in the fitting of eq 7 to their data of positive-charge scavenging. Thus, $\nu(R)$ is underestimated if the square-barrier model is applied to analysis of the data of positive-charge scavenging.

A model which appears to be pertinent to this case is illustrated in Figure 8, where a potential barrier is represented as the sum of Coulomb fields due to both cationic electron acceptor A_e^+ and cation of an electron donor molecule D_e. Note that the electron donor, which is initially neutral, behaves as a cation when an electron goes far from the nucleus. Using the WKB approximation,[11,26] $\nu(R)$ is written as

$$\nu(R) = \nu_0 \exp\left[-\frac{2(2m)^{1/2}}{\hbar} \times \int_{r_0}^{R-r_0} \left\{B_0 + \frac{e^2}{\epsilon R} - \frac{e^2}{\epsilon r} - \frac{e^2}{\epsilon(R-r)}\right\}^{1/2} dr\right] \quad (9)$$

where r_0 is the radius at which the term in the integrant square root equals zero, and accordingly a function of R; B_0 is the binding energy of a singly isolated donor trap; e is the electronic charge; ϵ is a dielectric constant of the medium. The integrals in eq 4 and 9 were numerically calculated for simulation. For eq 4 numerical integration was performed up to 200 Å. Incidentally, the values of R (in Å) for which the reaction probability becomes $1/2$ are calculated to be 14 at 1 μs, 18 at 1 ms, and 21 at 1 s for $\nu_0 F = 10^{15}$ s^{-1}, $\epsilon = 2$, and $B_0 = 6.2$ eV; the values calculated for $B_0 = 4.4$ eV are 4-5 Å larger than these.

The curves based on eq 4 and 9 are depicted in Figures 3 and 4. If ϵ is assumed to be 2.0, which is reasonable for the bulk dielectric constant of the glass, the calculated curves for $B_0 = 4.4$ eV and $\nu_0 F = 10^{15}$ s^{-1} agree with the data of hole scavenging by triethylamine, as shown in Figure 3. In the model under discussion, B_0 is regarded as I_s. The above value of B_0 is still smaller than the estimated values of I_s, 5.6-6.1 eV, but much closer to them than the value requested by the square-barrier model is. If ϵ is assumed to be 1.0, good simulation curves can be drawn, as also shown in Figure 3, for a value of 6.2 eV for B_0, which is consistent with the above estimated values for I_s. It is considered that the effective dielectric constant may be close to unity for small r and approach a bulk value as r increases; therefore, the simulations for $\epsilon = 1.0$ and 2.0 correspond to both extreme cases. The results of the simulations suggest that good agreement with the data can be attained for some of the above values of I_s by adequate

parameterization of ϵ, though such attempts were not made in the present calculation. Thus, it can be concluded that the method of estimation of $\nu(R)$ based on a tunneling model is valid for electron transfer from neutral molecules to cations, provided that an appropriate Coulomb field is taken into account.

Simulation was also made for hole scavenging by propylamine using the bulk value of ϵ, 2.0. If B_0 for triethylamine is 4.4 eV as mentioned above, the value for propylamine can be set 5.7 eV, since the difference in the ionization potentials of two compounds is identical in both gas phase and solid solutions according to eq 8. As shown in Figure 4, the curves calculated for $B_0 = 5.7$ eV fit the data if $\nu_0 F$ is 1×10^{14} s^{-1}, i.e., if F is smaller by one order of magnitude than that of triethylamine. It should be added that, if the above presumption on B_0 for propylamine is disregarded, then another set of the parameter values, e.g., $B_0 = 6.2$ eV and $\nu_0 F = 1 \times 10^{15}$ s^{-1}, can also give good simulation curves as shown in Figure 4.

In previous studies[27-31] the effect of Coulomb field has been discussed for trapped-electron scavenging by cationic scavengers and charge recombination, both of which are modeled as tunneling from a square-potential well of either trapped electrons or anions to a Coulombic sinkhole of cations. The equation of the rate constant for this model is analytically solvable.[28,31] The rate constants have been evaluated as a function of R or time,[27-30] but these cannot be compared immediately with experimental data without consideration of the spacial distribution of reactants. Theoretical calculation where the distribution was taken into account was successful in the explanation of the data of electrophotoluminescence resulting from charge recombination in the presence of external electric field, though comparison between the Coulombic and square-barrier models was not made.[31]

The present results provide poor materials for the discussion of the Franck–Condon factor. The theories predict that the Franck–Condon factor increases first with the free-energy difference $-\Delta G$ to a maximum, $-\Delta G_m$, and then decreases, and that $-\Delta G_m$ is governed by vibrational properties of a super molecule consisting of donor, acceptor, and solvent molecules.[13-15] The values of $-\Delta G$ for electron transfer to matrix holes from propylamine and triethylamine are estimated crudely at 1.8 and 3.1 eV, respectively. The increase in F by a factor of 10 was observed for this increase in $-\Delta G$. The decrease in F with increasing $-\Delta G$ was not observed for the donor–acceptor pairs used in the present experiments. The similarity in the survival curves of different electron acceptors, viz., bleachable and unbleachable holes and biphenyl cations, indicates that the F values for electron transfer to these acceptors are practically identical in spite of considerable difference in $-\Delta G$. A possible explanation for this is that the $-\Delta G$ values for the electron transfer to different acceptors happen to be nearly symmetric with respect to the $-\Delta G_m$ so as to lead to close values of F. Disagreement between observation and theory has been found for the dependence of the Franck–Condon factor on the acceptor energy level in trapped-electron scavenging,[32] and it has been suggested that this discrepancy is due to the con-

tribution of the electron transfer resulting in formation of excited states of the acceptor molecule. However, this type of reaction is unlikely in the present case, since the known excited states of the acceptor molecule, s-BuCl or biphenyl, lie at higher energies than the value of $-\Delta G$.

In conclusion, we should like to emphasize that data of the time evolution of electron transfer in glasses cannot be explained satisfactorily without explicit evaluation of the electronic perturbation matrix element, though stress is put on the Franck–Condon factor in current theories. In other words, those data will be good material to examine theories of electronic interactions at long distance. Recently, super-exchange mechanism has been suggested for long-range electron transfer,[13,33] but its formulation is not made yet.

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