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Pulse Radiolysis Study of Positive-Charge Transfer in Freon-Mixture Matrix at 77 K

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The pulse radiolysis of a Freon mixture (FM), an equivolume mixture of $CFCl_3$ and CF_2BrCF_2Br, at 77 K gave transient absorption bands with peaks at 360, 490, and 530 nm, whose decay was enhanced by cation scavengers: propylamine, triethylamine, *N,N'*-diethylaniline, and biphenyl. The degree of the enhancement was independent of the difference in the ionization potential between the matrix and the solute molecules. In the FM matrix, positive-charge transfer from biphenyl cations to some other solute molecules showed energy dependence similar to that observed in the *s*-butyl chloride matrix. The rate of inter-solute positive-charge transfer was faster in the FM matrix than in the *s*-butyl chloride matrix. These results were discussed in relation to current electron transfer theories.

An equivolume mixture of Freon 11 ($CFCl_3$) and Freon 114B2 (CF_2BrCF_2Br), which will be referred to as the Freon mixture or FM, provides an optically transparent glass at 77 K, which is used as an excellent matrix for preparation of radical cations by irradiation with ionizing rays.[1)] The optical absorption spectra of (radical) cations of aromatic hydrocarbons and other compounds have been measured in the γ-irradiated FM matrix.[2—4)] The formation of cations probably results from positive-charge (PC) transfer from trapped holes in the FM matrix produced by irradiation, as in the *s*-butyl chloride (*s*-BuCl) matrix;[5—8)] however, no kinetic studies have been carried out concerning PC transfer in the FM matrix.

From the theoretical point of view, the vibrational mode of both matrix and solute molecules can affect the rate of electron or hole transfer.[9)] The FM matrix which consists of carbon–halogen bonds differs in the vibrational mode from the *s*-BuCl matrix dominated by the carbon–hydrogen bond. Thus, the PC-transfer rate in FM may differ from that in *s*-BuCl, and comparative measurement of the same donor-acceptor pair in FM and in *s*-BuCl seemed to be the best feasible experiment to examine the effect of matrix vibrations.

This paper deals with a pulse radiolysis study on PC transfer in FM matrices at 77 K. Two types of PC transfer, matrix-to-solute and solute-to-solute, were studied. This study also revealed the presence of two or three types of holes or radiation-induced cationic entities in the FM matrix, although their nature is not yet elucidated. The compounds used as solutes and their ionization potentials in the gas phase are: biphenyl, 8.27 eV; pyrene, 7.55 eV; propylamine (PrA), 8.78 eV; triethylamine (TEA), 7.50 eV; *N,N*-dimethylaniline (DMA), 7.10 eV.

Experimental

A pulse radiolysis apparatus at Nuclear Engineering Research Laboratory, University of Tokyo, was used.[10)] A 10-ns pulse of 35-MeV/1-A electron beam focused to a diameter of 2 mm was irradiated to a sample placed in a Dewer vessel filled with liquid nitrogen. The monitoring light passes through the sample to the opposite direction to the electron beam on the identical axis and is detected with a Hamamatsu-TV R-928 photomultiplier after monochromatized with a Ritsu MC-10 monochromator. The photoelectric signal was fed to a Riken-Denshi TCH-4000 transient digitizer whose time base was operated by a logarithmic time clock.[5)] The shortest accessible time of this detection system was 1 μs, but measurememt was also made in the nanosecond region by the use of conventional detection devices.[10)] The dosimetry was carried out by using hydrated electrons in water at room temperature on the basis of a value of 3.5 for *G*-value (molecules/100 eV) at 10 ns and 1.3×10^4 $M^{-1}cm^{-1}$ (1 M=1 mol dm^{-3}) for the molar absorption coefficient (ε) at 600 nm.[11)]

Daifron S1 and 114B2 ($CFCl_3$ and CF_2BrCF_2Br, respectively) purchased from Daikin Ind. Co. were dried on Drierite. Other chemicals (Tokyo Kasei) were used as received. Samples were deaerated by the freezing-pumping method in early experiments but were aerated later, since aeration was found to cause no practical effects.

Results

Transient absorption spectra in the FM glass containing no solutes are exhibited in Fig. 1 and some decay curves are shown in Fig. 2. Although the shortest time indicated in Figs. 1 and 2 is 3 μs, no other transient bands were found before this time in the nanosecond measurement. As shown in Fig. 2, the transient absorptions at peaks of 360 and 490 nm decay with the logarithm of time but the absorption at 600 nm scarcely decays initially. This apparent constancy in the 600-nm absorption is probably ascribed to cancellation of the decrease in the 600-nm absorbing species by the increase due to its production from a transient with the 360-nm and/or the 490-nm band. In the spectrum at 10 ms, the 360-nm band is still alive but the 490-nm band has already been replaced by a broad band with a peak near 530 nm which will be called tentatively the 530-nm band, although this band can really be a composition of the 490-nm band and another band which may be a long-lived one with a peak near 560

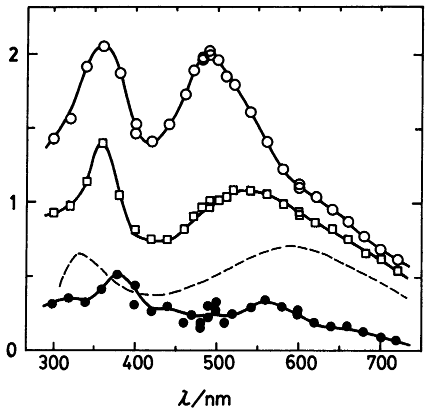

Fig. 1. Transient absorption spectra in an FM glass at 77 K at 3 μs ○, 10 ms □, and 3.7 s ● after the pulse. Thin dashed curve: the spectra taken after γ irradiation (Ref. 1).

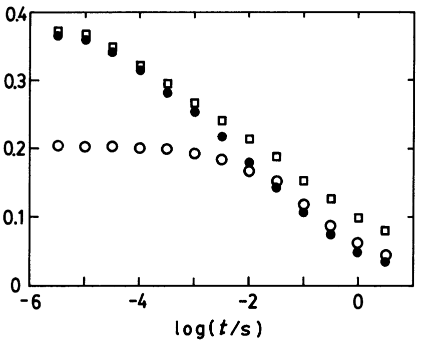

Fig. 2. The decay in the absorbances at 360 nm □, 490 nm ●, and 600 nm ○ in an FM glass plotted as a function of the logarithm of time.

nm.

The spectrum at 3.7 s differs from the one observed in steady-state measurement as shown in Fig. 1. Discrepancy between pulse and steady-state experiments also occurs in the absorption intensity: The Gε at the 560-nm peak at the 3.7-s spectrum of the pulse radiolysis is $3.3\times10^3\ \mathrm{M^{-1}cm^{-1}}$, which is smaller than the values for a 585-nm peak in the γ-irradiated FM glass: $4.5\times10^3\mathrm{M^{-1}cm^{-1}}$ in measurement by Grimison and Simpson[1] and $7.1\times10^3\ \mathrm{M^{-1}cm^{-1}}$ in our re-measurement.[12] In the rather soft FM matrix, the rise in local temperature caused by the strongly focused electron beam in the pulse radiolysis may enhance charge recombination which removes these matrix transients. In fact, the fast decay of the matrix transients in FM glass as shown in Fig. 2 contrasts with the very slow decay of trapped electrons in the alkaline-ice[13] and the 2-methyltetrahydrofuran[14] matrices as well as of trapped holes in the *s*-BuCl matrix.[5–8] However, it should be remarked that the decay of the biphenyl cation in the FM matrix is as slow as its decay in the *s*-BuCl matrix, as will be shown later.

As shown in Figs. 3 and 4, the decay of these matrix transients was enhanced by addition of a solute like triethylamine, propylamine, *N*,*N*-dimentylaniline, and biphenyl; the first three are typical cation scavengers that do not act on anionic species, and biphenyl scavenges both cationic and anionic species. Furthermore, the 490-nm absorption band of the DMA cation[4] and the 390- and 690-nm bands of the biphenyl

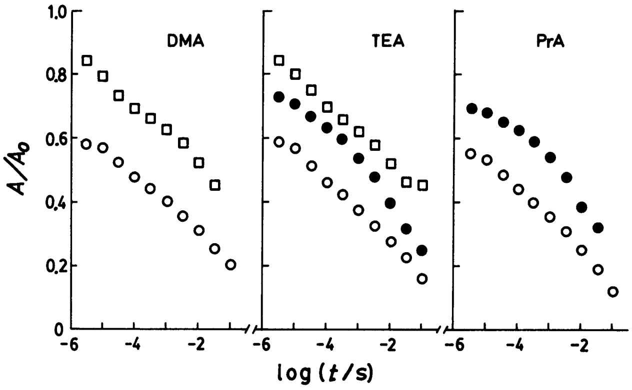

Fig. 3. Survival curves of trapped holes measured at 360 nm □, 490 nm ●, and 600 nm ○ in the presence of DMF, TEA, and PrA, each at 0.1 M.

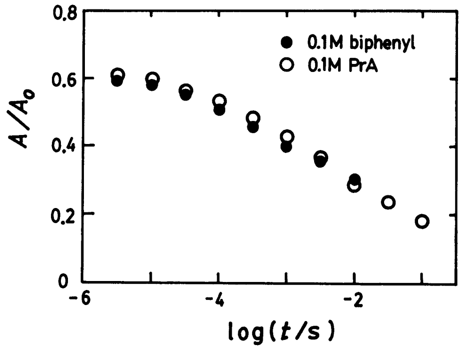

Fig. 4. Survival curves of the 490-nm hole band in the presence of biphenyl and PrA, each at 0.1 M.

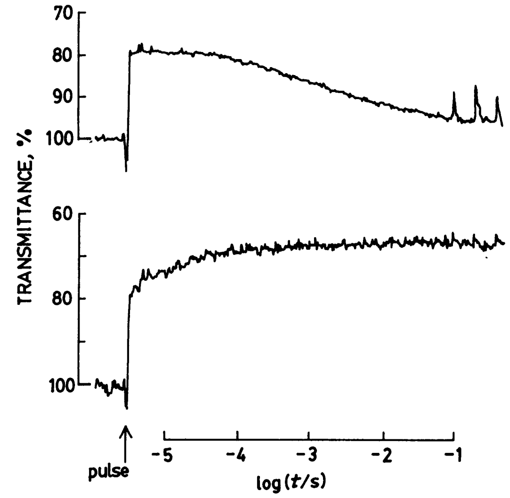

Fig. 5. The decay of the hole absorption at 490 nm and the corresponding growth of the biphenyl-cation absorption at 700 nm in an FM glass containing 0.03 M biphenyl.

cation were oserved in these experiments (see also Fig. 5); cations of TEA and PrA were not detected simply because of their weak absorptions.[4] Thus, these matrix transients which are probably composed of a few entities can be regarded as cationic species originating in the matrix, and will be referred to the (trapped) holes in this paper, although some of them may not really be the hole but cationic fragment radicals of a solvent component or certain ion pairs.

In steady-state γ radiolysis at 77 K, absorption maxima appear at 330 and 585 nm in the FM matrix, at 310 and 535 nm in the $CFCl_3$ matrix, and at 360 nm in the CF_2BrCF_2Br matrix;[1] the last two matrices are opaque. Comparison of the wavelengths of these maxima suggests that the 360-nm transient band observed in the pulse radiolysis may be assigned to a cationic species originating in CF_2BrCF_2Br and the 530-nm transient to a cationic species from $CFCl_3$. Decisive assignment of these bands seems difficult; such assignment has been unsuccesful for transient bands of carbon tetrachloride on which extensive studies have been made.[15]

In Figs. 3 and 4, survival ratios, A/A_0, where A and A_0 denote the absorbances in the presence and in the absence of a solute, respectively, are plotted against the logarithm of time; the decay that proceeds with the logarithm of time is common to reactions in rigid matrices.[5–7] This type of plot is usually used for presentation of the kinetic data in rigid matrices, and is called a survival curve. No corrections in the absorbance were made for possible overlap of the bands, since the spectrum of each component could not be isolated. The absorbance for the broad 530-nm band was measured at 600 nm in order to avoid the influence of the tail of the 490-nm band. Cations of biphenyl and DMA possess intense absorption bands in the visible region as mentioned above; therefore, the change in the net hole absorption at such wavelengths could not be measured in systems containing these solutes. A survival curve for a single species is given by[16]

$$A/A_0 = \exp\left[-C\int_0^\infty \{1-\exp(-kt)\}4\pi R^2 \mathrm{d}R\right] \qquad (1)$$

where C is the solute (PC acceptor) concentration and k is the first-oder rate constant of PC transfer which depends on the donor-acceptor distance, R. Thus, if two survival curves measured for the same concentration of different solutes agree with each other, the rate constants of the PC transfer to these solutes are identical. Note that the parallel survival curves do not indicate the same rate constant.

In Fig. 3 the survival curves of the holes measured at different bands do not agree. This disagreement means that these bands should be assigned to different species, i.e., there are three kinds of holes or cationic species. The disagreement of these survival curves, however, may be due to an experimental reason that the absorbance could not be corrected for the overlap of other bands. The survival curves of the hole measured at the same wavelength agree with one another among glassy solutions containing different solutes, as shown in Fig. 3. This coincidence can be interpreted as that the rate is independent of the energy gap which is measured as the difference in the ionization potential between the matrix and the solute molecules. This independence contrasts with the previous result that the survival curve of trapped holes in the s-BuCl matrix shifts downward as the ionization potential of the solute compound decreases.[5]

A time profile of the absorption signal for the biphenyl-cation band at 700 nm is depicted in Fig. 5 in comparison with that of the 4901nm band of the hole. Monitoring of the holes at 360 and 600 nm was unable because of masking by the strong biphenyl-cation bands. The absorption at 700 nm already formed at the initial time can be attributed to the tail of the 530-nm band and also to a band of biphenyl cations produced within 1 μs. The growth of the biphenyl-cation band in parallel with the decay of the trapped hole absorbing at 490 nm suggests that the biphenyl cation is formed by PC transfer from this hole, although other holes may also contribute to the formation of biphenyl cations. The rather slow decay of biphenyl cations contrasts with the rapid decay of the holes in the neat FM glass. This contrast in decay suggests that the FM matrix is softer than the s-BuCl matrix so that small trapped holes can move to attain certain rearrangement but larger biphenyl cations cannot.

Positive-charge transfers from biphenyl cations to TEA, DMA, and pyrene molecules were also studied in FM matrices containing both 0.14 M biphenyl and 0.03 M of each of the acceptor solutes, where the positive charge is first trapped by excess biphenyl and then trasferred from biphenyl cations to acceptor molecules. The survival curves of these donor-acceptor pairs in FM are shown in Fig. 6. The curve shifts downward, i.e. the rate increases, with decreasing ionization potential of a PC acceptor. The similar dependence has also been observed in s-BuCl[5,6] and poly(methyl methacrylate) matrices[17] at 77 K. Thus such a dependence is normal, although it contrasts with the energy-gap-independent rate observed in PC transfer from the solvent holes. In Fig. 6 the curves in s-BuCl[5b] are also depicted for comparison. In each donor-acceptor pair, the curve for the FM matrix lies lower than that for the s-BuCl matrix. It should be noted, however, that this comparison is made under the conditions of different biphenyl concentrations: 0.2 M for s-BuCl and 0.14 M for FM, the latter being limited by solubility. As the biphenyl concentration decreases, the biphenyl cation yield may decrease owing to the competition with the acceptor which can also scavenge the hole. A decrease in the biphenyl cation yield was estimated at 5% for a biphenyl-pyrene system on the basis of previous results of steady-state experiments.[18] The magnitude of the observed shift is more than 15%; thus there seems to

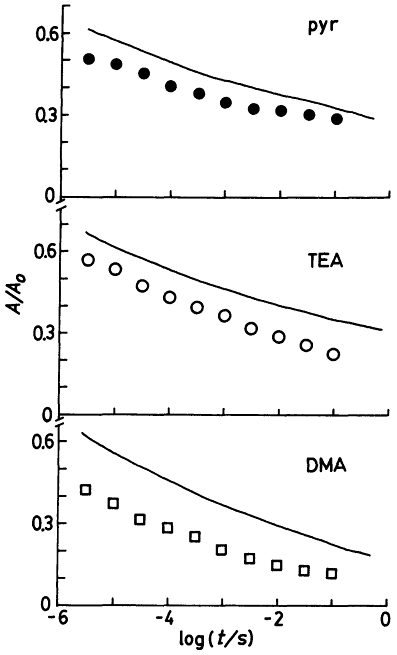

Fig. 6. Survival curves of biphenyl cations in the presence of PC acceptors at 0.03 M: pyrene, TEA, and DMA in FM (points) and in *s*-BuCl (lines) (Ref. 3).

be the shift of the survival curve with the change of matrix from *s*-BuCl to FM.

Discussion

Electron and hole transfers are explained on the basis of the Fermi golden rule, and the first-order rate constant is expressed as the product of a term associated with electronic interactions, ν, and the thermally-avaraged Franck-Condon factor, F:[5,6,9]

$$k = \nu F \tag{2}$$

Early theories[19] predict that the (thermally-averaged) Franck-Condon factor first increases with the energy gap and then decreases. The regions where the Franck-Condon factor increases and decreases are called the normal and the inverted region, respectively. On the other hand, some experimental results[20] indicate that the rate reaches a plateau above a certain value of the energy gap in contrast to the theories. A new theoretical explanation has recently been presented for this plateau.[21]

Equation 2 indicates that the Franck-Condon factor can be estimated from the rate constant if the value of the electronic interaction term is known. However, its reliable evaluation is very difficult both experimentally and theoretically. In most data analyses, the electronic interaction has been regarded implicitly as being identical regardless of donors and acceptors. A modified assumption that it is identical for the same donor has also been adopted in analysis of long-range electron transfer.[5–7] In this paper, we assume that for donor-acceptor pairs containing a common PC donor electronic interactions are identical. i.e. the relative Franck-Condon factor is proportional to the observed rate.

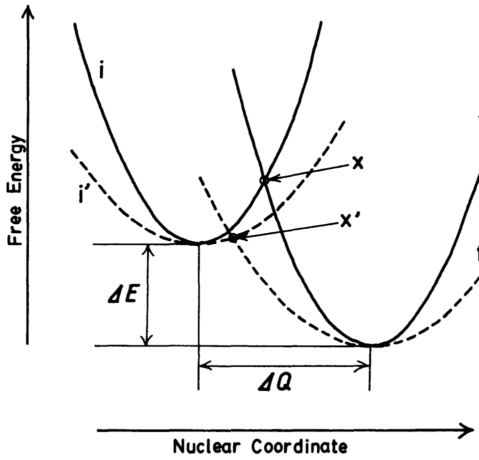

Fig. 7. Possible energy-surface diagrms of a donor-acceptor system in *s*-BuCl (solid curves) matrix and in FM matrix (dashed curves); *i* and *i*′ indicate the initial states and *f* and *f*′, the final states.

A feature of PC transfer from the hole in the FM matrix is the lack of the energy dependence over a rather wide ΔE-range of 1.28 eV. The energy independent rate is known to occur actually if the energy gap of a systems is very large.[20] In other words, if a hole has such a high energy that the ΔE against a solute molecule becomes large enough, the rate will be almost constant irrespective of solute. In *s*-BuCl the rate of PC transfer from the hole to the same solute as that used in the present experiments increases with increasing energy gap. This fact indicates that the energy gap of the hole-acceptor pair in *s*-BuCl is as low as to correspond to the normal region. The ionization potential of FM is probably higher than that of *s*-BuCl (10.65 eV), since the ionization potentials of CF_2BrCF_2Br and $CFCl_3$ are 11.4[22] and 11.7 eV,[23] respectively. Thus, for PC transfer from a trapped hole, the energy difference of a system with the same solute will be larger in the FM matrix than in the *s*-BuCl matrix.

The results of the studies on carbon tetrachloride[15] suggest that the matrix transients in the FM glass may not be assigned to cations of solvent molecules but to other complicated species such as ion pairs similar to $CCl_3^+Cl^-$ proposed for carbon tetrachloride. If ion pairs are involved, the energetics of the system will be complicated, and the above simple consideration may not immediately apply.

The normal energy-gap dependence was observed for the positive-charge transfer from the biphenyl cation where energy gaps are not so large. The point of interest with this reaction is acceleration caused by change of a matrix from *s*-BuCl to FM. Freons and their mixtures are characterized by poorer solvation abilities than *s*-BuCl. Major molecular vibrations in Freon are carbon–halogen vibrations whose frequency is lower than carbon–hydrogen vibrations dominating *s*-BuCl. These comparisons indicate that an energy surface for a donor-acceptor pair in the FM matrix is represented by a weaker function (or broader curve) than that for the same pair in the *s*-BuCl matrix. The energy diagram as illustrated in Fig. 7 can explain the faster rate in FM matrix in the normal energy-gap dependence region on the assumption that both energy gap (ΔE) and shift in nuclear coordinate (ΔQ) are unchanged. This diagram indicate that broadning of the energy surface lowers the crossing point from x to x' and reduces the activation energy to accelerate the reaction.

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