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# Positive-charge transfer in irradiated sec-butyl chloride glassy solutions at 77 K as studied by the pulse radiolysis method

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bands of Y and/or Z are eligible for the charge resonance bands of trimer cations.

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## Positive-Charge Transfer in Irradiated *sec*-Butyl Chloride Glassy Solutions at 77 K as Studied by the Pulse Radiolysis Method

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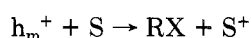
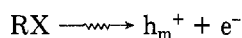
The Institute of Physical and Chemical Research, Wako-Shi, Saitama 351, Japan (Received February 12, 1979)

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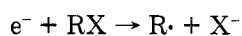
The time evolution of optical absorptions of cationic species in *sec*-butyl chloride glasses at 77 K was observed over the range of  $10^{-5}$  to 1 s after irradiation with electron pulses. A band tail newly found at wavelengths shorter than 420 nm in a pure glass is assignable to a precursor of the trapped hole characterized by the 480-nm band. In the presence of an aromatic solute, trapped holes decay over the above time range and solute cations grow concurrently. In biphenyl-pyrene solutions, the decay of biphenyl cations is accompanied by the growth of pyrene cations. The observed positive-charge transfer is consistent with long-range electron transfer.

## Introduction

Radical cations of aromatic solutes are produced by the radiolysis of butyl chloride (BuCl) glasses.<sup>1</sup> This cation formation has been explained in terms of mobile hole capture:



where RX and S denote solvent and solute molecules, respectively, and  $\text{h}_m^+$  is the mobile hole. Electrons ejected by irradiation are captured effectively by the solvent molecules by a dissociative electron capture process:



The nature of the mobile hole is little known. Hamill and co-workers<sup>2,3</sup> suggested that both ground and excited states of solvent cations can be precursors of the solute cations. Shida and Hamill<sup>1c</sup> found absorption bands at 550 nm in *n*-BuCl and at 480 nm in *s*-BuCl, which are assignable to holes trapped in the matrices. They also revealed that these bands consist of photobleachable and photoresisting components, which were later assigned to BuCl cations and butene cations, respectively.<sup>4a</sup> These species will be inclusively referred to as the trapped hole henceforth. Arai and co-workers<sup>4</sup> observed that cationic species in BuCl glassy solutions at 90–100 K neither decrease nor increase during 100  $\mu\text{s}$  after a 1  $\mu\text{s}$  pulse, and concluded that no positive charge transfer occurs after the end of the pulse.

Steady-matrix measurements of  $\gamma$ -irradiated glasses have revealed (1) that the logarithm of the trapped hole

yield decreases linearly in the solute concentration,<sup>5a</sup> and (2) that in some binary solute systems the yield of one solute cation is almost independent of the concentration of the other solute.<sup>5</sup> The selective capture of two kinds of mobile holes has been proposed to explain the latter result.<sup>5</sup> As an alternative scheme, it was suggested that positive-charge transfer by quantum-mechanical tunneling from trapped holes to solute molecules followed by that from cations of one solute to molecules of the other solute.<sup>5b</sup>

There are many studies on electron scavenging in irradiated glasses of alkaline ices, alcohols, and ethers.<sup>6</sup> Similar peculiar concentration dependences were also observed for electron scavenging.<sup>7,8</sup> Using the pulse-radiolysis method, Miller observed that trapped electrons decay over a wide time range of  $10^{-6}$  to  $10^2$  s with a rate which increases with solute concentration<sup>9</sup> and that in a binary solute system the decay of donor anions is accompanied by the growth of acceptor anions.<sup>10</sup> These results indicate the occurrence of long-range electron transfer, for which models of tunneling,<sup>6,9,10</sup> non-Gaussian diffusion,<sup>11</sup> and multiphonon assisted transfer<sup>12</sup> have been proposed.

Thus, pulse-radiolysis experiments for hole scavenging must clarify which mechanism, mobile-hole capture or long-range electron transfer, applies to the positive-charge transfer. No measurement has ever been made for either trapped holes or solute cations over such a wide time range. The present paper describes the evolution of trapped holes and solute cations in *sec*-BuCl glasses at 77 K measured over the time range of  $10^{-5}$  to 1 s by means of pulse radiolysis.

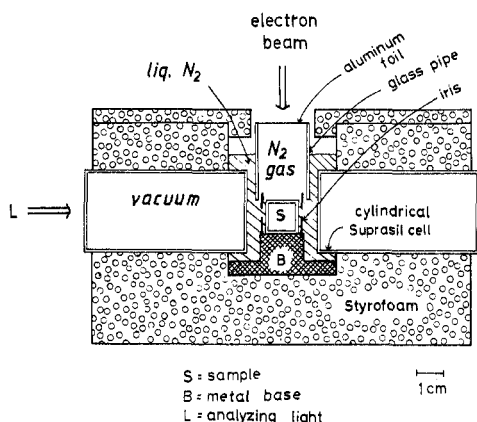


Figure 1. Sectional view of a sample housing for irradiation and absorption measurement at 77 K.

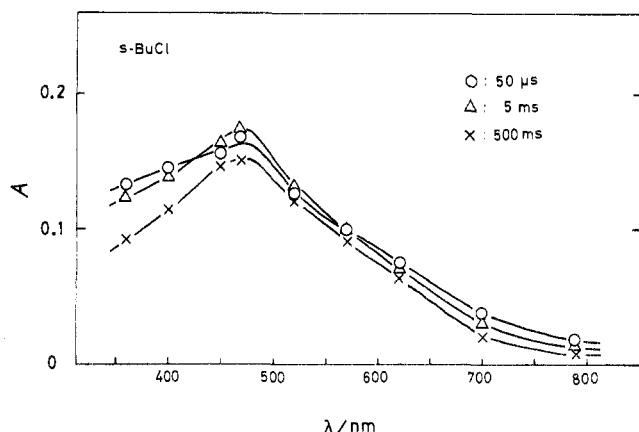


Figure 2. Transient absorption spectra of *sec*-butyl chloride at 77 K and 50  $\mu$ s, 5 ms, and 500 ms after irradiation by 5- $\mu$ s pulses.

### Experimental Section

Electron pulses were delivered by a Mitsubishi van de Graaff accelerator operated at 2.5 MV. Pulse widths were 2 and 5  $\mu$ s and the peak current was about 120 mA. A housing used for the low-temperature pulse radiolysis, illustrated in Figure 1, was designed so that nitrogen gas evaporating from liquid nitrogen lowers the level to remove the liquid from the path of the electron beam. An actual dose, however, may be smaller than a dose estimated from an incident beam intensity because of scattering and attenuation by the foil and gas layer. The change in the optical transmission for one shot was recorded simultaneously on both Iwasaki 5305B dual-beam (10  $\mu$ s/cm and 1 ms/cm) and Tektronix 7623A (100 ms/division) oscilloscopes. No special attention was paid to the photobleaching of samples by analyzing light, since the measurement period was as long as 1 s.

*sec*-Butyl chloride (Tokyo Kasei) was treated with sulfuric acid and fractionally distilled. Zone-refined reagents of biphenyl, naphthalene, and fluorene were purchased from Tokyo Kasei. Pyrene was refined by means of column chromatography. *trans*-Stilbene was recrystallized four times.

### Results and Discussion

The absorption spectrum in a pulse-irradiated pure *s*-BuCl glass changes with time as shown in Figure 2. The spectrum at 0.5 s after the pulse agrees with that of the trapped holes measured at several minutes after  $\gamma$  irradiation. The absorbance of the trapped holes near the 480-nm peak has not risen in full at the end of the pulse but grows over a long period, as also shown in Figure 3. Note that pulse intensities differ between the measure-

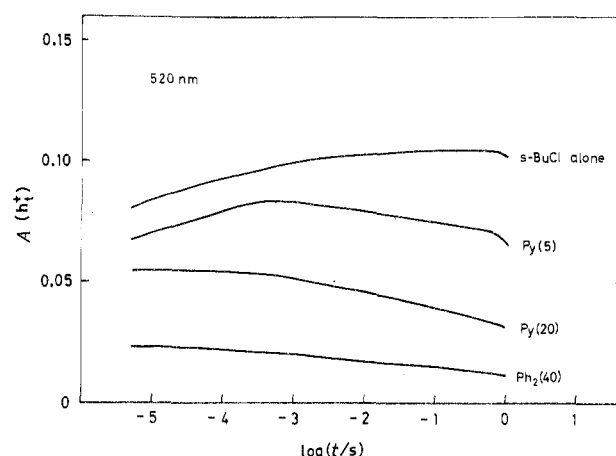


Figure 3. Changes in the absorbance ( $A$ ) at 520 nm with time for trapped holes in pure *sec*-butyl chloride glass and glassy solutions of pyrene (Py) and biphenyl ( $\text{Ph}_2$ ). Solute concentrations are shown in the parentheses in units of  $\text{mmol kg}^{-1}$ . Absorbances at each time have been corrected for the absorption of solute cations. The pulse duration was 2  $\mu$ s.

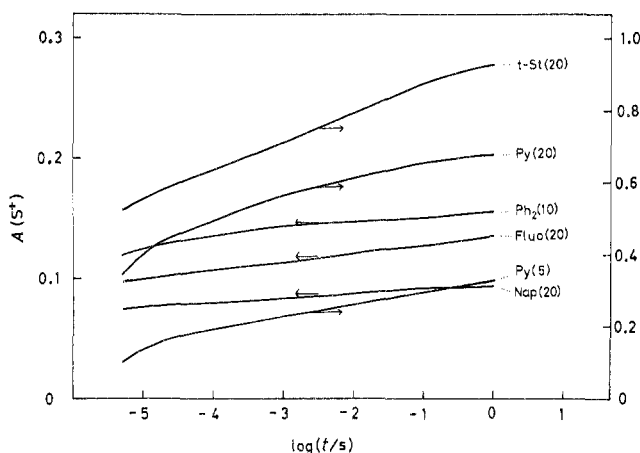
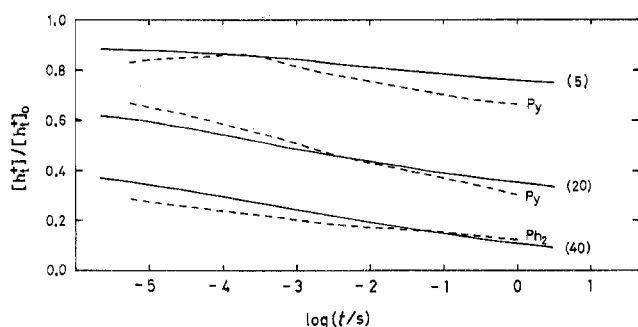


Figure 4. Growth of solute cations for various aromatic molecules. The absorbances were measured at 480 nm for *trans*-stilbene (*t*-St), 457 nm for pyrene, 700 nm for biphenyl, 660 nm for fluorene (*Fluo*), and 690 nm for naphthalene (*Nap*). The solute concentrations are shown in the parentheses in units of  $\text{mmol kg}^{-1}$ . The pulse duration was 2  $\mu$ s for pyrene and 5  $\mu$ s for other solutes.

ments for Figures 2 and 3. The time profile of the 520-nm absorption in the measurement for Figure 2, which is not illustrated, did not agree accurately with that shown in Figure 3. This discrepancy is due to the poor reproducibility in the time region later than  $10^{-2}$  s, which may result from hole scavenging by impurities in solvent and/or radiation-induced products. The absorbance at wavelengths shorter than 420 nm decreases at the initial stage as shown in Figure 2. This new band whose peak seems to be located in the UV region is most likely assigned to a precursor of the trapped holes.

Absorbances of the trapped holes at 520 nm are plotted in Figure 3 as a function of the logarithm of time. It is obvious from these plots that the aromatic solutes enhance the decay of the trapped holes. The concurrent growth in the absorbance of pyrene cations is illustrated in Figure 4, which also includes the growth curves for other aromatic cations measured at wavelengths near their absorption peaks.<sup>1,13,14</sup> The absorbances in Figures 3 and 4 were those corrected for the absorptions of other species on the basis of their absorption spectra which were obtained in steady-matrix measurements. The results shown in Figures 3 and 4 indicate that positive charges are moving from the trapped holes to solute molecules over a fairly



**Figure 5.** Decay of the survival probability of trapped holes: (solid curves) based on eq 1 and 2 with the parameter values shown in the text; (broken curves)  $A(h_t^+)$  for glassy solutions divided by that for pure *sec*-butyl chloride glass, calculated from the curves in Figure 3.

long period after the pulse. The slopes of the growth curves of solute cations shown in Figure 4 seemingly vary from solute to solute; however, the trapped-hole decay curves for the same solutions shown in Figure 3 do not vary considerably. This seeming discrepancy between the growth curve and decay curve may result from either incomplete correction of the absorbance of the trapped holes or the intricacy of real processes as will be mentioned later.

The observed time evolution resembles that measured by Miller for trapped electrons and solute anions,<sup>9</sup> which he explained in terms of a tunneling mechanism, formulating a simple model. A similar formulation is feasible if the positive-charge transfer is modeled as follows. An electron in a solute molecule can reach a distance  $a(t)$ , which increases with time, by quantum-mechanical tunneling. Provided that a trapped hole is located in a sphere of a radius  $a(t)$ , the electron transfers to the hole, that is, a positive charge moves from the hole to the solute molecule. The same mathematical procedures as those for electron scavenging<sup>6,9</sup> lead to an equation for the probability of survival of trapped holes:

$$[h_t^+]/[h_t^+]_0 = \exp\{-0.00251a(t)^3[S]\} \quad (1)$$

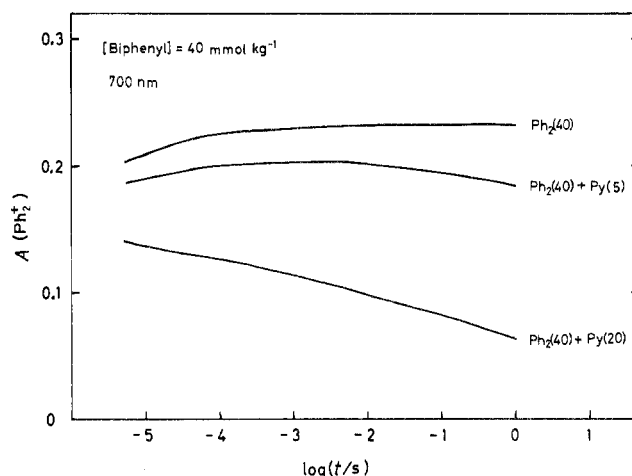
where

$$a(t) = a_0 + 2.26(\log \nu + \log F + \log t)B^{-1/2} \quad (2)$$

where  $[h_t^+]$  and  $[h_t^+]_0$  denote the amount of trapped holes in the presence and absence of a solute, respectively,  $[S]$  is a solute concentration in  $\text{mol dm}^{-3}$ ,  $a_0$  and  $B$  are an orbital radius and a binding energy of the tunneling electron in the solute molecule, respectively,  $\nu$  is a frequency factor for the solute molecule, and  $F$  is an efficiency factor for tunneling.

The binding energy  $B$  can be approximated by the ionization potential of solute molecules in glassy solutions, which is thought to be lower than that in the gas phase by a finite value.<sup>15</sup> The radius  $a_0$  can be estimated from the size of solute molecules. Equation 1 demands that the decay of trapped holes or the growth of solute cations should become faster as the ionization potential of solutes decreases. The data in Figure 4 seem to meet this demand. The solute compounds can be arranged in increasing order of the slope of the cation growth curve in Figure 4; biphenyl (8.27), naphthalene (8.12), fluorene (7.78), *trans*-stilbene (7.60), pyrene (7.55), where the values in parentheses indicate ionization potentials in electronvolts.

Figure 5 shows decay curves calculated by eq 1 for the values  $B = 4 \text{ eV}$ ,  $a_0 = 5 \text{ \AA}$ ,  $\nu = 10^{15} \text{ s}^{-1}$ , and  $F = 10^5$ . These parameter values were chosen so that the calculated curves fit the data presented in Figure 3, which are replotted in Figure 5 after conversion of the units to  $A(h_t^+)$  for a solution divided by that for the pure glass. The calculated



**Figure 6.** Changes in the absorbance at 700 nm with time for biphenyl cation ( $\text{Ph}_2^+$ ) in the presence and absence of pyrene. The solute concentrations are shown in the parentheses in units of  $\text{mmol kg}^{-1}$ . Absorbances have been corrected for pyrene cations at each time. The pulse duration was  $2 \mu\text{s}$ .

curves can reproduce the features of the observed decays, though the agreement is not quantitatively good. It should be noted that the observed change is not singly due to a simple positive-charge transfer from a single hole to a solute. The entity referred to as the trapped hole here actually consists of two components which may possess different reactivities to a solute. The probable direct positive-charge transfer from the precursor of the trapped hole to a solute may affect the decay and growth of both trapped hole and solute cation in complicated ways. If quantitative comparison of the data with any model is intended, corrections for these points will be essential. No solid material for such corrections can be obtained at present.

The concentration changes of biphenyl cations and pyrene cations were also measured in *s*-BuCl glasses containing both biphenyl and pyrene. Absorbances of biphenyl cations in the presence and absence of pyrene are plotted in Figure 6 as a function of the logarithm of time. The features of the curves in Figure 6 resemble those in Figure 3. In other words, biphenyl cations in biphenyl-pyrene solutions behave like the trapped holes in single-solute solutions. Growth curves of pyrene cations in the biphenyl-pyrene solutions, which are not illustrated, were found to be almost the same as those for solutions containing only pyrene at the same concentrations. It should be noted that the minor effect of biphenyl on the pyrene-cation formation, which seems strange superficially, is consistent with previous results of steady-matrix experiments.<sup>5</sup> The results mentioned in this section indicate that the positive-charge transfer between different kinds of solutes proceeds in the same manner as that from the trapped hole to solutes.

Observation of positive-charge transfer in biphenyl-pyrene solutions excludes the possibility that diffusion may be mainly responsible for this process. Both biphenyl cations and pyrene molecules are not considered to diffuse appreciably in *s*-BuCl glass at 77 K, since diffusion-induced dimer-cation formation<sup>14</sup> does not take place for biphenyl and pyrene in steady-matrix experiments with the same glass. Note that our present knowledge on the species referred to as the trapped hole is insufficient to state definitely that they do not diffuse at 77 K, though their immobility has been assumed so far.<sup>1c,4</sup>

All the present results are consistent with a scheme that positive-charge transfer occurs as a result of a long-range electron transfer, but inconsistent with a mobile-hole

capture mechanism and a selective capture scheme both proposed previously,<sup>5</sup> the latter should be replaced by the successive tunneling scheme.<sup>5a</sup> However, the results do not exclude thoroughly the possibility of the partial contribution of mobile holes in cation formation in glasses.

**Acknowledgment.** We thank Dr. M. Tachiya for suggestions concerning theoretical aspects.

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## Thermal Diffusion across Porous Partitions. The Process of Thermodialysis

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Coupling of mass flow to a flux of thermal energy is a well-known occurrence in various experimental situations. We have shown that in condensed matter these transport phenomena are produced by the radiation pressure developed by the flow of heat. We extend here this approach to nonisothermal transport through porous partitions characterized by a reflection coefficient nearly equal to zero. Analytical expressions, which allow qualitative and quantitative predictions for the mass flow occurring through the partition, can be derived from the theoretical approach. The phenomenon, which we call "thermodialysis", is theoretically and experimentally proved to be capable of producing matter flow proceeding "uphill", that is against gradients of hydrostatic pressure and/or of electrochemical potential. Also experimental evidence lending support to other fundamental predictions of the theory is presented.

## Introduction

The flow of heat through a liquid solution can cause a reduction of the entropy of the fluid mixture by inducing selective migration of its components. Such an ordering effect takes place in ionic, molecular, and macromolecular solutions of any degree of complexity. This phenomenon, called thermal diffusion or the Soret-Ludwig effect, from the names of its discoverers, has been known for nearly a century.<sup>1-4</sup>

When the flow of thermal energy takes place across dense membranes permeated by the solution, the associated transport of matter has been called thermoosmosis.<sup>5-27</sup> Nonequilibrium thermodynamics has provided a theoretical framework for the treatment of these processes. Such a general and powerful theoretical approach, however, has the shortcoming of being unable to yield a molecular description of the phenomena. The coupling between the heat flow and the associated fluxes of matter is expressed by means of coefficients whose dependence on the nature of the substances involved in the process is not specified. Experimental studies of thermoosmosis, on the other hand, have generally been concerned with semipermeable, selective membranes. Much less attention has been devoted to the case of porous partitions, having a Staverman reflection coefficient equal to zero, that is to partitions utterly unable to discriminate between solute and solvent. Perhaps this has been due to the feeling that the investigation would not be worth trying, owing to the lack of osmotic and/or ultrafiltration effects across such partitions.

Let us, however, try to consider the problem from an unconventional point of view. Imagine a porous partition sandwiched between two solutions maintained at different

temperatures. All components of the solutions can freely diffuse across the existing pores. The pore diameter, however, is supposed to be small enough to quench hydrodynamical convection and turbulent motions inside each channel. Under these conditions each liquid-filled pore constitutes a microscopic Soret cell in which thermal diffusion will take place at a very fast rate, when the thickness of the partition (i.e., the height of each equivalent Soret cell) is small. The "characteristic time" for the establishment of equilibrium is given by  $\theta = d^2/\pi^2 D$ , where  $d$  is the height of the thermodiffusive column (in our case the partition thickness) and  $D$  ( $\text{cm}^2\cdot\text{s}^{-1}$ ) is the ordinary coefficient of diffusion.

We have proposed a theory of thermal diffusion in liquids which attributes the redistribution of the components of a solution in a temperature gradient to radiation pressure generated by the flow of thermal excitations.<sup>28-30</sup> These excitations are supposed to consist of very high-frequency elastic waves (Debye waves). We have published much experimental evidence supporting the radiation-pressure approach.<sup>31-36</sup>

Without going into details concerning the genesis of thermal forces produced by a flux for thermal energy in condensed phases, which we have extensively treated elsewhere,<sup>28-30,37</sup> we shall recall here that, on the grounds of the radiation-pressure theory of thermal diffusion, the force acting upon a molecule of cross section  $\sigma_p$  contained in a nonisothermal liquid will be given by

$$F = -2\tau_{1,p}^2 \left[ \left( \frac{K}{v} \frac{dT}{dx} \right)_1 - \left( \frac{K}{v} \frac{dT}{dx} \right)_p \right] \sigma_p \quad (1)$$

where the  $K$ 's are the thermal conductivities and the  $v$ 's