BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2578—2586 (1968)

Formation and Decay of the Transient Species in Radiation Chemistry. Radiolysis of Alkyl Halide Systems

Hisashi UEDA

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, U.S.A., and Tokyo Kogyo Shikenjo, Mita, Meguro-ku, Tokyo

(Received April 15, 1968)

Biphenyl and *trans*-stilbene were irradiated by a pulse of 300 mA × 0.5 μsec in two types of solvents, alkyl halides and methyltetrahydrofuran. The spectra obtained by *n*-butylchloride, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane were concluded to be those of the cations, while the spectra obtained by CCl_4, 1,1,1-trichloroethane, and pentachloroethane were concluded to be due to something other than the cations. The spectra of *o*-terphenyl in 1,1,2-trichloroethane and in 2-methyltetrahydrofuran were different, the reason for this was discussed. The decay curves of the optical densities due to both the cations and the anions all exhibited first-order rates. The decay of the cation of the aromatic solute was concluded to consist of two processes, the transportation of the charged species and the neutralization of the ion pair thus formed. The rate-determining step is the neutralization process, the activation energies of which are 2.17 and 3.62 kcal/mol for *trans*-stilbene and biphenyl respectively. The transportation of the charged species was concluded to be not by the movements of the anion and the cation across the solution, but by the electron-trap- and hole-conductions, such as have been observed in semiconductors.

Shida and Hamill¹⁾ established the existence of the cations of aromatic compounds in the frozen-glass or polycrystalline matrices of alkyl halides. Unfortunately, however, the absorption spectra of the cation and the anion of an aromatic hydrocarbon are, in most cases, very similar to each other. It is, therefore, rather difficult to establish the exstence of either one of these ions with complete definiteness. In spite of such difficulties, however, it seems fairly reasonable to accept the conclusions of Shida and Hamill. It is for this reason that the present work was planned with the hope of establishing the formation and the decay of the radiation-chemical transient species in a solution of an aromatic hydrocarbon in an alkyl halide solvent in the liquid phase.

The present author²⁾ has studied the effects of additives on the radiolysis of 1,2-dichloroethane. In that study it was shown that those additives with larger reaction-rate constants with hydrated electrons than that of 1,2-dichloroethane decreased the *G*-values of ethylene and HCl, while those additives with smaller rate constants increased the *G*-values of ethylene and HCl, except in the cases of such additives as NH_3. It was also found that there is a parallel relation between the decrease in the *G*-value of ethylene and the increase in the rate constant with hydrated electrons. These facts suggested the existence of both positively- and negatively-charged species as the precursors of the radiolysis products, and also revealed the very quick and efficient charge transfer from the originally-formed solvent cation to the solute molecule.

Arai and Dorfman³⁾ studied the decay rate and the kinetics of an anion of aromatic hydrocarbon formed in isopropyl alcohol and found that the decay rate curve obeys a first-order reaction rate. This does not agree with a collision-initiated charge neutralization model, which predicts a second-order reaction. They interpreted this phenomenon as possibily resulting from an unknown impurity which still existed in the solution despite the greatest possible efforts at purification. The present author, therefore, also desired to see if such impurity effects are found with alkyl halide solvents.

The rigid-glass method is undoubtedly one of the best ways to take the spectrum of a radiation-chemical transient species, provided that the nature of the species formed is well known. Though in some instances a "fast detection" is equivalent to a "detection after freezing," there are several advantages to the pulse radiolysis method compared to the rigid matrix method. 1) It is possible to ascertain the kinetics of the formation and the decay of the transient species. 2) The successive transformations of the transient species, if any,

---

1) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375 (1966).
2) H. Ueda, *J. Phys. Chem.*, **71**, 3084 (1967).
3) S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964).

can be traced. 3) More varied types of compounds can be employed as solvents (matrix). 4) The effects of added impurities, which crystallize out if the solution is solidified by cooling, can easily be observed. Because of these considerations, it is important to study again, this time by pulse radiolysis techniques, the kind of system which has already been investigated by the rigid matrix method.

Experimental

The details of the experimental procedures of pulse radiolysis have appeared in many places[4,5] and so will not be particularly described here. Two or three different types of solvents were used after they had been purified. The alkyl halides were shaken with concentrated sulfuric acid and then distilled three times in a vacuum. The ethers, 2,2-dimethoxypropane, 2,5-dimethoxytetrahydrofuran, and 2-methyltetrahydrofuran (abbreviated as MTHF) were treated with sodium, distilled in a vacuum, distilled over a sodium mirror, and then distilled into the cell under a vacuum. The solute hydrocarbons, special reagent grade, were recrystallized twice from alcohol. The polaroid pictures (105 mm × 82 mm for 100 mm × 60 mm graticule) were enlarged to twice their original dimensions and used for the reaction-rate and absorption-rate analyses.

Results

In Figs. 1—7, Table 1 and Table 2 the results obtained with *trans*-stilbene as the solute are shown. In Fig. 1, the intensity of light absorption by the transient species is plotted as a function of the solute concentration. It may be seen in the figure that the intensity of light absorption is saturated if the solute concentration exceeds 10^{-2} mol/*l*. The effects of the solvents on the intensity of absorption

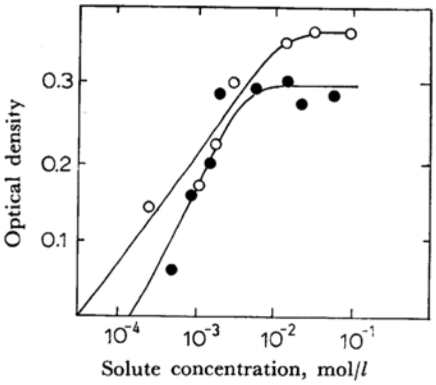

Fig. 1. The dependence of the optical densities of the solute cations on the concentration of *trans*-stilbene in *n*-butylchloride (●) and in 1,1-dichloroethane (○).

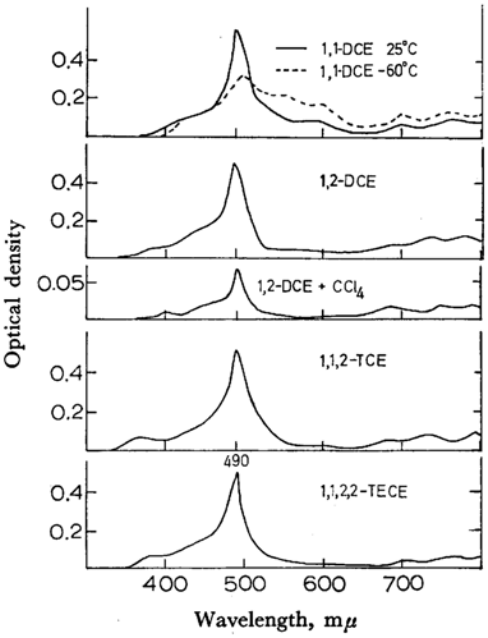

Fig. 2.

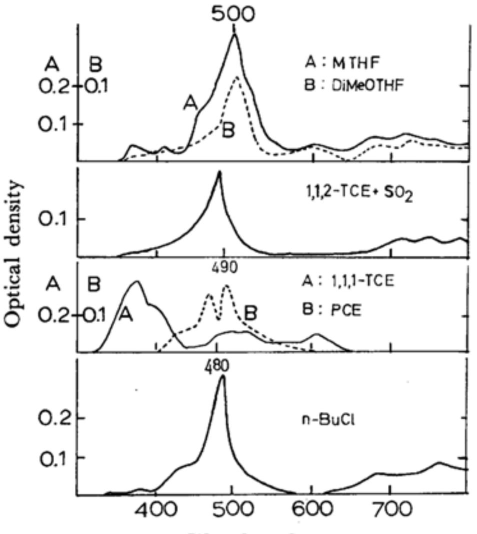

Fig. 3.

Fig. 2 and Fig. 3. The absorption spectra of the transient species of *trans*-stilbene in various solvents. About the abbreviations of the names of the solvents, see text. In the spectrum, third from top of Fig. 2, the ratio of 1,2-DCE and CCl_4 is 15 m*l*: 5 m*l*. In Fig. 3, top spectrum, DiMeOTHF signifies 2,5-dimethoxytetrahydrofuran. A similar, but far weaker, absorption spectrum was observed with 2,2-dimethoxy propane as solvent.

---

[4] M. Ebert, J. P. Keene, A. J. Swallow and J. H. Baxendale, Ed.; "Proceedings of the International Symposium on Pulse Radiolysis at Manchester April 1965," Academic Press, New York (1965).

[5] L. M. Dorfman and M. S. Macheson, "Pulse Radiolysis," American Chemical Society, Washington, D. C., to be published.

TABLE 1. TRANSIENT SPECIES OF *trans*-STILBENE IN VARIOUS SOLVENTS

Solvent	Additive	Observed wavelength	Optical density[a]	O.D./E.D.[b]	k_1[c]
n-Butylchloride	none	490 mμ	0.236	8.0×10^{-25}	2.03×10^{5} [d]
1,1-Dichloroethane	none	490 mμ	0.673	18.8	2.24
1,2-Dichloroethane	none	490 mμ	0.567	14.9	1.57
1,1,2-Trichloroethane	none	490 mμ	0.701	16.3	1.61
1,1,2,2-Tetrachloroethane	none	490 mμ	0.750	17.1	1.38
1,1,2,2-Tetrachloroethane	Hydroquinone 4.51×10^{-3} mol/*l*	490 mμ	0.160	3.64	1.42
1,1,2-Trichloroethane	β-Naphthol 1.53×10^{-3} mol/*l*	490 mμ	0.630	14.7	1.63
1,1,2-Trichloroethane	SO_2[e]	490 mμ	0.220	5.11	1.49
1,1,2-Trichloroethane	N_2O[f]	490 mμ	0.376	8.75	0.79
1,1,2-Trichloroethane	CCl_3CCl_3 1.91×10^{-1} mol/*l*	490 mμ	0.493	11.5	0.67
1,1,2-Trichloroethane	NH_3[g]	490 mμ	0.000	0	—
1,1,2,2-Tetrachloroethane	MTHF, 8 mol%	490 mμ	0.066	1.54	
2-Methyltetrahydrofuran	none	500 mμ	0.390		1.83
2,5-Dimethoxytetrahydrofuran	none	500 mμ	0.130		1.85

a) At 0.5 μsec after pulse (300 mA $\times$ 500 *n*sec).
b) Optical density/Electron density.
c) First-order decay rate constant.
d) sec^{-1}.
e) 2.00 mmol in 70 m*l* cell and 17.2 m*l* solution.
f) 3.85 mmol in 70 m*l* cell and 17.2 m*l* solution.
g) 3.54 mmol in 70 m*l* cell and 17.2 m*l* solution.

TABLE 2. EFFECT OF MIXED SOLVENTS ON THE FORMATION OF THE TRANSIENT SPECIES OF *trans*-STILBENE

Mol% of *n*-butylchloride	0	22	45	70	100
Mol% of 1,1-dichloroethane	100	78	55	30	0
Optical densities at 0.5 μsec after pulse and at 490 mμ	0.351	0.339	0.328	0.316	0.251

TABLE 3. TRANSIENT SPECIES OF BIPHENYL IN VARIOUS SOLVENTS

Solvent	Additive	Observed wavelength	Optical density[a]	O.D./E.D.[b]	k_1[c]
n-Butylchloride	none	690 mμ	0.051	1.67×10^{-25}	1.57×10^{5} [d]
1,1-Dichloroethane	none	690 mμ	0.070	1.92	2.40
1,2-Dichloroethane	none	690 mμ	0.152	4.00	1.72
1,1,2-Trichloroethane	none	690 mμ	0.140	3.20	1.81
1,1,2-Trichloroethane	NH_3[e]	690 mμ	0.000	0.00	
1,1,2-Trichloroethane	N_2O[f]	690 mμ	0.157	3.6	1.78
1,1,2,2-Tetrachloroethane	none	690 mμ	0.178	4.05	1.58
Carbon tetrachloride	none	680 mμ	0.027	0.6	
1,1,1-Trichloroethane	none	685 mμ	0.015	0.4	
Pentachloroethane	none	650 mμ	0.017	0.3	
Methyltetrahydrofuran	none	625 mμ	0.080		

a) At 0.5 μsec after pulse.
b) Optical density/electron density.
c) First order decay rate constant.
d) sec^{-1}.
e) 3.43 mmol in 70 m*l* cell and 19.9 m*l* solution.
f) 3.66 mmol in 70 m*l* cell and 17.8 m*l* solution.

by the transient species were studied using solutions containing the solute at higher concentrations than this saturating concentration. The results are shown in Table 1. A similar procedure was taken when determining the values in Table 3.

Figures 2 and 3 show the absorption spectra of the transient species of *trans*-stilbene in various solvents. The spectra shown are not the entire absorption corresponding to all the species existing in the system at the time of measurements, but are the differences between the two spectra at 1 and 9 μsec after pulse: (Spectrum at $t=1.0$)—(Spectrum at $t=9.0$ μsec). In Fig. 4 the absorption spectra of the transient species of *trans*-stilbene

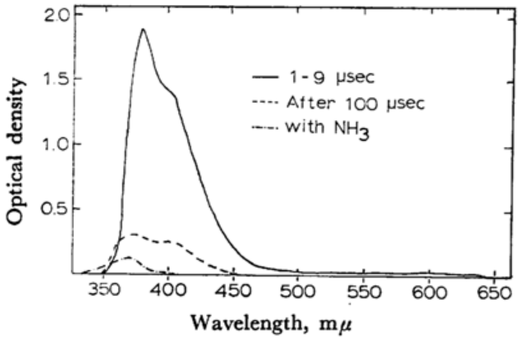

Fig. 4. The absorption spectra of the transient species of *trans*-stilbene in CCl_4. "1—9 μsec," means the difference of the spectra: (absorption at $t=1$ μsec)—(absorption at $t=9$ μsec). "After 100 μsec" means the entire absorption still left at $t=100$ μsec.

in carbon tetrachloride are shown.

It will be seen in Figs. 2, 3, 4, 8, and 9 that there are two types of alkyl halides. The one type consists of *n*-butylchloride (BuCl), 1,1-dichloroethane (11DCE), 1,2-dichloroethane (12DCE), 1,1,2-trichloroethane (112TCE), and 1,1,2,2-tetrachloroethane (TECE). These are called DCE type solvents in this report. The other group consists of 1,1,1-trichloroethane (111TCE), Pentachloroethane (PCE), and carbon tetrachloride. These are called CCl_4-type solvents in this report. The DCE-type solvents give almost identical absorption spectra, which are also quite similar to those reported by Shida and Hamill,[1] when biphenyl and *trans*-stilbene are the solutes, while the CCl_4-type solvents give spectra which are completely different from those observed with the DCE-type solvents.

Figure 5 shows the decay-rate curves of the transient species of *trans*-stilbene in 11DCE at various temperatures between −60°C and +20°C. The intensity of absorption was observed at 490 mμ. The Arrhenius plots of the rate constants are shown in Fig. 6. The activation energy for the first-order rate constant, k_1, was 1.27 kcal/mol.

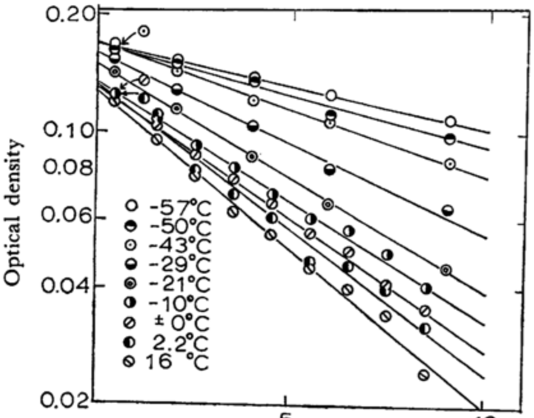

Fig. 5. The decay rate curves of the cations of *trans*-stilbene formed in 1,1-DCE at various temperatures.

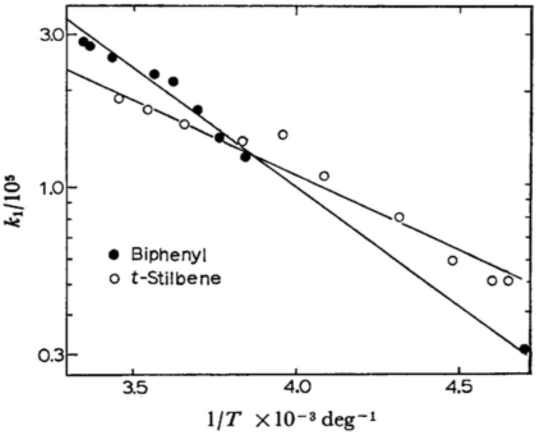

Fig. 6. Arrhenius plots of the 1st order rate constants k_1s in the temperature range between −60°C and +10°C.

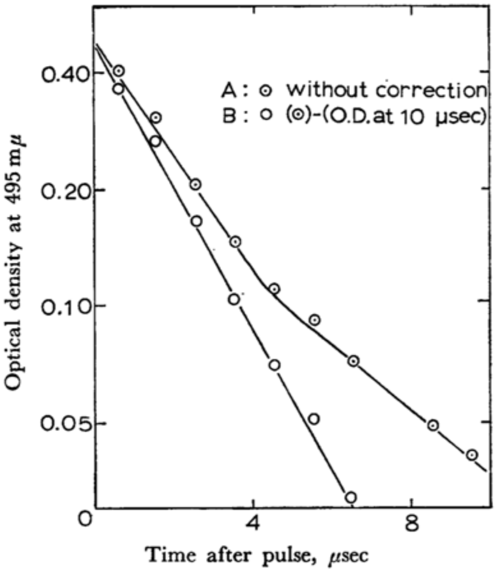

Fig. 7. The decay rate of the anion of *trans*-stilbene in methyltetrahydrofuran.

In Fig. 7 the decay rate of the transient species in MTHF observed at 495 mμ is shown. The A curve indicates that the absorption curve does not obey the first order decay. However, the absorption spectra showed a clear change in shape after 10 μsec. This means that the species existing during an initial 1—9 μsec, and the species existing after 10 sec, are somehow different. In view of this fact, the optical densities until 9 μsec were corrected by subtracting the value at 10 μsec. The corrected optical densities fall along the straight line B, which indicates a first-order decay. Such is also true with most of the transient species of *trans*-stilbene in various solvents at 25°C. In other words, all the decay-rate curves, after correction, obey the first-order rate and are identified by the initial optical density at $t=0$, and the rate constant, k_1. Table 1, therefore, shows the initial optical density, at $t=0.5$ μsec, and the k_1.

Though it seems to be beyond question that the effects of the DCE-group solvents on the formation of the transient species are all the same in quality, the present author tested this point by mixing many pairs of the solvents in the group. For example, the results obtained by mixing BuCl and 11DCE are shown in Table 2. However, the effects of 12DCE and CCl_4 are not added to each other when these two solvents are mixed and used. As is shown in Fig. 2, the optical density of the transient species which is qualitatively the same as that obtained by 12DCE is greatly reduced by adding CCl_4. Also, MTHF and TECE have opposite effects. The mixing of 0.08 mol of MTHF with 0.92 mol of TECE reduced the optical density of the transient species of *trans*-stilbene at 490 mμ from the 0.750 of pure TECE to 0.066, as is shown in Table 1.

Figures 8 and 9 show the absorption spectra by the transient species formed from biphenyl in various solvents. In Fig. 10 the decay curves of the transient species of biphenyl in 11DCE at various temperatures between −60°C and 20°C are shown. The intensity of absorption was measured at 370 mμ. The results show first-order rate curves, and the temperature dependence

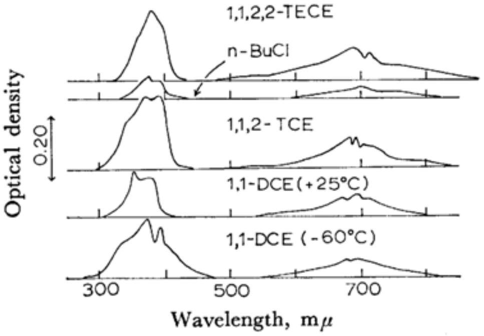

Fig. 8.

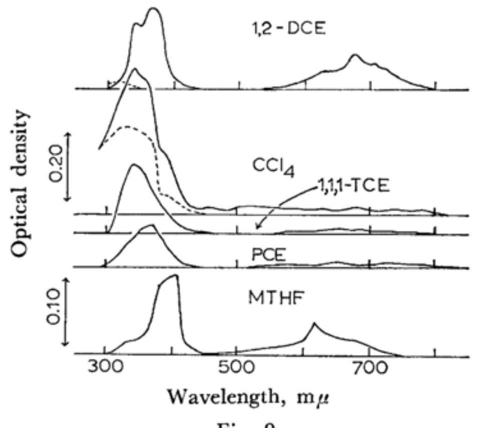

Fig. 9.

Fig. 8 and Fig. 9. The absorption spectra of the transient species of biphenyl in various solvents. In the spectra marked as CCl_4 and 1,2-DCE the dotted lines indicate the spectra after 100 μsec. All the others are the differences as are used in the caption for Fig. 4.

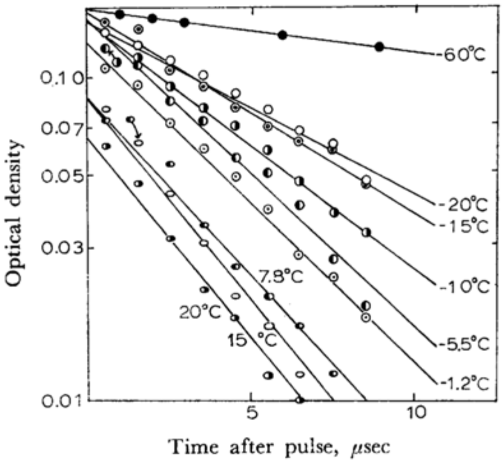

Fig. 10. The decay rate curves of the cation of biphenyl formed in 1,1-DCE at various temperature.

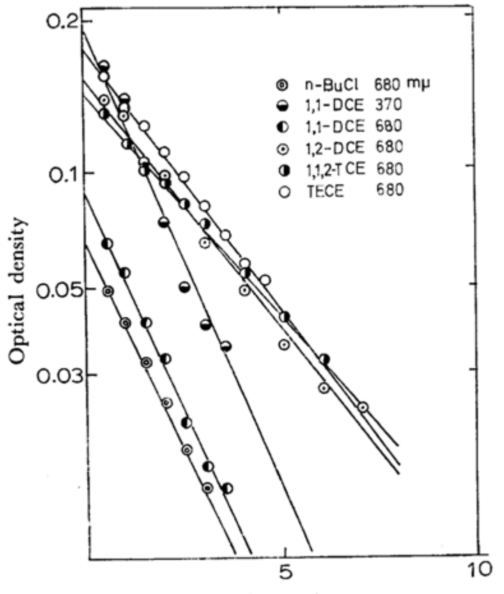

Fig. 11. The decay rates of the cation of biphenyl formed in various solvents. The wavelengths shown are those at which optical density measurements were made.

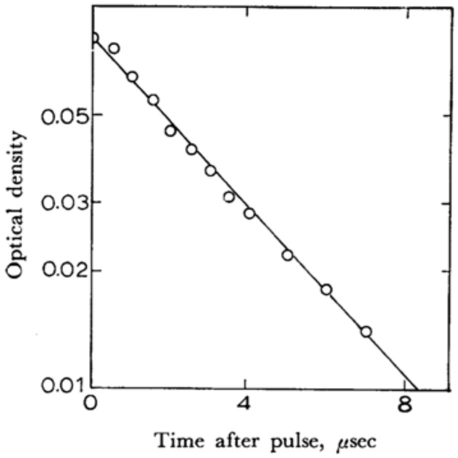

Fig. 12. The decay rate of the anion of biphenyl in MTHF.

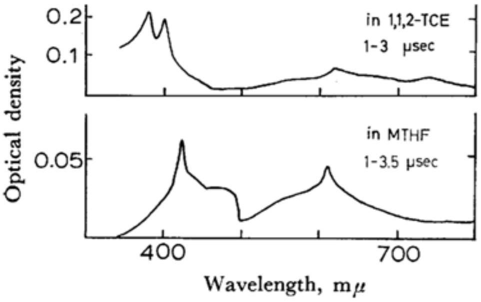

Fig. 13. The absorption spectra of the transient species of *o*-terphenyl formed by pulse radiolysis of *o*-terphenyl in MTHF and 1,1,2-trichloroethane. The upper spectrum is the difference: (absorption at $t=1.0$ μsec)$-$(absorption at $t=3.0$ μsec), and the lower spectrum is the difference between 1.0 and 3.5 μsec, respectively.

of the rate constant, shown in Fig. 6, gives 3.62 kcal/mol as the activation energy. Figure 11 shows the various decay rates of the transient species of biphenyl in several alkyl halide solvents. Figure 12 shows the decay rate of the transient species of biphenyl in MTHF. The absorption was measured at 625 mμ. The formation and the decay of the radiation-chemical transient species of biphenyl in various solvents are summarized in Table 3.

Though *trans*-stilbene and many other aromatic hydrocarbons give almost identical spectra⁶⁾ in both types of solvents, *i. e.*, alkyl halides and aliphatic ethers, biphenyl gives different spectra, as shown in Fig. 8 and Fig. 9. For a reason to be discussed later, *o*-terphenyl was also expected to give two different spectra in the two types of solvents. Figure 13, therefore, shows the absorption spectra of the transient species of *o*-terphenyl in 112TCE and in MTHF.

Discussion

The light absorption of positive and negative ions of aromatic hydrocarbons have already been studied. Hoijtink⁷⁾ studied the negative ions formed with metallic sodium in tetrahydrofuran and the positive ions formed in concentrated sulfuric acid. In most cases the spectra of the cation and the anion were similar to each other. A simple Hückel MO calculation does not predict any difference in the values of the differences in energy levels corresponding to the light absorption by a cation and by an anion.⁸⁾ The rigid matrix method used by Shida and Hamill¹·⁹⁾ also gave many spectra of the unstable species trapped in the matrices of MTHF and alkyl halides (mostly CCl_4 and *s*-butyl chloride) at 77°K. In these cases, however, it is not possible to conclude strightforwardly the pure existence of either a cation or an anion.

There are many possible ways to detect an ion of an aromatic compound in the liquid phase by using some of its physical properties. One of them is the visible-light absorption method, and another is the ESR method. The transient species to be predicted for a system subjected to an ionizing radiation are not limited to only one. For example, the aromatic compound C_nH_m would form $C_nH_m{}^+$, $C_nH_m{}^-$, $C_nH_{m-1}\cdot$, $C_nH_{m+1}\cdot$ and so on, generally speaking, there is no reason to deny the existence of any one of them. If this system is investigated in the liquid phase by the use of the ESR method, the difference in the number of protons of the paramagentic species may be found rather easily. Thus the difference between $C_nH_m{}^+$ or $C_nH_m{}^-$ and $C_nH_{m-1}\cdot$ or $C_nH_{m+1}\cdot$ will be clear. In addition, some modified or improved MO calculations can predict some difference in the spin density distributions between $C_nH_m{}^+$ and $C_nH_m{}^-$, a difference which is to be observed as the difference in the spacings of the lines in the ESR spectrum. At any rate, the information obtained by the ESR method in the liquid phase is normally more useful than that obtained by light absorption specetroscopy. Therefore, if it be possible to apply ESR method to the liquid-phase pulse radiolysis studies, it would be quite powerful.

In the case of the rigid glass method, the ESR method is less powerful than the absorption spectroscopy because of the averaging out of the anisotropy of the resonance lines. Therefore, the results of this method cannot be precisely compared in detail with any MO calculations.

---

6) L. M. Dorfman and H. Ueda, unpublished results.

7) G. J. Hoijtink and W. P. Weijland, *Rec. Trav. Chim.*, **76**, 836 (1957); W. Ij. Aaldberg, E. L. Mackor and W. P. Weijland, *J. Chem. Soc.*, **1959**, 3049, 3055.

8) For example, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York (1961).

9) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 4372 (1966).

It has already been established that the negative ion of biphenyl is formed by the action of alkali metal in pure tetrahydrofuran or similar solvents. According to Hoijtink,7) the absorption maximum appears at 625 mμ. Absorption maximum at the same wavelength was also obtained by the pulse radiolysis of biphenyl in ethanol.3) The present results show that the absorption maximum of 625 mμ is observed only from the solution of biphenyl in MTHF. In the DCE-type solvents, the maximum is 690 mμ. These facts suggest that the species formed in MTHF is the same as that formed in ethanol and that, therefore, it is the anion. However, they do not necessarily indicate that the species formed in 12DCE is the cation. Nevertheless, the effects of gases on the formation of the transient species, Table 3, indicate that only NH_3 affects the formation. The decay kinetics, in all cases, are simple first-order rates, showing that only one short-lived species exists. Such a short-lived species, the origin of which is effectively cancelled by NH_3, must be a species with a positive charge. The only question left is whether or not it is a protonated biphenyl. However, the elimination and transfer of a proton from a DCE-type solvent at these velocities must be doubted.

The absorption spectra for the cation and the anion of *trans*-stilbene have not yet been established. The only available information is that reported by Shida and Hamill.1) They obtained an absorption spectrum by the use of a rigid glass of *trans*-stilbene in *s*-butylchloride, they ascribed it to the cation. The present pulse-radiolysis results show that there is no considerable difference between the spectrum in MTHF and that in an alkyl halide of the DCE type. The only difference, as may be seen in Fig. 3, is the position of the absorption maximum, which is at 500 mμ for MTHF and 2,5-dimethoxy tetrahydrofuran and at 490 mμ for the alkyl halides of the DCE type. As in the case of biphenyl, it is not easy to decide on the nature of the transient species of *trans*-stilbene formed in each type of solvent. However, the first-order rate curve suggests that there can be only one species which gives the spectrum. The results from the effects of gases, Table 1, show that the transient species formed in DCE type alkyl halides are not much affected by any added N_2O or SO_2, but completely disappear if NH_3 is added. This, it seems, is strong evidence for the formation of the cation in these solvents. Therefore, the species giving rise a spectrum with the peak absorption at 490 mμ can be concluded to be the cation. The mixing of two solvents such as 11DCE and BuCl shows that the effects of the two solvents are added in the mixed solvent. On the other hand, a mixture of 8 mol% of MTHF and 92 mol% of TECE decreased the optical density at 490 mμ to only 9% of that observed with pure TECE. The latter fact indicates that MTHF scavenges the species formed in TECE. Therefore, the electronic nature of the transient species formed in MTHF seems to be exactly the reverse of that formed in TECE. Hence, it is highly probable that the species with the absorption maximum at 500 mμ is the anion.

In the studies of the effect of additives on the radiolysis of 1,2-dichloroethane,2) it was shown that the *G*-value of ethylene goes down if those additives with larger rate constants with hydrated electrons are added. It was, therefore, concluded that ethylene is formed through a negative ion of 12-DCE. On the other hand, MTHF and tetrahydrofuran, which have smaller affinities with hydrated electrons, increase the *G*-value of ethylene from 2.1 to 3.6 and 5.2 respectively. The explanation of this was that the holes formed in pure 12DCE are normally neutralized by the negative ions. If MTHF or tetrahydrofuran exists, a hole is neutralized by this compound before a negative ion comes into contact with it. The result is an increase in the number of the negative ions which spontaneously disintegrate into ethylene and Cl_2. The conclusion of the product analysis method, therefore, agrees very well with the present pulse-radiolysis results.

The difference between the spectra of the cation and the anion of biphenyl seems to be due to a steric electronic interaction between the *o*-positions in two different benzene rings. If so, a stronger steric effect should be observed in the cation and the anion of *o*-terphenyl. The two spectra from the solutions of *o*-terphenyl in 112TCE and in MTHF are different, as shown in Fig. 13. Therefore, the above explanation may be worth consideration. The electronic charge is conducted through the systems under investigation very well in spite of the insulating nature of both the aromatic solutes and the solvents used, all of which contain only covalent bonds. The concentration dependence of the optical density, Fig. 1, shows that the optical density will be zero at a solute concentration of 10^{-4} mol/*l*. This concentration is equivalent to a cubic lattice model with a unit dimension of 255 Å, one in which all the lattice points are occupied by a *trans*-stilbene molecule while the space inside the lattice is filled with solvent molecules. Therefore, if a cation (hole) of the solvent molecule is formed, at least one of the solute molecules is within less than 220 Å from this hole. The positive charge must travel this distance in order to be transferred to the solute molecule.

A covalently-bonded insulator becomes a semiconductor if some excess electric charge is injected into the lattices. The present system during and immediately after pulsed irradiation seems to be such a semiconductor. This does not mean, however, that a measurable macroscopic conductivity is observed with an aid of some external circuit connected to the cell. The hole travels only 220 Å before it is captured by the anion. If a solute molecule with a lower ionization potential exists within this range from the hole of the solvent molecule, the hole will migrate to the solute molecule.

Such a semiconduction process also explains the charge transfer within a rigid glass matrix. Unless there is such a conduction, it will be difficult to trap the holes and electrons formed in the matrix molecules completely with less than 10^{-1} mol/*l* of the solute molecules.

The electricity in the present systems is carried in two ways, by an electron and by a hole. The total conductivity is the sum of the two conductivities, σ_h and σ_e. These quantities are functions of the ionization potential, the electron affinity, the temperature, and so on. In the case of MTHF, the σ_h is small due to the low ionization potential. As a result, the conductivity by the electron traps, σ_e, is dominant, and a negative ion is formed far more easily than a positive ion. The slowly-travelling holes, therefore, are mostly caught by the solvated electrons before they meet a solute molecue. In the case of 12DCE, the σ_h is larger as a result of the high ionization potential. Therefore, only the cation of the solute molecule is formed. In some media in which the σ_h and σ_e are comparable, the simultaneous formation of both the ionic species can be expected. Such is the case with 3-methyl pentane.

To ignore the minor conductivity, however, is not possible, especially more than 1 μsec after a pulse. The ionic species of the solute molecule formed begin to meet the counter electric charge, which is conducted by the minor conductivity. This is observed as the decay of the solute ions. Another piece of experimental evidence to support such a conductivity theory is, then, the kinetics of the decay of the optical densities resulting from the ionic species of the solute.

By analogy with the recombinations of free radicals in the gas-phase photolysis, it has been generally believed that a cation or an anion disappear by the recombination process and that the charge carriers are individual ions. In the present theory, the movements of each molecule are ignored; rather the entire solution is handled as one continuous system. The rate-determining step in the collision-recombination theory is the movement of each molecule, while in the present theory the activation energy for the neutralization of the hole and the trapped electron (or the electron itself) determines the rate. The transportation of a hole or an electron trap is not considered to be rate-determining. It will be helpful to use an ion-pair model to interpret this theory. By, say 0.5 μsec after a pulse, each electron trap has already moved and occupied one of the lattice points which are close to or next to the site which is occupied by a solute cation. By 10 μsec after a pulse all the ion pairs have recombined by going over the activated state. This activation energy is supplied thermally by the surrounding lattices. This theory, therefore, predicts a first-order decay rate of the solute cation. Actually the rate is first-order. Arai and Dorfman(3) suggested the first-order decay rates of the solute anions in isopropyl alcohol with some unknown impurities. It may not have been correct, and the evidence may more properly be interpreted by the present theory.

Though in Shida and Hamill's experiments CCl_4 was a good matrix for observing a cation, in the present study it has been found that CCl_4 gives something else. The fact that a cation is not formed in CCl_4 has already been postulated.(10) The effect of NH_3 on the CCl_4 - *trans*-stilbene system has indicated that the transient species, whose spectrum is entirely different from that of the cation, is also effectively quenched by NH_3. This result can be explained as follows. The initial radiation-chemical product of CCl_4 will be an e^- and a cation, CCl_4^+. CCl_4^+ is, however, extremely unstable. Before a solute cation is formed by a hole conduction started from CCl_4^+, it decomposes to CCl_3 and Cl^+. As Cl^+ is quite different in shape from the matrix molecules, the hole conduction from it to a CCl_4 molecule is rather difficult, and Cl^+ is a stable hole. The transient species observed will have been formed through a direct molecule-to-molecule reaction of Cl^+ and the solute. If NH_3 exists, Cl^+ will react with NH_3 leaving almost nothing to be detected in the visible region. For the cases of other CCl_4-type solvents, namely, 111TCE and PCE, the instability of $CCl_3CH_3^+$ and $CCl_3CCl_2H^+$ will explain the odd transient species formed.

CCl_4, CCl_3CH_3 and, CCl_3CCl_2H all have a CCl_3 group, and none of them gives a cation of an aromatic compound in the liquid phase. However, it seems that $CHCl_3$(11) gives a solute cation. Therefore, it is possible to say that a -CCl_3 group without a hydrogen atom connected to it makes the original cation very unstable. In a frozen solid, all the Cl atoms are rigidly fixed by the surounding lattice, as a result, the lifetime of CCl_4^+ is long enough to allow a charge transfer by the hole conduction. If CCl_4 is added to 12DCE, the hole conduction through 12DCE lattice points is greatly disturbed by the presence of CCl_4 molecules. One possible reason is that the conducting holes are not in their ground state (the shallowest holes), but that some deeper holes are contributing to the conduction. Therefore, if the hole arrives at a site of the lattice which is occupied by a CCl_4 molecule, which may have a higher ionization

---

10) R. E. Bühler and T. Gäumann, p. 279, Ref. 4.
11) S. Arai, private communication.

potential than 12DCE, such an "excited" hole will become a " ground-state " hole of CCl_4 and no longer contribute to the conduction. This impurity effect can also serve to explain the effects of added N_2O and CCl_3CCl_3 on the formation and decay of the cation of *trans*-stilbene in 112TCE, shown in Table 1. As N_2O has a large rate constant with hydrated electrons, it is expected that it will fix negatively-charged species and, as a result, the life of the cation will become longer. This actually happens. However, N_2O also reduces the formation of the solute cation. This indicates that the hole conduction is also reduced by the presence of the N_2O molecule in the system. N_2O^+ as well as N_2O^- is, probably formed, and the charge transfer from a N_2O^+ to a 112TCE molecule is, like that from a N_2O^- to a 112TCE molecule, not easy. This is what the postulate in the previous work of the present author has meant[2]: all electron scavengers would undoubtedly behave both as electron scavengers and as hole scavengers, but after the overall competetion with the solvent molecules, they will behave as electron scavengers. In the case of CCl_3CCl_3, the formation of the cation is not distrubed much, but the decay rate is considerably lower.

The generally-accepted idea of the dissociative attachement process in the gas phase can be doubted in the liquid phase. If the negative charge (or an electron) is permanently trapped in the form of Cl^-, no semiconductivity by the negative charge, σ_e, can be expected. As a result, the decay curve must obey a second-order rate because of the collision-initiated nature of the neutralization. Therefore, the formation of a negative ion, $(RCl)^-$, is more suitable as an explanation of the formation of the cations in these solvents in either the solid or the liquid phase.

The author is greatly indebted to Mr. E. G. Wendell for his technical assistance in this work. He also wishes to thank Dr. L. M. Dorfman for his interest. The helpful opinions of Dr. S. Arai are also appreciated.