BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 297—300 (1970)

Kinetic Studies of the Pulse Radiolysis of *trans*-Stilbene in Several Solvents*[1]

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(Received June, 10, 1969)

The kinetics of the transient species of *trans*-stilbene in several solvents were studied using single pulsed electron beam (0.5 μsec × 300 mA) and the spectroscopic method. The species existing immediately (0—20 μsec) after a pulse is found to disappear according to a sum of two first-order decay-rate equations. The temperature dependence of the formation and decay of this species shows that there are two different *trans*-stilbene cations, R_s and R_f, which have almost identical absorption spectra but different formation and decay rates. The rate constants for R_s were not affected by the temperature, however, those for R_f were strongly affected. R_f is not found in the solution of *trans*-stilbene in 1,2-dichloroethane if a small amount of CCl_4 is added. Some effects of the dielectric constant were observed on the decay-rate constant of R_f. From these facts, it can be concluded that R_f is formed by an ordinary transfer of a hole from the solvent cation to the solute molecule. As R_s seems to be formed by a mechanism other than that of R_f, a possible scheme for it has been discussed.

The decay kinetics of the ionic species in solution have already been studied by the electrochemical method.[1,2] It was found that the solvation or the dielectric properties of the solvent greatly affect the decay kinetics of the ions. In the present work, therefore, the effect of the dielectric constant on the decay kinetics of the ionic transient species formed by ionizing radiation was investigated.

The kinetic data for the formation and the decay of the cation of *trans*-stilbene in alkyl-halides have already been included in a previous paper, together with the spectroscopic data.[3] The kinetic analyses in the previous paper, however, were carried out only for the time period of 0—9 μsec after a pulse; this method has, the present author believes, led to the right conclusion. Nevertheless, it is expected that some more information can be obtained by including the variation of the optical densities due to the ions still left 10—20 μsec after a pulse. Therefore, some further analyses of the rate curves are another purpose of the present study.

Experimental

The experimental procedures are the same as those reported in the previous paper.[3] The acetonitrile (AN) was purified by passing it through a vacuum-dried layer (30 cm) of alumina in a vacuum and by successive distillations in a vacuum. The solvents used were AN, carbon tetrachloride (possessing the two extreme values of dielectric constants, 35.99 and 2.25, at 25°C), *n*-butylchloride (BuCl), 1,1-dichloroethane (11DCE), 1,2-dichloroethane (12DCE), 1,1,2-trichloroethane (TCE), 1,1,2,2-tetrachloroethane (TECE), and 2-methyl tetrahydrofuran (MTHF) whose dielectric constants are between those two extremes.

Results

Figure 1 shows that the attempts to analyse the kinetic data with second-order rate curves were unsuccessful. For this reason, analyses with first-order rate curves were attempted; however, here the results were not successful, either. However, Fig. 2 shows that the decay rate of the transient species of *trans*-stilbene in AN consists of two processes with two different first-order rate constants, k_s and k_f, where the suffix *f* signifies that the rate is faster than that with *s* at 25°C. It will be seen that the decay curve, C, of the total light absorption can be interpreted as the sum of the two rate curves, S and F, the faster and the slower decays at 25°C. The rate curves obtained with 11DCE, CCl_4 MTHF, and all the other solvents have exactly the same shape, each consisting of two first-order rate curves, S and F. The kinetic constants for the S and F curves obtained with various solvents are listed in Table 1. In Fig. 3, the values of A_f and A_s (the relative values of the initial amount of the

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*[1] Supported by the U. S. Atomic Energy Commission.

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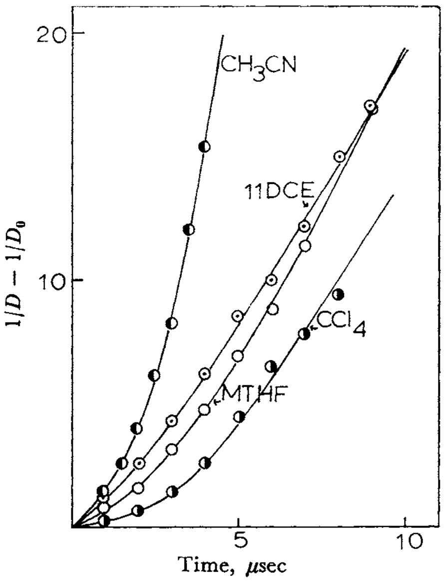

Fig. 1. Analyses of the results with second order rate equations. The ordinate indicates the difference of the inverse of the optical densities, $1/D$ and $1/D_0$, where D_0 signifies the optical density at the end of a pulsed irradiation and at 25°C. The abscissa indicates the time after a pulse.

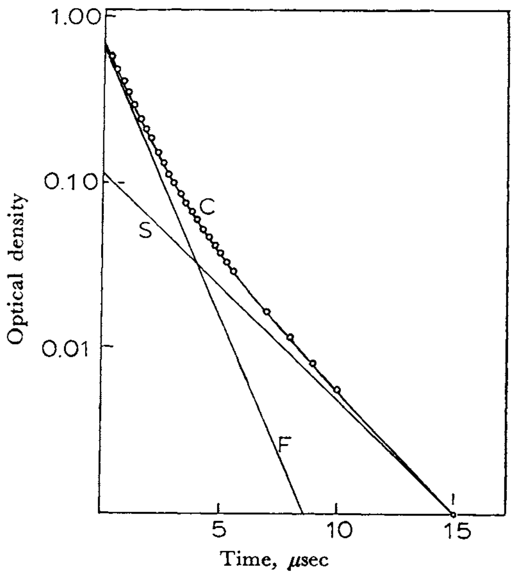

Fig. 2. Analyses of the results with first order decay rates. The ordinate shows the optical density, at 25°C, of the sample cell on a log scale and the abscissa shows the time after a pulse, in μsec.
Solvent: CH_3CN
trans-Stilbene: 1.76×10^{-2} mol/*l*

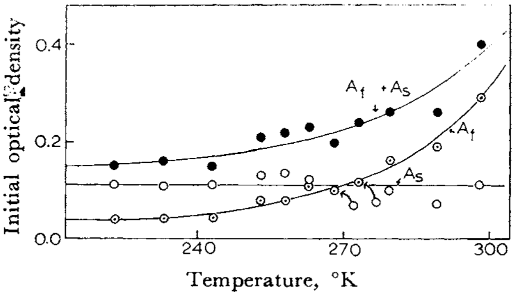

Fig. 3. The temperature dependence of the initial optical density, at 490 mμ, of the solution of *trans*-stilbene in 11DCE at the concentration of 1.40×10^{-2} mol/*l*. Explanations of A_f and A_s are in text.

transient species decaying with k_f and k_s) expressed in the scale of optical density are plotted against the temperature. The solvent used for this experiment was 11DCE because that substance has the lowest melting point (−98°C) among the solvents used. It was found that A_s is constant in the temperature region studied and that it is 0.11. It was also found that k_s is constant in the same temperature region and is 3.70×10^4 sec^{-1}. In Table 1, the A_f, A_s, k_f, and k_s values are shown for various solvents and mixed solvents of BuCl and 11DCE. In Table 2 the effects of the solute concentration on the k_f, A_f, and A_s values are shown.

Discussion

A second-order rate has been observed for a recombination process of free radicals; for this reason, a second-order rate has been expected for the decay of ions in a solution. In the present study, however, second-order rates can not be used for the analyses of the results. All are precisely interpreted by the sums of first-order rate equations. Similar types of decay rates have also been observed for the decay of trapped electrons in rigid glass matrices.[4] In these cases, however, the analyses of the rate curves were qualitative and the components were selected rather arbitrarily. Recent work[5,6] has indicated (I) that the ratio of the two (though in some papers three components have been postulated[4]) components is affected by the temperautre, the wavelength of the bleaching light, *etc.*, and (II) that the addition of a scavenger affects only the component with the slower decay rate.

In the present case, the consideration of a pseudo-first-order reaction might be necessary. In Table 2, the values of k_f slightly depends on that of A_f, but the values of the k_f/A_f ratio is not constant. The value of k_s does not depend on that of A_s and can ont be interpreted by a pseudo-first-order reaction. Another possibility is that the cation disintegrates spontaneously: $(RH^+) \rightarrow R\cdot + H^+$. This, however, would leave a free radical R· which should have some light absorption in the near UV region. No such formation has been found in the solutions studied. Therefore, some other type of charge neutralization with a first-order rate must be considered.

Table 1. The rate constants and the initial optical densities for various solutions of *trans*-stilbene at 25°C

Solvents	Concn.	A_f[a]	A_s[a]	A_f/A_s	k_f[b]	k_s[c]
n-Butylchloride	5.75[d]	0.30	0.11	2.7	4.15	6.94
75% BuCl[e] + 25% 11DCE[f]	1.92	0.29	0.10	2.9	2.86	4.23
50% BuCl + 50% 11DCE	2.13	0.32	0.10	3.2	2.69	4.17
25% BuCl + 75% 11DCE	2.12	0.29	0.11	2.6	2.15	3.66
1,1-Dichloroethane	1.73	0.29	0.11	2.9	2.17	3.70
1,2-Dichloroethane	2.22	0.43	0.28	1.5	2.17	5.38
1,2-Dichloroethane with 25 vol% CCl_4	1.60	—	0.09	—	—	4.53
1,1,2-Trichloroethane	1.87	0.73	0.38	1.9	2.67	5.30
1,1,2-Trichloroethane with 0.19 mol/*l* of C_2Cl_6	1.21	0.32	0.20	1.6	1.67	3.45
1,1,2,2-Tetrachloroethane	2.10	0.60	0.14	4.2	0.86	1.60
Carbon Tetrachloride[g]	2.99	12.1	0.14	86	3.34	1.78
Acetonitrile[h]	1.76	0.65	0.11	5.9	3.36	13.8
2-Methyltetrahydrofuran[i]	5.41	0.42	0.12	3.5	2.05	4.50

a) all except g—i were observed at 490 mμ. b) $\times 10^5$ sec^{-1} c) $\times 10^4$ sec^{-1} d) $\times 10^{-2}$ mol/*l*
e) *n*-Butylchloride f) 1,1-Dichloroethane g) at 380 mμ h) at 495 mμ i) at 500 mμ

Table 2. Effects of *trans*-stilbene concentration on the kinetic constants at 25°C

Concentration	A_f	A_s[a]	k_f $\times 10^5$ sec^{-1}	k_f/A_f
2.70×10^{-4}[b]	0.13	0.044	1.34	1.06×10^6
1.16×10^{-3}	0.18	0.060	1.62	0.90
1.70×10^{-3}	0.24	0.081	1.72	0.72
3.19×10^{-3}	0.26	0.088	2.02	0.78
1.30×10^{-2}	0.29	0.099	2.16	0.75
1.73×10^{-2}	0.30	0.099	2.14	0.72
3.48×10^{-2}	0.30	0.102	2.08	0.69
8.97×10^{-2}	0.31	0.103	2.00	0.65

a) k_s is constant and is 3.70×10^4 sec^{-1}.
b) mol/*l*.

In the previous paper it was established that the cation of *trans*-stilbene is formed in the solvents typically represented by 11DCE. Also, an anion can be assigned to the spectrum from a solution in MTHF.[3,7] In CCl_4 the spectrum[3] is almost completely different from that of the cation reported to be formed in polycrystalline CCl_4 by Shida and Hamill.[7] This fact might lead to the conclusion that the transient species formed in CCl_4 in the liquid phase is not an ionic species. However, the addition of a small amount of NH_3 destroyed the optical density due to the transient species observed in CCl_4 almost completely.[3] This indicates that the transient species observed in CCl_4 is also of cationic origin. In AN it is uncertain if the existing species is either one of the ions or both. The shape of the decay curve obtained with AN, shown in Figs. 1 and 2, is identical with those in the other solvents used in this study. Therefore, it is highly probable that the transient species observed have ionic natures in all the cases studied.

In Table 1, it will be seen that the number of C-Cl bonds in a unit volume of the solvent determines A_f. If CCl_4 or C_2Cl_6 exists in the solution, A_f decreases or disappears. The addition of a small amount of CCl_4 or C_2Cl_6 may result in a small decrease in the overall dielectric constant of the solution. The real effect of these compounds, however, will not be through the dielectric constant, but by a means similar to the one by which CCl_3CH_3 and CCl_3CHCl_2, when used as solvents, did not give the solute cations.[3] The absorption spectra of the transient species obtained by CCl_4 are entirely different from those obtained by other solvents, *e.g.*, 12DCE; therefore, the extinction constant at 380 mμ may be considerably larger than that of the pure stilbene cation, at 490 mμ. This would make it possible to interpret the large A_f and A_f/A_s values for CCl_4.

The k_f values for BuCl, 11DCE, and TECE decrease in that order. As the dielectric constant is also expected to increase in that order, it seems that the larger the dielectric constant of the solvent, the smaller the k_f. Such a tendency has also been found for the mixtures of BuCl and 11DCE.

Let the species with the k_f rate constant be named R_f, and that with k_s, R_s. The facts that the temperature strongly affects the formation of R_f, and that the decay rate of R_f, *i.e.*, k_f, is affected by the dielectric constant of the solvent, lead to the conclusion that the normal charge-transfer mechanism from the solvent cation to the solute molecule yields R_f. The effect of CCl_4, which acts as if it were a scavenger to the solute cation, R_f, in 12DCE can also be well explained by this mechanism. The charge transfer between 12DCE is intercepted by one of the added CCl_4 molecules during the

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[7] T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375 (1966).

charge transportation to a solute molecule; then, some chemical reaction at this CCl_4 molecule is started. At any rate, CCl_4^+, if once formed in the liquid phase, should not be good for the production of the solute cation.

It is hard to say if A_s is affected by the dielectric constant of the solvent, as is shown in Table 1. The difference between R_s and R_f is that A_s is little affected by either the temperature or the added CCl_4. The A_s value for MTHF, in which the *trans*-stilbene anion has been obtained, is also similar to those obtained by several of the alkyl halides used.

The k_s values, it seems, do not depend on the dielectric constant of the solvent. The large value for acetonitrile is puzzling, but it is possible to say that the large dielectric constant of acetonitrile does not contribute to the stability of the R_s.

As the R_s is not affected by the temperature or the added CCl_4, the formation of R_s should be different from that of R_f. As the absorption spectra for R_f and R_s are identical,[3)] they must be identical species with different routes of formation and decay.

The main purpose of this work, to establish the effect of the dielectric constant of the solvent on the formation and decay kinetics of the solute ions, has not been achieved conclusively, on the other hand, our knowledge of the values of the dielectric constants of the solvent compounds used in this study, especially those values under the influence of a strong electrostatic field, is very little. If these values were known exactly, the present data could perhaps be interpreted in a different way.

The formation and the decay of the solute cation include many steps such as: (A) the excitation of the solvent molecule to form $S^{*\prime}$; (B) the partial stabilization of $S^{*\prime}$ to form S^*; (C) excitation transportation to a solute molecule; (D) excitation transfer to the solute molecule to form $R^{*\prime}$ (E) the partial stabilization of $R^{*\prime}$ to form R^*; (F) the transportation of the excitation or the counterexcitation, and (G) recombination. Here "excitation" is taken in a wide sense and can include both ionization and simple excitation. The rate-determining steps for the formation and the decay processes will be only a few of them. Therefore, a direct determination of the entire process based on the observed reaction rate, which is determined by the rate-determining steps only, will be imperfect. The decay process of the solute cation includes at least the (E), (F), and (G) steps. Even when only the rate-determining step is temperature-independent and proceeds by a first-order rate, while the remaining two steps are not temperature-independent and do not so proceed, the overall result to be observed can be temperature-independent and can proceed with a first-order rate. On the other hand if any one of these steps is destroyed by the scavenger like CCl_4, all the steps seem to be destroyed by the scavenger. For these reasons, it would not be safe to say that the temperature independent kinetic data-obtained for R_s allow us to exclude the possibility of any thermal movements of charged species leading to the formation and decay of R_s.

However, the formation of R_s should be somehow different form that of R_f. As it has been concluded that R_f is formed by a normal charge transfer from a solvent cation to the solute molecule, some other mechanism should be found for R_s. A tentative scheme for R_s may be the following excitation transfer leading to an ion-pair formation:

$$\text{Solvent}_a \rightsquigarrow \text{Solvent}_a^*$$

$$\text{Solvent}_a^* + \text{Solvent}_b \rightarrow \text{Solvent}_a + \text{Solvent}_b^*$$

$$\text{Solvent}_p^* + \textit{trans}\text{-stilbene} \rightarrow \text{Solvent}_p^- + R_s^{(+)}$$

$$R_s^{(+)} + \text{Solvent}_p^- \rightarrow \textit{trans}\text{-stilbene} + \text{Solvent}_p,$$

where the asterisk signifies a non-ionic excited state. The suffix letters are for the identification of each solvent molecule. The plus sign in the parentheses indicates that this R_s species has a net positive charge. As no charge transfer is involved in these schemes, a temperature-independent rate can be expected. Since no transportation of a positive or a negative charge is involved in the decay process of the solute cation, it can proceed with a first-order rate.

The determination of the *G*-value for the formation of the cation of *trans*-stilbene has not been attempted in this work. The determination of the *G*-value is essentially the determination of the extinction constant of the light abosrption by the cation of *trnas*-stilbene. This naturally includes the preparation of a solution of the cation of *trans*-stilbene with a known concentration, and such a preparation can not be done easily. For this reason, the *G*-value determination was reserved for future experiments.

The author wishes to thank Mr. Jerome Brandon for his cooperation in the experiments involved in this study.