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Pulse Radiolysis Studies of Solvent Radical Cations in Liquid 1,2-Dichloroethane

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Transient absorption spectra with maxima at 270 and 550 nm were observed in liquid pure 1,2-dichloroethane by means of ps and ns pulse radiolysis. The broad absorption band with a maximum around 550 nm decayed according to a first-order reaction with $t_{1/2}$=0.2 ns in ps pulse radiolysis and $t_{1/2}$=200 ns in ns pulse radiolysis. These short lived species were attributed to solvent cations on the basis of scavenger experiments. The slowly decaying species with $t_{1/2}$=1.2 μs which absorbs around 400 nm superimposed on the 550 nm band, was tentatively assigned to carbocations. The 270 nm band formed during and after the electron pulse decayed over several microseconds by second-order kinetics. Those radicals which were produced by the dissociative electron attachment to the solvent and by the reaction of cations were responsible for this UV band.

Radiolysis of chlorinated hydrocarbonds such as carbon tetrachloride,[1] 1,2-dichloroethane (1,2-DCE),[2] and butyl chloride[3] has been applied to studies on solute cations by many workers. In these solvents electrons are dissociatively attached to solvent molecules to form stable chloride ions. The absorption spectra of solvent cations of carbon tetrachloride[4,5] and butyl chloride[6–8] have been observed and the rate constants of charge transfer with various solutes have been determined in pulse radiolysis experiments. However, it is reported that 1,2-DCE shows only a very weak absorption in the μs pulse radiolysis.[9] We initiated this study in order to obtain the spectral and kinetic information of 1,2-DCE cations. This paper reports the observation of radical cations of 1,2-DCE by means of ns and ps pulse radiolysis at room temperature and the rate constants of charge transfer for various cation scavengers.

Experimental

1,2-Dichloroethane was spectrograde of Wako Junyaku. The stroboscopic picosecond pulse radiolysis system[5] with a time resolution of 30 ps and the nanosecond pulse radiolysis system[10] with a time resolution of 10 ns were described earlier. Electron pulses of 45 MeV and 10 ns width from an S-band LINAC were used as a radiation source. The absorbed doses were determined with the KSCN dosimeter[11] for the 10 ns pulse and the hydrated electron dosimeter for the 30 ps fine-structure electron pulse applying $G(e_{aq}^-)$ at 30 ps as 4.8.[12] The detection system consisted of a monochromator (Bausch and Lomb, 33-86-25) and a photomultiplier (HTV, R928). The bandwidth of the monochromator was 10 nm. Samples were bubbled with argon in a quartz cell which has an optical path length of 1 or 2 cm and sealed with a teflon bulb for the ns pulse radiolysis. In the case of ps pulse radiolysis the solution was circulated through the 2 cm path length cell by a pump to prevent the deposition of radiation products. All experiments were carried out at 18 °C.

Results

Picosecond Pulse Radiolysis. Pure liquid 1,2-DCE was irradiated with a train of 30 ps fine structure electron pulses spacing at 350 ps each other. A typical kinetic trace observed at 550 nm is presented in Fig. 1. The solid line is the computer simulated first-order decay curve with parameters $G\varepsilon$=2.4×10^4 mol^{-1} dm^3 cm^{-1} and $t_{1/2}$=200 ps. The dose of the macro pulse whose time profile can be approximated as a gaussian with a half width of 10 ns was 38 Gy. Figure 2 shows the transient absorption spectra obtained immediately after the 30 ps pulse in the range of 350 to 700 nm. The spectrum exhibits a maximum at 550 nm.

Nanosecond Pulse Radiolysis. Figure 3 shows the

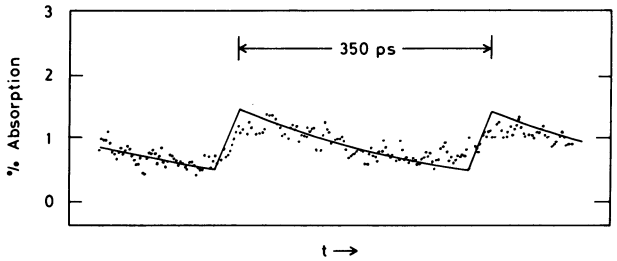

Fig. 1. The picosecond kinetic trace observed at 550 nm in pure 1,2-dichloroethane at 18 °C. The solid line is the simulated trace with $G\varepsilon$=2.4×10^4 mol^{-1} dm^3 cm^{-1} and $t_{1/2}$=200 ps.

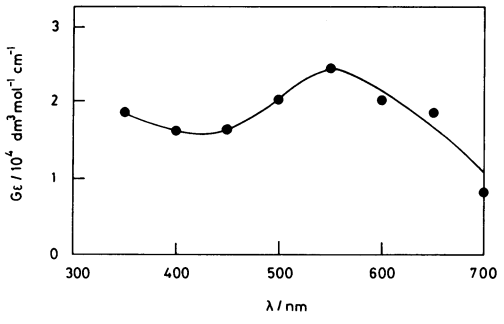

Fig. 2. The absorption spectrum obtained at the end of 30 ps electron pulse irradiation of pure 1,2-dichloroethane.

transient absorption spectra observed at the end of the 10 ns pulse, 120, 600 ns and 2 μs after the pulse in pure 1,2-DCE by the ns pulse radiolysis. Two distinguished transient absorption bands could be observed at 550 and 270 nm. However, the kinetic behavior is not identical for both absorption bands as shown in the insets of Fig. 3. The visible absorption spectrum immediately after pulse is quite similar to that was observed in the ps pulse radiolysis. The maximum of the visible band shifts from 550 to 500 nm in the first 120 ns then to 450 nm in 600 ns. This change can be also demonstrated by the different kinetic behavior observed at 400 and 650 nm as presented in Fig. 4. The decay trace at 650 nm consists two first-order components, i.e., $k_1=(2.5\pm0.5)\times10^7\ s^{-1}$ and $k_2=(3.5\pm0.5)\times10^6\ s^{-1}$. On the other hand, the kinetic trace at 400 nm is the superposition of these two components and a much slowly decaying component with $k_3=6\times10^5\ s^{-1}$. Therefore, the blue shift of the visible band is due to the rather long-lived species which absorbs near UV region.

The 270 nm band is formed during and after the pulse (Fig. 5a) and decays by a second-order reaction with $2k/\varepsilon=2\times10^7$ cm s^{-1}.

Typical electron scavengers such as N_2O, oxygen and CCl_4 have been added to the solution and it was found that they do neither reduce the initial absorbance of both 270 and 550 nm bands nor increase the decay rate. On the other hand, solutes which have a lower ionization potential than that of 1,2-DCE (11.41 eV)[14] increase the decay rate of 550 nm band and decrease the absorbance of the 270 nm band. Typical results obtained with cyclohexane (IP=10.32 eV)[14] as a cation scavenger are illustrated in Figs. 5a—c. The high concentration of cyclohexane ($>10^{-1}$ mol dm^{-3}) supresses the visible band almost completely

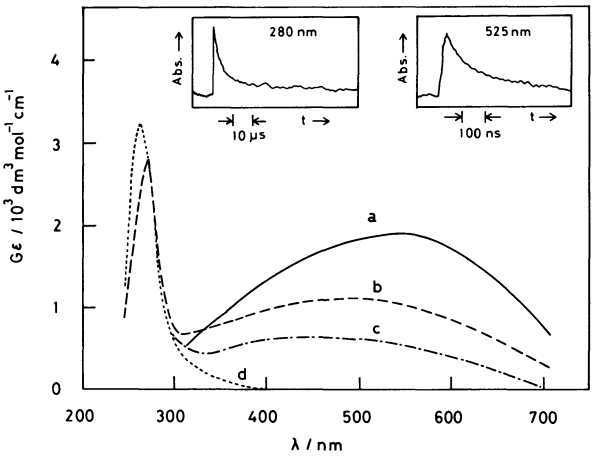

Fig. 3. Absorption spectra recorded at the end of the 10 ns electron pulse (a) and 120 ns (b), 600 ns (c) and 2 μs (d) after the pulse. Dose was 82 Gy and optical path length was 2 cm.
Insets: kinetic traces illustrating the decay of the absorbance at 280 and 525 nm.

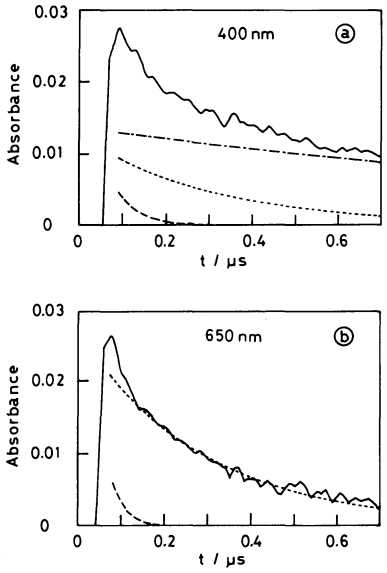

Fig. 4. Kinetic traces observed in pulse irradiated 1,2-DCE at 400 (a) and 650 nm (b). First-order components; (-----): $k_1=2.5\times10^7\ s^{-1}$, (------): $k_2=3.5\times10^6\ s^{-1}$, (—·—·—): $k_3=6\times10^5\ s^{-1}$.

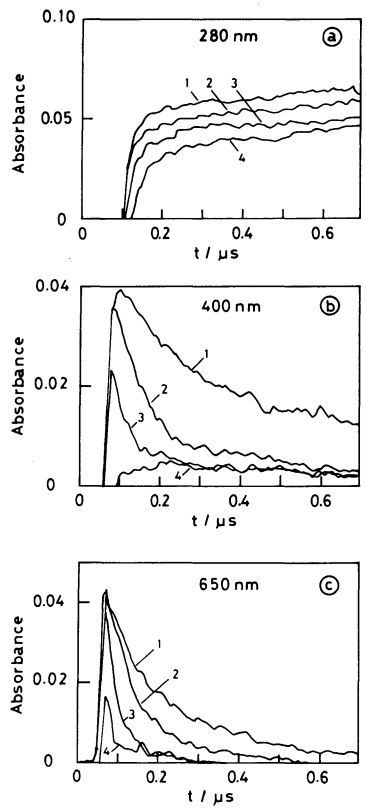

Fig. 5. Effects of cyclohexane on the transient absorption decay at 280 (a), 400 (b) and 650 nm (c). Dose was 110 Gy. Optical path length was 1 cm. Concentration of cyclohexane (in mol dm^{-3}); 1: 0; 2: 4.6×10^{-3}; 3: 1.8×10^{-2}; 4: 9.2×10^{-2}.

but the UV band to about a half. These results strongly indicate that the visible band is due to cationic species and reaction product of this primary cationic species contribute to the UV band to a certain extent. Obviously, the decay rate increases with increasing concentration of cyclohexane (Figs. 5b and 5c). Upon application of pseudo-first order kinetic treatment, the rate constant of positive charge transfer to cyclohexane was determined to be 1.5×10^{9} mol^{-1} dm^{3} s^{-1}.

In the case of pure 1,2-DCE, the absorbance vs. time profiles at 400 and 650 nm are different due to the contribution of the slowly decaying component as mentioned above. However, on addition of cyclohexane decay rate constants obtained at both wavelengths become same as shown in Figs. 5b and 5c. The initial signal intensity at 650 nm does not decrease significantly on addition of cyclohexane up to 2×10^{-2} mol dm^{-3}. On the contrary, the initial absorbance at 400 nm decreases with increasing cyclohexane concentration. These results suggest that the slowly decaying component at 400 nm reacts more rapidly with cation scavenger than the fast component or might be a secondary reaction product of cationic species.

The charge transfer rate constants have been obtained with 13 solutes. The rate constants determined are then correlated with the difference of ionization potential between 1,2-DCE and the added solute as shown in Fig. 6.

Aniline (IP=8.00 eV)[14] is well-known as a cation scavenger and the yield of the solvent cation can be estimated based on the maximum yield of aniline cation radicals.[15-17] The aniline cation radical exhibits an absorption maximum at 423 nm in aqueous solution[18] and at 385 nm in pure aniline.[19] Its extinction coefficient was established to be 2000 mol^{-1} dm^{3} cm^{-1}.[18] Figure 7 shows the typical transient absorption spectrum of the aniline cation radical observed in 2.75×10^{-2} mol dm^{-3} aniline solution. The spectral shape is the same with those observed in aqueous solution[18] and in pure aniline,[19] indicating that only one species is present. Figure 8 shows the decrease of the absorbance at 525 nm and the increase of 410 nm band with increasing aniline concentration. At higher concentration of aniline (>10^{-2} mol dm^{-3}) the absorbance of aniline cation radical is too strong to determine the reduced absorbance of the solvent cations. In spite of this difficulty, the increase of aniline cation radical absorbance seems to correspond with the decrease of the absorbance at 525 nm. The yield of the aniline cation radical has been estimated to be G=2.8 based on the plateau yield of it (OD_{max}=0.088) at the concentration larger than 10^{-1} mol dm^{-3}.

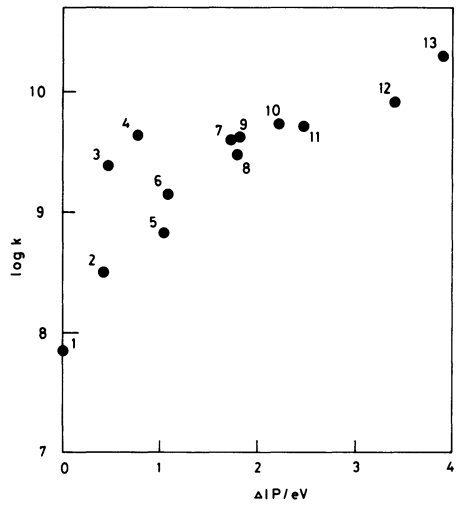

Fig. 6. Dependence of charge transfer rate constant on the ionization potential difference between 1,2-DCE and the solute.
Solutes; 1: dichloromethane; 2: cyclopentane; 3: methanol; 4: ethanol; 5: nonane; 6: cyclohexane; 7: 1-pentene; 8: diethyl ether; 9: 1-hexene; 10: cyclopentene; 11: cyclohexene; 12: aniline; 13: triethylamine.

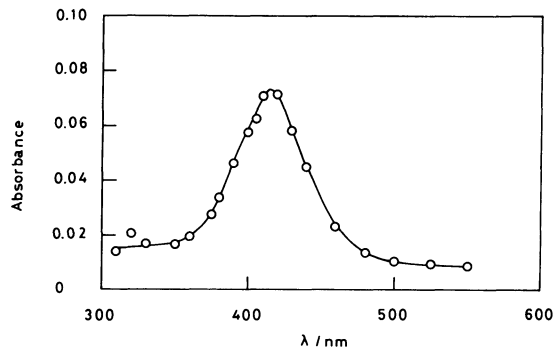

Fig. 7. The absorption spectrum obtained at 500 ns after the pulse in 2.75×10^{-2} mol dm^{-3} aniline in 1,2-DCE. Dose was 120 Gy.

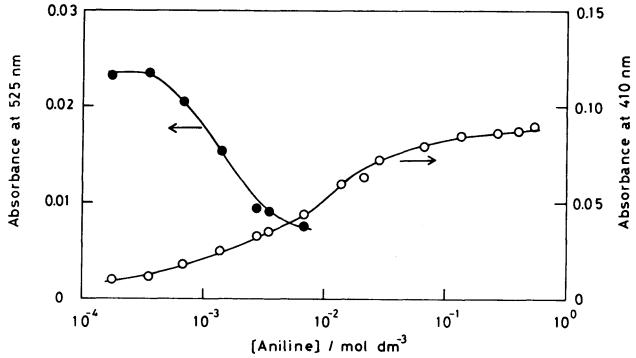

Fig. 8. Effect of aniline concentration on the absorbance at 525 nm of the 1,2-DCE radical cation and at 410 nm of the aniline cation. The absorbance was obtained at the end of pulse and 500 ns after the pulse, at 525 and 410 nm, respectively. Dose was 120 Gy. Optical path length was 1 cm.

Discussion

Assignment of the Transient Species. The transient absorbing species with a maximum at 550 nm has been observed in both ps and ns pulse radiolysis. This visible band can be assigned to 1,2-DCE radical cations based on the experimental evidence of the effects of the electron and cation scavengers on this band. This assignment is also supported by the relation between decay rate constants and the difference of ionization potential between 1,2-DCE and added solutes. The reaction rate constant of the added solute with the visible band increases with increasing difference of the ionization potential as illustrated in Fig. 6.

The $G\varepsilon$-value at 550 nm are 2.4×10^4 mol^{-1} dm^3 cm^{-1} at the end of 30 ps pulse and 1800 mol^{-1} dm^3 cm^{-1} at the end of 10 ns pulse. The higher G-value for ps pulse radiolysis and the short half lifetime of 200 ps indicate that more than 90% of primary 1,2-DCE radical cations disappears by geminate ion reactions. The faster decay observed at 400 and 650 nm during the first 120 ns is indicative of the tail of such geminate ion reactions.

The spectral shift from 550 to 500 nm in the first 120 ns can be due to the slowly decaying species with $k_3=6\times10^5$ s^{-1}. This species absorbs around 400 nm, and disappears almost completely by addition of cyclohexane larger than 5×10^{-3} mol dm^{-3}. These results show that the slow component is very reactive cationic species or has solvent cations as a precursor.

With respect to the spectral shift, it is interesting to note that the similar spectral change was observed in the case of butyl chloride cations.[6,7] Upon irradiation of butyl chloride the initial spectrum with a peak at 520 nm was obtained. However, the peak shifted to 450 nm within 80 μs at 133 K.[6] The short-lived species with a peak at 520 nm and the long-lived species with a peak at 450 nm were attributed to butyl chloride radical cations and butene radical cations, respectively. In that work, Arai et al. suggested that butene and butyl chloride cations must originate from a common precursor such as a vibrationally excited butyl chloride cations on the basis of cation scavenging experiments.

The formation of additional cationic species originating from the solvent was also suggested in the case of irradiated 1,2-DCE by Wang et al.[13] It was reported that there are two kinetically distinguishable cationic species of the 1,2-DCE solvent which react selectively with different solutes to form the phenylcarbenium ion. It was suggested that one is a 1,2-DCE radical cation and other a carbocation formed after C–Cl bond cleavage.

Therefore, we conclude that the fast decaying visible band with $k=(3.5\pm0.5)\times10^6$ s^{-1} is due to the 1,2-DCE radical cation and the slowly decaying visible band with $k=6\times10^5$ s^{-1} might due to cationic species such as CH_2CHCl^+ and $CH_2ClCH_2^+$ originates from 1,2-DCE.

The UV band with a peak at 270 nm was formed during and after pulse then decayed with a second-order reaction. This band can be ascribed to radicals which are produced by the dissociative electron attachment (reaction 1) and reactions of solvent cations such as deprotonation (reaction 2) and ion-molecular reactions (reaction 3).

$$CH_2ClCH_2Cl + e^- \longrightarrow CH_2ClCH_2\cdot + Cl^- \quad (1)$$

$$CH_2ClCH_2Cl^+ \longrightarrow CH_2ClCHCl\cdot + H^+ \quad (2)$$

$$CH_2ClCH_2Cl^+ + CH_2ClCH_2Cl \longrightarrow CH_2ClCH_2ClH^+ + CH_2ClCHCl\cdot \quad (3)$$

Yield of Solvent Cations. Wang et al.[13] estimated the yield of 1,2-DCE cations to be $G=0.87$ based on the yields of phenylcarbenium ions. The yield of solvent cations determined in the present experiment from the limiting absorbance of aniline cation radicals was $G=2.8$. Three times difference of cation yields can not be explained in the present situation. Since the extinction coefficient of the aniline cation radical was determined in water,[18] there might be a changing of the value depending on solvents. Also we have to consider the efficiency of cation scavenging. Since the yields of phenylcarbenium ion varies from $G=0.18$ to 0.87 depending on the solutes,[13] the solutes which were used by Wang et al. might be less effective than aniline to scavenge the solvent cation radical. Further experiments with various cation scavengers which have a well-defined extinction coefficient of cations are needed.

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References

1) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2369 (1966).
2) S. Arai, H. Ueda, R. F. Firestone, and L. M. Dorfman, *J. Chem. Phys.*, **50**, 1072 (1969).
3) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 4372 (1966).
4) R. Mehnert, O. Brede, J. Bös, and W. Naumann, *Ber. Bunsenges. Phys. Chem.*, **83**, 992 (1979).
5) T. Sumiyoshi, S. Sawamura, Y. Koshikawa, and M. Katayama, *Bull. Chem. Soc. Jpn.*, **55**, 2341 (1982).
6) S. Arai, A. Kira, and M. Imamura, *J. Phys. Chem.*, **80**, 1968 (1976).
7) R. Mehnert, O. Brede, and W. Naumann, *Ber. Bunsenges. Phys. Chem.*, **86**, 525 (1982).
8) T. Sumiyoshi, T. Yamada, A. Ohtaka, K. Tsugaru, and M. Katayama, *Chem. Lett.*, **1986**, 307.
9) J. Mönig, K-D. Asmus, L. W. Robertson, and F. Oesch, *J. Chem. Soc., Perkin Trans. 2*, **1986**, 891.

10) Y. Kondo, M. Aikawa, T. Sumiyoshi, M. Katayama, and J. Kroh, *J. Phys. Chem.*, **84**, 2544 (1980).
11) E. M. Fielden and N. W. Holm, "Manual on Radiation Dosimetry," ed. by N. M. Holm and R. J. Berry, Marcel Dekker, New York (1970), p. 261.
12) T. Sumiyoshi, K. Tsugaru, T. Yamada, and M. Katayama, *Bull. Chem. Soc. Jpn.*, **58**, 3073 (1985).
13) Y. Wang, J. J. Tria, and L. M. Dorfman, *J. Phys. Chem.*, **83**, 1946 (1979).
14) K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, "Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules," Japan Scientific Societies Press, Tokyo (1981), p. 92.
15) R. Cooper and J. K. Thomas, *Adv. Chem. Ser.*, **82**, 351 (1968).
16) R. E. Bühler and B. Hurni, *Helv. Chim. Acta*, **61**, 90 (1978).
17) H. D. Burrows, D. Greatorex, and T. J. Kemp, *J. Phys. Chem.*, **76**, 20 (1972).
18) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963).
19) R. Cooper and J. K. Thomas, *J. Chem. Phys.*, **48**, 5103 (1968).