Pulse Radiolysis-Laser Flash Photolysis Study of Xanthene in 1,2-Dichloroethane/Carbon Tetrachloride

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The photochemistry of 9-xanthenyl radicals produced by pulse radiolysis of xanthene in 1,2-dichloroethane (1,2-DCE) and CCl_4 was studied by means of successive laser flash photolysis. Photobleaching due to chlorine atom transfer from solvents to the excited 9-xanthenyl radical was observed with quantum yields of 0.04 and 0.29 in 1,2-DCE and CCl_4, respectively.

Combined pulse radiolysis-laser flash photolysis techniques are powerful tool to investigate the photochemistry of short-lived transient species such as radicals,[1] radical ions[2] and π-complexes.[3] Xanthene has been used as one of efficient hydrogen donors,[4] and the photochemical studies have been carried out extensively.[5-8] However, photochemical reactions of the resulting 9-xanthenyl radical have not been reported so far. Pulse radiolysis is a convenient method to produce transient species if adequate solvents were chosen. In the present study, 1,2-DCE was used to produce solute cations,[9] and CCl_4 was used as a Cl atom source.[10] Xanthene was recrystallized from ethanol and 1 x 10^{-3} mol dm^{-3} solutions were deaerated by bubbling with argon before irradiation. Successive electron pulse irradiation and flash photolysis were carried out by the pulse radiolysis-laser flash photolysis system with a time resolution of 10 ns described before.[3]

Figure 1 shows transient absorption spectra observed at 50 ns and 4 μs after irradiation of xanthene in 1,2-DCE with a 30 ns, 45 MeV electron pulse. The UV-Vis absorption bands at 50 ns (340 and 940 nm) can be easily characterized as those due to the xanthene radical cation ($XH^{\cdot+}$).[11] After 4 μs, these bands disappeared and a new band at 340 nm was formed. The inset of Figure 1 illustrates the decay of $XH^{\cdot+}$ at 900 nm and grow-in of the 340 nm band. The 340 nm band can be assigned to 9-xanthenyl radicals ($X\cdot$)[6] which was produced via deprotonation of $XH^{\cdot+}$ as shown in Eq. 1. The deprotonation

$$XH^{\cdot+} \longrightarrow X\cdot + H^+ \qquad (1)$$

of $XH^{\cdot+}$ has been reported for the photolysis of xanthene in H_2O/CH_3CN in the presence of *p*-nitrobenzoic acid[7] and for the photobleach[11] and annealing[8] of $XH^{\cdot+}$ in low temperature glassy matrices. On the other hand, the radical cation was not produced upon irradiation of xanthene in CCl_4. Nevertheless, the 9-xanthenyl radical was produced directly via hydrogen abstraction by chlorine atoms in CCl_4 (Eq. 2).

$$XH + Cl \longrightarrow X\cdot + HCl \qquad (2)$$

Figure 2 shows kinetic traces obtained by pulse radiolysis-laser flash photolysis of xanthene in 1,2-DCE/CCl_4 (0, 50, and 100 vol% CCl_4). Laser flash photolysis (6 ns width pulses of 337.1 nm from an N_2-laser) caused rapid and permanent photobleaching of $X\cdot$. Actinometry was performed with solutions of benzophenone (1.0 x 10^{-3} mol dm^{-3}) containing

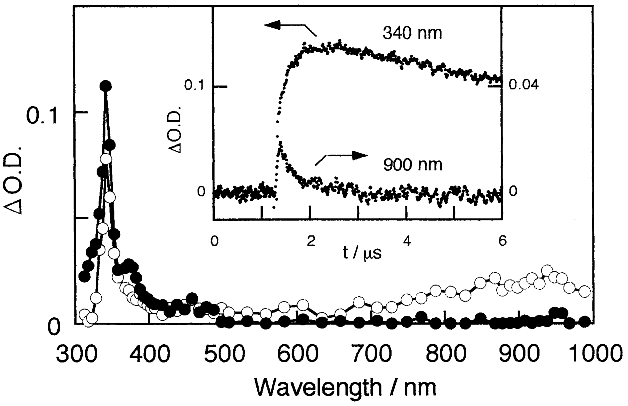


Figure 1. Transient absorption spectra observed at 50 ns (○) and 4 μs (●) after pulse radiolysis of 1 x 10^{-3} mol dm^{-3} xanthene in 1,2-dichlororethane. Inset shows the changes in the absorbances at 340 and 900 nm after pulse radiolysis.

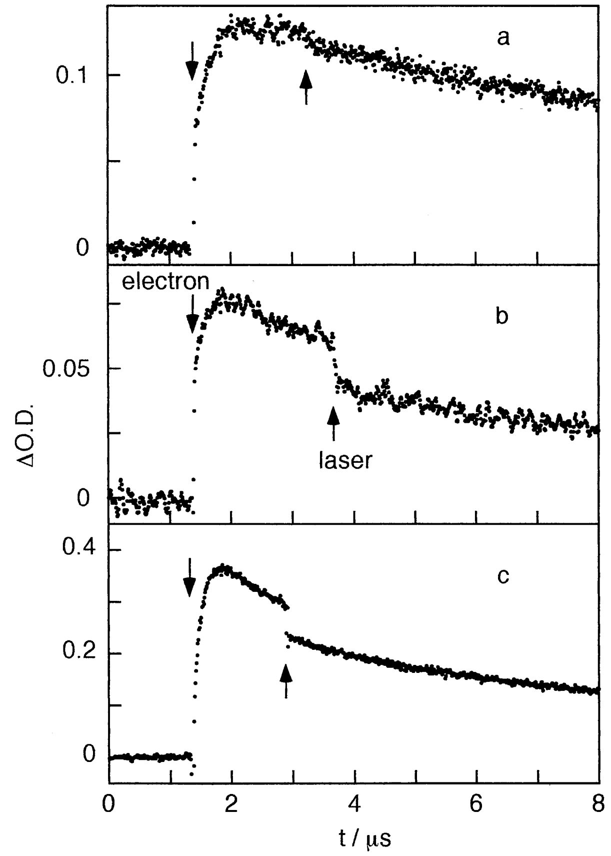


Figure 2. Kinetic traces observed at 348 nm by combined pulse radiolysis-laser flash photolysis of 1 x 10^{-3} mol dm^{-3} xanthene in 1,2-DCE (a), 50% CCl_4 (b), and CCl_4 (c).

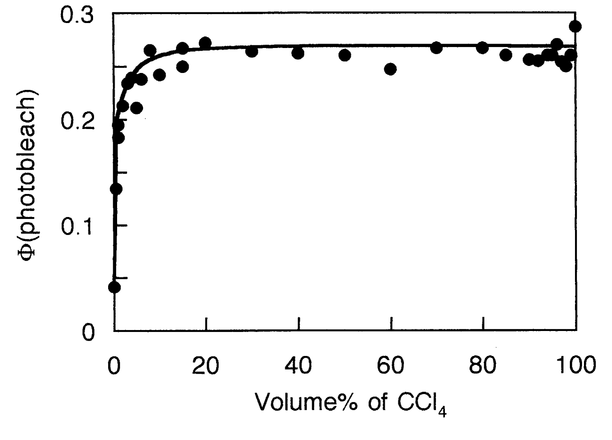
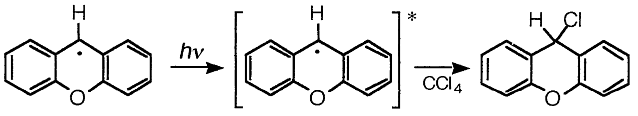


Figure 3. Quantum yields of photobleaching of 9-xanthenyl radicals in 1,2-DCE / CCl_4 at different volume percents of CCl_4.

naphthalene (1.0 x 10^{-1} mol dm^{-3}), and the extinction coefficients ($\varepsilon_{337\ nm}$ = 20700 and $\varepsilon_{348\ nm}$ = 22000 dm^3 mol^{-1} cm^{-1}) of X· in CCl_4 were estimated assuming the radiation chemical yield of the chlorine atom in CCl_4 to be 0.17 μmol J^{-1} as described previously.[3] The quantum yields of photobleaching thus obtained were 0.04, 0.26, and 0.29 for 0, 50, and 100 vol% CCl_4, respectively. The effects of CCl_4 on the quantum yields of photobleaching of X· were investigated in detail and are illustrated in Figure 3. The quantum yields of photobleaching increased significantly on addition of small amount (< 5 vol%) of CCl_4 and reached a plateau value of 0.26 at 10% CCl_4. This constant value of quantum yields in the wide range of 1,2-DCE concentration indicates that 1,2-DCE does not quench the excited 9-xanthenyl radical. Both dimerization of X· which results in 9,9'-bixanthyl[7] and electron transfer from X· leading to the closed-shell cation formation[8,12] have been reported for the ground state X·. However, these types of reactions can be ruled out in the case of the excited X· on the basis of the solvent dependent photobleaching quantum yields and the fact that the photobleaching of X· is not accompanied by an occurrence of transient absorption of xanthyl cation at around 380 nm.[8,12] Since the present experimental results suggest the significant role of CCl_4 for the photobleaching of X·, it appears probable that the photobleaching observed in the this work is due to chlorine atom transfer from the solvent to the excited 9-xanthenyl radicals as shown in the following scheme.



Scheme 1.

Such a photochemical process in CCl_4 was reported previously for the reaction of the excited diphenylmethyl radical and a charge-transfer mechanism leading to halogen atom transfer was suggested.[13] Chlorine atom transfer from 1,2-DCE to the excited 9-phenylxanthenyl radical has been also documented.[14] However, the present results revealed a significant difference in the photobleaching quantum yields in CCl_4 and 1,2-DCE. Since the smaller value of electron affinity and the larger C-Cl bond dissociation energy than those of CCl_4 are expected for 1,2-DCE,[15] 1,2-DCE should be a less efficient reactant for the above photoreaction.

References and Notes

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