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Transient Species in Picosecond Pulse Radiolysis of Liquid Carbon Tetrachloride

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Formation and decay of transient species produced in pure liquid carbon tetrachloride by ionizing radiation were studied by using a stroboscopic pulse radiolysis technique in the time region 35—350 ps. Optical absorption spectra show two principal bands. One narrow band centered at 325 nm, which is formed during each fine structure electron pulse and decayed after pulse with $t_{1/2}=6.5$ ns, is attributed to CCl_4^+ cation. The other broad band centered at 470 nm built up after electron pulse is assigned to $(CCl_4^+\cdot Cl^-)$. A consideration on effects of cation scavengers on these bands furnishes a support for the above assignment.

Radiolysis of carbon tetrachloride in the condensed phase has been studied extensively over the past fifteen years. This is mainly because the comparatively high ionization potential of carbon tetrachloride ($I_p(CCl_4)=$ 11.47 eV) makes the carbon tetrachloride cation (CCl_4^+) quite suitable for transfer of a positive charge to a solute molecule. Optical spectra of a wide variety of solute cations have been obtained by the matrix isolation[1,2] and pulse radiolysis methods.[3,4] In pure CCl_4 and solutions of CCl_4 in alkane and argon matrices, many attempts have been made to establish the nature of primary species involved by means of low-temperature matrix isolation[1,5,6] and pulse radiolysis.[7—9] Both experiments revealed characteristic absorption bands with maxima located in two wavelength regions around 320—370 and 400—500 nm. However, the assignment of these absorption bands is not satisfactory as described below. Both the 367 nm band[5] observed in γ-radiolysis studies of CCl_4 in alkane hydrocarbons at 77 K and the 340 nm band[8] observed by pulse radiolysis on pure CCl_4 at 20 °C were assumed to be due to CCl_4^+. On the other hand, the band centered at 330 nm was assigned to dichlorocarbene radical (CCl_2) on the basis of an *ab initio* SCF CI study.[10] An earlier γ-radiolysis work with polycrystalline CCl_4 at 77 K revealed an absorption at 400 nm, which was assigned to positive hole.[1] Also, a spectrum of CCl_4, observed in an argon matrix at 25 K after argon discharge photoionization, exhibited a broad absorption at 425 nm,[6] which was assigned to CCl_4^+ cation since cation infrared absorptions in similar experiments exhibited the same photolysis behavior. On the contrary, both the broad absorption band centered around 470 nm,[5] observed in a γ-irradiated sample of CCl_4 in alkane hydrocarbons at 77 K, and the short-lived absorption band, observed at 480 nm[8] in an ns pulse radiolysis of CCl_4 at 20 °C, were assigned to a complex $(CCl_4^+\cdot Cl^-)$. A 500 nm band observed in a pulse irradiated liquid CCl_4 at −22 °C was assigned to another type of complex $(CCl_3^+\cdot Cl^-)$ on the basis of cation scavenger studies;[7,11] however, an *ab initio* configuration calculation[12] predicted no stability for any isolated contact ion-pairs between CCl_3^+ and Cl^-. We have constructed a stroboscopic pulse radiolysis instrument with time resolution of picoseconds and applied it to studying transient absorptions obtained in the pulse radiolysis of liquid CCl_4. By means of this instrument, it is possible to observe the formation and decay kinetics in the time region of 35—350 ps from the beginning of pulse.

The stroboscopic pulse radiolysis system was first designed and built by Bronskill *et al.*[13] Using 35 ns pulses from an S-band linear accelerator (LINAC) and a conventional photomultiplier optical detection system, they were able to study reactions of solvated electrons,[14] dry electrons,[15] and solvation of electrons in alcohols[16] in the time region of 20—350 ps. Jonah[17] applied this technique to a single picosecond pulse from an L-band LINAC[18] and was able to study similar aqueous systems in the time range 100 ps to as long as 3.5 ns after irradiation.[19,20] A distinct contribution of his method is that it has removed the upper limit on observation time (350 ps for an S-band LINAC and 770 ps for an L-band LINAC), which has inevitably accompanied experimental works using a train of fine structure pulses.

The present experiments were carried out with a 45 MeV S-band LINAC with no subharmonic prebuncher. Although the stroboscopic method using a train of electron pulses is essentially accompanied by a long time limit as mentioned above, it is capable of providing a good time resolution (≈20 ps) even with a conventional photomultiplier detection system.[13]

Experimental

Stroboscopic Pulse Radiolysis System. The stroboscopic pulse radiolysis system is shown in Fig. 1. The radiation source is 11 ns, 45 MeV electron pulse from the S-band LINAC installed in Hokkaido University. This 11 ns electron pulse consists actually of a train of fine structure pulses with time intervals of 350 ps. Simultaneous flashes of Čerenkov light are produced by these fine structure electron pulses in a 10 cm air path between the LINAC and a thin mirror. These light flashes are delayed 0.87 to 1.80 ns by a system of mirrors and are used as analyzing light flashes to observe absorption signals in irradiated samples. Čerenkov light has a continuous spectrum and is radiated outward from the path of 45 MeV electrons with an angle of 1.2°. A conical-shaped (axicon) lens was used to refract this conical beam of Čerenkov light into a pseudo-parallel beam.

In the stroboscopic pulse radiolysis system, three types of signals are required to obtain the absorption signal (S).[13] The electron beam and analyzing light are mechanically chopped to produce the three types of signals A, B, and C as illustrated in Fig. 2. Signal A is the sum of the analyzing light decreased in intensity by the absorption in the cell and the background Čerenkov light. Signal B consists of only the Čerenkov

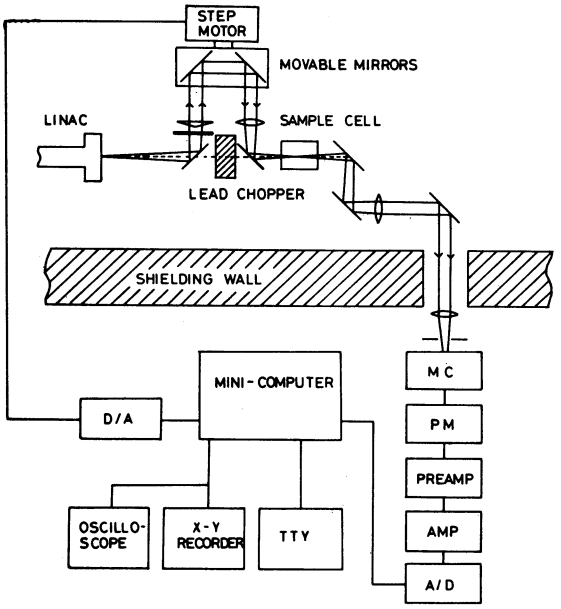

Fig. 1. Stroboscopic picosecond pulse radiolysis system. MC: Monochromator, PM: photomultiplier.

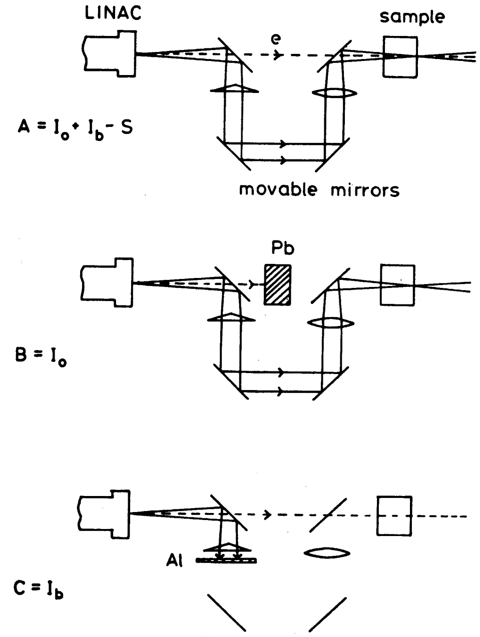

Fig. 2. Three types of Čerenkov light signals obtained by rotating the aluminum light chopper and the lead beam chopper.

analyzing light, and signal C consists of the background Čerenkov lights produced in and near the sample cell. The absorption signal can be obtained by addition and subtraction of these signals, *i.e.*,

$$S = B + C - A,$$

and the percent absorption is calculated as

$$(S/B) \times 100\,\%.$$

These three signals are produced sequentially at the rate of 50 Hz with line-locking to minimize 50 Hz ripple effects in the LINAC and detection system.

Detection System. The three types of light pulses are detected by a system which consists of a monochromator

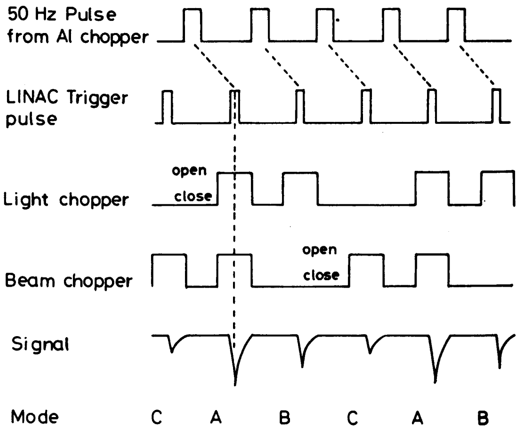

Fig. 3. Pulse timing sequence of the stroboscopic pulse radiolysis system.

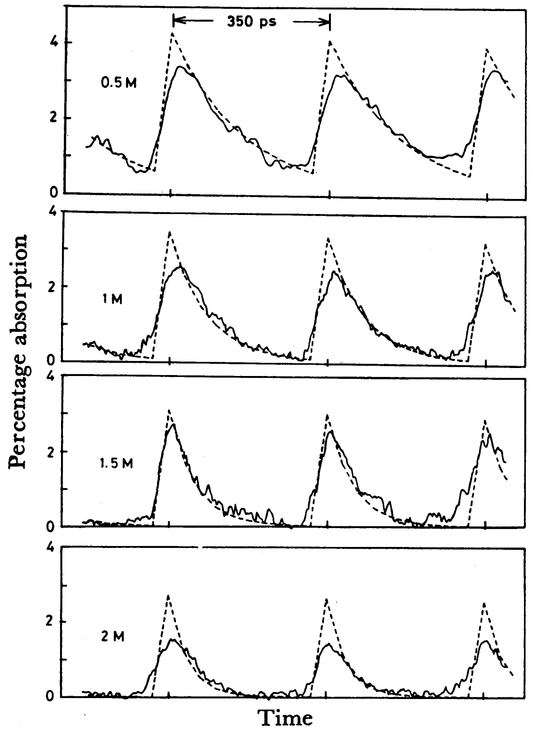

Fig. 4. Formation and decary of e_{aq}^- in 0.5—2 M $HClO_4$ (1 M = 1 mol dm^{-3}) solutions as observed at 633 nm. The dashed lines are simulated traces.

(Bausch & Lomb), a photomultiplier (Hamamatsu TV Co., R446UR), a preamplifier, an amplifier (ORTEC 451), and an A/D converter (NAIG D-161). The photomultiplier was used in a five-stage configuration that had a linear response of up to 4 mA with a rise time of less than 3 ns. The linearity of the detection system was carefully checked by using pulses from a pulse generator and actual, well-known absorption signals, as will be described in the following section. The output signal from the A/D converter is fed into an on-line minicomputer (TACC 1200M) and stored before arrival of the next signal. Both the averaging of signals and the operation of the movable mirrors in the optical delay system are performed by a minicomputer. The timing sequence for synchronization of pulses and choppers is shown in Fig. 3.

Linearity and Time Resolution. Observation on the formation and decay of e_{aq}^- and Br_2^- was carried out as a critical check on the performance of the stroboscopic pulse radiolysis system. Linearity was tested by use of the baseline and the first-order decay of e_{aq}^- in concentrated $HClO_4$ solutions. Results obtained at 633 nm in solutions of 0.5—2 M $HClO_4$ are shown in Fig. 4. The baseline approaches a near-zero level with increasing concentration of H_{aq}^+ as expected. The dashed lines in Fig. 4 are results from a computer simulation for the first order decay of e_{aq}^-. In these calculations it is assumed that a value of ε_{633nm} is 1.44×10^4 M^{-1} cm^{-1} for e_{aq}^-,[21] and the decay of e_{aq}^- during the electron pulse is taken into account. Agreement on the decay traces is quite satisfactory. The rate constant was calculated to be $(1.2\pm 0.06)\times 10^{10}$ M^{-1} s^{-1}, which is in good agreement with the reported value of $(1.2\pm 0.2)\times 10^{10}$ M^{-1} s^{-1} over the range of 0.5—5 M H_{aq}^+ by Bronskill *et al.*[22] A further test on the linearity of the detection system was carried out in the ultraviolet region. Figure 5 shows kinetic traces for the formation of Br_2^- at 360 nm in 0.5—2 M NaBr aqueous solutions. Both a fast and a slow component are shown, along with the contribution of the fast component, to increase with increasing NaBr concentration. These results are quite similar to those reported by Hunt *et al.*,[23] who suggested that the fast component is due to reactions of dry hole (H_2O^+) and Br^-:

$$H_2O^+ + Br^- \longrightarrow Br + H_2O,$$

followed by reaction

$$Br + Br^- \longrightarrow Br_2^-.$$

The observed rise time (10—90%) for the formation of hydrated electron in Fig. 4 is about 35 ps. Since the formation time of e_{aq}^- has been estimated to be less than 10 ps,[22] this rise time is attributed mainly to the following two factors: One is the width of fine structure electron pulses. The width of the fine structure pulse observed with a streak camera system (Hamamatsu TV Co., HTV-C979X) having a rise time of 10 ps is approximately 39 ps (FWHM), which is longer than the observed rise time of e_{aq}^-. It is thus thought that the real pulse width is less than 30 ps. The other factor is the desynchronization of pulses, which is due to different velocities of the high energy electrons and analyzing light in water. The 45 MeV electron pulse moves with a velocity close to that of light *in vacuo*, while the analyzing light moves more slowly with a velocity of c/n, where n is the index of refraction of light in solution and c is the velocity of light *in vacuo*. The desynchronization of pulses is given by

$$\Delta t = (n-1)l/c,$$

where l is the length of cell. The time difference of a 2 cm path in water is 21 ps. A shorter optical path is desirable for faster detection, though it will possibly decrease the absorption signal.

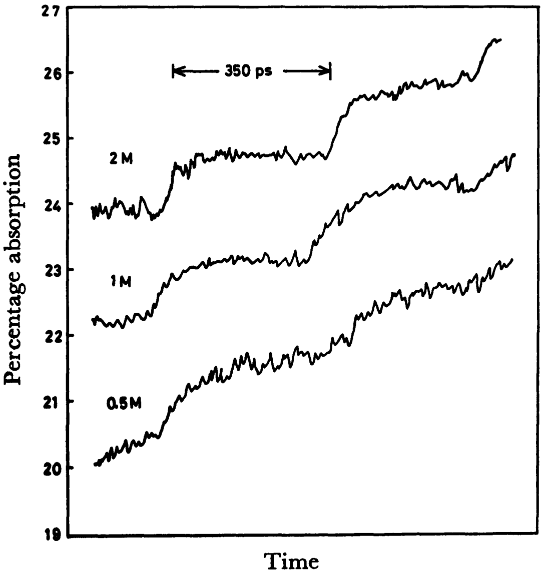

Fig. 5. Formation of the absorption signal of Br_2^- in 0.5—2 M NaBr at 360 nm.

Chemicals and Flow System. The chemicals used were NaBr, 60% $HClO_4$, cyclohexane, and CCl_4 (Wako Junyaku), and all were used without further purification since on the experimental time scale, any small amounts of impurities would have a negligible effect. Aqueous solutions were prepared with triply distilled water.

Experiments were carried out in a 2 cm sample cell which connects to a 1 dm^3 sample reservoir and a pump. To prevent buildup of heat and radiolytic products, the sample was circulated at 160 ml/min. No attempt was made to degas the sample solution since on the experimental time scale, O_2 is known to have no effect on experiment results in aqueous solutions[22] or in pure CCl_4.[8] All experiments were carried out at room temperature 15—20 °C.

Results

Kinetic Traces. Figure 6 shows typical kinetic absorption traces in pure CCl_4 at 320, 350, and 480 nm. These traces were obtained by averaging more than 30 runs including those conducted on different days and by applying correction for variation in irradiation doses. There appear to be at least two different main formation processes of transient species. The absorption at 320 nm grows only during the irradiation of fine structure electron pulses and decays after the pulse, while the absorption at 480 nm grows after the pulse. The trace at 350 nm shows a rather fast buildup and a slow one, and sould consist of a set of contributions from the two

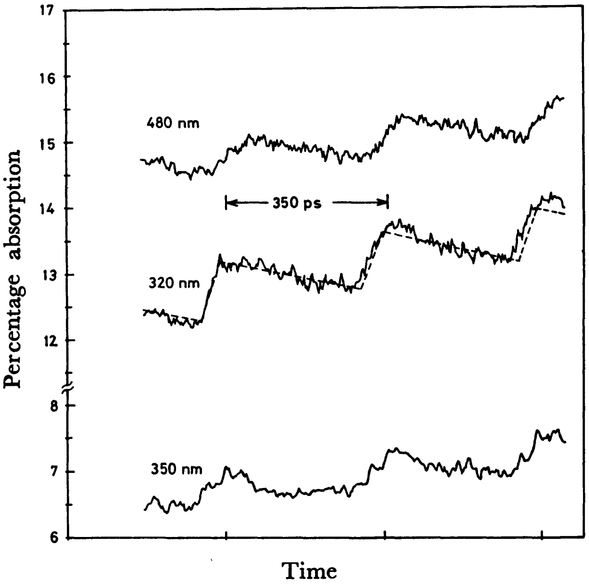

Fig. 6. Kinetic traces of the formation of the transient species observed at 320, 350, and 480 nm in CCl_4. The dashed line is a simulated trace with $t_{1/2}=6.5$ ns.

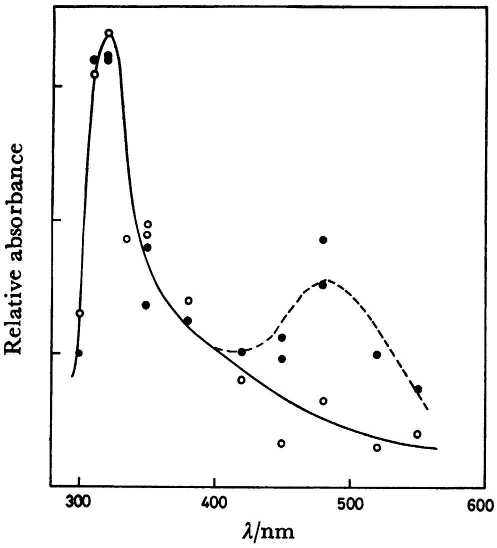

Fig. 7. Spectra of transient species in CCl_4.
○: Immediately after pulse, ●: 100 ps after pulse.

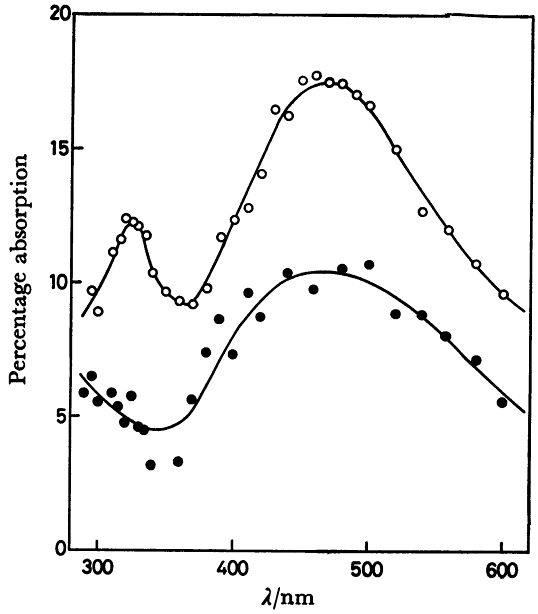

Fig. 8. Buildup spectra of CCl_4.
○: Pure CCl_4, ●: 0.5 M cyclohexane in CCl_4.

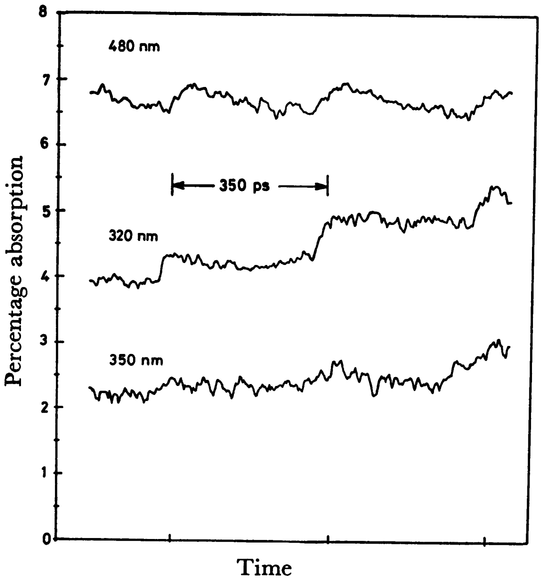

Fig. 9. Kinetic traces of the formation of the transient species observed at 320, 350, and 480 nm in 0.5 M cyclohexane in CCl_4.

components described above. The dashed line is a result from computer simulations of kinetic traces at 320 nm. The simulations were done assuming a first-order decay and a contribution from only one transient species. The best fitted curve was obtained when the half-life time and $G \times \varepsilon$ were assumed to be 6.5 ns and 25500 M^{-1} cm^{-1}, respectively.

Spectra. Figure 7 shows absorption spectra obtained immediately after pulse (17 ps from the middle of pulse) and 100 ps after the pulse. Only the narrow band centered around 320 nm was observed immediately after pulse. In addition, at 100 ps a broad band was observed around 480 nm. Since none of the transient species observed decays considerably within 350 ps, the absorption signal produced by the fine structure electron pulse is superimposed by the background absorption shown in Fig. 6. The background absorption spectrum obtained by fixing the movable mirrors at the position nearest to the beam is shown in Fig. 8. In this spectrum two absorption bands are clearly shown and the broad band centered at 470 nm is more intense than that at 325 nm, in contrast to the spectrum at 100 ps after pulse in Fig. 7. Since in the stroboscopic method it is essential that the analyzing light is absorbed by transient species of different ages, the slower decaying species will contribute more to the background absorption. The difference between the spectra in Figs. 7 and 8 is that the former shows absorption by a fine structure pulse and that the latter shows contributions of both absorption intensity and decay rate.

Effect of Cation Scavenger. Since cyclohexane has a lower ionization potential (9.88 eV) than CCl_4, it was used as a cation scavenger.[7,8] Figure 9 shows kinetic absorption traces observed at 320, 350, and 480 nm in 0.5 M cyclohexane. Both the step height of absorption signals (the maximum absorption signal by a fine structure pulse) and the buildup absorption signal decrease to less than half of those in pure CCl_4 in Fig. 6. The buildup absorption spectrum is compared with that of pure CCl_4 in Fig. 7. The band centered at 320 nm observed in pure CCl_4 could not be observed any more, and instead the band peaked at $<$290 nm began to be observed. The latter species does not show fast decay as clearly seen in Fig. 9. From these results it is apparent that the species, having given the band at 325 nm, was scavenged more effectively than the one for 470 nm.

Discussion

Identification of the 325 nm Band. In th epresent study, observations showed that radiolysis of liquid CCl_4 initially produces a sharp band centered at 325 nm as seen in Fig. 7. This band is reduced to almost zero by addition of 0.5 M cyclohexane, which is known as a scavenger for cationic species. The residual species which peaks below 290 nm does not show any decay. It was not clear whether this species originated from CCl_4 or from cyclohexane in this experiment. The 325 nm band can be assigned to a primary cation formed in the initial act of ionization for CCl_4. This assignment is consistent with previous works in which ns pulse radiolysis and low temperature matrix were used. Mehnert *et al.*[8] observed a transient absorption which peaked at 340 nm in pure liquid CCl_4 by ns pulse radiolysis and assigned it to CCl_4^+ cation. They determined rate constants of charge transfer reaction for 17 solutes from observations on the decay of cation. Ha *et al.*[10] carried out *ab initio* configuration calculations on electronic states of the CCl_2 radical and assigned a 330 nm band obtained by a pulse radiolysis experiment to it. Their assignment is based on a kinetic behavior which indicates that the band can be due to neither a transient ion nor any of the simple radicals of Cl and CCl_3; their experimental data have not yet been published. Also, in low temperature matrix studies, the CCl_4^+ cation was observed at 400 nm in a γ-irradiated polycrystalline CCl_4 at 77 K,[1] at 367 nm in a γ-irradiated CCl_4 in alkane hydrocarbons at 77 K,[5] and at 425 nm in an argon discharge photoionization during condensation at 25 K.[6] This variation in band peaks of CCl_4^+ cation seems to depend on the nature of matrix. For example, glassy solutions of CCl_4 in alkane hydrocarbons give a band maximum similar to that obtained in pulse radiolysis experiments. It should be pointed out that in an argon matrix, CCl_4^+ has been attributed to assymmetric $Cl_2CCl_2^+$ species by Prochaska and Andrews[24] through infrared studies. They suggested that one set of two carbon-chlorine bonds involves normal electron pair bonding, whereas the other set involves electron-deficient bonding with presumably delocalized electrons around the cation center.

Identification of the 470 nm Band. The present experiments revealed that the broad absorption band at 470 nm builds up after the electron pulse and is less sensitive to the cation scavenger than the species which peaked at 325 nm. These results suggest that the corresponding species should be an electrically neutral intermediate produced by reaction of primary radiation products, though more detailed investigations are needed before a precise conclusion is reached.

Mehnert *et al.*[8] observed a similar broad band centered at 480 nm by ns pulse radiolysis at 22 °C and assigned it to a complex ($CCl_4^+\cdot Cl^-$). Also Bühler and Hurni[7] observed by ns pulse radiolysis a transient spectrum which peaked at 500 nm in CCl_4 at −22 °C and decayed with a half-life time of 33 ns. They studied effects of cation scavengers on this band and found that, though reducing the pulse end absorbance of the 500 nm band, they have no effect on the life time. They concluded that the CCl_4^+ cation must be a precursor to the 500 nm species and that the 500 nm species behaves like both cation and neutral species. They assigned the 500 nm band to another type of complex ($CCl_3^+\cdot Cl^-$) on the assumption of a very short life time of CCl_4^+ cation. Since no mass spectrum of CCl_4^+ has been observed,[25] CCl_4^+ is considered to eliminate Cl atom readily in the gas phase. In liquid phases, however, stabilization of CCl_4^+ by surrounding molecules can be expected.[5,6] Considering the life time of 6.5 ns for CCl_4^+ observed in this work, it is strongly suggested that the 470 nm band is due to rather a neutral complex ($CCl_4^+\cdot Cl^-$).

Louwrier and Hamill[5] observed an isothermal decay of 367 nm absorption and a growth of 470 nm absorption in γ-irradiation studies on solutions of CCl_4 in alkane hydrocarbons at 77 K and attributed these bands to CCl_4^+ and $CCl_4^+\cdot Cl^-$), respectively. Their observations are in good agreement with the present work.

In conclusion, the present picosecond pulse radiolysis studies have provided direct observations on the initial process in irradiated CCl_4 as follows, provided that the absorption at 325 nm can be assigned to CCl_4^+:

$$CCl_4 \rightsquigarrow CCl_4^+(325\text{ nm}) + e^-, \qquad (1)$$

and subsequent fomation of ion pairs

$$CCl_4 + e^- \longrightarrow CCl_3 + Cl^-, \qquad (2)$$

$$CCl_4^+ + Cl^- \longrightarrow [CCl_4^+\cdot Cl^-]\ (470\text{ nm}). \qquad (3)$$

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