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PICOSECOND PULSE RADIOLYSIS OF FLUOROTRICHLOROMETHANE AND BROMOTRICHLOROMETHANE

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Transient species in the radiolysis of $CFCl_3$ and $CBrCl_3$ was studied by stroboscopic picosecond pulse radiolysis. Two principal bands in the UV and Vis region were observed in both samples and identified as cations and charge transfer complexes of parent cations and halogen anions respectively.

Halomethanes have been used as a suitable solvent to transfer the positive charge to solute molecules with a lower ionization potential than their own.[1,2] However, the nature of their cationic species has not been well understood until now. Pulse radiolysis with picosecond time resolution can provide direct information about the elementary processes of radiation chemistry of halomethanes. In a previous paper, the transient species produced in CCl_4 was described in detail.[3] The present paper describes the formation kinetics and spectra of transient species produced in $CFCl_3$ and $CBrCl_3$ at room temperature. The experiments were carried out with a stroboscopic pulse radiolysis system using 11 ns pulses of 45 MeV electrons.[3] $CFCl_3$ and $CBrCl_3$, purchased from Tokyo Kasei, were the guaranteed reagents; they were used without further purification. The observation time was 35–350 ps from the beginning of the electron pulse because of the utilization of the interval of the fine structure electron pulse from an S-band LINAC. The kinetic traces obtained at 305 and 430 nm in $CFCl_3$ are shown in Fig. 1. Since the decay of the transient species is not completed in 350 ps, the absorption signal produced by each fine structure electron pulse is obtained superimposed on the buildup absorption level. Similar formation processes are observed at 375 and 610 nm in $CBrCl_3$ as shown in Fig. 2. The buildup spectra of both samples are shown in Fig. 3. The maxima of absorption are 305 and 430 nm in $CFCl_3$ and 360 and 520 in $CBrCl_3$. In the previous experiments, two absorption bands were observed in CCl_4 at 325 and 480 nm; they were assigned to CCl_4^+ and a charge transfer complex $[CCl_4^+ \cdot Cl^-]$ respectively.[3] The parallel shift of absorption bands in the UV and Vis region for $CFCl_3$ (305,430 nm), CCl_4 (325,480) and $CBrCl_3$ (360,520), and the fast and slow formation kinetics observed, indicated that the 305 and 360 nm bands of $CFCl_3$ and $CBrCl_3$ are assigned to parent cations, and the 430 and 520 nm bands of $CFCl_3$ and $CBrCl_3$ are assigned to CT complexes $[CFCl_3^+ \cdot Cl^-]$ and $[CBrCl_3^+ \cdot Br^-]$ respectively. Since cations do not show any fast decay during the formation of CT complexes, the presence of excited cations of parent halomethanes is strongly suggested. The following processes are

proposed to explain the present picosecond experimental results:

$$CFCl_3 \longrightarrow CFCl_3^+ + e \quad (1)$$

$$e + CFCl_3 \longrightarrow CFCl_2 + Cl^- \quad (2)$$

$$CFCl_3^+ + Cl^- \longrightarrow [CFCl_3^+ \cdot Cl^-]. \quad (3)$$

The excited cation CCl_4^+ in nanosecond pulse radiolysis has been suggested previously by Brede et al.[4] Further investigations on the nature of halomethane cations are being carried out to obtain a more detailed understanding of the primary processes involved.

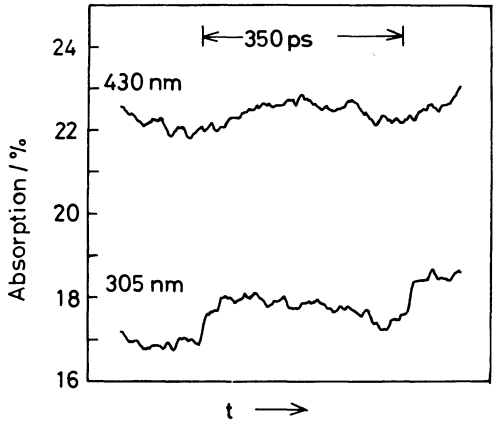

Fig. 1. Kinetic traces observed in $CFCl_3$.

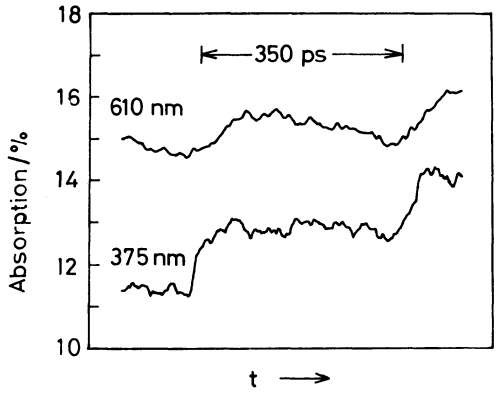

Fig. 2. Kinetic traces observed in $CBrCl_3$.

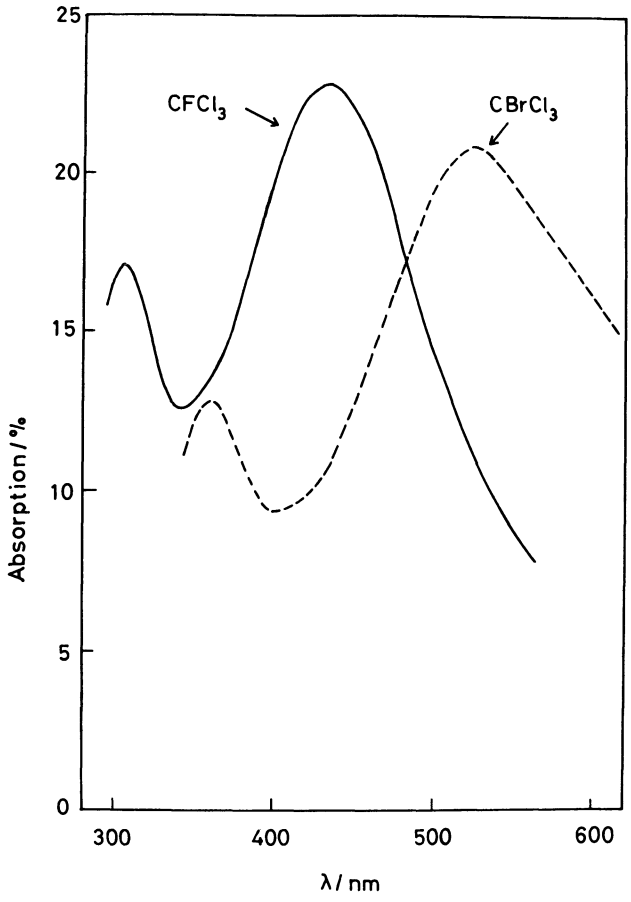

Fig. 3. Buildup spectra of $CFCl_3$ and $CBrCl_3$.

References

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