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PICOSECOND PULSE RADIOLYSIS STUDIES OF THE SHORT LIVED CATION PRODUCED IN BUTYLCHLORIDE AND BUTYLBROMIDE

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Transient species produced in neat butylchloride and butylbromide were observed by means of picosecond pulse radiolysis. The visible band which was produced during electron pulse and then decayed with a half lifetime of 2 ns was assigned to a vibrationally excited cation.

Butylchloride has been used as one of the suitable solvents to produce solute cations by charge transfer for its high ionization potential (10.67 eV).1,2) Pulse radiolysis studies at low temperature in the μs time range3) and at room temperature in the ns time range2) have been carried out. However, the nature of the solvent cations has not been well understood so far. Because of the short lifetime of cations in the liquid phase, the picosecond pulse radiolysis technique should provide important information on the behavior of cations in the very early stage after the irradiation. We studied the kinetic behavior of cations in the ps and ns time regions and found fast decaying cations which have much shorter lifetime than that observed in the ns pulse radiolysis.

Butylchloride and butylbromide used were guaranteed reagents of Tokyo Kasei and were purified by distillation. The stroboscopic picosecond pulse radiolysis system4) and the conventional ns one5) were described earlier. The absorbed dose was measured by the KCNS dosimeter6) for ns macro pulse and by the aqueous electron dosimeter for picosecond fine structure electron pulse using $G(e_{aq}^{-})$ at 30 ps as 4.8.7)

Figure 1 shows typical picosecond kinetic traces observed in neat butylchloride at indicated wavelengths. Since the decay of the transient species is not completed between fine structure electron pulses (350 ps), the absorption signal produced by each fine structure pulse indicated as h is superimposed on the buildup absorption indicated as H. Dashed lines are computer simulated kinetic traces. The simulation was carried out to obtain the best fit for h, H and the slope of traces. All kinetic traces could be reproduced by a single exponential decay with a half lifetime of 1.7 ± 0.3 ns, and estimated $G\varepsilon$ values were 11000, 14000, and 9000 at 450, 520, and 630 nm, respectively.
Figure 2 shows the buildup spectrum (H) and step signal (h) produced by fine structure electron pulses with a half width of 30 ps. Both spectra with peaks at

500 nm are quite similar to those reported already[1-3] and could be assigned to parent cations. On the contrary, the present ns pulse radiolysis experiment shows that the transient absorption with a maximum at 500 nm decays with a half lifetime of 50 ns which is in good agreement with that observed by Mehnert et al.[2] Further, the Gε value at 500 nm in ns pulse radiolysis was about 2000 $M^{-1}cm^{-1}$.

Figure 3 shows buildup spectra of butylbromide indicating two absorption peaks at 390 and 600 nm which are in good agreement with the spectrum observed by the ns pulse radiolysis. Gε values and half lifetimes obtained in the ns pulse radiolysis are given in Table 1. Figure 4 shows ps kinetic traces of butylbromide. The kinetic trace at 600 nm was reproduced by a single exponential decay with a half lifetime of 2 ± 0.2 ns. On the other hand, traces at 390 and 450 nm could be simulated by assuming two components which are given in Table 2. Dashed lines in Fig. 3 were estimated buildup spectra of two components. The band at 380 nm with the half lifetime of 4 µs can be assigned to Br_2^-.[8] And the visible band at 600 nm with the half lifetime of 2 ns can be assigned to parent cations.[3,8]

Present experimental results of both butylhalides can be better explained by the existence of vibrationally excited butylhalide cations as suggested in the low temperature pulse radiolysis experiment.[3] The observation of rapid formation of

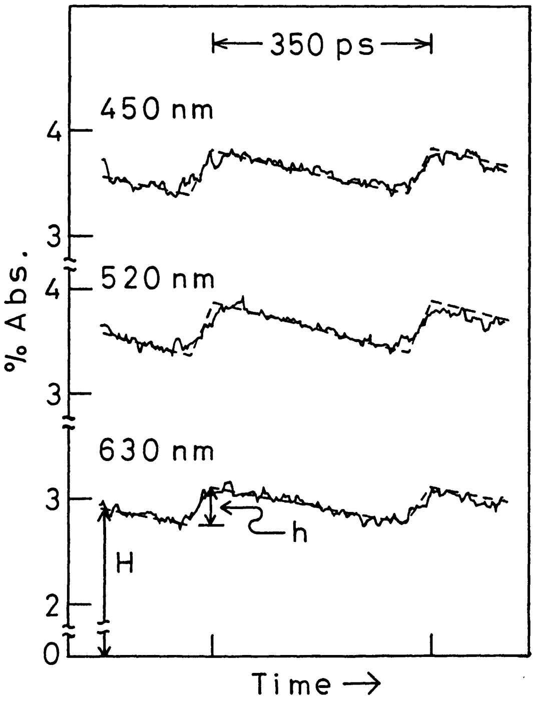

Fig. 1. Picosecond kinetic traces observed 450, 520, and 630 nm in neat butylchloride at room temperature. Dashed lines are simulated traces.

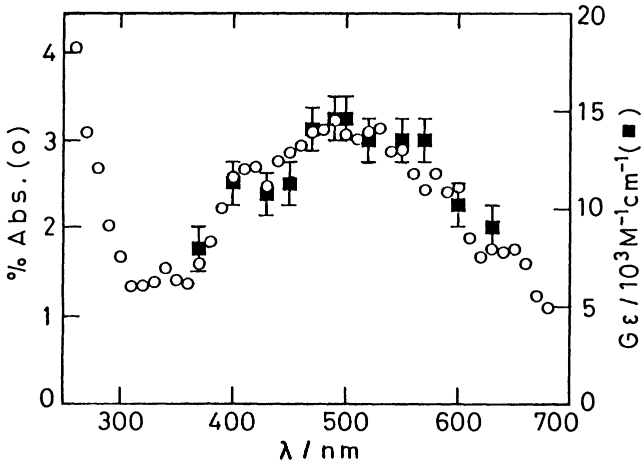

Fig. 2. The buildup spectrum (o) and the spectrum produced by fine structure pulse (■) in butylchloride.

Table 1. Gε and Half Lifetimes Observed by Nanosecond Pulse Radiolysis of Butylbromide

λ/nm	Gε	$T_{1/2}$
380	10000	4 μs
450	4500	2.3 μs
590	2500	100 ns

Table 2. Gε Values Obsreved by Picosecond Pulse Radiolysis of Butylbromide

λ/nm	$T_{1/2}$ = 2 ns	$T_{1/2}$ = 4 μs
390	5000	10000
450	9000	4000
600	17000	0

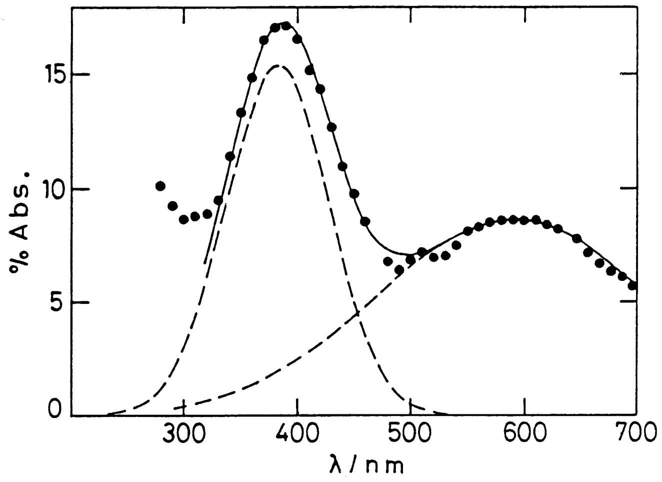

Fig. 3. Buildup spectra of butylbromide. Dashed lines are estimated two components.

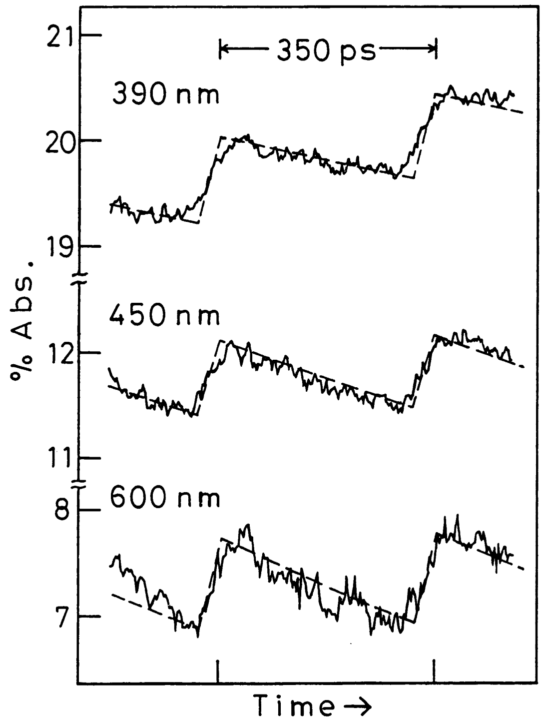

Fig. 4. Kinetic traces observed at 390, 450, and 600 nm in butylbromide at room temperature. Dashed lines are simulated traces with parameters given in Table 2.

visible bands (<30 ps), excludes the contribution of an ion-pair intermediate such as ($BuCl^{+}\cdots{}^{-}Cl$) which was suggested by the analogy of radiolysis of other alkyl halides.[2] The low Gε value and the relatively long half lifetime of cations observed in ns pulse radiolysis suggested that a part of vibrationally excited cations might be deactivated to the ground state. The existence of vibrationally excited cations has been also suggested in a series of picosecond pulse radiolysis experiments of alkyl halides and alkanes.[9-11] However, the contribution of spur reactions of ground state cations cannot be excluded.

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