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Ultrafast One-Photon (232 vs 266 nm) Bond-Selective Photochemistry of Bromoiodomethane (CH_2BrI) in Solution

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Abstract. Ultrafast broadband transient absorption spectra measured from the deep-ultraviolet to the near-infrared region following single-photon excitation of bromoiodomethane in acetonitrile at different wavelengths manifest chromophore - selective structural rearrangement and carbon-halogen bond dissociation in solution.

The control over photochemistry is possible, if one can manipulate the superposition of molecular vibrational or electronic states created by ultrafast laser excitation, the molecular chemical design, and the environment. For polyatomic molecules in solution, where most chemistry occurs, this is a challenging task because of the complexity and the lack of detailed understanding about such systems. CH_2BrI has two different carbon-halogen chromophores and has been of long-standing interest as a model system to study bond selectivity upon electronic excitation, [1-3]. The UV absorption spectrum of CH_2BrI exhibits two A- and B- bands centered at 266 and 214 nm, dominated by the $n(\mathrm{I}) \rightarrow \sigma^*(\mathrm{C–I})$ and $n(\mathrm{Br}) \rightarrow \sigma^*(\mathrm{C–Br})$ transitions, respectively. Previous gas-phase molecular-beam studies of CH_2BrI demonstrated that the A-band excitation favors C–I bond cleavage and the C–Br bond cleavage predominates upon excitation into the B-band, [1]. Chromophore-selective photochemistry of CH_2BrI in solution is addressed in this work using the ultrafast transient absorption method that exploits broadband probing, including the deep-UV/UV range, which is of superb advantage for the detection of small reaction intermediate and radical species.

Following 266-nm excitation into the A-band of CH_2BrI, a strong absorption band at 445 nm and a weaker absorption band at 640 nm due to the $CH_2Br–I$ isomer product are formed on a time scale of several picoseconds (Fig. 1A), consistent with previously experiments, [2]. At long times (100-1200 ps), the isomer bands noticeably decay (time constant, ~1.2 ns). In the deep-UV/UV regions, two absorption bands, an intense at 240 nm and a weaker one at 275 nm are detected at short times. The formation of these bands is faster than our instrumental response time limited by solvent coherent artifact to about 400 fs. The 275- and 240-nm absorption bands are ascribed to a $I{\cdot}CH_3CN$ charge-transfer complex (formation time in polar solvents, $\leq$ 0.3 ps, [4]) and a $CH_2Br{\cdot}$ radical, [5], respectively. The absorption of $CH_2Br{\cdot}$ and $I{\cdot}CH_3CN$ shows no change up to 500 ps, suggesting that these species once formed following excitation of CH_2BrI do not collapse within 500 ps to produce either the parent or the $CH_2Br–I$ isomer molecules. Some rise of 275- and 240-nm bands after 500 ps is concurrent with decay of $CH_2Br–I$, and therefore, is attributed to the formation of $CH_2Br{\cdot}$ and $I{\cdot}CH_3CN$ following radical decomposition of $CH_2Br–I$. Also, the decay of $CH_2Br–I$ is accompanied by the build up of ΔA signals between 300 and 380 nm, where absorption of a second isomer of

CH_2BrI, CH_2I–Br, was conjectured, [3]. The photochemical mechanism upon 266-nm excitation is illustrated in Fig. 2, left panel.

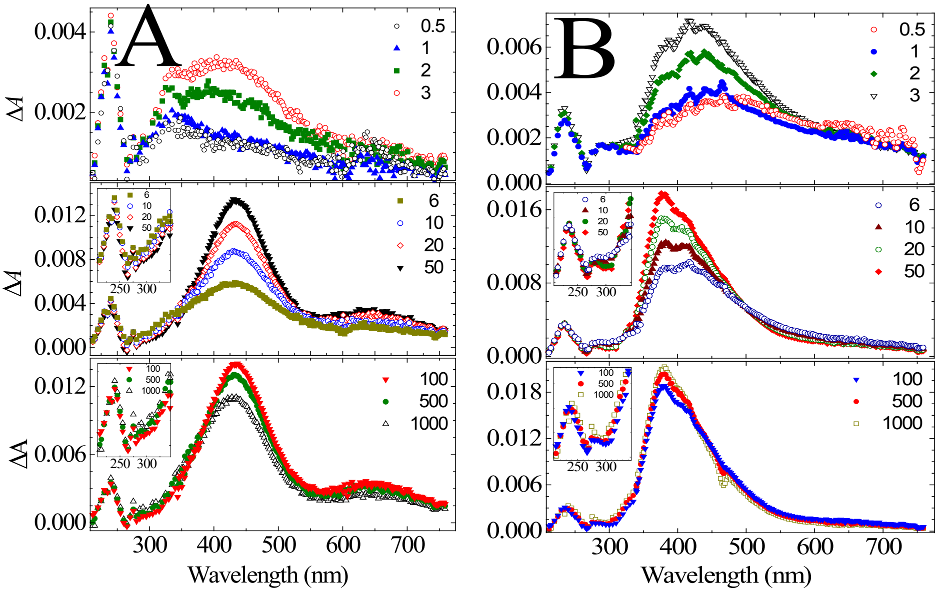

Fig. 1. Transient absorption ΔA spectra of CH_2BrI in CH_3CN following excitation at 266 nm (A) and 232 nm (B). Time delays (in picoseconds) between pump and probe pulses are given as legends.

Similarly to 266-nm excitation, the 235-nm product band due to $CH_2Br\cdot$ is observed in the transient absorption ΔA spectra upon 232-nm excitation of CH_2BrI (Fig. 1B), suggesting the C–I bond cleavage. Moreover, the short-time ΔA spectra exhibit the broad absorption feature at 275 nm as well as the 335-nm shoulder. The 275-nm feature signals the presence of $Br\cdot CH_3CN$, suggesting the C–Br bond cleavage, which is further supported by the shoulder at 355 nm where absorption of $CH_2I\cdot$ is known to occur, [6]. From 500 to 1200 ps, the 235-nm band of $CH_2Br\cdot$ slightly rises and a new weak absorption at 290 nm develops. This band is identical to that observed upon 266-nm excitation and can be assigned similarly to $I\cdot CH_3CN$. The 500-fs visible ΔA spectrum displays a band

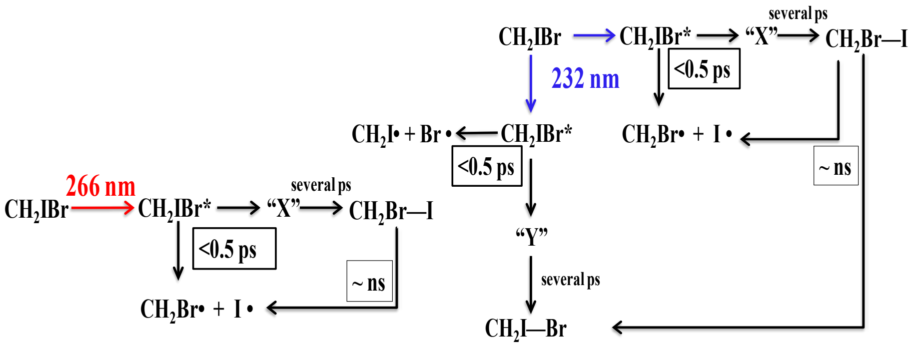

Fig. 2. Photochemical reaction pathways following 266-nm (left panel) 232-nm and (right panel) excitations of CH_2BrI in CH_3CN. The X or Y label the precursor states involved in the formation of isomers CH_2Br–I and CH_2I–Br.

with a broad 440 - 460 nm maximum, and with a long tail stretching to the near-IR wavelengths. On a time scale of several picoseconds this absorption reshapes to form a dual band spectrum with two maxima at ~378 and ~420 nm. With time increasing to several tens of picoseconds, the 378-nm band becomes major, but the 420-nm band as well as the red absorption remain appreciable, the latter shapes up to form a 640-nm band. Further rise of the 378-nm band at long times (100-1200 ps) is concurrent with both decay of the absorption for wavelengths longer than 430 nm and absorption rise in the deep-UV range (time constant, ~1.2 ns). The 640-nm transient absorption band and the decay time constant observed are characteristic of the formation and decomposition of CH_2Br–I. According to the 266-nm results, the decay of this isomer should lead to the formation of $CH_2Br\cdot$ and $I\cdot CH_3CN$, consistent with rise of the 235-nm band of $CH_2Br\cdot$ and the 290-nm band of $I\cdot CH_3CN$, as well as to the interconversion into CH_2I–Br, consistent with rise of the 378-nm band, Fig. 2, right panel.

In summary, we demonstrated that the mode-selective chemistry achieved by localizing electronic excitation in CH_2BrI in the gas-phase can also be accomplished for this molecule in solution. The transient spectra recorded in the present work include probing across deep UV wavelengths, and enable us to provide new insights into the photochemical dynamics of this system. Excitation into the A-band (266 nm) yields a radical pair ($CH_2Br\cdot$ + I·) and the isomer (CH_2Br–I). Single-photon excitation at 232 nm gives rise to two radical pairs ($CH_2Br\cdot$ + I· and $CH_2I\cdot$ + Br·) and two isomers (CH_2Br–I and CH_2I–Br). For both excitations, absorption of the radical species remains constant during the isomer formation and vibrational thermalization processes, providing the evidence that the isomers are not formed as result of recombination of these radicals. This finding indicates the existence of the short-lived precursor states in the isomerization processes and the complex topology of potential energy surfaces involved.

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