Photochemistry of 1,2-Dibromoethane in Solution. A Model for the Generation of Hydrogen Bromide

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Laser flash photolysis of 1,2-dibromoethane at 266 nm reveals the rapid formation of two bromine atoms as the primary photochemical step; the atoms are readily detected through their complexation with bromide to yield Br_2^{-}.

Halogenated compounds have been reported by a number of groups[1-3] to be efficient hydrogen halide photogenerators. *Vicinal* dibromides represent a particular subset of these materials whose direct, non-sensitized photochemistry is not well understood in this regard. While more complex molecules will likely be required for proper functionality in photoresist applications, the title compound is the simplest dibromide and should provide a simple model in which the basic photochemical steps can be invesigated.

In our experiments we have irradiated solutions of 1,2-dibromoethane in acetonitrile or diglyme [bis(2-methoxyethyl)-ether] with the pulses (266 mm, ~6 ns, < 30 mJ pulse^{-1}) from the fourth harmonic of a Surelite Nd/YAG laser. The concentrations of the solutions (deaerated unless otherwise indicated) were selected so as to achieve absorbances around 0.3 at the laser wavelength and a flow system was employed to ensure that a fresh portion of solution was irradiated by each pulse.

Bromine atoms are not readily detectable in experiments of this type. However, experiments at short wavelengths in the absence of bromide (*vide infra*) reveal the formation of an intense absorption. Inset (*a*) in Fig. 1 illustrates this observation. We tentatively suggest that this growth reflects predominantly the recombination of bromine atoms to yield Br_2 which absorbs very strongly below 300 nm. Oxygen had no effect on the kinetics or intensity of this growth, as could be expected given our assignment.

In order to 'make bromine atoms visible' we have explored the addition of bromides in an attempt to generate Br_2^{-} which is known to absorb strongly with $\lambda_{max} \sim 360$ nm.[4] Tetraethyl-ammonium bromide proved to have a suitable solubility in polar organic solvents and led to readily detectable signals from Br_2^{-}; Fig. 1 shows the spectrum recorded in acetonitrile. The quantum yield of bromine atom formation can be quantified by use of a suitable actinometer. In our case we have employed benzophenone which upon excitation yields its triplet state (λ_{max} 535 nm; $\varepsilon_{535} = 7800$ dm^3 mol^{-1} cm^{-1}) with a quantum yield of one.[5] Data extrapolated to zero laser dose

(to avoid any two-photon processes) led to a quantum yield of 2.3 ± 0.5 for the formation of Br_2^{-} based on a reported extinction coefficient of 9900 dm^3 mol^{-1} cm^{-1} at 360 nm.[6] Within our error limits this implies that two bromine atoms are formed per photon absorbed, as shown in eqns. (1)–(3).

$$CH_2BrCH_2Br \xrightarrow{266 \text{ nm}} CH_2BrCH_2{}^{\bullet} + Br^{\bullet} \quad (1)$$

$$CH_2BrCH_2{}^{\bullet} \xrightarrow{\text{Fast}} CH_2{=}CH_2 + Br^{\bullet} \quad (2)$$

$$Br^{\bullet} + Br^{-} \rightleftharpoons Br_2^{-} \quad (3)$$
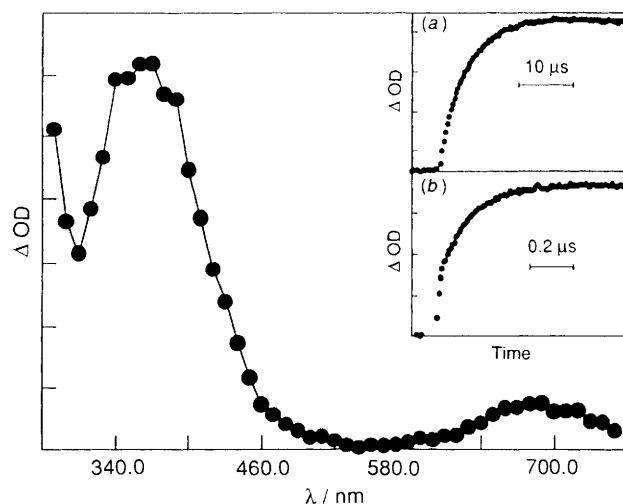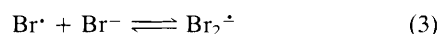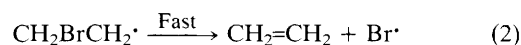

Fig. 1 Transient absorption spectrum of Br_2^{-} recorded after 266 nm laser excitation of 1,2-dibromoethane in acetonitrile solution in the presence of 0.03 mol dm^{-3} tetraethylammonium bromide (OD = optical density). Inset: (*a*) Transient growth at 290 nm recorded after 266 nm laser excitation of 1,2-dibromoethane in acetonitrile solution; (*b*) transient growth at 360 nm recorded after 266 nm laser excitation of 1,2-dibromoethane in acetonitrile solution in the presence of 0.3 mmol dm^{-3} tetraethylammonium bromide.

Given that at bromide concentrations $>10^{-2}$ mol dm^{-3} the formation of Br$_2^{-}$ is complete within the duration of the laser pulse, reaction (2) must be a very fast process, with a lifetime of less than 20 ns. The ability to study reaction kinetics of 'invisible' transients in solution using laser photolysis techniques has typically been a direct function of the development of suitable probes that make them detectable. While such reactions are not necessarily new, their identification as suitable probes has enabled numerous studies in systems such as alkoxyl radicals,[7] Type II biradicals[8] and carbenes.[9] We find that in the case of bromine atoms Br$_2^{-}$ is a useful probe.

While added bromide was required to obtain significant absorption from Br$_2^{-}$, we noted that in acetonitrile a weak signal was observed in the same region in the absence of added bromide. We believe that this may reflect interaction between Br· and some HBr formed *in situ*.

At low concentrations of added bromide it is possible to observe the growth of Br$_2^{-}$ [see inset (*b*) in Fig. 1] following a small prompt absorption that was not characterised in detail. This growth follows first-order kinetics; a plot of this rate constant against the bromide concentration led, from the slope, to a rate constant of 1.6×10^{10} dm^3 mol^{-1} s^{-1} for reaction (3) in acetonitrile.[10] If the Br$^-$ concentration is held constant and a Br· scavenger added, the growth kinetics for Br$_2^{-}$ changes reflecting the trapping process. In this case Br$_2^{-}$ acts as a 'probe'; a similar approach has been employed with other reaction intermediates.[7-9] Kinetic analysis of data obtained in this manner leads to rate constants (acetonitrile, room temp.) of 1.0×10^6 and 3.6×10^7 dm^3 mol^{-1} s^{-1} for Br· trapping by methanol and propan-2-ol, respectively. The reaction with the alcohols to yield HBr is expected to involve hydrogen abstraction from C–H bonds at the alcohol carbon; such abstractions may in fact be mediated by charge transfer.

Further verification of the role of hydrogen abstraction in the ultimate generation of H$^+$ was obtained by checking for H$^+$ following UV excitation of 1,2-dibromoethane in either acetonitrile of diglyme. In both solvents we observe little or no HBr generation. In contrast, irradiation in the presence of propan-2-ol as a hydrogen donor leads to strongly acidic solutions.

In conclusion, deep-UV irradiation of 1,2-dibromomethane leads to the rapid generation of two bromine atoms. Photoacid generation under these conditions seems to depend upon the presence of suitable hydrogen donors. Complexation of Br· by Br$^-$ yields the readily detectable Br$_2^{-}$ which may prove valuable to study the formation and reactions of the otherwise invisible bromine atoms.

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