Dynamics of the Photochemical Debromination of Silicon-Substituted Vicinal Dibromides

Dean Weldon,[†] Mónica Barra,[†] Roger Sinta,[‡] and
J. C. Scaiano*[,†]

*Department of Chemistry, University of Ottawa,
Ottawa, Canada K1N 6N5, and Research and Development
Laboratories, Shipley Company, 455 Forest Street,
Marlborough, Massachusetts 01752*

Received January 9, 1995

The photochemical debromination of acyclic vicinal dibromides leads to the rapid formation of two bromine atoms. For example, photolysis of 1,2-dibromoethane yields ethylene and bromine atoms. The latter are formed with a quantum yield of 2.0 within the time resolution (<20 ns) of our laser flash photolysis experiments.[1,2]

$$CH_2BrCH_2Br \xrightarrow{h\nu} Br^\bullet + CH_2BrCH_2^\bullet \quad (1)$$

$$CH_2BrCH_2^\bullet \xrightarrow{k_2} Br^\bullet + C_2H_4 \quad (2)$$

Thus, in this case, $k_2 > 5 \times 10^7\ s^{-1}$. Attempts to detect the intermediate radical $CH_2BrCH_2^\bullet$ by ESR spectroscopy have also been unsuccessful.[3] Efficient debromination has also been proposed on the basis of product studies in the bromination of 1-bromobutane.[4] The bromine atoms formed in reactions 1 and 2 cannot be detected easily with laser photolysis techniques because they do not have any strong absorptions in the spectral region normally accessible. We have reported earlier[1,2] that this problem can be easily overcome by adding bromide ions to the system so that the bromine atoms will form the readily detectable $Br_2^{\bullet -}$.[5] This simple technique has allowed us to measure many bimolecular rate constants involving bromine atoms.[1]

$$Br^\bullet + Br^- \xrightarrow{k_3} Br_2^{\bullet -} \quad (3)$$

While the β-cleavage leading to the loss of bromine in reaction 2 and related systems proved too fast for nanosecond techniques, we reasoned that the reaction could be slowed down if β-cleavage involved a somewhat stabilized radical. In the extreme case, McGimpsey et al.[6] have shown that β-bromoethyl aryl radicals are stabilized to the point that they do not undergo β-bromine elimination in the time scale of their experiments. Laser flash photolysis (266 nm) of tetrakis(1,2-dibromoethyl)silane[7] in the presence of 6 mM tetrabutylammonium bromide in acetonitrile at 23 °C led to the trace of Figure 1 (▲ and △), consisting of a rapid "jump", followed by a resolved growth with a lifetime of ~43 ns.[8] By contrast (Figure 1, ● and ○), this growth is absent in the case of 1,2-dibromoethane where a similar analysis yields a lifetime of 10.5 ns, reflecting pulse duration and system response. We attribute the data for tetrakis(1,2-dibromoethyl)silane to reactions 4 ("instantaneous") and 5 (growth-resolved), followed by rapid bromine atom trapping by reaction 3. We note that, under these conditions (vide infra), bromide trapping is fast ($\tau \sim 10$ ns).

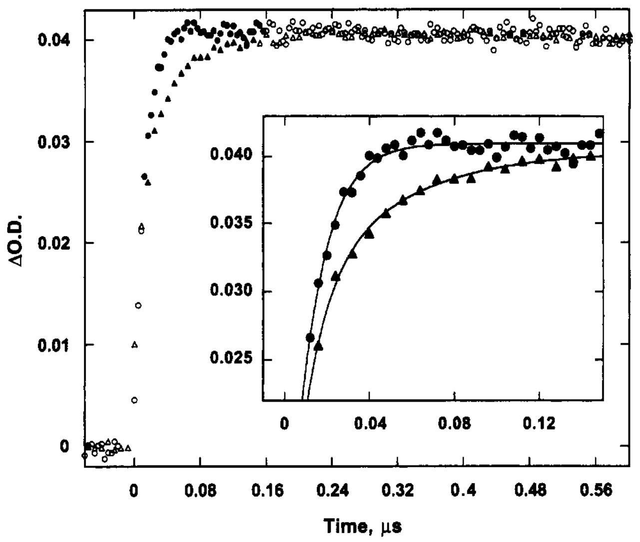


Figure 1. Normalized traces monitored at 360 nm (corresponding to $Br_2^{\bullet -}$) following 266 nm excitation of vicinal dibromides in acetonitrile at 23 °C. ▲ and △, tetrakis(1,2-dibromoethyl)silane with $[Br^-]$ = 6 mM; ● and ○, 1,2-dibromoethane with $[Br^-]$ = 6 mM. Filled points show the data used for the kinetic fit.

$$(CH_2BrCHBr)_3SiCHBrCH_2Br \xrightarrow{h\nu} (CH_2BrCHBr)_3SiCHBrCH_2^\bullet + Br^\bullet \quad (4)$$

$$(CH_2BrCHBr)_3SiCHBrCH_2^\bullet \xrightarrow{k_5} (CH_2BrCHBr)_3SiCH{=}CH_2 + Br^\bullet \quad (5)$$

At lower concentrations of bromide, the rate-determining step becomes the trapping process of reaction 3; under these conditions, a plot of the pseudo-first order rate constant for $Br_2^{\bullet -}$ growth (k_{obs}) against bromide concentration yields k_3 from the slope. We have measured a value of $1.6 \times 10^{10}\ M^{-1}\ s^{-1}$ for k_3 in acetonitrile earlier,[1] in line with literature values.[9] Similar experiments with

---

[†] University of Ottawa.

[‡] Shipley Co.

(1) Scaiano, J. C.; Barra, M.; Krzywinski, M.; Sinta, R.; Calabrese, G. *J. Am. Chem. Soc.* **1993**, *115*, 8340.

(2) Scaiano, J. C.; Barra, M.; Calabrese, G.; Sinta, R. *J. Chem. Soc., Chem. Commun.* **1992**, 1418.

(3) Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 6485.

(4) Tanner, D. D.; Darwish, D.; Mosher, M. W.; Bunce, N. J. *J. Am. Chem. Soc.* **1969**, *91*, 7398.

(5) Hug, G. L. *Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution*; National Bureau of Standards: Washington, DC, 1981; Vol. NSRDS-NBS 69, p 160.

(6) Zhang, B.; Pandit, C. R.; McGimpsey, W. G. *J. Phys. Chem.* **1994**, *98*, 7022.

(7) The laser system employed was the same used in earlier work.[1,2] Tetrakis-(1,2-dibromoethyl)silane was prepared as follows: Bromine (9.4 g, 58 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a solution of tetravinylsilane from Aldrich (2.0 g, 14 mmol) in CH_2Cl_2 (40 mL) while the solution was maintained at 0 °C. After 3 h, the reaction mixture was allowed to warm to room temperature and washed (2 × 20 mL) with a saturated aqueous solution of sodium bisulfite. The organic layer was next washed with water (20 mL) and dried over $MgSO_4$. After filtration, the solvent was removed under vacuum and a white solid was obtained. After recrystallization from CH_2Cl_2, 7.0 g (63.5%) of product (mp 144–146 °C) was obtained: ^1H NMR (DMSO-d_6) δ 4.15 (1H, t), 4.40 (1H, m), 4.62 (1H, m). Anal. Calcd for $C_8H_{12}Br_8Si$: C, 12.39; H, 1.56; Br, 82.43; Si, 3.62. Found: C, 12.53; H, 1.60; Br, 82.55.

(8) These traces were fitted with a double exponential expression fixing one rate constant (i.e., $k_3[Br^-]$) to $9.6 \times 10^7\ s^{-1}$. This value corresponds to the rate of formation of $Br_2^{\bullet -}$ from instantaneously formed $Br^\bullet$ in reactions 1 or 4 in the presence of 0.006 M bromide.

(9) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330.

0022-3263/95/1960-3921$09.00/0

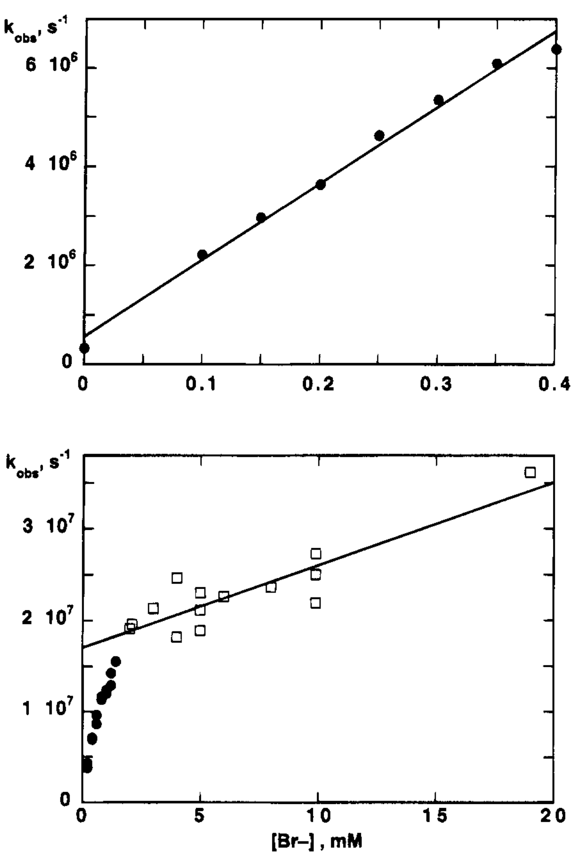


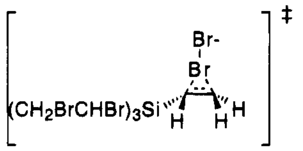
Figure 2. Concentration dependence of the growth of $Br_2^{\bullet-}$ for tetrakis(1,2-dibromoethyl)silane in acetonitrile at 23 °C. Top: formation of $Br_2^{\bullet-}$ at very low bromide concentrations. Bottom: comparative dependence of k_{obs} in the low and high bromide concentration ranges.

tetrakis(1,2-dibromoethyl)silane led to a rate constant of 1.5×10^{10} M^{-1} s^{-1} (see Figure 2, top). We had anticipated that a plot of the rate constant for the growth of $Br_2^{\bullet-}$ against the concentration of Br^- should yield a line with slope k_3 at low concentration (as observed), turning to a plateau at the value of k_5, when this reaction becomes the rate-determining step for the formation of the second $Br_2^{\bullet-}$ molecule. Experimentally (see Figure 2, bottom), we observe a dramatic change of slope, but not a plateau. The second segment (at high bromide) yields a slope of 9.0×10^8 M^{-1} s^{-1}. While k_{obs} changes with bromide concentration in this range, the total $Br_2^{\bullet-}$ yield remains essentially constant. The results are consistent with β-cleavage occurring by two mechanisms: the unimolecular elimination of reaction 5 and the "assisted" elimination of reaction 6.

$$(CH_2BrCHBr)_3SiCHBrCH_2^{\bullet} + Br^- \xrightarrow{k_6} (CH_2BrCHBr)_3SiCH{=}CH_2 + Br^{\bullet-} \quad (6)$$

To the best of our knowledge, reaction 6 is unprecedented in bromine atom chemistry. However, β-cleavage of other radicals is known to be accelerated by stabilization of the reaction products. For example, the β-cleavage of alkoxyl radicals is accelerated in polar solvents that stabilize the carbonyl products.[10-12] Reaction 6 is somewhat analogous to the well-known synthesis of alkenes by reaction of vicinal dibromides with iodide.[13]

We assume that reaction 6 involves a bridged intermediate or transition state, probably the same species as in the attack of $Br_2^{\bullet-}$ on olefins. Unfortunately, while numerous rate constants are available for $Br_2^{\bullet-}$, these studies tend to exclude alkenes and concentrate on water soluble substrates, reflecting the fact that most data originate from pulse radiolysis.[14]



The "true" rate constant for reaction 5 can be obtained by extrapolation of the high-concentration data to zero bromide concentration, where reaction 6 does not influence the kinetics. This analysis leads to $k_5 = 1.71 \times 10^7$ s^{-1}, corresponding to a lifetime of 58 ns for **I**, in acetonitrile at 23 °C.

Neighboring group participation in the formation of radicals has received considerable attention.[4,15-20] Stabilization of radicals has been observed for compounds having, for example, a β-silyl,[21-23] a β-bromo,[24-27] and a β-chloro[3,15,28] group. In all cases, it is observed that the most effective stabilization occurs when the neighboring group eclipses the newly formed radical center, suggesting that the neighboring group bridges to the radical center. Walsh reports the β-stabilizing effect of silicon as ~12 kJ/mol,[21] and Skell and Traynham report the β-stabilizing effect of bromine also as ~12 kJ/mol.[24] These stabilizing effects may explain why the radical of tetrakis(1,2-dibromoethyl)silane is moderately long lived, but it does not unambiguously establish which bromine atom leaves first. The β-bromine will leave upon photolysis if the β-directing effects of the geminal silicon and bromine are additive (they would not be expected to be 100% additive since both groups could not simultaneously eclipse the developing radical center). The β-bromine will also leave if silicon bridges more readily than bromine. If bromine bridges preferentially, then the α-bromine would cleave because it is on the more substituted carbon.

---

(10) Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466.

(11) Davies, A. G.; Roberts, B. P.; Scaiano, J. C. *J. Organomet. Chem.* **1972**, *42*, C27.

(12) Walling, C.; Wagner, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 3368.

(13) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 875. Original reference: Winstein, S.; Pressman, D.; Young, W. G. *J. Am. Chem. Soc.* **1939**, *61*, 1645.

(14) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027.

(15) Kochi, J. K.; Krusic, P. J. In *Essays on Free Radical Chemistry, Special Publication No. 24*; Norman, R. O. C., Ed.; The Chemical Society: London, 1970; Vol. 24; p 147.

(16) Lyons, A. R.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 622.

(17) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846.

(18) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 6459.

(19) Norman, R. O. C.; Storey, P. M. *J. Chem. Soc. B* **1971**, 1009.

(20) Cooper, J.; Hudson, A.; Jackson, R. A. *Tetrahedron Lett.* **1973**, 831.

(21) Walsh, R. *Pure Appl. Chem.* **1987**, *59*, 69.

(22) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207.

(23) Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 208.

(24) Skell, P. S.; Traynham, J. G. *Acc. Chem. Res.* **1984**, *17*, 160.

(25) Symons, M. C. R.; Smith, I. G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1362.

(26) Skell, P. S.; Tuleen, D. L.; Readio, P. D. *J. Am. Chem. Soc.* **1963**, *85*, 2849.

(27) Thaler, W. *J. Am. Chem. Soc.* **1963**, *85*, 2607.

(28) Chen, K. S.; Elson, I. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 5341.

Unfortunately, the lifetime is too short to attempt trapping experiments.

No aliphatic vicinal dibromide, until now, had produced a detectable β-bromo radical upon photolysis; therefore, bromine bridging is not sufficient. Stabilization due to silicon bridging is comparable to that of bromine; therefore, it too would not be sufficient. The β-effects of silicon and bromine must be at least partially additive; therefore, we tentatively assign the nascent radical to the β-position.

Observation of the resolved growth of $Br_2^{\bullet -}$ at a bromide concentration high enough to trap instantaneously (<10 ns) all bromine atoms implies that the β-bromo radicals are decaying at a resolvable rate. It was expected that oxygen would quench these radicals, thus influencing the growth kinetics and decreasing the yield of bromine atoms. This was not observed. In our earlier studies of 1,2-dibromoethane, the yields of $Br_2^{\bullet}$ were also insensitive to oxygen. McGimpsey et al.[6] made similar observations for their dibromoethyl aryl systems. The unusual properties of β-bromo radicals have been attributed to bridging of the bromine atom to both the α- and the β-carbons.[24]

In conclusion, our results provide the first reliable value for the rate of bromine atom elimination from a β-bromoalkyl radical (k_5), further evidence for bromine bridging, and mechanistic and kinetic data for the assisted debromination of reaction 6.

Acknowledgment. J.C.S. thanks the Natural Sciences and Engineering Research Council of Canada and the Canada Council (Killam Research Fellowships Program) for support of this research.

JO9500693