

Laser Flash Photolysis Determination of Absolute Rate Constants for Reactions of Bromine Atoms in Solution

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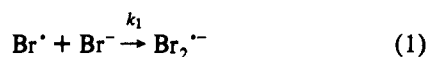
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Received April 12, 1993

Abstract: The photodecomposition of vicinal dibromides at 266 nm produces bromine atoms with a quantum yield of ~2.0. This results from an efficient primary photocleavage of a C-Br bond, followed by rapid elimination of a second bromine atom from radicals of the type RCH-CH₂Br. This cleavage occurs with a lifetime of <20 ns at room temperature. Bromine atoms react with bromine ions with a rate constant of $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ to yield Br₂^{•-}, an easily detectable and long-lived radical ion. This reaction can be used as a probe in order to determine absolute rate constants for other reactions of bromine atoms. For example, the rate constants for methanol, 2-propanol, and triethylamine are 9.3×10^5 , 4.1×10^7 , and $2.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, respectively. It is suggested that these hydrogen atom transfer reactions may involve a considerable degree of charge transfer. α -Bromoacetophenone also serves as a convenient bromine atom source in those cases where vicinal dibromides cannot be employed. The advantages and disadvantages of using probe techniques in the determination of absolute rate constants are discussed in some detail.

Introduction

Photoresist technology³ is a field where vicinal dibromides have found applications as UV photoacid generators.^{4,5} Recent work on this subject led to the development of laser techniques allowing the absolute determination of rate constants for reactions of bromine atoms.⁶ In this report we take advantage of these developments in order to study the kinetics of reactions of bromine atoms in solution. Much to our surprise, we were unable to find in the literature any rate constants for reactions of bromine atoms with organic substrates in solution. In contrast, a recent review⁷ lists over 200 rate constants for reactions of Br₂^{•-}, in turn formed by reaction of bromine atoms with bromide, i.e.



The rate constant for reaction 1 in aqueous medium has been determined by flash photolysis by Nagarajan and Fessenden⁸ as $k_1 = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and is in agreement with values published earlier by Treinin and Hayon.⁹ Bromine atoms also have a tendency to form complexes with bromine-containing organic molecules, and Shoute and Neta¹⁰ have examined these complexes using pulse radiolysis techniques.

While reports on absolute rate constants for reactions of bromine atoms in solution are virtually nonexistent,¹¹ a number of studies have been concerned with these processes in the gas

phase. Hydrogen, methane, and other hydrocarbons have been frequent substrates in these studies.¹² We note that in the case of substrates that are good candidates for charge-transfer interactions, gas-phase studies would be unlikely to provide a reasonable basis for understanding processes in solution.

Bromine atoms and hydrogen bromide (a frequent product of bromine atom reactions) are not readily detectable using laser photolysis techniques with UV-visible absorption detection. In order to monitor the kinetics of these reactions, it is important to identify a molecule that would react efficiently with Br[•] yielding a readily detectable species. In principle, aromatic substrates could serve this purpose, since they are well-known to form detectable complexes with halogen atoms.¹³ However, in practice their use is prevented by the fact that they are strongly absorbing at the excitation wavelengths employed in the photocleavage of vicinal dibromides (266 nm in our case). We have found that reaction 1 provides an ideal probe reaction, since Br₂^{•-} absorbs strongly ($\epsilon_{360} = 9000 \text{ M}^{-1} \text{ cm}^{-1}$) at 360 nm.¹⁴ In a preliminary communication⁶ we reported the importance of this application of Br₂^{•-} in the study of deep-UV photoacid generators. Further details of these studies, including the use of chain dehydrobrominations as amplified photoacid generators, will be discussed elsewhere. The present article is concerned with the dynamics of bromine atom reactions which take advantage of the techniques developed as part of our work related to photoresist systems.

Results

Several vicinal dibromides have been used as sources of bromine atoms; these include 1,2-dibromoethane (I), 1,2-dibromodecane (II), and tris(2,3-dibromopropyl) isocyanurate (III). Compound III has found application as a photoacid generator for photoresists.⁴

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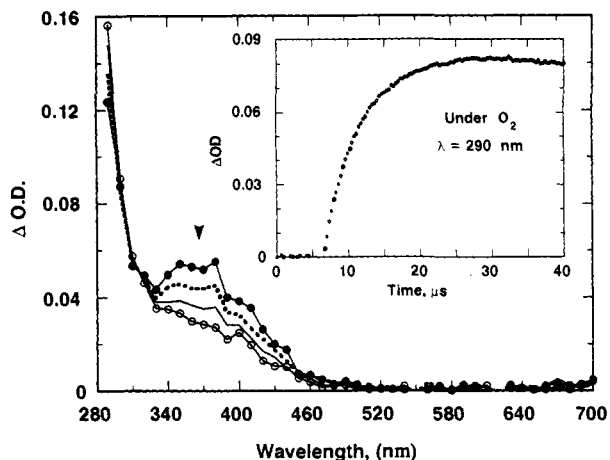


Figure 1. Transient spectra recorded following 266-nm excitation of III in acetonitrile. The spectra (that decay at 350 nm) were recorded 4.4, 17, 42, and 77 μs after excitation. Inset: Formation of the signal at 290 nm (attributed to Br_2^-) under the same conditions as those in the main figure, but under oxygen.

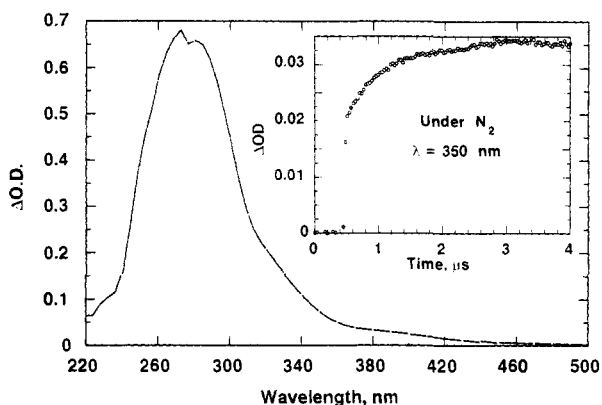


Figure 2. Difference spectrum recorded in a conventional spectrophotometer, following 15-min irradiation of III in acetonitrile at 254 nm. Inset: Growth trace recorded at 350 nm when the same sample was excited with a laser at 266 nm.

Laser photolysis (266 nm) of III in acetonitrile solution yields weak signals at $\lambda > 320$ nm (Figure 1). In contrast, at shorter wavelengths we observe the growth of a signal which persists for a long time (see insert in Figure 1). This is clearly the absorption from a stable product, since it can be recorded with a conventional UV spectrophotometer following the completion of the laser experiment. The spectrum is shown in Figure 2 and has been established to correspond to molecular bromine by comparison with the spectra of authentic samples. In fact, it is not surprising that, in the absence of good hydrogen atom donors, bromine atoms undergo self-reactions in acetonitrile, since typical concentrations generated under laser photolysis conditions are usually in the 10–50- μM range. Further, the formation kinetics for these signals (see insert in Figure 1) are not affected by oxygen, as would be expected if the signal arises from self-reaction of bromine atoms.

The signals at $\lambda > 320$ nm are probably due to weak complexation of bromine atoms with their bromine-containing precursors. Shoute and Neta¹⁰ have characterized these processes in considerable detail. In addition, it is likely that some $\text{Br}_2^{\cdot-}$ is also formed *in situ*. This suggestion is also supported by the observation that the absorptions in this region increase considerably if the sample flow is stopped allowing the accumulation of HBr produced by several laser pulses.

Laser excitation of samples of vicinal dibromides containing $(\text{C}_2\text{H}_5)_4\text{NBr}$ leads to strong absorptions at 360 nm, readily characterized as due to $\text{Br}_2^{\cdot-}$.¹⁴ The spectrum of this intermediate is shown in Figure 3. Note also the weak band at ~ 680 nm,

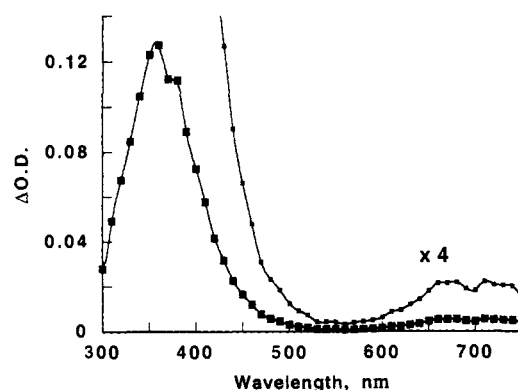


Figure 3. Transient spectrum recorded following 266-nm excitation of I in acetonitrile in the presence of 5 mM Et_4NBr under nitrogen.

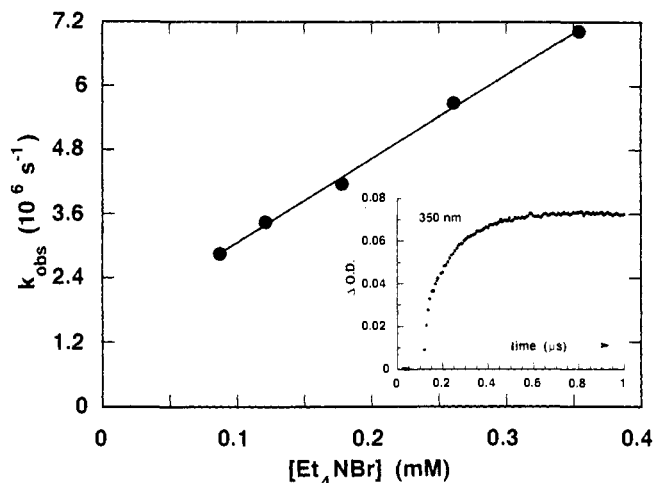


Figure 4. Plot according to eq 2 for reaction of bromine atoms (from I in acetonitrile) with bromide ions. Inset: Representative trace showing the buildup of $\text{Br}_2^{\cdot-}$.

which is known to be characteristic of $\text{Br}_2^{\cdot-}$.¹⁴ The same spectrum is obtained regardless of which one of the precursors is employed.

At bromide concentrations ≥ 3 mM (such as in Figure 3), the formation of $\text{Br}_2^{\cdot-}$ appears to be instantaneous, and typical decay lifetimes in acetonitrile are in the microsecond range. In contrast, at low bromide concentrations it is possible to resolve the formation of $\text{Br}_2^{\cdot-}$, as illustrated in the insert in Figure 4. The buildup profile always appears to be preceded by a small "jump" or instantaneous growth of signal at 360 nm. While small, this effect is quite reproducible. As indicated in connection with Figure 1 (*vide supra*), weak complexation with the molecules employed as bromine atom precursors can be expected to lead to some signals in this region.¹⁰ The growth of signal due to $\text{Br}_2^{\cdot-}$ is related to the kinetics of reaction 1 according to eq 2

$$k_{\text{obs}} = k_0 + k_1[\text{Br}^-] \quad (2)$$

where k_{obs} is the rate constant associated with the first-order fit to the growth traces such as that in the insert of Figure 4, k_1 is the rate constant for reaction 1, and k_0 is the rate constant for bromine atom decay in the absence of added bromide ions.¹⁵ A plot according to eq 2 in acetonitrile as solvent is shown in Figure 4 and leads to $k_1 = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The value is somewhat higher than that reported in water,⁸ probably reflecting the lower viscosity of acetonitrile.

Yields of Bromine Atom Formation. Under conditions where reaction 1 is used to trap quantitatively bromine atoms, the yield of $\text{Br}_2^{\cdot-}$ should be identical to the photochemical yield of bromine

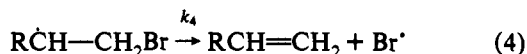
(15) Given the self-reaction of bromine atoms, k_0 may incorporate some second-order contributions; however, these do not introduce significant error provided that k_0 is considerably smaller than k_{obs} .

Table I. Quantum Yields for the Formation of Bromine Atoms

precursor	Φ_{Br^\bullet} ^a
I	2.6
II	2.0
III	1.8

^a Typical errors $\pm 25\%$.

atoms. In this sense $\text{Br}_2^{\bullet-}$ provides a straightforward way of "counting" bromine atoms, since they give rise to a readily detectable and well-characterized signal. In order to carry out these measurements, we employed the triplet state of benzophenone as an actinometer. Triplet benzophenone is known to be formed with a quantum yield of 1.0, having a strong absorption at 525 nm and an extinction coefficient of $7800 \text{ M}^{-1} \text{ cm}^{-1}$.¹⁶ These experiments were carried out in the presence of 5 mM $(\text{C}_2\text{H}_5)_4\text{NBr}$ to ensure quantitative trapping of bromine atoms. The literature value of $9000 \text{ M}^{-1} \text{ s}^{-1}$ was employed for the extinction coefficient of $\text{Br}_2^{\bullet-}$.¹⁴ The results obtained have been summarized in Table I. The errors given ($\pm 25\%$) take into account that some systematic error may have been introduced due to the errors in the extinction coefficients for $\text{Br}_2^{\bullet-}$ and benzophenone triplets. Within experimental error, all the values in Table I can be taken as 2.0. We propose that this quantum yield reflects that all the precursors used undergo efficient photocleavage of a C–Br bond, followed by further elimination of a second bromine atom with formation of a C–C double bond, i.e.



We were somewhat concerned with the fact that the yields of $\text{Br}_2^{\bullet-}$ could be severely affected if the errors in literature values of extinction coefficients were larger than reported. In order to further test this point, quantum yields of product formation were determined under steady-state (254 nm) irradiation. In fact, II was included in this series because its product, 1-decene, could be readily analyzed by gas chromatography. Quantum yield studies were carried out using the photocleavage of valerophenone to yield acetophenone as a relative actinometer.¹⁷ 1-Decene was produced with a quantum yield of approximately 1.0, confirming that each photon leads to the formation of a C–C double bond. Further, 1-decene was the only detectable product from II.

Experiments with III using HPLC analysis confirm that photodecomposition of III leads to products where allyl groups replace the original substituents. On prolonged irradiation, the corresponding triallyl compound is formed, the same compound from which III is produced commercially.

Analysis for HBr was somewhat more complex because of formation of Br_2 in acetonitrile and the triggering of chain reactions in alcohol-containing mixtures,^{18,19} however, with diglyme as solvent the quantum yields were systematically around 2.0.

Attempts To Determine the Rate Constant for Reaction 4. Examination of the mechanism of reactions 3 and 4 indicates that the formation of bromine atoms should occur in two stages, reflecting the two-step mechanism. Thus 50% can be expected to be formed essentially instantaneously (reaction 3), while the second half should grow-in following the kinetics of reaction 4. At sufficiently high concentrations of bromide, the formation of $\text{Br}_2^{\bullet-}$ should mimic exactly the time profile for bromine atom generation.

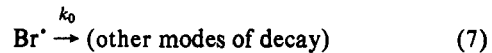
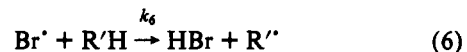
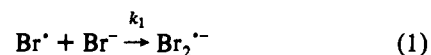
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(19) The ketyl radicals from the alcohols reduce the dibromides to initiate their chain decomposition. We will report on this elsewhere.

In a variety of experiments following the rationale given above, and using precursors I–III, we systematically failed to detect anything other than an "instantaneous" formation of $\text{Br}_2^{\bullet-}$, which, as already indicated (*vide supra*), is produced with a quantum yield of ~ 2.0 . We are therefore forced to conclude that in acetonitrile at room temperature reaction 4 occurs within our time resolution. Thus $k_4 \geq 5 \times 10^7 \text{ s}^{-1}$ represents a conservative lower limit for this rate constant.

Dynamics of Bromine Atom–Molecule Reactions in Solution. The readily detectable absorption from $\text{Br}_2^{\bullet-}$ can be used to advantage not only in the determination of k_1 (see Figure 4) but also in the determination of other rate constants where all the reactants and products of the reaction are invisible to the technique employed. This technique is usually referred to as the "probe technique" and was introduced by our group in the late seventies to study reactions of biradicals and alkoxyl radicals.²⁰ It has also been employed in the study of a variety of other systems.^{21–23}

The substrate, R'H, is added to a system which, in addition to the precursor of bromine atoms, contains a fixed concentration of bromide ions. The following mechanism shows the relevant steps in the reaction



where reaction 5 is the sum of reactions 3 and 4 and reflects our observation that the latter is instantaneous and quantitative (*vide supra*). We assume that $\text{Br}_2^{\bullet-}$ is long lived in the time scale of these measurements and that, therefore, its decay does not need to be taken into account. k_0 has the same meaning here as it does in eq 2.

Kinetic analysis for the mechanism above leads to eq 8

$$k_{\text{obs}} = k_0 + k_1[\text{Br}^-] + k_6[\text{R}'\text{H}] \quad (8)$$

where k_{obs} results from the first-order fit to the growth profile for $\text{Br}_2^{\bullet-}$. Thus, determination of k_{obs} values for various concentrations of R'H and constant $[\text{Br}^-]$ leads to the values of k_6 from plots of k_{obs} vs $[\text{R}'\text{H}]$. Representative plots are illustrated in Figure 5. A series of rate constants obtained using this approach is listed in Table II.

Attempts to determine rate constants for representative hydrocarbons, such as cyclohexane, were unsuccessful, suggesting that these rate constants are at least an order of magnitude smaller than the smallest values in Table II. Reaction rate constants are generally based on the use of I (typically 0.16 M) as a bromine atom precursor. However, in the cases of methanol and 2-propanol we looked for possible influence of the precursor and/or precursor concentration on the rate constants obtained according to the analysis of eq 8. It was reassuring to find no dependence on these parameters.

The yield of $\text{Br}_2^{\bullet-}$ in the plateau region of the growth curves can also be related to the corresponding rate constants using a Stern–Volmer type of approach, i.e.

$$\frac{\Delta\text{OD}_0}{\Delta\text{OD}} = 1 + k_6\tau[\text{R}'\text{H}] \quad (9)$$

where ΔOD and ΔOD_0 are the transient optical densities due to

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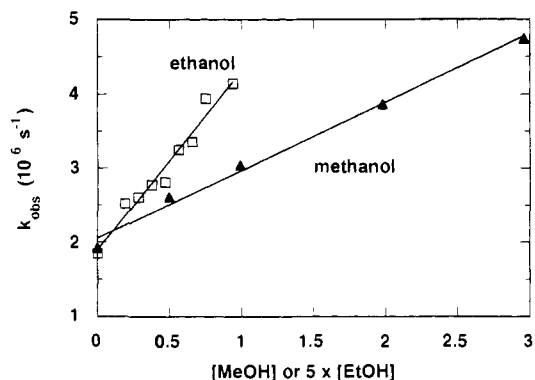


Figure 5. Plots according to eq 8 for reaction of bromine atoms with ethanol (\square) and with methanol (\blacktriangle) in acetonitrile. Ethanol concentrations have been multiplied by five for display clarity.

Table II. Rate Constants for Reactions of Bromine Atoms with Various Hydrogen Donors in Acetonitrile at Room Temperature

substrate	$k_6, 10^6 \text{ M}^{-1} \text{ s}^{-1}$
methanol	0.93
ethanol	16
1-pentanol	11
1-octanol	12
2-methyl-1-propanol	17
2-propanol	41
2-octanol	35
dioxane	1.2
diethyl ether	17
diglyme	21
triethylamine	29000 ^a
<i>p</i> -cresol	30000 ^a

^a Using α -bromoacetophenone as bromine atom source, see text.

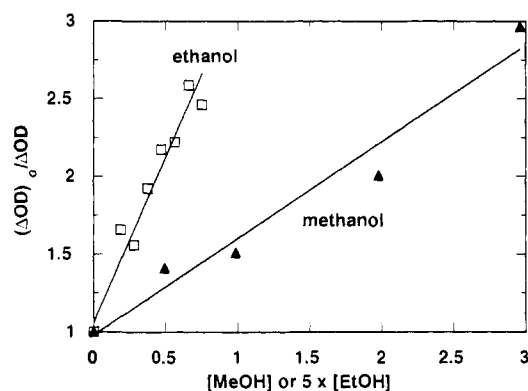


Figure 6. Plot according to eq 9 for data derived from the same experiments as those in Figure 5.

$\text{Br}_2^{\cdot-}$ in the presence and absence of R'H. The lifetime τ , in the absence of R'H is given by

$$\tau^{-1} = k_0 + k_1[\text{Br}^-] \quad (10)$$

Figure 6 shows plots according to eq 9 for methanol and 2-propanol under the same conditions as in Figure 5.

The data in Figure 6 lead to $k_6\tau$ values of 0.62 and 10.7 M^{-1} for methanol and ethanol, respectively. For 2-propanol (not shown) we obtained a value of 21 M^{-1} . These values should correspond to the ratio of slope to intercept in Figure 5; this calculation leads to values of 0.4, 8.3, and 20 M^{-1} for methanol, ethanol, and 2-propanol, respectively. Given the errors of $\pm 25\%$ that can be expected in Stern–Volmer plots of this type, the kinetic and quantum yield data show good consistency.

Finally, while photolysis of vicinal dibromides provides a convenient and exceptionally clean source of bromine atoms, its use is limited to substrates that are essentially transparent at the excitation wavelength (266 nm). In order to extend the appli-

cability of the probe approach, we have also used α -bromoacetophenone as a source of bromine atoms.¹³



Reaction 11 has been studied in detail¹³ and is known to lead to formation of bromine atoms with a quantum yield of 0.41 within 10 ns of excitation. This precursor of bromine atoms was used to study kinetics of reactions with triethylamine and *p*-cresol. The corresponding values of k_6 have been included in Table II.

Discussion

Our results show that the primary step in the photocleavage of vicinal dibromides (reaction 3) occurs systematically with a quantum yield of 1, suggesting that the process may involve a dissociative state of the C–Br bond. Recent gas-phase studies support this conclusion.²⁴ In addition, the α -bromoalkyl radical that results from the photocleavage undergoes further debromination (reaction 4) to produce a second bromine atom with 100% efficiency. Our results show that the rate constant for reaction 4 exceeds $5 \times 10^7 \text{ s}^{-1}$ in acetonitrile at room temperature. If we assume a preexponential factor for this process of around 10^{13} s^{-1} , then the activation energy for reaction 4 must be less than 7.5 kcal/mol.

In order to carry out detailed kinetic studies, it is not sufficient to identify a good source of bromine atoms. In addition, it is necessary to rely on a detectable signal, with a reasonable extinction coefficient. $\text{Br}_2^{\cdot-}$, generated via reaction 1, yields such a signal, with a convenient band at 360 nm and a weak (but useful for characterization purposes) band in the 680-nm region, see Figure 3. The probe method, centered around the use of eq 8, allows the determination of a wide range of rate constants, as illustrated in Table II.

A note of caution is worthwhile in connection to the application of the probe method. The technique allows the determination of absolute rate constants for reactions where all the reactants and all the products are invisible to the technique employed. Clearly there must be a price to be paid by using this approach. This is that the rate constants obtained contain no information regarding the mode or site of reaction. Thus, in the case of bromine atoms, the fact that the reaction involves hydrogen abstraction is inferred from the formation of HBr, while the site of attack relies on an educated guess based on the known reactivity of the substrates or on product studies. For example, it is clear that the methanol/ethanol/2-propanol reactivities follow the order of bond energies and known reactivities at the C–H bonds on the alcohol moiety.

In the examples listed in Table II, the mode and site of reaction do not represent a problem. However, we note that in the case of toluene we determined a rate constant of $6.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This case has been excluded from Table II because it is unclear what this value represents. Aromatic substrates are known to form complexes with halogen atoms quite easily; at the same time toluene is also a good hydrogen donor. Is this a case of complexation followed by hydrogen transfer within the complex, or is this a case where toluene acts both as a reactant and a "moderator" of the bromine atom concentration *via* complexation? Our data cannot answer these questions, but the case is brought up to illustrate the type of systems where the probe technique may have severe shortcomings.

As pointed out in the Results section, the rate constants measured are independent of parameters such as the concentration of bromide ions and the concentration and nature of the bromine atom precursors employed. This suggests that any complexation between bromine atoms and their precursors must be extremely weak, at least at the concentrations employed in this work. Shoute and Neta¹⁰ have reported rate constants for reactions of the

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bromine atom complexes $\text{CBr}_4\cdot\text{Br}$ and $\text{CH}_2\text{Br}_2\cdot\text{Br}$. In view of our results, it seems likely that the latter complex is sufficiently weak that their observed reactivity reflects largely bromine atom reactivity. In the only system where rate constants are readily comparable, the value reported for *p*-methoxyphenol was $1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in cyclohexane¹⁰ and is very similar to that for *p*-cresol in Table II. In contrast, in the case of $\text{CBr}_4\cdot\text{Br}$ it is clear that reactivities are greatly moderated,¹⁰ presumably reflecting stronger binding within this complex.

We note that reactions with hydrocarbon substrates are much slower, to the point that we were unable to measure any reliable rate constants under our experimental conditions. We take this observation to indicate that charge-transfer interactions must play an important role with the substrates in Table II, all of which contain at least one oxygen or nitrogen atom. The high rate constants obtained for triethylamine and *p*-cresol support this view. Further to this point, Shoute and Neta¹⁰ noted that the reaction of $\text{CH}_2\text{Br}_2\cdot\text{Br}$ with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine leads to its readily detectable radical cation.

It is clear that vicinal dibromides will not be convenient bromine atom sources where substrates absorbing at 266 nm, such as aromatic molecules, need to be used in significant concentrations.²⁵ In these cases, we have demonstrated that α -bromoacetophenone can be employed as an alternate source, although it is clear that reaction 11 is not as clean a source as vicinal dibromides. In this case it may also be possible to use the complexation between bromine atoms and aromatic molecules (e.g. benzene)¹³ as a probe reaction. This would facilitate work in nonpolar solvents.

Finally, the photodecomposition of vicinal dibromides thus provides a remarkably clean source of bromine atoms. Not surprisingly, these compounds have been found to be convenient photoacid generators for photoresist applications. Since the films employed in this type of use are frequently phenolic polymers (e.g. such as novolak),^{26,27} the bromine atoms readily abstract a hydrogen to form HBr.

Experimental Section

Materials. 1,2-Dibromoethane (I) and tris(2,3-dibromopropyl) isocyanurate (III), both from Aldrich, were used as received. We note that commercially available III is a mixture of diastereoisomers; the same applies to II.

(25) The same would apply to 248 nm, the other laser wavelength that would be convenient for this type of work. Even in cases where only very low substrate concentrations are required (see last two entries in Table II), we found it more convenient to find an alternate bromine atom source.

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1,2-Dibromodecane (II) was prepared by bromination of 1-decene (Aldrich). A stirred solution of 1-decene (28.05 g, 0.2 mol) in 70 mL of CH_2Cl_2 was cooled to 5 °C. A solution of Br_2 (31.85 g, 0.2 mol) in 30 mL of CH_2Cl_2 was then added dropwise while maintaining the temperature below 10 °C. After 4 h the reaction mixture was washed with 10% NaHSO_3 , followed by a H_2O wash, and dried over MgSO_4 . The solvent was then removed by evaporation, and the product was isolated by vacuum distillation: Yield 57 g (95%); bp 108–110 °C at 1.5 mm Hg.

Bromide ions were added as $(\text{C}_2\text{H}_5)_4\text{NBr}$ from Aldrich, which had suitable solubility in acetonitrile for our experiments. Acetonitrile, spectra grade from BDH, was used as received.

General Techniques. UV-visible spectra were recorded using a Hewlett-Packard 8451 diode array spectrometer. Gas chromatographic analyses were carried out on a Perkin Elmer Model 8320 capillary instrument fitted with a 15-m DB-5 bonded-phase column from J&W Scientific. HPLC analyses were performed on a Varian Instrument fitted with a 15-cm column (Varian) type MicroPak SP-C18.

Steady-state irradiations were performed in a photoreactor equipped with nine RPR-254 lamps. The temperature in this reactor was typically between 32 and 35 °C. The samples were contained in deaerated quartz tubes and were rotated with a "merry-go-round" to ensure that all samples received the same irradiation dose.

Laser Flash Photolysis. Experiments with dibromides were carried out using the fourth harmonic of a Surelite Nd-YAG laser for excitation (266 nm, ~6 ns, ≤ 20 mJ/pulse). In the few cases where α -bromoacetophenone was employed, it was irradiated with the third harmonic from the same laser (355 nm) or the pulses from a Lumonics EX-510 excimer laser (Xe/HCl, 308 nm, ~6 ns, ≤ 40 mJ/pulse). The system was controlled by a Macintosh II-ci computer running LabVIEW-2.2 software from National Instruments. This computer was also interfaced (GPIB) to a Tektronix Model 2440 digital oscilloscope that was used for data acquisition. Other aspects of the laser photolysis instrument resemble closely the setups described in other reports.^{28,29}

Unless otherwise indicated, the samples were deaerated by bubbling oxygen-free nitrogen through a container attached to the photolysis flow cell with Teflon lines. The photolysis cell was constructed of 7×7 mm² Suprasil tubing. All experiments were performed under flow conditions and (unless otherwise indicated) under a nitrogen atmosphere. The temperature of the photolysis samples was 20–22 °C.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada through an operating grant (J.C.S.) and a summer scholarship (M.K.). Thanks are due to Dr. J. Luszyk for valuable comments.

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