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Chain Amplified Photoacid Generation from Vicinal Dibromides. A General Strategy for the Efficient Generation of Hydrogen Bromide across the Ultraviolet and Visible Spectrum

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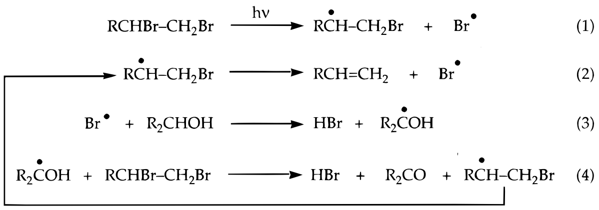
Vicinal dibromides are efficient HBr photogenerators that have found application in several acid-hardened photoresists. In this report we describe the photodecomposition of vicinal dibromides as a general chain reaction for HBr generation; a reaction that propagates in the presence of many substrates (i.e., alcohols, amines, sulfides) having the correct hydrogen-donor and reducing properties. In addition, we show that entry into the chain propagation steps of these reactions can be photoinduced by numerous initiation processes (e.g., hydrogen abstraction, fragmentation, electron transfer). Thus, provided a suitable photoinitiator is identified, it is possible to not only amplify the acid generation process but also use vicinal dibromides as photoacid generators across the UV and visible spectrum (and possibly the near infrared).

Introduction

Vicinal dibromides are efficient photochemical sources of hydrogen bromide. These photoacid generators (PAGs) have found application in several acid-hardened advanced negative resists. The mechanism of acid generation has been the subject of recent attention in our laboratory[1,2] and elsewhere.[3,4] In essence, most simple dibromides undergo rapid photoinduced C−Br bond cleavage with a quantum yield of 1. In nonstabilized systems, the β-bromo-substituted alkyl radical formed undergoes rapid cleavage to yield a second bromine atom and the corresponding alkene. Thus, reactions 1 and 2 in Scheme 1 combined lead to bromine atom formation with quantum yields approaching 2.[2,5]

We have recently shown that in the presence of alcohols containing the HCOH functionality, it is possible to trigger a chain reaction that effectively amplifies the acid-generation process.[5] The reaction involves reduction of the dibromide by the ketyl radical produced by hydrogen abstraction by the bromine atom, reactions 3 and 4 in Scheme 1. Thus, vicinal dibromides are effective bromine atom sources, and it is simply the tendency of the bromine atom to abstract hydrogen that makes them effective PAGs.

Scheme 1



β-Bromoalkyl radicals have lifetimes of <20 ns in simple systems such as 1,2-dibromoethane or 1,2-dibromododecane[2] but become very long-lived in systems involving stabilized (e.g., benzylic) radical centers.[3] We have recently shown that silicon stabilization [e.g., $Si(CHBrCH_2Br)_4$] can make these radicals sufficiently long-lived for reaction 2 to be accessible by nanosecond laser photolysis techniques.[6]

Bromine atoms are not readily detectable in the spectral region normally accessible in laser flash photolysis experiments. Addition of bromide ions leads to the rapid formation ($k_5 = 1.6 \times 10^{10}$ M^{-1} s^{-1})[1] of $Br_2^{\bullet -}$ which has an intense absorption at 370 nm, and a weak but very characteristic band in the 600 nm region.[7,8] Thus, $Br_2^{\bullet -}$ can be used as a “probe” for the identification of bromine atoms. This simple technique has allowed the determination of numerous rate constants for reactions of bromine atoms with a wide range of substrates.[2]

$$Br^{\bullet} + Br^{-} \rightarrow Br_2^{\bullet -} \qquad (5)$$

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

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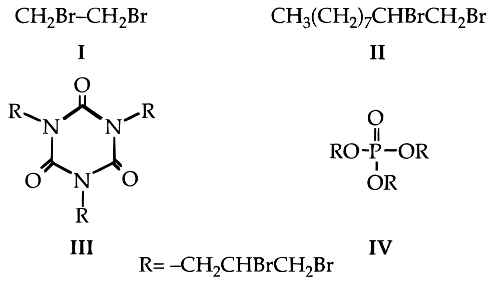
Chart 1



In this report we show that the chain decomposition of vicinal dibromides is a rather general reaction that can be triggered by many substrates with the correct hydrogen donor and reducing properties. We illustrate this with several amines, dialkyl sulfides, and alcohols. Further, entry into the propagation steps of these reactions does not require the direct photolysis of the dibromides, but instead, numerous other initiator processes can be employed as effective triggers for the reaction. In effect, this means that the compounds described here can be employed as PAGs across the UV and visible spectrum, provided a suitable initiator can be identified. In this regard, recent reports have explored the potential of visible light initiating systems.[9−11]

Work reported here has concentrated on four vicinal dibromides, **I**−**IV** (Chart 1), which were selected for various reasons. **I** is the simplest vicinal dibromide, **II** offers the possibility to monitor the progress of the reaction readily by analysis of the 1-decene formed, and **III** is important because it has found commercial applications.

A typical photoresist composition may incorporate the PAG, a polymer such as novolak, and, in the case of negative resists, an acid-activated cross-linker. The term “amplified resist” is normally used to indicate that cross-linking (during baking) uses the acid generated by the PAG as a catalyst. Thus, each acid molecule can lead to many cross-linking events that result in polymer insolubilization. Normally the acid generation step is not amplified. That is, each photon can lead to a maximum of one or exceptionally two (see reactions 1 and 2 in Scheme 1) molecules of acid. In this paper we demonstrate that the acid generation step can also be an amplified process. Thus, each photon can lead to many molecules of acid, each of which can in turn trigger numerous cross-linking steps. We also develop the strategies which can make these *doubly-amplified* resists available across the UV and visible spectrum. While our work concentrates on photoinduced initiators, it is clear that thermal sources may work just as well in those systems where image transfer is not important.

Experimental Section

Materials. 1,2-Dibromoethane (**I**), tris(2,3-dibromopropyl)isocyanurate (**III**), α-bromoacetophenone, triethylamine, trihexylamine, piperidine, 1-ethylpiperidine, morpholine, 4-ethylmorpholine, *N*,*N*-diethylaniline, *N*,*N*-diisopropylethylamine, 1-methylimidazole, naphthalene, pyrene, perylene, rubrene, and erythrosin B (spirit soluble), all from Aldrich, merocyanine 540, from Kodak, tris(2,3-dibromopropyl)phosphate (**IV**), from ICN, 2-isopropylthioxanthone from Biddle-Sawyer and Irgacure 907, Irgacure 369, Irgacure 184, and Darocur 1137, all from Ciba-Geigy, were used as received. 1,2-Dibromodecane (**II**) was prepared and purified as previously reported.[2] Quinuclidine and di-*n*-propyl sulfide, both from Aldrich, were purified as described in the literature.[12] All solvents, spectra grade from BDH, were 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. 1,2-Dibromodecane showed no thermal decomposition under the conditions of these analyses.

Steady-state irradiations were performed in a photoreactor equipped with RPR-2540, RPR-3000, or RPR-3500 lamps from the Southern New England Ultraviolet Co. The temperature in this reactor was typically between 32 and 35 °C. The samples were contained in quartz cells of the same type used for laser flash experiments and were rotated with a “merry-go-round” apparatus to ensure that all samples received the same irradiation dose. A few irradiations using long-wavelength sensitizers were also performed using either the pulses from the second harmonic of a Surelite Nd/YAG laser (532 nm, $\sim$6 ns, $<$40 mJ/pulse) or the pulses from a Lumonics HD-500 dye laser (420 nm, $\sim$6 ns, $<$20 mJ/pulse).

1-Decene Determination as a Measurement for HBr Generation. Monitoring of the progress of the chain reaction by analysis of 1-decene rather than HBr offered considerable analytical convenience. To ensure that these products were formed in the correct stoichiometric relationship, several samples were analyzed by both techniques.

Samples (2×3 mL) of solution containing 50 mM **II** in methanol or 2-propanol were deaerated by bubbling with oxygen-free nitrogen (20−30 min) in quartz cells and then irradiated at 254 nm for 10 min. After irradiation, HBr concentrations were determined by acid-base titrations as previously described.[5] The extent of photoconversion of 1,2-dibromodecane into 1-decene was determined by gas chromatography using dodecane as internal standard. Comparison of concentrations of 1-decene and HBr were in the expected 1:2 stoichiometric relationship. Thus, quantum yields (and therefore chain lengths) can be calculated either by acid−base titration or by chromatographic analysis of the corresponding alkene.

Laser Flash Photolysis. Experiments with α-bromoacetophenone were carried out using a Lumonics EX-510 excimer laser (Xe/HCl, 308 nm, $\sim$6 ns, $\leq$40 mJ/pulse) for excitation, while for vicinal dibromides we employed the fourth harmonic of a Surelite Nd:YAG laser (266 nm, $\sim$6 ns, $\leq$20 mJ/pulse). The system is controlled by a Macintosh II-ci computer running Lab-

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VIEW-2.2 software from National Instruments. This computer is also interfaced (GPIB) to a Tektronix Model 2440 digital oscilloscope used for data acquisition. Other aspects of the laser photolysis instrument resemble closely the set-ups described in other reports.[13,14]

Solutions were contained in quartz cells constructed of 7 × 7 mm^2 Suprasil tubing and deaerated by bubbling with oxygen-free nitrogen. All measurements were performed at room temperature.

Results

Laser Flash Photolysis. We have shown earlier that while bromine atoms do not have a convenient absorption in the spectral region accessible, they can be readily monitored by addition of bromide ions.[1,2] As a matter of convenience, bromide anions are usually added as their tetrabutylammonium salt. Formation of $Br_2^{\bullet -}$ according to reaction 5 provides a simple method for the study of these reactions.

Reaction 5 occurs with a rate constant of 1.6×10^{10} M^{-1} s^{-1} in acetonitrile at room temperature.[1] When bromide ions and a second substrate (as in the case of reaction 3) compete for reaction with bromine atoms, the experimental first-order rate constant for the growth of $Br_2^{\bullet -}$ is given by:

$$k_{obs} = k_0 + k_5[Br^-] + k_r[X] \qquad (6)$$

where X is the substrate of interest and k_0 the rate constant for bromine atom disappearance in the absence of quenchers. Thus, at constant bromide concentration a plot of k_{obs} against [X] yields k_r from the slope. While this method determines absolute rate constants, it yields no information on the site or mode of attack. For the substrates selected for this work, it is reasonable to assume that the dominant mode of reaction is hydrogen abstraction from the weakest C−H bond by $Br^\bullet$, consistent with the formation of HBr. For example, in the case of triethylamine, reaction 7 illustrates the process leading to HBr formation.

$$Br^\bullet + (C_2H_5)_3N \rightarrow HBr + CH_3\dot{C}HN(C_2H_5)_2 \qquad (7)$$

In a number of cases, we found that the substrates of interest compete for light absorption with the vicinal dibromide at the laser wavelengths of 248 and 266 nm. In these cases (e.g., amines), it was more convenient to use α-bromoacetophenone as a bromine atom source at 308 nm (reaction 8), an approach that circumvents the

$$PhCOCH_2Br \xrightarrow{h\nu} PhCO\dot{C}H_2 + Br^\bullet \qquad (8)$$

substrate absorption problems. We emphasize that this alternate precursor is needed only as a tool for the determination of rate constants; the initiation and chain reactions work quite well at the shorter wavelengths also. We do not envisage α-bromoacetophenone as a common ingredient in photoresist compositions due to its thermal instability.

Table 1 summarizes the rate constants determined in this work using the approach of eq 6, along with those rate constants reported earlier.[2] Representative plots using this technique have been included in earlier publications.[2] The reasons for the selection of this group of substrates will become apparent in sections of this article dealing with the chain reaction generation of HBr.

Table 1. Rate Constants for Reactions of Bromine Atoms in Acetonitrile at Room Temperature

substrate	k_r, M^{-1} s^{-1}	ref
methanol	9.3×10^5	2
ethanol	1.6×10^7	2
2-propanol	4.1×10^7	2
benzhydrol	4.1×10^9	5
p-cresol	3.0×10^{10}	2
dioxane	1.2×10^6	2
diethyl ether	1.7×10^7	2
triethylamine	2.9×10^{10}	2
piperidine	2.2×10^{10}	this work
morpholine	2.7×10^{10}	this work
ethylmorpholine	4.2×10^{10}	this work
ethylpiperidine	3.2×10^{10}	this work
N,*N*-diethylaniline	4.5×10^{10}	this work
methylimidazol	3.7×10^{10}	this work
quinuclidine	3.0×10^{10}	this work
di-*n*-propyl sulfide	2.2×10^{10}	this work
cyclohexane	$<1.0 \times 10^5$	2

Table 2. Rate Constants for the Reaction of Representative Chain Carriers with Excited States in Acetonitrile at Room Temperature

sensitizer	excited state	chain carrier	k, M^{-1} s^{-1}	ref
acetone	triplet	2-propanol	9.7×10^5	24
benzophenone	triplet	2-propanol	2.8×10^6	this work
acetone	triplet	triethylamine	2.9×10^8	24
benzophenone	triplet	triethylamine	3.2×10^9	17
2-isopropylthioxanthone	triplet	triethylamine	4.0×10^9	this work
naphthalene	singlet	triethylamine	9.4×10^9	25
pyrene	singlet	triethylamine	3.9×10^{8} [a]	26

[a] Value in acetonitrile:water (1:1).

Reaction 2 in Scheme I is fast ($k_2 > 5 \times 10^7$ s^{-1}) for all the molecules studied in this work.

In principle, any photosensitizer that provides a direct or indirect entry yielding the reaction intermediates involved in the chain propagation steps (reactions 2−4) in Scheme 1 could behave as a photoinitiator for the PAGs discussed herein. Knowledge of radical photoinitiators for chain reactions is abundant in the literature and a wide range of products is commercially available for this specific purpose. To test the generality of this concept, we have examined the kinetics of a few photoinitiator systems; these are summarized in Table 2. This list is in no way comprehensive but serves to illustrate the versatility of the approach. Many other systems could be readily identified depending on the specific requirements of each system. It is important to note that intermolecular initiation does not necessarily require hydrogen transfer; in fact, some of the examples in Table 2, such as pyrene−triethylamine are well-known to involve electron transfer.[15] Further, some of the initiators employed (vide infra) such as the Irgacure series are known to induce photoinitiation by intramolecular bond cleavage, frequently via the Norrish Type I reaction, to yield free radicals.

Chain Reactions Initiated by Benzophenone. To test the ability of several hydrogen donors to act as

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Table 3. Relative Yields of 1-Decene for the Benzophenone-Sensitized Decomposition of II in Acetonitrile in the Presence of Various Amines[a]

amine	rel yield
triethylamine	43
ethylpiperidine	43
trihexylamine	28
ethylmorpholine	25
diisopropylethylamine	24
N,*N*-diethylaniline	1[b]
piperidine	n.r.
morpholine	n.r.
quinuclidine	n.r.

[a] [**II**] = 0.015−0.020 M; [amine] = 0.6 M; [benzophenone] = 0.020 M; $\lambda_{\text{irrad}} = 350$ nm. [b] Taken as a reference for product yields.

chain carriers for the generation of hydrogen bromide, we decided to utilize a constant set of conditions with benzophenone as a photosensitizer. Benzophenone initiates the reaction by hydrogen abstraction by its triplet state, efficiently formed by rapid intersystem crossing of the singlet state.[16] Reactions 9 and 10 illustrate the process for the cases of 2-propanol and triethylamine.

$$\mathrm{Ph_2CO^* + (CH_3)_2CHOH \rightarrow Ph_2\dot{C}OH + (CH_3)_2\dot{C}OH} \tag{9}$$

$$\mathrm{Ph_2CO^* + (C_2H_5)_3N \rightarrow Ph_2\dot{C}OH + CH_3\dot{C}HN(C_2H_5)_2} \tag{10}$$

These processes occur with rate constants of 2.8 × 10^6 and 3.2 × 10^9 M^{-1} s^{-1} in acetonitrile for 2-propanol[17] and triethylamine, respectively. The radicals resulting from reactions 9 and 10 are all known to be good reducing agents[18] and react with vicinal dibromides according to reactions 11−13.

$$\mathrm{Ph_2\dot{C}OH + RCHBrCH_2Br \rightarrow Ph_2CO + R\dot{C}HCH_2Br + H^+ + Br^-} \tag{11}$$

$$\mathrm{(CH_3)_2\dot{C}OH + RCHBrCH_2Br \rightarrow CH_3COCH_3 + R\dot{C}HCH_2Br + H^+ + Br^-} \tag{12}$$

$$\mathrm{CH_3\dot{C}HN(C_2H_5)_2 + RCHBrCH_2Br \rightarrow CH_2{=}CHN(C_2H_5)_2 + R\dot{C}HCH_2Br + H^+ + Br^-} \tag{13}$$

In the case of reaction 11, the rate constants have been determined in earlier work in tetrahydrofuran solution and lead to k_{10} values ranging from 8.9 × 10^2 M^{-1} s^{-1} for **I** to 5.6 × 10^3 M^{-1} s^{-1} for **IV**.[5] No rate constants are known for reactions 11 and 12, although they are anticipated to be faster than that for reaction 10. The cycle is completed by the fragmentation of the bromoalkyl radical according to reaction 2. In the case of alcohols we have shown that vicinal dibromide reduction by the ketyl radicals (e.g., reactions 10 and 11) are rate determining in the overall chain propagation process.[5] Table 3 compares the efficiencies observed for several amines. We have shown earlier that in the case of **II**, the yields of hydrogen bromide are always twice the yield of 1-decene, as expected (see Experimental Section);[5] thus, as a matter of analytical convenience reaction yields are based on the formation of 1-decene. It is evident from these data that aromatic amines are substantially less efficient than their aliphatic counterparts; further, the ability to react is greatly reduced in cyclic systems such as quinuclidine. We note that under the conditions of these experiments cyclic systems (e.g., piperidine) give virtually no detectable amounts of 1-decene.

Table 4. Quantum Yields of 1-Decene for the Benzophenone-Sensitized Decomposition of II in Acetonitrile/Hydrogen Donor Mixtures

hydrogen donor, HD	% v/v HD	[**II**], M	conditions	$\Phi_{\mathrm{c=c}}$[a]
none	0	0.019	350 nm (1 lamp), 60 min	$\ll 10^{-3}$
methanol	85	0.019	350 nm (1 lamp), 60 min	0.11
2-propanol	85	0.019	350 nm (1 lamp), 40 min	0.14
di-*n*-propyl sulfide	85	0.019	350 nm (1 lamp), 30 min	0.13
triethylamine	85	0.019	350 nm (1 lamp), 1 min	23
methanol	85	0.136	350 nm (2 lamps), 60 min	0.3
2-propanol	85	0.128	350 nm (2 lamps), 30 min	0.5
triethylamine	85	0.126	350 nm (2 lamps), 1 min	44
methanol	100	0.040	350 nm (2 lamps), 60 min	0.068
2-propanol	100	0.048	350 nm (2 lamps), 40 min	1.3
triethylamine	100	0.045	350 nm (2 lamps), 1 min	8.0

[a] Quantum yield.

To compare amines with other types of substrates, a series of experiments was carried out in the hydrogen donor−chain carrier as solvent or cosolvent (85% v/v) with acetonitrile (15%). These results are summarized in Table 4. Quantum yields (and therefore chain lengths) are expected to depend upon the detailed irradiation conditions (including light intensity) α. The series in Table 4 was carried out under matched experimental conditions. A few initial experiments were carried out with 100% hydrogen donor. However, the precipitation of ammonium salts from triethylamine posed some problems that were overcome by use of 15% acetonitrile.

We note the inclusion of di-*n*-propyl sulfide in Table 4, which as a chain carrier has an efficiency comparable with 2-propanol, which we earlier showed to be a very efficient chain carrier among a series of alcohols.[5] The low yields shown in Table 4 however clearly indicate that benzophenone is actually not an efficient initiator when using alcohols as chain carriers.

Sensitized and Photoinitiated Chain Acid Generation. Table 5 gives a listing of the photosensitizers that have successfully been used as chain initiators for the production of HBr, along with the wavelengths at which they have been tested. We note that our time resolved evidence from laser flash photolysis (vide supra) suggests that most of these reactions involve the lowest excited states of the photosensitizers; thus, one would expect their efficiency as photoinitiators to extend to the red edge of their absorption band. For example these limits for merocyanine-540, erythrosin-B, and rubrene are 610, 580, and 575 nm,[19] respectively.

Among the group labeled ketones in Table 5, we expect the chain reaction to be triggered by hydrogen abstraction from the chain carrier. The group labeled radical initiators is usually composed of ketones capable of cleavage according to the Norrish type I reaction.

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(19) These wavelengths are the longest for which the extinction coefficient exceeds 100 M^{-1} cm^{-1}.

Table 5. Photosensitizers That Succesfully Initiated the Chain Reaction between II (0.015−0.020 M) and Triethylamine (0.6−0.7 M) in Acetonitrile Solution at Room Temperature[a]

ketones[b]	radical initiators	aromatic hydrocarbons	dyes
acetone (300 nm)	Irgacure 907 [0.44] (300 and 350 nm)	naphthalene (300 nm)	merocyanine 540 (532 nm)
benzophenone [1] (300and 350 nm)	Irgacure 369 [0.72] (350 nm)	pyrene [1.1] (300 nm)	erythrosin B, spirit soluble (532 nm)
2-Isopropylthioxanthone [0.28] (350 nm)	Irgacure 184 [1.1] (300 nm)	perylene [0.33] (350 and 420 nm)	
	Darocur 1137 [1.0] (300 nm)	rubrene (300 nm)	

[a] Wavelength of testing shown in parentheses (−); efficiency relative to benzophenone given in square brackets whenever available [-]. [b] These ketones normally initiate the process via ketone photoreduction.

Chart 2

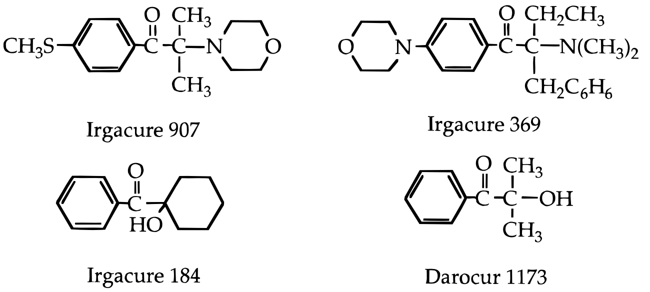


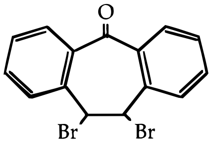
Chart 2 gives the structures of the initiators in this group included in Table 5. The aromatic hydrocarbons of Table 5 have no tendency toward hydrogen abstraction in either their singlet or triplet excited states, but they do have a tendency toward electron-transfer reactions, which are well established in the case of amines.[15] Depending upon the experimental conditions some of the amine radical cations produced by electron transfer may deprotonate to yield the neutral radical. Systems mediated by excited singlet states may operate at longer distances than those involving triplet states and thus have some desirable characteristics under the conditions of limited diffusion prevailing in polymer films.

Finally, the last group includes a couple of dyes that probably trigger the chain reaction by photoinduced electron transfer reactions from either the singlet or triplet state with the amines. No attempt was made to compile a comprehensive list of photoinitiators, or to select them to include all possible wavelength ranges. We note that in one case we have shown that a commonly used cross-linker can also act as photosensitizer (albeit with limited efficiency) for the decomposition of vicinal dibromides.[20]

Efficiencies can be compared only for values determined at the same wavelength. In those cases where the values are available, they have been included in square brackets in Table 5 using benzophenone as a reference.

Discussion

Vicinal dibromides are excellent sources of bromine atoms under deep-UV irradiation, where in simple aliphatic systems reactions 1 and 2 couple to produce $Br^{\bullet}$ with a quantum yield of 2.0. Under some conditions it is possible to extend the spectral response to the near-UV spectrum, while maintaining high quantum yields; for example, **V** has been examined by McGimpsey and co-workers, who established that reaction 2 is also rapid with this substrate.[4]



V

The strategy is unfortunately not general, and McGimpsey has shown that molecules such as 1-(1,2-dibromoethyl)naphthalene undergo efficiently reaction 1, but the radicals are stabilized such that reaction 2 becomes too slow to be useful.[3] Clearly, molecules of this type have little to gain energetically by fragmenting to yield the corresponding vinylaromatic compound. In any event, quantum yields of direct photolysis are limited to a maximum of 2 for bromine atom production.

As already indicated, bromine atoms are usually sufficiently reactive toward hydrogen atom abstraction[2,5] that in general it can be assumed that their conversion to hydrogen bromide will be near-quantitative. This is clearly the situation in phenol-rich environments such as some of the polymers (e.g., novolak) that are widely employed in photoresist applications. In poor hydrogen donating solvents such as acetonitrile, bromine atoms frequently recombine to yield molecular bromine.[2,5]

The formation of hydrogen bromide can be greatly enhanced by adding a suitable chain carrier so as to trigger the chain propagation process of reactions 2−4 (alcohols) or 2, 7, and 13 (triethylamine). We believe that proper optimization of the experimental conditions could readily lead to increases in acid generation of 2 or 3 orders of magnitude compared with the non-chain process discussed above.

In the context of a general strategy for these chain reactions, it is important to identify the properties required for a molecule to act efficiently in this role. Table 6 shows the types of reactants, intermediates, and products involved in the systems examined by us. These three groups of compounds have in common that the reagent is a good hydrogen donor (see Table 1), that the intermediate radical is a strong reducing agent, leading to the reduction of the dibromide with formation of a double bond. Conceivably comparable strategies leading for example to aromatization could yield similar results. For example, we thought that 1,4-cyclohexadiene, an excellent hydrogen donor, would be an effective chain carrier (leading to benzene via the cyclohexadienyl radical). To our surprise, these experiments did not lead to any significant enhancement of the HBr yields. We presume that the reduction of the dibromide by cyclohexadienyl radicals was slow, although the matter was not pursued any further.

While much of our work was carried out with 1,2-dibromodecane as the HBr source, this reflected the

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Table 6. Reagents, Intermediates, and Products for Some Molecules Capable of Chain Generation of Hydrogen Bromide

functional group	example		
	reagent	intermediate	product
alcohol	$CH_3CHOHCH_3$	$CH_3\dot{C}(OH)CH_3$	CH_3COCH_3
amine	$(C_2H_5)_3N$	$CH_3\dot{C}HN(C_2H_5)_2$	$CH_2{=}CHN(C_2H_5)_2$
sulfide	$(C_3H_7)_2S$	$CH_3CH_2\dot{C}HS\text{-}(C_3H_7)$	$CH_3CH{=}CHS(C_3H_7)$

convenience of analytical work in the case of the product, 1-decene. However, experiments with the other precursors of Chart 1 also led to hydrogen bromide generation with comparable efficiency. In particular, in the case of **III** we were able to detect the mono-, di-, and triallyl derivatives. The triallyl compound is in fact the precursor from which **III** is prepared commercially.

Our tests of a variety of photoinitiators and photosensitizers (see Table 5) clearly show that essentially any absorber that can lead to reactive radicals or radical ions can effectively trigger the chain generation of hydrogen bromide in the presence of a chain carrier of one of the types included in Table 6. The importance of this versatility is that it allows the generation of hydrogen bromide across the UV and visible spectrum. Further, we are certain that a careful selection of available sensitizers would allow the same strategy to be applied in the near-infrared region, at wavelengths such as those readily available from diode lasers.

Conclusion

The term *amplified* is used in photoresist technology to indicate that each molecule of acid, such as HBr, is able to catalyze a cascade of chemical reactions which lead to image definition. In the case of amplified negative resists (ANRs for short) it indicates that each molecule of acid can cause many of the polymer cross-links required for adequate insolubilization. The catalytic cross-linking reaction normally occurs during postexposure baking of the resist film. The acid-generating strategy presented in this work provides an additional amplification stage, by generating acid using a photoinduced chain reaction. This should lead to a dramatic increase in photoresist speed by providing in effect a *doubly amplified* mechanism for the cross-linking of ANRs or deblocking in the case of positive-tone resists.

The individual chain carriers tested here are not without limitations. Thus, for example, it could be claimed that amine addition requires a base to enhance acid formation, thus effectively compensating for at least some of the increase in acid production. While this is true, there may be instances in which a small amount of amine may be desirable as a way of limiting diffusion. Given that hydrogen donor ability and pK_a are relatively independent parameters, it may be possible to select amines with modest basicity. Further, careful choice of the amine can lead to HBr−amine complexes that dissociate during the critical baking process. Other substrates, such as alcohols and sulfides should not have these problems. Additionally, these represent solution studies, and it is recognized that the situation may differ in polymer films.

It should be noted that other bromo compounds, in addition to vicinal dibromides, can also carry similar chains, although they yield only one molecule of HBr per propagation cycle.[21−23] Such is the case for α-bromoacetophenone.[21]

Finally, one of the major expected applications of these systems resides in their potential for use at a wide range of wavelengths, thus making them applicable for the deep-UV to the visible region and possibly even the near infrared.

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