Photohydrolysis of 1,2-Dibromo-3-chloropropane

C. E. Castro,* Steve Mayorga, and N. O. Belser

Irradiation of dilute aqueous solutions of 1,2-dibromo-3-chloropropane (1) with a 450-W medium-pressure mercury lamp results in a rapid photohydrolysis ($t_{1/2}$ = 25 min) to the isomers 2-bromo-3-chloropropanol-1 (2) (72%) and 1-bromo-3-chloropropanol-2 (3) (28%). Both 2 and 3 undergo sequential photocatalyzed conversions to nonhalogenated products. The former is converted to acrolein polymer via the sequence 3-chloropropanaldehyde → acrolein → acrolein polymer. The latter (3) is converted to a mixture of products including chloroacetone, epichlorohydrin, and 1-chloropropanol-2, but the predominate pathway leads to glycerine and hydroxyacetone via the intermediate 1-chloro-2,3-dihydroxypropane. The overall conversion of 1 to acrolein is fast, with the slowest step having a $t_{1/2}$ of 41 min. However, the path to glycerine and hydroxyacetone proceeds with a final $t_{1/2}$ of 58 h. The branched reaction pathway and rates for each step are presented. The rate enhancement for the hydrolysis of 1 by photolysis is ~10^5. The products of these reactions can be rationalized by carbocationic intermediates, but the regioselectivity and relative rates suggest other mechanisms may be operative.

The photodecomposition of pesticides in water represents an important set of environmental transformations. Photoreactions of aromatics and heterocyclic derivatives have been examined for some time (Crosby et al., 1971), and selected studies of aryl halide hydrolysis have recently appeared (Dullin et al., 1986).

The chemistry and general mechanism of the photolysis of aliphatic halides in the gas phase (Steacie, 1958; Major and Simons, 1964) and in solution (Sammes, 1973; Lodder, 1983) is well charted. Under these conditions, reaction products emanate from free radicals that result from the initial photoinduced homolysis of the carbon–halogen bond. Reactions in polar millieu, however, can generate products that derive from carbocations (Kropp, 1984). In methanol, for example, the cationic pathway can predominate. Indeed, the reactions can be used to generate vinyl (Kropp et al., 1983; Kitamura et al., 1986) and bridgehead (Kropp, 1984) carbocations that are not easily obtained by ground-state means. Generally, alkyl iodides have been employed in these reactions, and they seem to yield the highest ratio of cation to radical products. Thus, photolysis of 1-bromonorbornane in methanol does yield the corresponding methyl ether, but the reduction (radical) product norbornane predominates. Recently copper(II) salts have been shown to force the generation of cations from the photolysis of vinyl bromides (Kitamura et al., 1986). Still, little is known about the processes aliphatic bromides and chlorides may undergo in a more polar solvent like water.

We have been interested in the simple C_1–C_3 organic halides that have been extensively employed as soil fumigants for the control of nematodes and fungi. Photolysis (Castro and Belser, 1981, 1985) of dilute aqueous solutions of these substances results in a remarkable rate enhancement of hydrolysis, but the actual path of the reaction can be surprising. For example, chloropicrin (Castro and Belser, 1981) produces NO_3^- quantitatively. Ethylene dibromide (Castro and Belser, 1985) does yield ethylene glycol, but the pathway proceeds quantitatively through ethylene oxide.

In this work we focus on the nematicide 1,2-dibromo-3-chloropropane. The reaction is more complicated than observed with the C_1 or C_2 compounds. Initially the reaction produces cleanly a mixture of the isomeric hy-

droxybromochloropropanes. Each of these undergo further phototransformations that result in seven products. While the results can be explained by cationic intermediates, other pathways may be involved.

EXPERIMENTAL SECTION

1,2-Dibromo-3-chloropropane was a commercial sample that was distilled under vacuum before use. 2-Bromo-3-chloropropanol-1 was prepared and purified by the method of Dela Mare (1962). The 2-hydroxy-1-bromo-3-chloropropane isomer was prepared by the reaction of anhydrous magnesium bromide with epichlorohydrin; bp 52 °C (17 mm). Epichlorohydrin and acrolein were distilled before use. Chloroacetone, 1-chloro-2-propanol, hydroxyacetone, β-chloropropionaldehyde, diethyl acetal, and glycerine were reagent-grade standards and were used without purification. 1,2-Dihydroxy-3-chloropropane was obtained and purified as previously described (Castro and Bartnicki, 1968) and refractionated before use; bp 90 °C (3 mm).
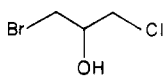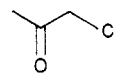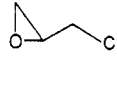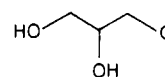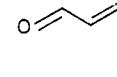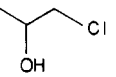
Reactions. General reaction conditions entailed irradiation of a 10^{-2}–10^{-3} M substrate solution in water with a 450-W medium-pressure quartz mercury lamp (Hanovia) in the manner previously described for ethylene dibromide (Castro and Belser, 1985). The photoreactions in this work were conducted in air or under argon in the presence or absence of 0.1 M phosphate buffer at pH 5.6. The buffer had no effect on the pathway and was employed to diminish any acid-catalyzed reaction during workup. Neutralization of reaction mixtures with NaOAC before workup had the same effect, and this procedure was adopted. The results under argon were the same as those obtained in air.

1,2-Dibromo-3-chloropropane (λ_{max} 205 nm). A 600-mL sample of 1.58 × 10^{-3} M solution of DBCP was irradiated for varying times with stirring in the tube-shaped quartz finger-reactor. Temperature was maintained at 30 °C by a water bath.

After 40 min, the bromide ion concentration was 10^{-3} M and the reaction solution was clear. Gas chromatographic analysis upon a 12 ft 30% SE Gum 30 column at 180 °C showed two product peaks coemergent with 1-hydroxy-2-bromo-3-chloropropane and 2-hydroxy-1-bromo-3-chloropropane. Both were qualitatively identified by GC–MS, the 2-hydroxy isomer showed P^+ at 172, 174, and 176. The 1-hydroxy compound showed the highest mass ion at 136 and 138 corresponding to P – HCl. The mass spectrum of each isomer was identical to that of an

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Table I. Time Course for 1-Bromo-3-chloropropanol-2

time, min	[Br⁻]ᵃ	Br~OH Cl	O~Cl	O~Cl epoxide	HO~OH Cl	O~	OH Cl
0		100					
21	6	90	2	2	(2)ᵇ	0	0
45	16	80	4	2.5	(8.5)	1.0	0
63.5	26	70	4.5	3.0	(17.5)	1.0	1.0
90	40	54	5.0	3.5	(27)	2.0	2.5
120	53	38.5	5.0	4.0	(38)	3.0	3.0
240	80	10.9	2.0	4.0	(62)	4.0	5.0
300	89	9	2.0	5.0	(68)	4.5	6.0
360	95	4	1.0	5.0	(73)	3.0	6.5
420	100	2	0.5	3.0	72	2.0	6.0

ᵃConcentration of all products in (M × 10⁴). ᵇCalculated values in parentheses.

authentic standard. Quantitation of the isomeric halo alcohols was accomplished by comparison with authentic standards. At this time yields of the 1-hydroxy and 2-hydroxy isomer were 72 and 28%, respectively. Further irridation for 2 h resulted in a turbid solution that contained a white precipitate. The solution was vacuum filtered, neutralized with sodium acetate to pH 5, and extracted with ether in a liquid–liquid extractor. The ether solution was dried over sodium sulfate and concentrated to a volume of 1–2 mL. Gas chromatographic analysis of the concentrate showed none of the hydroxybromopropanols, but an early peak corresponding to acrolein was apparent. A red (2,4-dinitrophenyl)hydrazone prepared and isolated from the ether concentrate had a melting point and mixed melting point with acrolein DNP (mp 165 °C) that was somewhat depressed (155–165 °C). The mass spectrum of a TLC-purified fraction was identical with that of acrolein DNP.

Analysis of the aqueous phase for bromide ion by direct potentiometry indicated all the bromine had been removed from the substrate: [Br⁻] = 3.2 × 10⁻³ M. Note: An identical sealed solution allowed to stand 20 months in the dark at 22 °C showed a Br⁻ concentration of 3.1 × 10⁻⁵ M. This corresponds to a $t_{1/2}$ of ~54 years.

The white precipitate and turbidity was deduced to be acrolein polymer. This was confirmed by comparison of the IR spectrum of the polymer with that resulting from the irradiation of acrolein at 10⁻³ M under identical conditions.

Repeat reactions were monitored by direct flame ionization gas chromatography with time. Usually 1-μL aliquots were injected on the SE-30 column at 180 °C. The first new product peaks corresponded to the hydroxy-bromo-3-chloro derivatives. As these declined, peaks corresponding to chloropropionaldehyde and acrolein were observed on the 1-ft Porapak P column at 180 °C.

Kinetics. Reactions exactly like the one above were monitored with time for Br⁻ production, substrate disappearance, and product generation. For DBCP, ethylene dibromide was added as an external standard to the reaction aliquot before GC analysis. For all other substrates, authentic standards of the substrate or product were employed for quantitation. Reproducibility of GC analysis was usually ±5%. A clearer picture of the overall transformation was obtained by independent study of the photoreactions of the first generated chlorobromopropanols.

1-Hydroxy-2-bromo-3-chloropropane ($\lambda_{max} < 190$ nm). Reaction was conducted with 600 mL of 10⁻² M substrate in the manner described for DBCP. Bromide ion was monitored by direct potentiometry of 1-mL aliquots, and organics were followed by gas chromatography on a 2-ft Porapak P column at 150 °C. The first product peak

corresponded to 3-chloropropionaldehyde. The nature of the substrate was confirmed by GC–MS (parent at 108 and 110). As the chloropropionaldehyde disappeared, acrolein appeared. The latter diminished with time and the solution became turbid. The polymer precipitate was present at the end of the run.

3-Chloropropionaldehyde (λ_{max} 265 nm). A 600-mL solution of 10⁻² M aldehyde prepared by acid hydrolysis of the dietyl acetal was irradiated and monitored in the manner described above. Chloride ion from 1-mL aliquots was determined by direct potentiometry. As the chloro aldehyde disappeared, acrolein appeared and fell off. After 90 min the Cl⁻ yield was 80% (8 × 10⁻³ M). The aqueous solution contained a trace of chloroaldehyde (1.5 × 10⁻³). The bulk of the product was in the polymer.

Acrolein (λ_{max} 210, 315 nm). A 600-mL solution of 10⁻² M acrolein irradiated as above afforded 95% of acrolein polymer in 2 h.

2-Hydroxy-1-bromo-3-chloropropane ($\lambda_{max} < 190$ nm). A 600-mL sample of 10⁻² M solution was irradiated and monitored in the manner described above.

In this case very early samples subjected to gas chromatography indicated a partial isomerization of the 2-hydroxy isomer to the 1-hydroxy isomer. First new product peaks corresponded to chloroacetone and epichlorohydrin 2.5 and 3.0 min (30 M RSL 150 capillary column, 35–100 °C). These were confirmed by GC–MS (P⁺ at 92 and 94). These were followed by acrolein (1.6 min) and 1-chloro-2-propanol (2.8 min) (GC–MS parent at 94 and 96) and acrolein polymer. The material balance in these runs decreased with time (cf. Table I).

While throughout the remaining, starting substrate (8.0 min) and Br⁻ balanced well, the total organics did not. The compound 1,2-dihydroxy-3-chloropropane was suspected but was not easily detected by flame ionization.

Subsequent runs at 10⁻² M were carried to completion in 7 h (Br⁻ concentration 10⁻² M). The acrolein polymer was filtered, the reaction mixture was neutralized with sodium acetate to pH 5, and the entire aqueous solution was concentrated on a rotary evaporator to a thick partially crystalline syrup. The salt mixture was repeatedly triturated with acetone. The acetone solution was dried over Na₂SO₄ and concentrated. Analysis by gas chromatography on a 6-ft SE 30 column at 150 °C with a thermal conductivity detector showed a dominant peak coemergent with the expected dihydroxychloropropane (at 2.1 min). The nature of the substance was confirmed by GC–MS using a silicone capillary column. The peak coemerging with 1,2-dihydroxy-3-chloropropane exhibited a mass spectrum identical with that of an authentic standard. The high mass peak at 79 corresponds to P – Cl.

The substance was subsequently quantitated by flame ionization gas chromatography on a 30 M RSL 150 ca-

pillary column at 90 °C. The yield was 72%. The weight of dried acrolein polymer, 0.0267 g, corresponded to 8% of the product.

1-Chloro-2,3-dihydroxypropane ($\lambda_{max} < 190$ nm). This substance was slow to photolyze. A 600-mL sample of a 10^{-2} M solution irradiated as above for 62 h showed chloride ion at 0.52×10^{-2} M (52% conversion). Direct GC analysis (6-ft. 30% SE 30 column at 180 °C) showed product peaks corresponding to acetol (0.7 min), starting chlorodihydroxypropane (1.6 min), and glycerine (3 min). The products were confirmed by GC–MS: P+ at 74 and 92, respectively. The mass spectra were identical with those of authentic samples. The yields of hydroxyacetone and glycerine were 15 and 85%, respectively.

RESULTS

Stoichiometry and Pathway. The photolysis of 1,2-dibromo-3-chloropropane in aqueous solution results in an overall (>95%) conversion to the completely dehalogenated products acrolein (and acrolein polymer), glycerine, and hydroxyacetone. The stoichiometry is that given in eq 1. The overall time course for organic halide consumption and bromide ion release is shown in Figure 1. This process however is complex and proceeds by two main pathways. The general overall sequence of reactions is given in Figure 7.
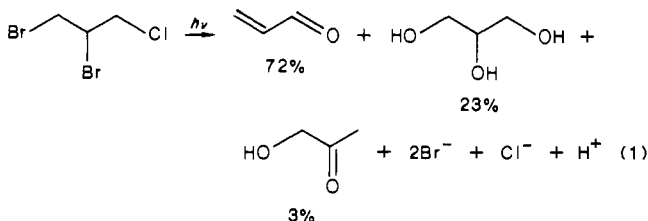
Initial Step. The first conversion of the trihalo compound results in the isomeric bromohydroxychloropropanes. The 1-hydroxy isomer predominates (eq 2).
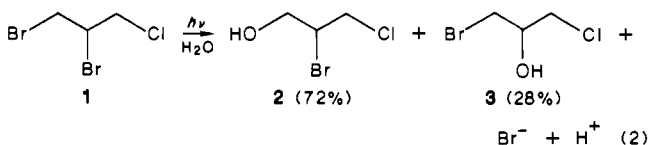
The reaction is quantitative in the initial stages, and the time course for one of the runs is depicted in Figure 2. Each of the dihalo alcohols undergoes photoconversion by sequential processes. The figure also illustrates the slight lag time associated with beginning with a cold lamp.

2-Bromo-3-chloropropanol-1. This substance is converted to acrolein in two steps. The first step entails the production of β-chloropropionaldehyde (eq 3). Reaction
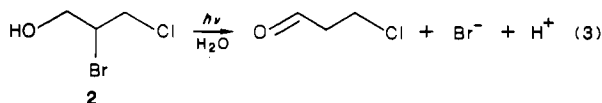
3 is quantitative and is followed by the conversion of the chloroaldehyde to acrolein (eq 4). The latter polymerizes
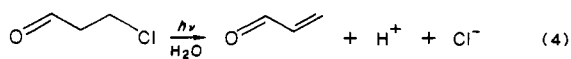
(eq 5). The overall material balance between starting

chloro aldehyde and acrolein and acrolein polymer was good at any time, and the time course of the reaction is shown in Figure 3.
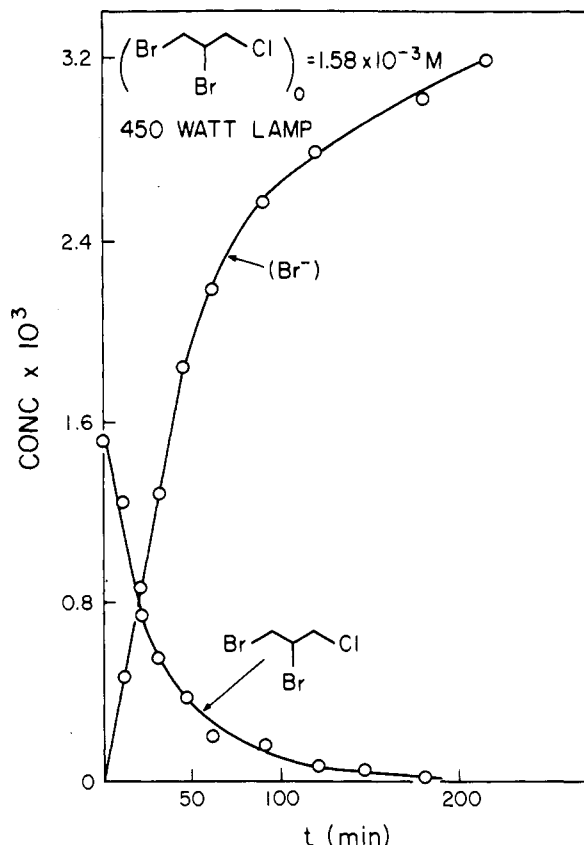
Figure 1. Overall rates of 1,2-dibromo-3-chloropropane disappearance and Br⁻ release.
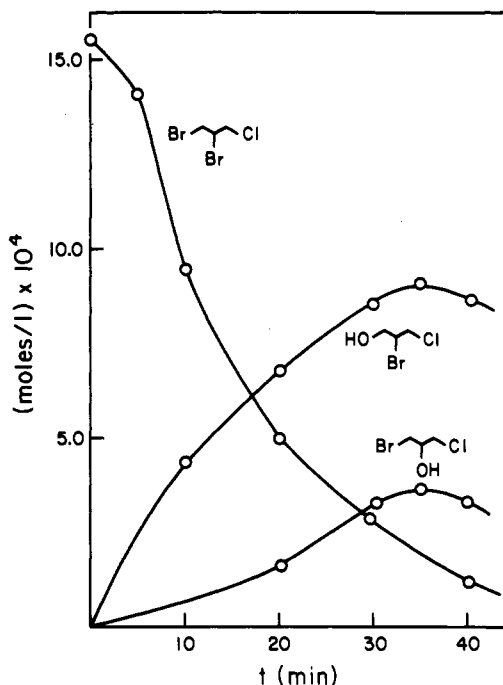
Figure 2. Initial time course of the DBCP photohydrolysis (eq 2).

1-Bromo-3-chloropropanol-2. Quantitation of all products from this alcohol was difficult. The results reflect a multiplicity of reaction pathways (see below). In the initial phases aqueous photolysis produced the 1-hydroxy isomer, epichlorohydrin, and chloroacetone. While the yield of Br⁻ corresponded well with the amount of starting alcohol, the material balance for organics was not good and lessened with time (cf. Experimental Section and Table I). A major portion of the product (40%) was missing from the first

Figure 3. Time course for 2-bromo-3-chloropropanol-1 (eq 3).

time point. It was subsequently demonstrated that this was accounted for by 1-chloro-2,3-dihydroxypropane. The latter was not easily detected by flame ionization gas chromatography of the reaction mixture. This was subsequently accomplished. The final yield of this material reached 72% in 6 h. The reaction produces a complex mixture of products at the outset (eq 6) including the

reduction product chloropropanol-2 (6%). β-Chloropropionaldehyde, acrolein, and acrolein polymer subsequently derive from **2** (eq 3–5). The yield of the isomerization product **2** in the first step (eq 6) is calculated from the final yield of acrolein 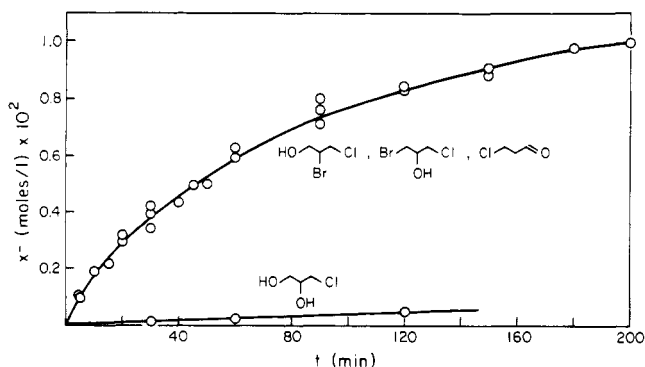and acrolein polymer. A partial time course for one of the runs is shown in Figure 4. The dihydroxy chloro compound is a main product of the initial interaction, and it is the dominant final product in the short term. In part this must be the result of the hydrolysis of epichlorohydrin (eq 7), though we have no evidence

idence for a photocatalysis of eq 7. (We have previously demonstrated that the hydrolysis of ethylene oxide is not catalyzed under these photolytic conditions.) Consequently, it was of interest to learn whether or not an organic chloride of this type may undergo further photohydrolysis albeit more slowly than the precursor bromo compounds. The chloro diol does undergo a photoreaction.

3-Chloro-1,2-dihydroxypropane. Reaction proceeds smoothly but slowly to glycerine and hydroxyacetone (eq

Figure 4. Time course for 1-bromo-3-chloropropanol-2 (eq 6).

8). Whether or not the epoxide glycidol is an intermediate was not established, but it could not be detected in the reaction mixture.

Given this conversion (eq 8) we presume the other chlorinated products 3-chloropropanol-2 and chloroacetone would be hydrolyzed slowly under these conditions (eq 9 and 10).

Kinetics. While the disappearance of substrate monitored by gas chromatography corresponded well with the rate of halide release, the latter was more reliably measured. The rates of bromide or chloride release assessed by direct potentiometry are presented in Figures 1 and 5. The upper curve in Figure 5 is a composite of separate runs for reactions 3, 4, and 6. The graph illustrates that these reactions proceed at the same rate within experimental error. Moreover, the rate of acrolein disappearance (eq 5), determined separately and plotted inversely would also fit on this line. Individual rate constants were assessed by first-order plots of the data like that shown in Figure 6. The constants are collected in Table II. There are no striking differences in the rates. DBCP reacts about twice as fast as the isomeric bromo alcohols, and the chloro diol is much slower to react than the chloro aldehyde. Under identical conditions the DBCP photohydrolysis proceeds 10 times faster than the photolysis of potassium ferrioxalate. The results presented in the table were obtained within a 3-month period. However, a set of runs 1 year

Figure 5. Composite plot of halide release from 2-bromo-3-chloropropanol-1, 1-bromo-3-chloropropanol-2, 3-chloropropionaldehyde, and 1-chloro-2,3-dihydroxypropane (bottom) all at 10^{-2} M.
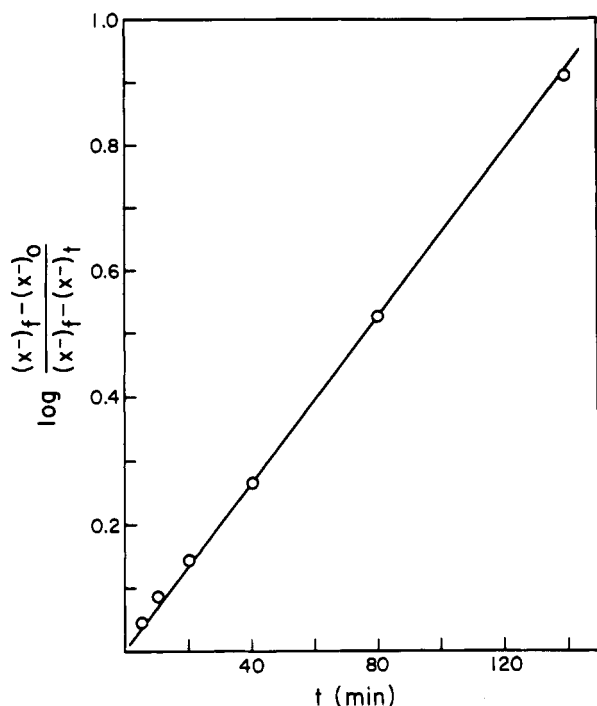

Figure 6. First-order plot for halide release from the isomeric bromochloropropanols and 3-chloropropionaldehyde.

Table II. Rates of Reactions at 30 °C, Irradiation with a 450-W Medium-Pressure Mercury Lamp

substrate	$k,$[a] $s^{-1} \times 10^4$	$t_{1/2}$, h	eq
1,2-dibromo-3-chloropropane	4.7[b]	0.4	2
2-bromo-3-chloropropanol-1	2.4	0.68	3
1-bromo-3-chloropropanol-2	2.4	0.68	6
3-chloropropionaldehyde	2.4	0.68	4
acrolein	2.4	0.68	5
1-chloro-2,3-dihydroxypropane	0.032	58	8

[a] Calculated from linear log plots. [b] Under identical conditions $k_{Fe^{III}OX} = 4.7 \times 10^{-5}$ s^{-1}.

later with 2-bromo-3-chloropropanol under the same conditions, while consistent with themselves, proceeded at a rate 3 times slower than that noted in Table II (see Figure 4). We presume this was due to an aged lamp.

DISCUSSION

The generation of cations by the photolysis of organic halides in alcoholic solution has been studied broadly by Kropp and associates (1984). Recently vinyl cations have been generated from the corresponding iodides by this means (Kropp et al., 1983% Kitamura et al., 1986). Re-
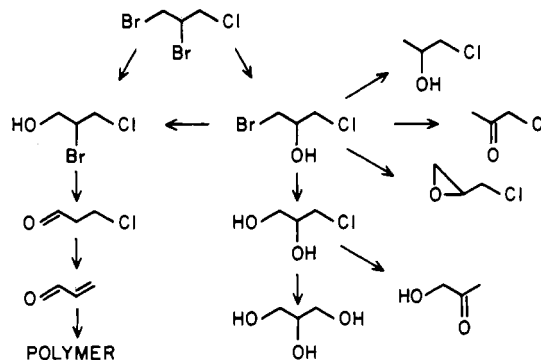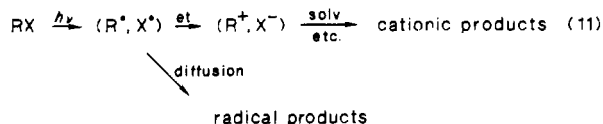

Figure 7. Overall reaction pathway.

action is proposed to occur via an initial homolytic scission followed by back electro transfer (eq 11, X = halogen) to yield products derived from the carbocation as well as those emanating from the radical (e.g. RH via hydrogen extraction).


To our knowledge the present case is the first example of a simple substrate that has the potential for production of two isomeric cations. Also it is one of the few examples of a reaction in the aliphatic class conducted in water, and there are several interesting features to it.

Regioselectivity of Carbocation Generation. Initial cleavage of DBCP (1) would seem to result primarily in the least stable primary cation. From the ratio of hydroxy isomers produced (eq 2) originally, the 2-bromo-chloropropanyl cation predominates (eq 12). This is surprising
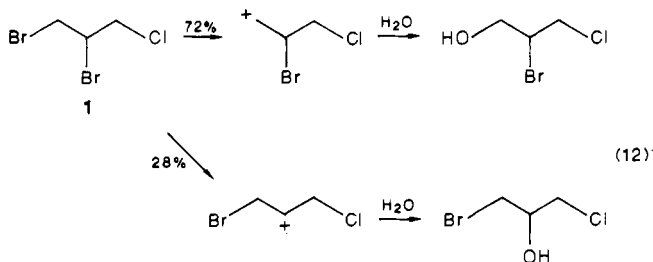

on two counts: (i) initial scission would be expected to favor the secondary C–Br cleavage; (ii) the secondary cation would seem to be more favorably disposed to internal solvation by adjacent halogens. On the other hand these results could reflect the selectivity of solvent water attack upon a single bromine-bridged cation. The same bromonium ion could derive from initial C–Br cleavage at either site.

Relative Rates of Reaction. Another surprising aspect of this work is that the rates of cleavage of the isomeric bromochloropropanols are the same. Presuming the back-electron-transfer rate (eq 13) is fast, an initial scission

$$RX(H_2O)_n \longrightarrow RX^*(H_2O)_n \xrightarrow{k_{rate}} products \qquad (13)$$
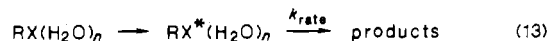
to a radical pair may favor dissociation of the 2-bromo isomer. (However, corresponding bond dissociation energies for isopropyl and n-propyl bromide are the same, 68 kcal/mol.) These results suggest an alternate and perhaps simpler mechanistic path in which solvent water participates. In this formulation cations may or may not be intermediates, but the key step in the overall process would be the direct reaction of water with the photoexcited halide solvate. Thus hydrolysis, substitution, and rear-

Scheme I

3
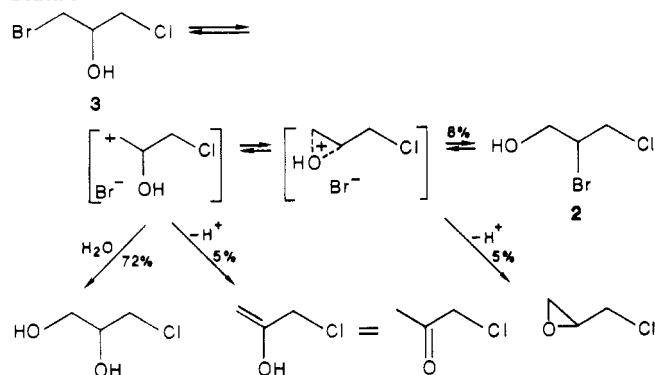
rangement may occur, but the rates and selectively would reflect the nature of the reaction of the excited state with water rather than the stability of the generated cation or the intrinsic rate of homolytic scission.

Scheme I portrays the fragmentation of **3** to the corresponding primary cation and its relative fate. The reactions observed are a textbook example of what might be expected for the reactivity of the 3-chloro-2-hydroxypropanyl cation in water. However, all of the products may as well be explained by reaction of the photoexecuted halide directly with water or with itself.

A radical product chloropropanol-2 was obtained in this reaction to a minor extent (6%). Presumably the radical abstracted hydrogen from starting substrate (eq 14).
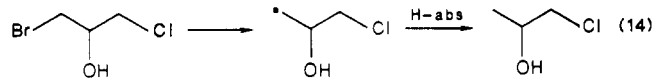
A cationic process can also be envisioned for the 1-hydroxy isomer (**2**) (eq 15). Oddly though, decomposition of the cation would proceed exclusively via β-proton loss. It is also possible that the reaction proceeds by a radical path or that the chloro enol is produced directly by hydrogen bromide loss to water from photoexcited **2**.
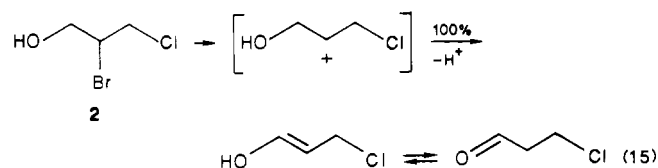
Obviously radical processes proceeding by H-atom abstraction should be diminished in water solvent, and this

would contribute in part to the near lack of photoreduction products obtained (overall 2%). However, the influence of solvent on these polar reactions has not been studied broadly. An increased ratio of cationic to radical processes was obtained in ethylene glycol (Kropp, 1984). The result was interpreted in support of reaction 11. That is, in the more viscous ethylene glycol the lifetime of the caged radical pair would increase and allow electron transfer to more favorably compete with diffusion to bulk solvent. However, another interpretation could be that the solvent dielectric was higher in ethylene glycol. Thus, in our work with the aliphatic bromides in water, a still more polar solvent ($D = 78.5$), the apparent ionic pathway proceeds nearly exclusively in all cases. Two alternate mechanisms can explain these results: (i) The solvated photoexcited halide dissociates directly to cation and anion. (ii) The photoexcited halide solvate reacts directly with water, perhaps from within the inner solvation sphere.

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