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Photohydrolysis of Ethylene Dibromide

Charles E. Castro* and Nao O. Belser

Ethylene dibromide in aqueous solution undergoes a rapid photohydrolysis upon irradiation with a 450-W medium-pressure mercury lamp. The photoreaction proceeds in two steps: (i) conversion of ethylene dibromide to bromoethanol ($t_{1/2}$ 7.6 min); (ii) cyclization of bromoethanol to ethylene oxide ($t_{1/2}$ 64 min). The rate of hydrolysis of ethylene oxide to ethylene glycol is not enhanced by light ($t_{1/2}$ ~10 days). The rates of reactions i and ii are respectively 32 and 3.8 times faster than the reduction of ferrioxalate ion under identical conditions. For ethylene dibromide the photo process represents a rate enhancement of the order of 10^5 over the nonphotolytic pathway.

INTRODUCTION

Ethylene dibromide (EDB) has been used as a soil fumigant, a sterilant for grains and wheat products as well as an antiknock additive to gasoline. The substance is a known carcinogen (U.S. Dept. of Health, Education & Welfare, 1979). Trace amounts of EDB have been detected in well water, and ppb levels have also been found in processed food products (Sheneman, personal communication). The presence of even small quantities of EDB in the environment has been the basis for serious concern.

In soil the substance can be dehalogenated by bacteria (eq 1) (Castro and Belser, 1968). The same transformation to ethylene has been observed to occur with the nematode *Aphelenchus avenae*. The main low level conversion of EDB by these animals however results in *o*-acetylserine (eq 2) (Castro and Belser, 1978). The ethylene dibromide carbon atoms were those of the acetyl moiety.

$$BrCH_2CH_2Br \rightarrow CH_2{=}CH_2 + 2Br^- + 2H^+ \quad (1)$$

$$BrCH_2CH_2Br \rightarrow CH_3C(=O)OCH_2CHNH_2CO_2H \quad (2)$$

Nonbiological conversion in the environment might be expected to be slow. For example, the rate of hydrolysis of EDB in neutral water is quite slow ($t_{1/2}$ ~16 years).

We report here that ethylene dibromide will undergo rapid photohydrolysis. The process could be a means of environmental detoxification.

EXPERIMENTAL SECTION

Materials. Ethylene dibromide, Matheson, Coleman and Bell, mp 9–10 °C, ethylene oxide, Matheson, and ethylene glycol, Mallenckrodt analytical reagent, were employed without purification. Bromoethanol, Eastman Kodak white label, was distilled (bp 55–56 °C (20 mm)) before use. All substances exhibited a single peak upon gas chromatography and showed correct mass spectra. Potassium ferrioxalate was prepared according to the procedure of Parker (1953). Water was deionized and glass distilled.

Methods. Product Identification and Analysis. Bromide ion was determined potentiometrically from 3-mL aliquots of the reaction in the manner previously described (Castro and Belser, 1968). Ethylene dibromide, (138 °C, 8.0 min), bromoethanol (138 °C, 5.4 min), ethylene glycol (138 °C, 4.0 min), and ethylene oxide (90 °C, 3.0 min) were determined from 1-μL reaction aliquots by direct flame ionization gas chromatography on a 3.5 ft, $^1/_8$ in. Poropak P column containing 3% DEGS and 6% DC-710. Ethylene oxide was monitored on a 2 ft, $^1/_8$ in. Poropak R column (90 °C, 3 min). The temperature and emergence

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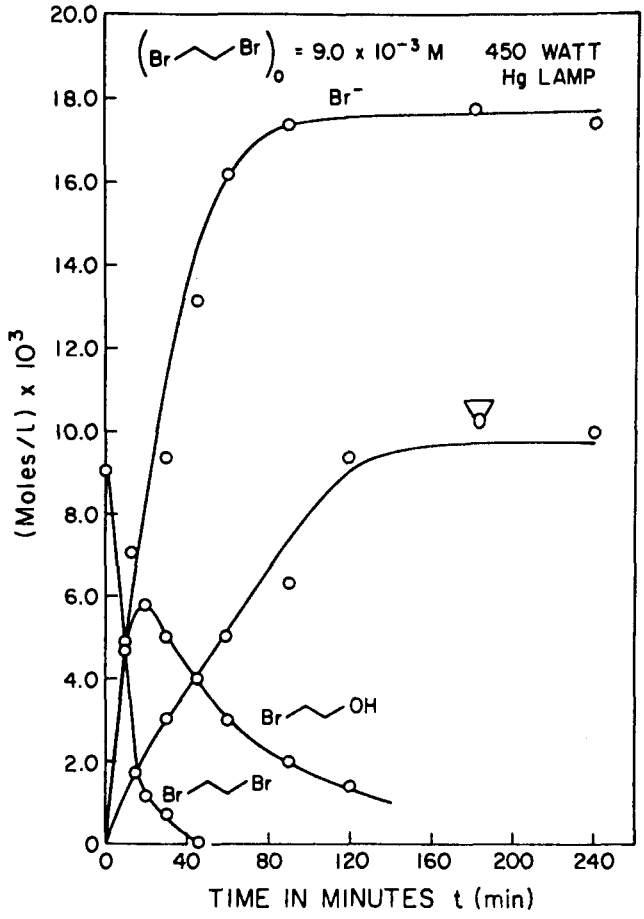

Figure 1. Time course of the photolysis of ethylene dibromide.

times are given in parenthesis. Quantitation was accomplished by comparison with authentic standards over a linear range of machine response. The nature of the photoproducts was confirmed by GC–MS. A 4 ft Poropak R column was directly connected to a quadrupole mass spectrometer. MS, bromoethanol (parents 126, 124) 126, 124 (CH_2CH_2 – OH, 45) 45; ethylene oxide (parent 44) 44.

Reaction Conditions. A 700-mL tube-shaped reactor was fitted with serum capped stopcocks for gas and solution removal, a manometer, and magnetic stirring bar. The light well was a concentric, water-jacketed quartz finger. Solution levels were 2–3 cm above the top of the tubular 450-W Hanovia medium-pressure mercury lamp. Starting concentrations for all substrates were in the range of 9.0×10^{-3} to 1.0×10^{-2} M. The reactor was charged with 600 mL of an aqueous solution in air. The entire apparatus was placed in a water bath held at 22 °C.

Ethylene Dibromide. The absorption maximum for this substance, 218 nm, ϵ 600, tails only slightly toward the visible (at 250 nm, ϵ 3.3). Nonetheless EDB undergoes rapid decay upon irradiation with the medium-pressure lamp. The rate of reaction was assessed from linear first-order plots of the disappearance of EDB with time. Alternately the corresponding first slope of the biphasic plot of bromide appearance vs. time could be employed. Reproducibility was ±10%. The time course of a typical photolysis of EDB at 9.0×10^{-3} M is shown in Figure 1. The results in the figure are a composite of two separate runs. At each time point the material balance was good. Reaction was complete in 2 h. During the course of the reaction, there was no detectable pressure change. Nevertheless, gas samples subjected to gas chromatography and mass spectroscopy indicated traces (<0.1%) of ethyl bromide, ethane, and ethylene.

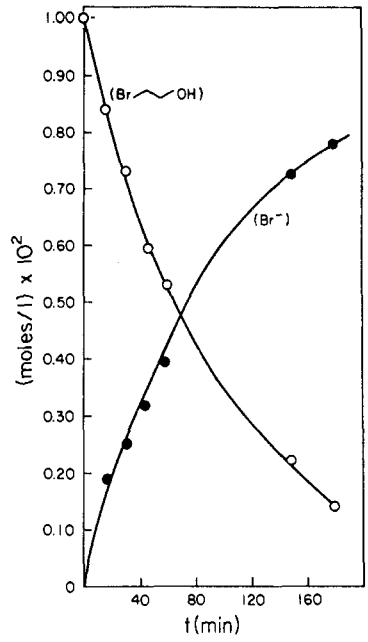

Figure 2. Time course of the photolysis of bromoethanol.

As a blank, Br^- was determined in a 1.0×10^{-2} M solution of EDB that had been standing in a sealed flask for 0.77 years. The concentration of Br^- was 3.2×10^{-4} M. This corresponds to a $t_{1/2}$ of 16 years.

Bromoethanol. Under identical conditions 80% of the bromoethanol (λmax 197, ϵ 1860) was consumed in 3 h (Figure 2). Ethylene oxide was produced quantitatively. Rate constants were evaluated from linear log plots of Br^- appearance or bromoethanol disappearance with time. Reproductivity was ±5%.

Ethylene Oxide. Aqueous solutions of ethylene oxide at 1.0×10^{-2} M exhibited no change upon irradiation for 3 h. The ethylene oxide peak was undiminished upon gas chromatography and ethylene glycol was not detected.

Potassium Ferrioxalate. A 6.00×10^{-3} M solution of potassium ferrioxalate was irradiated under the same conditions employed for ethylene dibromide. Initial rates of reduction were assessed at 15 min (4% conversion). The reaction was monitored according to the procedure of Hatchard and Parker (1956).

Relative rates of EDB and ferrioxalate were also assessed under sunlight irradiation. For this purpose stock solutions of EDB and ferrioxalate were placed in sealed quartz tubes. The latter were placed on the roof and sampled for Br^- and Fe^{II}.

RESULTS

The general time course of the photohydrolysis of ethylene dibromide is illustrated in Figure 1. The initial rates of bromide production parallel the initial rate of decay of the starting halide. This is followed by the rise and fall of bromoethanol and the gradual buildup of ethylene oxide. Rate constants for C–Br cleavage from the two halides, Figures 1 and 2, are given below. Results establish a quantitative reaction sequence for the photolytic process. The internal second hydroxylation is somewhat slower than the initial hydrolysis.

$$BrCH_2CH_2Br \xrightarrow[H_2O]{h\nu} BrCH_2CH_2OH + H^+ + Br^- \quad (3)$$

$$k_1 = 1.5 \times 10^{-3}\ s^{-1}$$

$$BrCH_2CH_2OH \xrightarrow[H_2O]{h\nu} \overline{CH_2CH_2O} + H^+ + Br^- \quad (4)$$

$$k_2 = 1.8 \times 10^{-4}\ s^{-1}$$

Ethylene oxide, itself a biocide and soil sterilant, is well known to hydrolyze in aqueous solution to ethylene glycol (eq 5). The process is general acid or base catalyzed (Long and Pritchard, 1956). Clearly the rate of eq 5 is not enhanced by light. At pH 7 $t_{1/2}$ is approximately 10 days.

$$\overbrace{CH_2CH_2O} \xrightarrow[H_2O]{H^+, OH^-} HOCH_2CH_2OH \qquad (5)$$

The relative rates of reactions 3 and 4 compared to the rate of reduction of ferrioxalate are ($k_{RX}/k_{Fe^{III}O_X}$) 32 for EDB and 3.8 for bromoethanol, respectively. With sunlight irradiation, EDB reacts 2.7 times faster than ferrioxalate. An estimate of the rate for Br^- release from EDB based upon 53 days (and nights) of exposure to roof sunlight, (10% conversion) corresponds to a $t_{1/2}$ ~380 days or a ~15-fold rate enhancement over the dark reaction.

DISCUSSION

The general photo enhanced substitution observed here (eq 6) suggests cationic intermediates. These results

$$>C\text{-}Br \xrightarrow{ROH} >C\text{-}OR \qquad (6)$$

would accord with a variety of studies of the photolysis of primarily aliphatic iodides in polar millieu (Kropp, 1984) and with the products obtained and the paths of reaction of chloropicrin and methyl bromide (Castro and Belser, 1983). Quantum yields cannot be calculated from the data at hand. Nevertheless, the absorption spectrum of ferrioxalate solutions is well-known, and clearly the actinometer solution absorbs more light than the organic halides over the entire wavelength region generated by the medium-pressure lamp. For ferrioxalate the extinction coefficient at 218 nm (λ_{max} for EDB) is ca 10^4 (Parker, 1953) and the absorption of light by the salt extends well into the visible. The faster rates of decay of the less absorbing halides indicate quantum yields considerably above one. A chain reaction is implied and the reactions bear further mechanistic scrutiny.

The rate enhancement for the photo process noted here with EDB is remarkable (~10^5). The actual photohydrolysis of ethylene dibromide in the environment could be an important means of its decay. Moreover, it is conceivable that photoprocesses could be employed to destroy relatively substitution inert aliphatic halides in the environment.

Registry No. EDB, 106-93-4; bromoethanol, 540-51-2; ethylene oxide, 75-21-8; ethylene glycol, 107-21-1.

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Methiocarb Residues in Grapes and Wine and Their Fate during Vinification

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An analytical method developed for the determination of total methiocarb residues on grapes included initial extraction with acetonitrile, oxidation of residues to methiocarb sulfone with *m*-chloroperbenzoic acid, derivatization with methanesulfonyl chloride, and quantitation by sulfur specific flame photometric gas chromatography. Grape juice, pomace, and wine were analyzed to determine the fate of methiocarb during vinification. Samples were also analyzed for the individual metabolites of methiocarb by using similar methods but omitting the oxidation step. Total residue on Pinot noir grapes treated 4 times at 4.5 kg AI/ha was 46 ppm 7 days after a handgun application and 7.4 ppm if the material was applied by airplane. Residues on White Riesling grapes treated with a concentrate sprayer at the same rate ranged from 12 to 19 ppm 7 days after last application. About 50–80% of the residue on fruit was removed from the vinification process with pomace and additional reductions occurred during the settling of juice. Total residue in wines made from grapes treated 7 days before harvest was 4.9 ppm in White Riesling wine and 4.6 ppm in Pinot noir wine which represented 26 and 13% of the initial residue on grapes.

INTRODUCTION

Birds cause considerable damage to maturing grapes and growers suffer financial losses estimated to be over 4 million dollars annually (Crase et al., 1976). The usual techiques utilized to reduce bird damage, such as noise, netting, live trapping, and poisoning, are expensive and not always effective (Boudreau, 1972). Recently it has been found that chemicals which repel birds are more effective and more economical to use. One such chemical useful against bird depredation is methiocarb [mesurol, 3,5-dimethyl-4-(methylthio)phenyl methyl carbamate] (Schafer and Brunton, 1971; Bollingier et al., 1971; Bailey and Smith, 1979). However, before this compound could be used on grapes, the magnitude of residues on grapes and the fate of residues during the vinification process needed to be determined.

Methiocarb is metabolized to its sulfoxide and sulfone by plants (Abdel-Wahab et al., 1966), and since these compounds are also toxic, any analytical method developed for methiocarb should also detect the oxidative metabolites. Carbamates, such as methiocarb, are thermally

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