

photolyzing light absorbed by C is given by (3).

$$f_C = 2.303\epsilon_C[C]l \quad (3)$$

If the flux of photolyzing light is  $N_i$  quanta  $\text{cm}^{-2} \text{s}^{-1}$ , then the mean rate of absorption of quanta within the vessel, in quanta per unit volume per unit time, is given by

$$I_a = \frac{N_i(1 - 10^{-A})}{l} \quad (\text{quanta cm}^{-3} \text{ s}^{-1})$$

However, we are concerned with the two components of this figure: the rates of absorption of quanta by species B and C, respectively. Subject to the conditions detailed above, these are given by eq 4 and 5. Thus, the instan-

$$I_a^B = 2.303N_i\epsilon_B[B] \quad (\text{quanta cm}^{-3} \text{ s}^{-1}) = \frac{2.303N_i\epsilon_B[B]}{10^3N_A} \quad (\text{einsteins dm}^{-3} \text{ s}^{-1}) \quad (4)$$

$$I_a^C = \frac{2.303N_i\epsilon_C[C]}{10^3N_A} \quad (\text{einsteins dm}^{-3} \text{ s}^{-1}) \quad (5)$$

taneous rate of the photochemical conversion of B to C would be given by the product of  $I_a^B$  and the quantum yield,  $\phi_1$ , for this process (eq 6). The solution to this

$$-\frac{d[B]}{dt} = \phi_1 I_a^B = \frac{2.303N_i\epsilon_B\phi_1[B]}{10^3N_A} \quad (6)$$

equation is eq 7, which shows that the concentration of B should decrease exponentially with time from its initial value  $[B]_0$ . Thus, the concentration of B decreases in the same manner as for a reaction following first-order kinetics. However, the counterpart of the pseudo-first-order rate constant is a function of the light flux, the extinction coefficient, and the quantum yield.

$$[B]_t = [B]_0 e^{-(2.303N_i\epsilon_B\phi_1 t/10^3N_A)} \quad (7)$$

If the quantum yield for the conversion of C to D is  $\phi_2$ , then the rate of this second process is given by (8). Since this is proportional to the concentration of C, it means that this step also would progress as if it followed pseudo-first-order kinetics, with the same qualification as in the preceding paragraph.

$$\phi_2 I_a^C = \frac{2.303N_i\epsilon_C\phi_2[C]}{10^3N_A} \quad (8)$$

With regard to the report by Castro and Belser (1985), it may be pointed out that while a medium-pressure mercury lamp emits strongly at around 313 and 365 nm

(Calvert and Pitts, 1966), neither ethylene dibromide nor 2-bromoethanol absorb at those wavelengths. Thus, the only light capable of causing these reactions would have been the relatively small output at around 265 nm and the 254-nm resonance line. In this range, the absorbance of a few centimeters of a  $9 \times 10^{-3} \text{ M}$  solution is comfortably less than unity, so one would expect the concentration of ethylene dibromide to fall exponentially under the influence of the ultraviolet lamp.

A measurement of the quantum yield of this process thus requires a knowledge of the flux of light of wavelengths effective in causing reaction. The reported experiments with ferrioxalate do not serve this purpose, chiefly because this system is photosensitive well into the visible and so is affected by light that is irrelevant to the photohydrolysis. But in addition it must be pointed out that even 1 cm of  $6 \times 10^{-3} \text{ M}$  ferrioxalate solution is totally absorbing over this wavelength range. Consequently, the mean rate of light absorption can be shown to be given by (9), which indicates that the concentration of ferrioxalate

$$I_a = N_i/10^3lN_A \quad (\text{einstein dm}^{-3} \text{ s}^{-1}) \quad (9)$$

should fall linearly and not exponentially and also that the mean rate of this photoreaction is not in any way a function of the coefficient of absorption,  $\epsilon$ . Thus, the relative rates of  $\text{Br}^-$  production from ethylene dibromide and  $\text{Fe}^{2+}$  production from ferrioxalate bear no simple relationship to the quantum yields of these two reactions. Clearly the factors of 32 and 3.8 quoted (Castro and Belser, 1985) have no fundamental significance and pertain only to the particular experimental conditions of their work.

In summary, it would seem eminently desirable that the measured efficiency of any reaction brought about by the action of light is reported in terms of its quantum yield, which is widely understood as the ratio of the number of molecules reacting to the number of quanta absorbed.

**Registry No.** Ethylene dibromide, 106-93-4.

#### Literature Cited

- Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1966; p 696.  
Castro, C. E.; Belser, N. O. *J. Agric. Food Chem.* 1985, 33, 536-538.

S. R. Logan

Department of Chemistry  
University of Ulster  
Coleraine BT52 ISA, Northern Ireland

Received for review August 19, 1987. Accepted April 13, 1988.

## Rebuttal on Photohydrolysis of Ethylene Dibromide

*Sir:* The theory drawn by Dr. Logan is correct, if rather well-known. It is consistent with our observations.

We are interested in discerning those processes that may be relevant to the transformation of biocides in the environment. Hence, in this work and a more recent one (Castro et al., 1987), we have chosen to irradiate simulta-

neously over a range of wavelengths that approximate relevant sunlight irradiation at earth. The total radiant energy of the medium-pressure Hanovia lamp we have employed in this and subsequent work is 175.8 W and, according to the manufacturer, is distributed over the following wavelengths (nm): 220-280 (15%), 280-320

(16%), 320–400 (16%), 400–600 (43%). The remaining 10% is emitted at longer wavelengths and in the infrared. While it is well suited to our purpose, irradiation in this fashion does not allow the determination of the quantum yield (as stated in our paper). It does allow for the occurrence of a variety of photoprocesses by differently absorbing species (including uncharacterized ones). This is especially important to any multipathed reaction sequence that may not take place with monochromatic light but could still be significant environmentally. In order to give the readers an idea of the relative speed of these processes, we have chosen to compare them with the rates for ferrioxalate reduction under identical conditions. The latter salt is a standard actinometer employed by and familiar to many.

To the extent that our presentation may have misled others in addition to Dr. Logan, we welcome his comments.

**Registry No.** Ethylene dibromide, 106-93-4.

#### Literature Cited

Castro, C. E.; Belser, N. O.; Mayorga, S. "Photohydrolysis of 1,2-Dibromo-3-chloropropane". *J. Agric Food Chem.* 1987, 35, 865–870.

**Charles E. Castro**

*Department of Nematology  
University of California  
Riverside, California 92521*

Received for review February 2, 1988. Accepted April 13, 1988.