Photodecomposition of Gaseous Bromoethane at 163.4 nm

Kyung-Hoon Jung,* Young Sik Choi, Hee Soo Yoo,

Department of Chemistry, Korea Advanced Institute of Science of Technology, Chongyangni, Seoul 131, Korea

and E. Tschuikow-Roux*

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4 (Received: October 6, 1983; In Final Form: November 6, 1985)

The 163.4-nm photolysis of gaseous C_2H_5Br has been investigated at 298 K over the pressure range 2–100 torr, using a bromine lamp. The effects of additives, N₂, CF₄, and NO, were also studied. In the pure system the observed reaction products and their respective quantum yields are C_2H_4 (~0.36), C_2H_6 (0.42–0.79), C_2H_3Br (0.1–0.24), CH_3CHBr_2 (0.24–0.32), and $n-C_4H_{10}$ (<0.01), most yields increasing with substrate pressure. An opposite trend is observed with increasing pressure of inert gases. The addition of NO as a radical scavenger completely suppresses the formation of C_2H_6 , C_2H_3Br , CH_3CHBr_2 , and $n-C_4H_{10}$, and partially reduces the yield of C_2H_4 . The results are interpreted in terms of the initial formation of two electronically excited states which are linked by way of a pressure dependence, one of which yields C_2H_4 by molecular elimination of HBr, while the second decomposes by carbon-halogen bond fission. The kinetics of the secondary process are discussed in some detail.

Introduction

The primary processes in the photolysis of a number of haloethanes have been shown to depend on wavelength¹⁻⁴ as well as the number, identity, and position of halogen substitution.^{4,5} In the shorter wavelength region two or more reaction channels may compete.⁴⁻⁶ In this aspect the photolysis of ethyl bromide is no exception and the secondary reaction kinetics are intricate. Friedman, Bernstein, and Gunning⁷ reported the photolysis of gaseous C₂H₅Br between 210 and 260 nm over the temperature range 30-250 °C in the presence of mercury and excess cyclopentane. Under these conditions ethane was found as the principal product, while the amount of C_2H_4 was very small (<5%), and brominated C₂ products were not observed. The results were interpreted in terms of C-Br bond rupture as the major primary process, in agreement with an earlier photolysis study at 313 nm by Roof and Daniels.⁸ Barker and Maccoll⁹ studied the gas-phase photolysis of C₂H₅Br at 253.7 nm in the temperature range 150-300 °C and reported a radical chain reaction yielding C₂H₄ and HBr. In the absence of propene as inhibitor, the formation of $C_2H_4Br_2$ in a chain termination step was implied in this work. More recently, the 253.7-nm photolysis of gaseous C₂H₅Br at 23 °C has also been examined by Frank and Hanrahan,¹⁰ who measured product quantum yields as a function of time. Reported major products at an early stage of the reaction were HBr, C_2H_6 , C₂H₄, and CH₃CHBr₂, with lesser yields of CH₂BrCH₂Br, C₂-H₃Br, plus a number of other minor products. At longer photolysis times the only significant products were C_2H_6 and $1,1-C_2H_4Br_2$. The behavior of the system was interpreted in terms of two parallel primary processes: C-Br bond scission ($\phi = 0.8$) and molecular HBr elimination ($\phi = 0.2$). Most recently, Jung and co-workers¹¹⁻¹⁵ investigated the photolysis of C_2H_5Br in the vacuum-ul-

- (4) Ichimura, T.; Kirk, A. W.; Tschuikow-Roux, E. J. Phys. Chem. 1977, 81, 1153.
- (5) Yano, T.; Tschuikow-Roux, E. J. Chem. Phys. 1980, 72, 3401.
 (6) Fujimoto, T.; Wijnen, M. H. J. J. Chem. Phys. 1972, 56, 4032.
 (7) Friedman, H. L.; Bernstein, R. B.; Gunning, H. E. J. Chem. Phys.
- 1957, 26, 528.
 - (8) Roof, J. G.; Daniels, F. J. Am. Chem. Soc. 1940, 62, 2912.
 - (9) Barker, R.; Maccoll, A. J. Chem. Soc. 1963, 2839
 - (10) Frank, A. J.; Hanrahan, R. J. J. Phys. Chem. 1978, 82, 2194.

traviolet at 25 °C. The emphasis in these studies at wavelengths (λ/nm) 104.8–106.7,¹¹ 123.6,¹² 147,¹³ 174.4,¹⁴ and 193.1¹⁵ has been on the determination of the quantum yields of C_2H_6 and C_2H_4 , which showed that the primary processes in the photodecomposition of C_2H_5Br are strongly wavelength dependent,¹⁴ and that molecular elimination of HBr increases with photon energy. In this paper we report on the 163.4-nm photolysis of gaseous ethyl bromide which complements previous work and attempts to clarify secondary processes.

Experimental Section

Photolyses were carried out at 298 K in a conventional static apparatus. The reaction vessel consisted of a 19.5-cm-long cylindrical borosilicate glass cell (330 cm³) equipped with an all-glass circulating pump. The light source was a sealed bromine atom resonance lamp¹⁶ which was fitted with a 1-mm-thick Suprasil window, and incorporated a cold finger for the control of the bromine vapor pressure. The lamp was operated by a microwave generator, KIVA MPG-4M, and its spectral purity was checked routinely with a 0.3-m GCA/McPherson 218 vacuum-ultraviolet monochromator. A Suprasil window, which has a cutoff at 160 nm,¹⁷ was chosen to eliminate all undesired lines^{17,18} at shorter wavelengths. Over prolonged periods of operation, a slow intensity decrease of the lamp was experienced, which ranged from 2.4 \times 10^{14} to 9.1×10^{13} photon s⁻¹. The lamp intensity was restored in between runs by cleaning the window with spectral grade acetone. In order to reduce possible distortion of the photolysis results due to intensity fluctuations, actinometric readings were performed twice before and after each run, and used as a guide to screen the data. The criterion chosen for acceptable runs was $\pm 5\%$ deviation between those two readings. Actinometry was based on the production of acetylene from the photolysis of ethylene¹⁹ ($\phi_{C_{2}H_{2}} = 0.7$ at 163.4 nm). Total conversions were held

- (12) Yoo, H. S.; Jung, K.-H. Bull. Korean Chem. Soc. 1980, 1, 35. (13) Jung, K.-H.; Yoo, H. S.; Hahn, J. H. Int. J. Chem. Kinet. 1984, 16,
- 397.
- (14) Jung, K.-H.; Yoo, H. S.; Hwang, J. S. J. Photochem. 1983, 23, 289.
 (15) Jung, K.-H.; Lee, C. M.; Yoo, H. S. Can. J. Chem. 1983, 61, 2486.
 (16) Loucks, L. F.; Cvetanovic, R. J. J Chem. Phys. 1972, 56, 321.
- (17) Okabe, H. "Photochemistry of Small Molecules"; Wiley: New York, 1978; p 120.
- (18) Davis, D.; Braun, W. Appl. Opt. 1968, 7, 2071

⁽¹⁾ Calvert, J. G.; Pitts, Jr., J. N. "Photochemistry"; Wiley: New York, 1966; p 522-528, 647 and references cited therein.
(2) Cremieux, L.; Herman, J. A. *Can. J. Chem.* 1974, 52, 3098.
(3) Ichimura, T.; Kirk, A. W.; Tschuikow-Roux, E. J. Photochem. 1976, 6, 77.

⁽¹¹⁾ Kim, H. L.; Yoo, H. S.; Jung, K.-H. Bull. Korean Chem. Soc. 1981, 2.71

⁽¹⁹⁾ Potzinger, P.; Glasgow, L. C.; von Bünau, G. Z. Naturforsch. 1972, 27a, 628.



Figure 1. Dependence of the product quantum yields on C_2H_5Br pressure: \Box , C_2H_6 ; O, C_2H_4 ; \bullet , CH_3CHBr_2 ; Δ , C_2H_3Br .



Figure 2. Dependence of the quantum yield ratio $\phi_{C_2H_6}/\phi_{C_{2H_4}}$ on substrate and inert gas pressure: O, C_2H_5Br ; Δ , CF_4 ; \Box , N_2 .

to less than 1% throughout. Product analysis was carried out by flame ionization gas chromatography (Hewlett Packard, Model 5840 A, twin F.I.D.) using two columns: 30% OV 101 80/100 mesh Chromosorb PAW 1/8 in. \times 4 m nickel at 80 °C to isolate C_2H_4 , C_2H_6 , n- C_4H_{10} , C_2H_3Br , and CH_3CHBr_2 ; and 100/120 mesh Spherocarb 1/8 in. \times 1.1 m S.S. at 100 °C for the actinometry product, C_2H_2 . The identification and quantitative determination of the carbon-containing products were made by comparison of their retention times with those of authentic samples, and subsequent determination of the respective sensitivities to the detector response. Though HBr is undoubtedly an important product, the adopted analytical procedure was unsuitable for its determination and was not attempted.

Ethyl bromide (Eastman Kodak) was purified on a spinning band column (Perkin Elmer, Model 251) and by trap-to-trap distillation to better than 99.99% by GC analysis. Nitric oxide, stated purity 99.0% minimum, and nitrogen, stated purity 99.998%, both obtained from Matheson Co., were used without further purification. Carbon tetrafluoride (Matheson) was used after passing through a 1-m Pt-coated Cu₂O column which was activated by hydrogen at 200 °C for 5 h. Bromine (Mallinckrodt), Analytical Grade, was passed through a P_2O_5 column before entering the lamp body.

The extinction coefficient of C_2H_5Br at 163.4 nm has been determined as $\epsilon = -(1/lP) \ln (I/I_0) = 202.0 \pm 6.5 \text{ atm}^{-1} \text{ cm}^{-1}$.

Results

The major carbon-containing products in the 163.4-nm photolysis of ethyl bromide are C_2H_6 , C_2H_4 , CH_3CHBr_2 , and C_2H_3Br . Trace amounts of n- C_4H_{10} ($\phi < 0.01$) were also identified but could not be determined quantitatively. Brominated C_4 products (1- C_4H_9Br , 2- C_4H_9Br , and 1,3-, 2,3-, and 1,4-dibromobutanes) were specifically searched for, but none were found. The quantum yields of the major products are listed in Table I as a function



Figure 3. Quantum yields of nonscavengeable (\odot) and scavengeable (\odot) ethylene as a function of ethyl bromide pressure.



Figure 4. Dependence of product quantum yields on photolysis time: \Box , C_2H_6 ; O, C_2H_4 ; \oplus , CH_3CHBr_2 ; \triangle , C_2H_3Br . C_2H_3Br pressure: 15 torr.

of reactant and/or additive gas pressure.

In the photolysis of pure C_2H_5Br at low pressures, all product quantum yields show some increase with substrate pressure. Above 20 torr this increase becomes more gradual in the case of C_2H_6 , C_2H_3Br , and CH_3CHBr_2 , while the yield of C_2H_4 is almost pressure independent (Figure 1). The addition of the inert gases N_2 and CF_4 to a fixed pressure of C_2H_5Br (runs 19–30, Table I) shows the opposite trend; the quantum yields generally decrease with increasing inert gas pressure. The ratio of the quantum yields $\phi_{C_2H_6}/\phi_{C_2H_4}$ is also listed in Table I and shows approximately a linear increase with the substrate or total pressure (Figure 2). The relative increase in $\phi_{C_2H_6}/\phi_{C_2H_4}$ with pressure is in the order of molecular complexity, $C_2H_5Br > CF_4 > N_2$.

The addition of NO as a scavenger (runs 31-44, Table I) suppresses completely the formation of C_2H_6 , C_2H_3Br , CH_3CHBr_2 , and *n*- C_4H_{10} , and reduces partially the yield of C_2H_4 . The pressure dependence of the residual (nonscavengeable) C_2H_4 in the presence of NO and that of the "scavengeable" C_2H_4 obtained by difference for experiments without NO at the same substrate pressure (Table I) are shown in Figure 3.

The effect of irradiation time on the product yields is presented in Table II and in graphical form in Figure 4. The quantum yields of C_2H_4 and C_2H_6 are unaffected by prolonged irradiation while C_2H_3Br decreases and CH_3CHBr_2 shows an opposite trend.

Discussion

The complete suppression of C_2H_6 , C_2H_3Br , CH_3CHBr_2 , and $n-C_4H_{10}$ by the addition of nitric oxide may be interpreted that these products derive from radical sources. Similarly, the partial suppression of C_2H_4 (ca. 30%) in the presence of NO also suggests a contribution from radical reactions to the total yield of ethylene. The residual C_2H_4 can then be attributed to the molecular elimination of HBr from C_2H_5Br upon photon absorption, as has been observed at other wavelengths, $^{10-15}$ and also in the case of chemical²⁰ and thermal²¹ activation. The gradual reduction of the

				quantum yields					
run no.	$P_{C_2H_5Br}$, torr	additives, torr	C_2H_4	C ₂ H ₆	C ₂ H ₃ Br	CH ₃ HBr ₂	$\phi_{C_2H_6}/\phi_{C_2H_4}$		
 1	1.7		0.324	0.38	0.09	0.22	1.17		
2	2.1		0.23	0.42	0.10	0.24	1.83		
3	2.45		0.30	0.38	0.11	0.24	1.27		
4	3.0		0.285	0.32	0.13	0.23	1.12		
5	5.0		0.35	0.507	0.14	0.24	1.44		
6	5.2		0.25	0.46	0.11	0.24	1.84		
7	6.2		0.344	0.516	0.13	0.22	1.50		
8	9.9		0.31	0.56	0.14,	0.25	1.81		
9	11.2		0.31	0.506	0.148	0.25	1.62		
10	15.0		0.416	0.63	0.15	0.26	1.53		
11	15.5		0.36	0.66	0.16	0.29	1.83		
12	15.8		0.34	0.63	0.165	0.30	1.85		
13	20.0		0.36	0.67,	0.19	0.32	1.87		
14	30.0		0.36	0.70_{4}^{-}	0.176	0.32	1.96		
15	40.0		0.36	0.73	0.165	0.29	2.03		
16	50.0		0.37	0.74	0.19	0.29	2.00		
17	75.0		0.36	0.76	0.21	0.30	2.11		
18	100.0		0.35	0.79	0.24	0.32	2.26		
19	5.0	N ₂ ; 9.8	0.33	0.57	0.14	0.23	1.72		
20	5.0	N_2 ; 20.0	0.30	0.52	0.12	0.21	1.76		
21	5.0	N ₂ ; 30.0	0.30	0.534	0.11	0.20	1.78		
22	5.0	$N_2; 41.7$	0.23	0.42	0.10	0.11	1.83		
23	5.0	N ₂ ; 50.6	0.20	0.37	0.09	0.10	1.85		
24	5.0	CF₄; 10.8	0.32	0.575	0.16	0.26	1.80		
25	5.0	CF ₄ ; 21.9	0.27	0.49	0.14	0.23	1.81		
26	5.1	CF ₄ ; 30.1	0.23	0.424	0.12	0.19	1.84		
27	5.0	CF ₄ ; 40.2	0.20	0.376	0.09	0.15	1.88		
28	5.0	CF ₄ ; 49.7	0.19	0.36	0.09	0.11	1.89		
29	5.0	CF ₄ ; 72.5	0.18	0.357	0.08	а	1.98		
30	5.1	CF ₄ ; 91.0	0.15	0.308	0.07	а	2.05		
31	1.7	NO; 4.1	0.264	0.0	0.0	0.0			
32	1.7	NO; 4.1	0.165	0.0	0.0	0.0			
33	2.45	NO; 2.4	0.265	0.0	0.0	0.0			
34	5.0	NO; 5.4	0.26,	0.0	0.0	0.0			
35	5.1	NO; 5.4	0.21	0.0	0.0	0.0			
36	10.0	NO; 3.0	0.25	0.0	0.0	0.0			
37	11.2	NO; 3.0	0.25,	0.0	0.0	0.0			
38	15.5	NO; 3.0	0.264	0.0	0.0	0.0			
39	20.0	NO; 4.2	0.27	0.0	0.0	0.0			
40	30.0	NO; 4.4	0.264	0.0	0.0	0.0			
41	40.0	NO; 4.7	0.26	0.0	0.0	0.0			
42	50.0	NO; 5.5	0.25	0.0	0.0	0.0			
43	75.0	NO; 6.7	0.23	0.0	0.0	0.0			
44	100.0	NO; 5.8	0.21	0.0	0.0	0.0			

quantum vielde

^aNot determined.

TABLE II: Dependence of Quantum Yields on Irradiation Time

run	P _{C2H5Br} , torr	irrad time, min	quantum yield				
no.			C_2H_4	C_2H_6	C ₂ H ₃ Br	CH ₃ CHBr ₂	
1	15.0	5	0.33	0.64	0.17	0.27	
2	15.8	10	0.34	0.63	0.165	0.30	
3	15.0	15	0.32	0.63	0.155	0.33	
4	15.0	20	0.34	0.65	0.15	0.35	
5	15.0	25	0.33	0.61	0.14	0.40	
6	15.0	30	0.33	0.65	0.14	0.34	
7	15.0	35	0.33	0.62	0.13	0.41	
8	15.0	45	0.33	0.67	0.12	0.37	
9	15.0	55	0.33	0.64	0.11	0.44	

product yields with increasing moderator pressure (N_2 and CF_4) is indicative of a general collisional stabilization of the respective precursors leading to reaction. While such collisional quenching must obviously also occur with increasing substrate pressure, the observed increase in the product yields must be interpreted in terms of secondary processes which are enhanced by an increase in reactant pressure. In this respect the results for the nonscavengeable ethylene at the lowest pressures show considerable scatter which we attribute to experimental and analytical difficulties in this region; hence further discussion is focused on the results above 10 torr total pressure.

Primary Processes. The production of C_2H_6 and CH_3CHBr_2 in the system points unequivocally to the presence of ethyl radicals and bromine atoms in the system. Further, from an interpretive point of view, the slow reduction in the yield of the nonscavengeable C_2H_4 with increasing reactant pressure (above 10 torr, Figure 3) is significant and could be construed as the result of collisional quenching of its precursor. However, a collisionally induced horizontal conversion of the initially formed photoexcited state to the electronic ground state is untenable, since such a process would result in a highly vibrationally excited species which, at the pressures in question, would rapidly decompose to C_2H_4 and further to $C_2H_{23}^{22}$ the latter being contrary to experimental observation. Searching for alternatives and in common with previous studies.^{3,4,10,13–15} we propose that two electronically excited states are responsible for the primary processes in the photolysis of C_2H_5Br at 163.3 nm. Deferring, for the moment, the discussion of the rationale for this "two-state" hypothesis with ostensibly monochromatic radiation, we postulate that the nonscavengeable C_2H_4 is produced by molecular elimination of HBr from an excited state, $C_2H_5Br^{+(1)}$, corresponding to a Rydberg transition, which may be long-lived,²³ and that the scavengeable C_2H_4 and C_2H_6

⁽²⁰⁾ Johnson, R. L.; Setser, D. W. J. Phys. Chem. 1967, 71, 4366. (21) Tsang, W. J. Chem. Phys. 1964, 41, 2487.

⁽²²⁾ Ogata, Y.; Obi, K.; Akimoto, H.; Tanaka, I. Bull. Chem. Soc. Jpn. 1971, 44, 2671.
(23) Majer, J. R.; Simons, J. P. Adv. Photochem. 1964, 2, 137.



Figure 5. Plot of $\phi_{C_2H_6}/\phi_{C_2H_4}$ (nonscavengeable) as a function of C_2H_5Br pressure.

derive from a second excited state, $C_2H_5Br^{\dagger(2)}$, corresponding to an antibonding $n \rightarrow \sigma^*$ transition,^{23,24} which decomposes directly by carbon-bromine bond fission to yield scavengeable C_2H_5 radicals and bromine atoms. In order to explain the observed pressure dependence of the product yields we invoke, furthermore, a collisionally induced cross-over³ from state 1 to state 2 which for simplicity we denote as a one-step process: $C_2H_5Br^{\dagger(1)}$ $C_2H_5Br^{\dagger(2)}$. Thus an increase in pressure would favor the formation of products with radical precursors while it would diminish the yield of C_2H_4 formed by the molecular elimination process. This proposition is in qualitative agreement with the data shown in Figures 1-3.

Since the postulated origin of C_2H_6 is from state 2 and that of the nonscavengeable C_2H_4 is from state 1, respectively, the ratio of their quantum yields can be equated to the concentration ratio of the excited states, i.e., $\phi_{C_2H_6}/\phi_{C_2H_4}$ (nonscavengeable) = $[C_2H_5Br^{\dagger(2)}]/[C_2H_5Br^{\dagger(1)}]$. Figure 5 shows a plot of this ratio vs. reactant pressure. The relation is linear with a nonzero intercept, which indicates that $C_2H_5Br^{\dagger(1)}$ is not the only source of $C_2H_3Br^{\dagger(2)}$. On the basis of this observation we therefore propose a second, pressure-independent source of $C_2H_5Br^{\dagger(2)}$ by allowing it to be also formed directly upon photon absorption. The concurrent formation of two excited states may be rationalized by an overlap²³ between Rydberg and the $n \rightarrow \sigma^*$ valence transitions, which appears to be plausible since the Rydberg transitions in C_2H_5Br [i.e., B (177 nm), C (171 nm), and D (157 nm) bands] are rather diffuse²⁵ and the absorption spectrum corresponding to $n \rightarrow \sigma^*$ shows an extension to shorter wavelengths from its absorption maximum at ~ 200 nm.²⁶

From the foregoing discussion, the primary processes may then be summarized as follows

$$C_{2}H_{5}Br + h\nu \rightarrow C_{2}H_{5}Br^{\dagger(1)} \qquad \phi_{1}^{0}$$
$$\rightarrow C_{2}H_{5}Br^{\dagger(2)} \qquad \phi_{2}^{0}$$

$$C_2H_5Br^{\dagger(1)} + M \xrightarrow{k_1} C_2H_5Br^{\dagger(2)} + M$$
(1)

$$C_2H_5Br^{\dagger(1)} \xrightarrow{\kappa_2} C_2H_4 + HBr$$
 (2)

$$C_2H_5Br^{\dagger(2)} \xrightarrow{k_3} C_2H_5 + Br$$
 (3)

where ϕ_1^{0} and ϕ_2^{0} are the primary quantum yields extrapolated to zero pressure. Assuming, for the moment, that the only fate of the C₂H₅ radicals is their removal by reaction with the product HBr or the substrate to yield C_2H_6 , it can be shown by application of the usual stationary-state approximation that

The Journal of Physical Chemistry, Vol. 90, No. 9, 1986 1819

$$\frac{\phi_{C_2H_6}}{\phi_{C_2H_4} \text{ (nonscavengeable)}} = \frac{\phi_2^0}{\phi_1^0} + \left(1 + \frac{\phi_2^0}{\phi_1^0}\right) \frac{k_1}{k_2}[M] \qquad (I)$$

Equation I is commensurate with the data in Figure 5. From the intercept and slope one obtains $\phi_2^0/\phi_1^0 \simeq 2.1$ and $k_1/k_2 \simeq 5.4$ × 10⁻³ torr⁻¹, respectively. If k_1 is now assumed to have its "usual" order of magnitude of ~10⁷ torr⁻¹ s⁻¹ we obtain $k_2 \simeq 2 \times 10^9$ s^{-1} and hence the lifetime of $C_2H_5Br^{\dagger(1)}$ is estimated to be ~5 \times 10⁻¹⁰ s, in reasonable agreement with the theoretical prediction of a lower limit of $\tau \approx 2 \times 10^{-10}$ s if one assumes a line width of 0.1 cm⁻¹ and considers Doppler broadening and predissociation.27

Direct evidence for the two-channel photodecomposition of haloalkanes has recently been reported by Kawasaki et al.28 who studied the photodissociation in molecular beams using an excimer laser at 193 nm and measured the time-of-flight (TOF) distribution of the X and HX photofragments to establish the primary processes and the dissociation dynamics after a model transformation of the TOF data to a center-of-mass (CM) reference frame translational energy distribution, $P(E_T)$.²⁹ Although the photodissociation of C_2H_5Br was not specifically investigated, the results on several alkyl chlorides, including C₂H₅Cl, and two bromoalkynes established the long life of excited state 1 and the short life of excited state 2.

Turning to a consideration of the energetics, we observe that since the photon energy at 163.4 nm is 175 kcal mol⁻¹ and the heat of reaction 2 is ~ 19 kcal mol^{-1 30} there are ca. 156 kcal mol⁻¹ of excess energy to be distributed between C_2H_4 and HBr. However, the absence of C_2H_2 among the photolysis products restricts the internal energy content of C_2H_4 to less than the activation energy for its nonequilibrium dissociation to C_2H_2 and H₂ which has been estimated³¹ as ~ 80 kcal mol⁻¹. The enthalpy change for reaction 3 is 70 kcal mol⁻¹, using the recently revised value³² for the heat of formation of the ethyl radical, $\Delta H_{\rm f}^{\rm o}({\rm C}_2{\rm H}_5)$ = 28 kcal mol⁻¹. Hence the excess energy is 105 kcal mol⁻¹ if the primary radical products are formed in their ground electronic states. The discussion of the subsequent reaction kinetics then depends, in part, on the question as to how this excess energy is partitioned between the fragments. The analysis of Kawasaki et al.²⁸ has shown that for C-Br bond scission in propargyl bromide at 193 nm the total CM translational energy (E_{T}) is ca 36% of the available energy (E_{avi}) . Here E_{avi} is the excess energy to be partitioned among the photofragments, the dissociation proceeding along the ground-state potential surface. For a simple bond rupture reaction one has, from the conservation of energy²⁹

$$E_{\text{avl}} = E_{\text{int}} + E_{\text{T}}$$
$$= E_{\text{int}}^{\text{P}} + h\nu - D_0^0$$

where E_{int} and E_{int}^{P} are the internal (vibrational and rotational) energies of the fragment(s) and parent molecule, respectively, $h\nu$ is the photon energy, and D_0^0 the bond dissociation energy.

If the above result for energy partitioning, $f_{\rm T} = E_{\rm T}/E_{\rm avi} = 0.36$, is used to provide a rough guideline for reaction 3 in the present study, the fractional amount of the excess energy that is channeled into internal excitation is ~ 67 kcal mol⁻¹, which must necessarily reside in the C_2H_5 fragment. This would render the C_2H_5 radical unstable with respect to decomposition to $C_2H_4 + H$, which, in our case, is not supported by experimental evidence. The formation in reaction 3 of Br* (${}^{2}P_{1/2}$) atoms is a possibility (~10.5 kcal mol⁻¹ above the ground state³³) and would reduce the fraction of the

⁽²⁴⁾ Robin, M. B. "Higher Excited States of Polyatomic Molecules"; Academic: New York, 1974; Vol. 1.

⁽²⁵⁾ Price, W. C. J. Chem. Phys. 1936, 4, 547.

⁽²⁶⁾ Porret, D.; Goodeve, C. F. Proc. R. Soc. London, Ser. A 1938, A165, 31.

⁽²⁷⁾ Herzberg, G. "Electronic Spectra and Electronic Structure of Polyatomic Molecules"; van Nostrand: Princeton, NJ, 1966; p 45

⁽²⁸⁾ Kawasaki, M.; Kasatani, K.; Sato, H.; Shinohara, H.; Nishi, N. Chem. Phys. 1984, 88, 135.
(29) Shinohara, H.; Nishi, N. J. Chem. Phys. 1982, 77, 234.

 ⁽³⁰⁾ Unless otherwise noted, thermochemical data were taken from:
 Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.;
 Bailey, S. M.; Churney, K. L.; Nuttall, R. L. J. Phys. Chem. Ref. Data, 1982, 11, Suppl. No. 2.

⁽³¹⁾ Kirk, A. W.; Tschuikow-Roux, E. J. Chem. Phys. 1969, 51, 2247.

⁽³²⁾ Cao, J. R.; Back, M. H. Int. J. Chem. Kinet. 1984, 16, 961.
(33) Moore, C. E. "Atomic Energy Levels"; Government Printing Office: Washington, DC, 1952; Natl. Bur. Stand. (U.S.) Cir. 467, Vol. II.

excess energy available to the C_2H_5 radical for internal excitation, but not below the threshold for its dissociation. Nevertheless, it is clear that the bulk of the excess energy must be carried by the C_2H_5 photofragment in the form of internal and translational energy. The extent of these excitations cannot be ascertained, but a consideration of the energy requirements for subsequent reactions of the C_2H_5 radicals impose some restrictions. We return to this point later in the discussion.

For HBr elimination from HCCCH₂Br the energy channeled into translation was found to be small, and Kawasaki et al.²⁸ established an experimental upper limit of $E_T \leq 5$ kcal mol⁻¹. Again, if this result is extended to C_2H_5Br , the total internal energy available to the C_2H_4 and HBr photofragments in reaction 2 is \geq 151 kcal mol⁻¹. In light of the abovementioned experimental restriction concerning the internal energy content of C_2H_4 , more than 71 kcal mol⁻¹ would have to be vested in the HBr molecule. Since the bond energy in HBr is ~ 87 kcal mol⁻¹, the energy balance for product stability could be met in this instance.

Formation of C_2H_6 . The formation of the major product C_2H_6 can be explained primarily, in terms of hydrogen abstraction by C_2H_5 radicals. The significant hydrogen donors to be considered are the substrate and, with increasing conversion, the product HBr produced in the system:

$$C_2H_5 + C_2H_5Br \rightarrow C_2H_6 + C_2H_4Br \tag{4}$$

$$C_2H_5 + HBr \rightarrow C_2H_6 + Br \tag{5}$$

Reactions 4 and 5 have been invoked by others in the photolysis of C₂H₅Br and it is relevant to assess their relative importance in the present system. Though, there appear to be no measured rate parameters for reaction 4, which is slightly exothermic,³⁴ we estimate for ground-state reactants an activation energy of no less than 10 kcal mol⁻¹ by analogy to metathetical reactions between C_2H_5 and alkanes.³⁵ Friedman et al.⁷ proposed reaction 4 to explain the *indirect* formation of small amounts of ethylene in the photolysis of C_2H_5Br at 220-260 nm in the presence of excess $c-C_5H_{10}$. This is not surprising since their study encompassed the temperature range 30-250 °C. Reaction 4 has also been invoked as a major source of the observed C_2H_6 yield by Frank and Hanrahan¹⁰ in the 253.7-nm photolysis of C_2H_5Br at a pressure of 100 torr and 23 °C. In this latter work the time evolution of the product yields was compared with computer simulations, based, in part, on estimated rate coefficients. To explain the observed decline in the quantum yield to HBr with photolysis time, Frank and Hanrahan further proposed reaction 5, noting that HBr is known to be a moderately good free-radical scavenger. The rate constant for the exothermic reaction 5 [$\Delta H_{(5)} = -12.8 \text{ kcal mol}^{-1}$], can be deduced from the literature. Fettis and Trotman-Dickenson³⁶ determined competitively the rate constant ratio $k_5/k_r =$ $10^{0.23} \exp(-2.3 \text{ kcal mol}^{-1}/RT)$ where k_r refers to the reaction

$$C_2H_5 + I_2 \rightarrow C_2H_5I + I$$

for which Hartley and Benson³⁷ report the Arrhenius parameters $\log (A_r/cm^3 \text{ mol}^{-1} \text{ s}^{-1}) = 12.5, E_r = 0.2 \text{ kcal mol}^{-1}$. The quoted activation energy is an estimate, but it is generally accepted³⁸ that for exothermic iodination reactions, $\mathbf{R} + \mathbf{I}_2 \rightarrow \mathbf{RI} + \mathbf{I}$, $E_a = 0$ \pm 1 kcal mol⁻¹. Combining these data one obtains

$$k_5/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 10^{12.73} \exp(-2.5 \text{ kcal mol}^{-1}/RT)$$

Since the A factors for reactions 4 and 5 are of the same order of magnitude, one estimates $k_5/k_4 > 3 \times 10^5$ at 25 °C and hence the rate ratio $R_5/R_4 > 300$ even for 0.1% HBr formation.

Therefore, for *thermal* reactants the contribution to the ethane yield from reaction 4 is negligible. Nevertheless, our results point toward a significant contribution from reaction 4 especially when viewed in conjunction with the brominated C_2 products. Further, inspection of the data in Table I shows that the quantum yield of ethane increases with C_2H_5Br pressure, while it is decreased by the addition of inert gases at a fixed substrate pressure. For example, the yield of C_2H_6 at 100 torr of C_2H_5Br is $\phi(C_2H_6) =$ 0.79 (run 18) while at roughly the same total pressure but 18-fold excess of CF_4 (run 30) the yield of C_2H_6 decreases by more than a factor of 2. This is indicative of collisional stabilization of the C_2H_5 radicals by inert gases and reactive collisions with the parent. The contribution to the ethane yield from reaction 4 at room temperature can be rationalized on the basis of the foregoing discussion concerning the distribution of the total excess energy among the photofragments in reaction 3, and the constraint derived from the apparent stability of the C_2H_5 radical with respect to further decomposition. Therefore, it appears not unreasonable to postulate that the translational energy of C_2H_5 is more than sufficient to overcome the energy barrier associated with reaction 4. The proposition of a "hot" radical reaction in this system is analogous to the well known case^{1,23} of the 253.7-nm photolysis of CH_3I where the formation of CH_4 has been shown to arise from the reaction

$$CH_3 + CH_3I \rightarrow CH_4 + CH_2I$$

with an observed activation energy near zero,¹ whereas the activation energy for the thermal reactants has been reported between 12.3³⁵ and 13.7 kcal mol^{-1.39}

Formation of CH₃CHBr₂. Among secondary products, CH₃-CHBr₂ stands next to ethane in order of importance. The formation of this product can only arise as a consequence of the presence of C_2H_4Br radicals and bromine in the system. Here we note that the C_2H_4Br radicals formed in reaction 4 can be structurally different depending upon the site of attack by C_2H_5 being α or β relative to the bromine in CH₃CH₂Br:

$$C_2H_5 + C_2H_5Br \rightarrow C_2H_6 + CH_3CHBr \qquad (4a)$$

$$\Rightarrow C_2H_6 + CH_2CH_2Br \tag{4b}$$

Based on thermochemical estimates³⁴ reaction 4a is favored by about 3 kcal mol⁻¹, and hence the predicted secondary product(s) resulting from reactions of the C_2H_4Br species should be largely due to the CH₃CHBr radical. This is confirmed experimentally: the observed dibromoethane product is CH₃CHBr₂, while 1,2dibromoethane was not found. These observations are in general agreement with the results of Frank and Hanrahan,¹⁰ and also in accord with the concept of "inert" or "wrong" radical playing an important role in chain termination as discussed by Benson.⁴⁰ On the other hand, the absence of CH₂BrCH₂Br as a product does not, in itself, preclude reaction 4b since, as discussed below, the CH₂CH₂Br radical may be unstable with respect to C-Br bond scission and/or is consumed by reaction with HBr to yield the starting material.

An additional source of C₂H₄Br radicals and HBr to be considered is the reaction of bromine atoms produced in reaction 3 with the substrate:

$$Br + C_2H_5Br \rightarrow HBr + C_2H_4Br$$
 (6)

In the 253.7-nm photolysis Frank and Hanrahan have argued against translational excitation of Br atoms as an adequate explanation for the observed large initial yield of HBr. These arguments were based on energy considerations, rapid thermalization,⁴¹ and an activation energy of 13 kcal mol^{-1} for reaction 6 estimated by Benson.⁴⁰ We have recently concluded a competitive photobromination study of $C_2H_5Br^{42}$ with visible light in

(41) Donovan, R. J.; Husein, D. Trans. Faraday Soc. 1966, 62, 2643.

⁽³⁴⁾ Based on $\Delta H_1^{\circ}[CH_2CH_2Br] = 32.7$ kcal mol⁻¹ evaluated from ref 40 and 44, and $\Delta H_1^{\circ}[CH_3CHBr] = 29.7$ kcal mol⁻¹ derived from bromination of C_2H_5Br , ref 42, and its reverse.

⁽³⁵⁾ Kerr, J. A., Moss, S. J., Eds. "CRC Handbook of Bimolecular and Termolecular Gas Reactions"; CRC Press: Boca Raton, FL, 1981; Vol. I. (36) Fettis, C. G.; Trotman-Dickenson, A. F. J. Chem. Soc. 1961, 3037.

⁽³⁷⁾ Hartley, D. B.; Benson, S. W. J. Chem. Phys. 1963, 39, 132.
(38) O'Neal, H. E.; Benson, S. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 17.

⁽³⁹⁾ Furuyama, S.; Golden, D. M.; Benson, S. W. Int. J. Chem. Kinet. 1969, 1, 283.

⁽⁴⁰⁾ Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 234

Photodecomposition of Gaseous Bromoethane

the temperature range 40-100 °C and obtained unequivocal evidence that below 90 °C bromine atom attack occurs almost exclusively at the substituted site

$$Br + C_2H_5Br \rightarrow HBr + CH_3CHBr$$
 (6a)

with an activation energy $E_{(6a)} = 10.6 \text{ kcal mol}^{-1}$. Thus, given the photon energy at 163.4 nm, the enthalpy change for reaction 3, $\Delta H_{(3)} = 70 \text{ kcal mol}^{-1}$, and making allowance for the maximum internal energy of the C₂H₅ radical below its decomposition threshold, $E_{int}^{R} < E_{a} \sim 40 \text{ kcal mol}^{-1}$,⁴³ we obtain from an elementary calculation of the energy balance involving the respective fragment masses

$$E_{\mathrm{T,Br}} = (h\nu - \Delta H_{(3)} - E_{\mathrm{int}}^{\mathrm{R}})[m_{\mathrm{R}}/(m_{\mathrm{R}} + m_{\mathrm{Br}})]$$
$$\simeq 17 \text{ kcal mol}^{-1}$$

as the minimum translational energy of the Br atom if it is formed in the electronic ground state. Inasmuch as this value exceeds the measured activation energy for hydrogen abstraction, reaction 6a cannot be excluded from providing an additional, if not alternate, source of CH_3CHBr radicals.

Since the three-body combination of bromine atoms

$$2Br + M \rightarrow Br_2 + M \tag{7}$$

is relatively slow,⁴⁰ the formation of CH₃CHBr₂ can then be readily explained by reaction 8 which is the generally accepted termination

$$CH_3CHBr + Br \rightarrow CH_3CHBr_2$$
 (8)

step in the pyrolysis of C_2H_5Br ,⁴⁰ with perhaps a minor contribution derived from reaction with molecular bromine produced in the system

$$CH_3CHBr + Br_2 \rightarrow CH_3CHBr_2 + Br \tag{9}$$

Reactions 4a and 6a in conjunction with (8) and (9) predict that the yield of CH_3CHBr_2 should increase with substrate pressure, which is roughly supported by the data at least in the lower range of pressures (Table I). However, a comparison with C_2H_6 shows that both the relative and absolute increase in the yield is somewhat less in the case of CH_3CHBr_2 . This suggests some collisional moderation in the production of its precursor, CH_3CHBr , which must be attributed mainly to reaction 6a since reaction 4a is common to both C_2H_6 and CH_3CHBr . In the presence of inert gases the yield of CH_3CHBr_2 decreases, not unexpectedly, as a consequence of collisional quenching of the reaction intermediates, C_2H_5 and Br.

Formation of Scavengeable C_2H_4 and C_2H_3F . As mentioned earlier, significant amounts of olefins of radical origin are formed in the 163.4-nm photolysis. It is tempting to assign the formation of this fraction of C_2H_4 simply to the dissociation of the primary C_2H_5 radicals formed in reaction 3

$$C_2H_5 \rightarrow C_2H_4 + H \tag{10}$$

The activation energy for reaction 10 is about 40 kcal mol^{-1,43} and from the foregoing discussion concerning the total excess energy available to the C_2H_5 radical this process could certainly be energetically feasible. However, the yields of C_2H_6 and the scavengeable C_2H_4 increase with substrate pressure, whereas, if reaction 10 provided the sole source of the scavengeable C_2H_4 , the net yield of the latter should *decrease* with increasing C_2H_5Br pressure as a result of the collisional stabilization of C_2H_5 and/or the competition from reaction 4. Consequently, reaction 10 cannot be considered to contribute significantly to the ethylene yield. This conclusion also places an upper limit, which has been mentioned earlier, on the internal energy content of C_2H_5 derived in the initial energy partitioning process, 3 and which, hence, must necessarily be below the threshold of ~40 kcal mol⁻¹, with a corresponding larger amount of the excess energy being channeled into translation, the latter favoring reaction 4.

The disproportionation of C_2H_5 radicals, reaction 11, cannot

$$2C_2H_5 \rightarrow C_2H_4 + C_2H_6 \tag{11}$$

$$\rightarrow n - C_4 H_{10} \tag{12}$$

account for the ethylene yield in question, again, because of the competition with reaction 4, and on the basis of kinetic and experimental evidence. The disproportionation/combination (D/C)ratio of C₂H₅ radicals is well established,³⁵ $k_{\rm dis}/k_{\rm comb} \sim 0.13$, yet the volatile *n*-butane, most likely produced in reaction 12, was only found in trace amounts. In fact, this observation places an upper limit to which reaction 11 may contribute to the scavengeable ethylene yield. Similarly, lack of experimental evidence for brominated butanes removes from consideration the disproportionation of C_2H_4Br radicals as a significant source of C_2H_3Br , or the cross-disproportionation of C_2H_5 and C_2H_4Br as a source of C_2H_4 . Though, in these cases, the D/C ratios have apparently not been determined, radical combination would be expected to be significant, if not necessarily predominant. What then is the source of the scavengeable C_2H_4 and C_2H_3Br ? As noted earlier the β -radical formed in reaction 4b may be unstable and decompose to yield Br atoms and ethylene. Wong and Armstrong⁴⁴ determined the relative rate parameters for the reactions

$$CH_2CH_2Br \rightarrow C_2H_4 + Br$$
 (13)

$$CH_2CH_2Br + HBr \rightarrow C_2H_5Br + Br$$
 (14)

as $E_{13}-E_{14} = 4.5 \pm 0.5$ kcal mol⁻¹, $A_{13}/A_{14} = 0.0216$ mol cm⁻³. These values may be combined with the rate constant k_{14}/cm^3 mol⁻¹ s⁻¹ = 10^{12.5} exp(-2 kcal mol⁻¹/RT) estimated by Benson⁴⁰ to yield $E_{13} \simeq 6.5$ kcal mol⁻¹ and $A_{13} \simeq 6.8 \times 10^{10}$ s⁻¹. Hence, at 298 K, $k_{13} \simeq 1.2 \times 10^6$ s⁻¹ and the lifetime of a thermal CH₂CH₂Br radical is estimated as ~8.5 × 10⁻⁷ s. Our recent results on the competitive photochlorination of ethyl bromide⁴⁵ suggest an even shorter lifetime; thus in addition to the expected major photochlorination product, CH₃CHClBr, we observe at 298 K a very low yield of CH₂ClCH₂Br but a very significant amount of C₂H₄ which can only derive from reaction 13. It is therefore not unreasonable to assume that reaction 13 is also operative in the present system, particularly so since some energy transfer must occur in the collision encounter, reaction 4b.

The formation of vinyl bromide is more difficult to interpret. As already mentioned, bromoethyl radical disproportionations are not considered significant since no dibromobutanes were found (though their analysis in this system was not without problems). The direct formation of C_2H_3Br from either of the two types of C_2H_4Br radicals via C-H bond fission is energetically not feasible, the processes being endothermic by 38-41 kcal mol⁻¹. The only other available routes for scavengeable olefin formation are the atom-radical disproportionations

$$Br + C_2H_5 \rightarrow HBr + C_2H_4 \tag{15}$$

$$Br + C_2 H_4 Br \rightarrow HBr + C_2 H_3 Br$$
(16)

While there are other reaction channels for the loss of bromine atoms, Frank and Hanrahan¹⁰ have shown that inclusion of reactions 15 and 16 in their computer simulation using plausible rate constants could account for part of the initial HBr yield. Noting that the "inert" CH₃CHBr radical will be present at higher concentration we propose the highly exothermic reaction 16a as Br + CH₃CHBr \rightarrow

+
$$CH_3CHBr \rightarrow$$

HBr + C_2H_3Br ($\Delta H \simeq -46 \text{ kcal mol}^{-1}$) (16a)

the most likely source of C_2H_3Br , and reactions 13 and 15 as the source of the scavengeable C_2H_4 .

In this connection it is worthy of note that the absence of CH_2BrCH_2Br and $CH_2BrCHBr_2$ among products might appear to provide a somewhat surprising diagnostic of the instability of the adducts formed between Br atoms and the product olefins.

⁽⁴²⁾ Salomon, D. R., Tschuikow-Roux, E., to be published.
(43) Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimo-

⁽⁴³⁾ Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions"; Natl. Stand. Ref. Data Ser. (U.S.) Natl. Bur. Stand. 1970, NSRDS-NBS 21.

⁽⁴⁴⁾ Wong, K. T.; Armstrong, D. A. Can. J. Chem. 1969, 47, 4183.

⁽⁴⁵⁾ Faraji, F.; Tschuikow-Roux, E., to be published.

In the case of C_2H_4 the resulting bromoethyl radical would necessarily be CH_2CH_2Br , and, unless one postulates a possible rapid isomerization to CH_3CHBr , the product would be CH_2 -Br CH_2Br after further reaction with bromine, in analogy to reactions 8 or 9. For C_2H_3Br the adduct would be either CH_2CHBr_2 or, possibly, $CH_2BrCHBr$, both leading to 1,1,2-tribromoethane by the same argument. An alternative and preferred explanation for the absence of the above products can be found by considering the reactions of bromoethyl radicals (formed by Br atom addition or otherwise) with the HBr in the system

$$Br + C_2H_4 \rightarrow CH_2CH_2Br \qquad (17)$$

$$Br + CH_2 CHBr \rightarrow CH_2 CHBr_2$$
(18a)

$$\rightarrow$$
 CH₂BrCHBr (18b)

$$CH_2CH_2Br + HBr \rightarrow C_2H_5Br + Br$$
 (19)

$$CH_2CHBr_2 + HBr \rightarrow CH_3CHBr_2 + Br$$
 (20)

$$CH_2BrCHBr + HBr \rightarrow CH_2BrCH_2Br + Br$$
 (21)

where reaction 17 is the reverse of (13), and reactions 19–21 are analogous to (5). In light of our product analysis the following conclusions can be drawn from this scheme: (a) the CH_2CH_2Br radical formed in reactions 4b or 17 leads to no products but generates the parent molecule via reaction 19; (b) the addition of Br atoms to vinyl bromide occurs primarily at the substituted site, thus reactions 18b and 21 can be neglected; (c) the depletion of C_2H_3Br in (18a) results in an enhanced yield of CH_3CHBr_2 via reaction 20. This conclusion is supported by experiment as shown in Figure 4: the yield of C_2H_3Br decreases with photolysis time, while that of CH_3CHBr_2 shows a roughly corresponding increase. The time independent yield of C_2H_4 shows that its production is quasi-stationary.

Acknowledgment. The financial support of the Korea Science and Engineering Foundation and the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. C_2H_5Br , 74-96-4; CF₄, 75-73-0; NO, 10102-43-9; C₂H₆, 74-84-0; C₂H₃Br, 593-60-2; CH₃CHBr₂, 557-91-5; C₄H₁₀, 106-97-8; C₂H₄, 74-85-1; N₂, 7727-37-9

Photosensitized Reaction of ³P Hg, Cd, and Zn Atoms with Difluorochloroethene in Krypton Matrix

Harry E. Cartland and George C. Pimentel*

Chemical Biodynamics Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720 (Received: October 28, 1985)

The reaction between $M(^{3}P)$ atoms (M = Hg, Cd, Zn) with diffuorochloroethene (CDFE) and deuteriodiffuorochloroethene (CDFE-*d*) in krypton matrix at 12 K has been studied. The usual gas-phase reaction caused by mercury-photosensitization of halogenated ethenes, elimination of HX (or H₂), is not observed. Instead, each of these class IIB (group 12 in the new notation) metal atoms gives a reaction product with an absorption spectrum that resembles that of the parent olefin but shifted significantly to lower frequencies. For mercury, the product is identified as 1,1-diffuorovinylmercuric chloride, (F₂C=CH)HgCl, the net result of mercury insertion into the carbon-chlorine bond. Cadmium and zinc apparently give analogous products. The preferential insertion into the C-Cl bond indicates that reaction is constrained in krypton matrix to a triplet reaction surface and suggests that there is an activation energy barrier connected with the change in shape of the olefin in its planar, ground state to the twisted triplet state. The reactivity of the Hg(³P) state relative to that of the ground state is attributed to its partially occupied valence orbitals. In view of the infrared spectrum of CDFE-*d*, the vibrational assignment deduced earlier for CDFE must be altered.

Introduction

The mercury photosensitization of many gas-phase reactions have been reported and they have been well reviewed.¹ Specific studies of the gaseous fluoroethenes have revealed HF elimination as a favored reaction path.² In addition, however, HgCl has been found as a reaction product in gas-phase photosensitization of chlorinated alkanes and alkenes.¹ Furthermore, the gaseous reactions of Hg(³P) atoms with H₂O, O₂, and N₂O produced oxides of mercury. Such mercury products intimate that chemical reactivity plays a role in photosensitization along with energy transfer. The relative importance of these two reaction paths is generally not clear.

We have undertaken a systematic study of the reactions that occur when mercury, cadmium, and zinc atoms are excited to the ³P state in a cryogenic matrix containing various halogenated ethenes.³ Such experiments cast additional light on this question of the extent to which behavior now classified as photosensitization can be further segregated into systems for which energy transfer suffices to explain the chemistry and systems for which transient reaction intermediates are likely to be involved. Of course, the chemical reactivities of group IIB (group 12)²³ metals are quite low in their ground ²S state because of the paired $(ns)^2$ valence orbital occupancies. This is evident in their low dimerization energies: Hg₂, 1.4 kcal/mol, Cd₂, 2.1 kcal/mol, and Zn₂, 6 kcal/mol. In contrast, the ³P states, with two unpaired valence electrons $(ns)^1(np)^1$, can be expected to be chemically reactive. Insofar as this reactivity may play a role in photosensitization, the matrix technique offers a favorable opportunity to interrupt the train of events and reveal any transient, but stable, intermediate.

A second issue of considerable interest is the extent to which such photosensitized chemistry is constrained to triplet reaction surfaces. Here, we expect contrasts between the behaviors of the Hg, Cd, and Zn to be informative. These atoms should display

⁽¹⁾ Gunning, H. E.; Strausz, O. P. Advances in Photochemistry; Interscience: New York, 1963; Vol. 1, pp 209-274.

⁽²⁾ Norstrom, R. J.; Gunning, H. E.; Strausz, O. P. J. Am. Chem. Soc. 1976, 98, 1454.

⁽³⁾ Cartland, H. E. Ph.D. Dissertation, University of California, Berkeley, 1985.