polarizable than first-row atoms, and therefore are more perturbed by positively charged holes in either their own cores, or the cores of adjacent atoms. Furthermore, the increased size of these heavier elements implies smaller one-center $\langle r^{-1} \rangle$ expectation values and thus smaller chemical shifts. Thus, the effects of valence electron relaxation should become relatively more pronounced. The equivalent cores approach, in both its thermodynamic[22] and electrostatic potential[23] applications, provides a simple method of accounting for the valence electron charge polarization which occurs during photoemission.

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Photochemistry of Organochalcogen Compounds. I. Photolysis of Benzyl Diselenide

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Abstract: The photolysis of benzyl diselenide (I) in acetonitrile under nitrogen at wavelengths above 280 nm results in extrusion of elemental selenium and formation of dibenzyl selenide. The quantum yield for disappearance of (I) is $\phi = 0.16$ independent of initial concentration. It was shown that homolytic Se–Se bond cleavage plays no role in formation of the observed products. A radical mechanism involving photolytic C–Se bond scission is proposed and accounts for all preparative and kinetic observations.

Photodecomposition and formation of the elemental chalcogens is frequently cited as a nuisance factor in the preparation and storage of organic selenium and tellurium compounds. However, this behavior is not universal, and many stable compounds of these elements are known and well documented.[1] It appears then rather remarkable that the literature to date contains little structure/property information and essentially no mechanistic details on these grossly observable photoeffects.

The study reported herein was undertaken to generate suitable mechanistic information on the photophysical and photochemical events leading to deposition of the free elements. Benzyl diselenide (I) was chosen as a model compound for the following reasons. Its photodecomposition was noted just 100 years ago by Jackson[2] and later confirmed by Price and Jones.[3] The photochemistry of benzyl disulfide is well documented[4] and does not lead to deposition of sulfur. While quantitative differences between analogous organic sulfur and selenium compound are always reasonable and expected, this appears to be one of the rare instances where compounds of these elements exhibit a qualitative difference. A recent note[5] added the information that irradiation of I at 350 nm yielded selenium and benzaldehyde in air, while dibenzyl selenide (II) and only traces of selenium were formed in the absence of oxygen.

We report herein a quantitative study on the photolysis of benzyl diselenide and propose a mechanism which accounts for all reported observations.

Experimental Section

General. Infrared spectra were taken on a Perkin-Elmer Model 267 spectrophotometer. Uv spectra were measured on a Cary 15 spectrophotometer. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. NMR spectra were determined on a JEOL C60H instrument with $CDCl_3$ or CD_3CN as solvent and tetramethylsilane as internal standard. Melting points were recorded with a Thomas Hoover melting point apparatus and are not corrected. Eastman silica gel chromagram sheets were used for thin-layer chromatography. For preparative-layer chromatography, plates (20 × 20 cm) coated with 2 nm of Merck silica gel F-254 were used, with benzene–hexane as eluent.

Table I. Photolyses of Benzyl Diselenide (I)

Light source	Time (hr)	Temperature	Products, % I	II	Se°
PEK, 365 nm	2.9	Ice water cooling	93	7	7
Rayonet, 350 nm	1.3	Ice water cooling	61	39	36
Rayonet, 350 nm	1.3	No cooling	70	25	Trace[a]

[a] Only a trace amount of *dark gray* selenium was in the photolysis products.

Materials. Benzyl diselenide was prepared by adapting the method of Günther and Mautner.[6] Potassium selenosulfate was treated with benzyl chloride followed by alkaline hydrolysis. The crude product was purified by multiple recrystallizations from ethanol and hexane: mp 92–93° (lit.[7] mp 92–93°); uv, λ_{max} (CH_3OH) 235 (log ϵ 4.18), 308 nm (log ϵ 2.85); NMR (CD_3CN) δ 3.67 (4 H, S), 6.91 (10 H, S).

Dibenzyl selenide was prepared by adapting the procedure of Klayman and Griffin.[8] The crude product was recrystallized from pentane: mp 45–46° (lit.[8] mp 44–45°); NMR (CD_3CN) δ 3.55 (4 H, S), 6.91 (10 H, S).

Solvents. Deuterated solvents were commercial spectral grade. Burdick & Jackson spectroquality acetonitrile was purified by drying with molecular sieves, followed by passing it through a column of alumina (e.g., Woelm, activity 1).

Irradiation Procedures. Preparative photolyses were carried out in a quartz, ice-water cooled immersion apparatus equipped with magnetic stirring and dry nitrogen purging. Degassed solutions were irradiated under nitrogen atmosphere with the output of an Hanovia 450-W mercury arc lamp filtered through Pyrex to eliminate light of wavelengths less than 280 nm. For quantum yield and kinetic studies the output of a PEK 112 high-pressure compact point source mercury arc was collimated using quartz lenses, passed through a 5-cm cold water filter, then through Corning glass filters to isolate wavelength regions of interest, through diaphragms into a quartz reaction cell a distance of 40 cm from the lamp. This experimental setup provides collimated light and eliminates unwanted thermal side reactions. Light intensity was determined using a 16-junction, circular, Eppley thermopile in conjunction with a Keithley Model 150A microvolt-ammeter. This actinometer system was calibrated using the potassium ferrioxalate actinometer.[9]

A Rayonet reactor supplied by the Southern New England Ultraviolet Co., Inc. consisting of a circular array of 3500 Å lamps was used for some photolyses.

Photolyses of Benzyl Diselenide (I). A solution of I (2.50 g) in purified acetonitrile (310 ml) was irradiated with a 450-W Hanovia lamp as described above. Selenium was precipitated from solution during the photolysis and a thin film was deposited on the cooling jacket, reducing the effectiveness of the irradiation. The progress of the photolysis was monitored by withdrawing small samples at fixed intervals. The samples were analyzed by NMR and thin layer chromatography. After 2 hr of irradiation (80% benzyl diselenide decomposed), the reaction mixture was filtered. The solid was washed with acetonitrile and dried in a vacuum oven to give 0.434 g of selenium. The filtrate and the acetonitrile washings were combined and concentrated to give 1.851 g of pale yellow liquid which solidified upon standing at room temperature. NMR analyses showed that the reaction products consisted of dibenzyl selenide (82%) and benzyl diselenide (18%). A portion of the reaction mixture (391 mg) was separated by preparative layer chromatography on a glass plate (20 × 20 cm) coated with a 2-mm layer of silica gel to give 282 mg of dibenzyl selenide and 77 mg of benzyl diselenide. Both organic species were identified by comparison with authentic samples. The precipitate of red amorphous selenium underwent a transition to the gray form (hexagonal selenium) at 70–80° and melted at 218° which is in good agreement with a literature value of 219°.[10] Reaction of the red precipitate with triphenylphosphine gave triphenylphosphine selenide[11] in quantitative yield.

A series of experiments were also run to determine the photolysis products of I (2.827 × 10^{-2} *M*) in degassed benzene at various irradiation conditions. Results appear in Table I.

NMR Method for Kinetic Study. Proton magnetic resonance techniques were used to determine concentrations of benzyl diselenide, dibenzyl selenide, and other photoproducts. The chemical shifts of the methylene protons for benzyl diselenide (δ 3.67) and dibenzyl selenide (δ 3.55) are sufficiently different to allow spectral peak areas to be compared, using the constant peak area for acetonitrile impurity in the deuterioacetonitrile solvent as an internal standard. Degassed solutions of I in deuterated acetonitrile were irradiated through a Corning 0-53 filter with the collimated emission of a PEK 112 high intensity mercury arc. This allows light having wavelengths greater than 280 nm to enter the reaction vessel.

Results

Product Formation. In our hands, a nitrogen purged solution of benzyl diselenide (I) in acetonitrile, after irradiation through Pyrex with a 450-W Hanovia mercury lamp for 2 hr gave dibenzyl selenide (II) (98% based on the benzyl diselenide consumed) and a *stoichiometric amount of amorphous elemental selenium* as the only detectable reaction products. After this irradiation time 18% benzyl diselenide was recoverable, prolonged photoexposure led to secondary photolysis of the monoselenide II.

$$\underset{\text{I}}{PhCH_2SeSeCH_2Ph} \xrightarrow[CH_3CN]{h\nu\ (\lambda > 280\ nm)} \underset{\text{II}}{PhCH_2SeCH_2Ph} + Se \qquad (1)$$

When Corning 7-39 and 7-54 glass filters, which transmit light between 350 and 375 nm (50% T) were used, and care was taken to prevent any unwanted thermal side reactions, a small yield of dibenzyl selenide and a stoichiometrically equivalent amount of red amorphous selenium were isolated after 3 hr of irradiation of a degassed solution of 10^{-2} *M* benzyl diselenide in benzene. Dibenzyl selenide and a stoichiometrically equivalent amount of red selenium were also produced when the photolysis was carried out in a Rayonet reactor using 350-nm light and ice water cooling (Table I).

Mechanistic Results. The observed quantum yield for disappearance of I using 313-nm light was 0.16 ± 0.02 at low conversions. The curves in Figure 1 show that changing the diselenide concentration by a factor of 1.6 has little effect on the initial rate of diselenide photodecomposition. We have varied the initial concentration of I from 0.025 to 0.25 *M*, and within our experimental error the initial rates of benzyl diselenide photodecomposition are independent of concentration. The nonlinear decomposition curves indicate a decrease with time of diselenide decomposition. This decrease is due to lowered light intensity impinging on the starting material due to scattering and absorption by the photochemically produced selenium.

Benzyl diselenide (I), 3.35 × 10^{-2} *M* in degassed acetonitrile at 23°, was photolyzed using neutral density filters to vary the incident light intensity. In Figure 2, are plotted the millimoles of I decomposed against absorbed light intensity I_a (einstein sec^{-1} cm^{-2}). The curve shows a near linear dependence of photodecomposition upon absorbed light intensity, photodecomposition increasing with increasing light absorption.

Discussion

Our results show that the photodecomposition of I is independent of initial concentration, but dependent upon absorbed light intensity and wavelength. At 313 and 350 nm, photodecomposition occurs readily to give monoselenide (II) and a stoichiometric amount of red selenium, but at 365 nm only a small amount of photodecomposition can be detected after several hours irradiation. Kumler et al.[5] reported that photolysis of 10^{-2} *M* benzyl diselenide solution in degassed benzene at 350 nm using a Rayonet reactor yielded II and only a trace amount of elemental selenium.

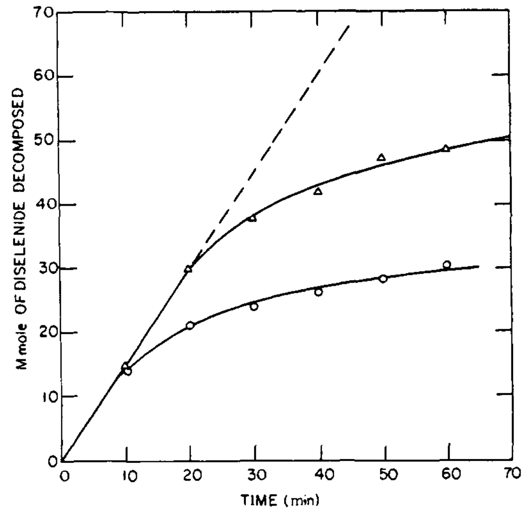

Figure 1. Photolysis of benzyl diselenide in CD_3CN: △, 0.056 *M*; O, 0.034 *M*.

We have repeated their experimental conditions (no ice water cooling) and confirmed their stated results. Only a trace of dark gray selenium was observed as a coating on the surface of the photolysis vessel. Also, the temperature in the reaction vessel (Hg thermometer) reached 61° after 40 min. These facts lead to the following conclusions. The transition from red amorphous selenium to the gray form requires heat; therefore, it seems clear that thermal processes play a major role under these conditions. The surprisingly small yields of elemental selenium are consistent with thermally induced reactions leading to polymeric selenides as reported by Lardon.[12] By analogy with Lardon's results, atomic selenium, produced photochemically, must play a major role in the thermal formation of polymeric selenides. Since the benzylselenoselenyl radicals produced at 0° dissociate readily at this temperature and are expected to be less stable at higher temperatures, these radicals are not likely to be involved in the thermal production of polyselenides. This explains the lack of selenium and in addition the color change from pale yellow to deep yellow upon irradiation which we have observed for reactions in which thermal processes play a role.

Photolyses carried out with care to prevent unwanted thermal side reactions result in the disappearance of the pale yellow color, due to the fact that colorless dibenzyl selenide is the primary photoproduct.

We feel confident that no thermal reactions occurred in our system and propose the following mechanism.

There are two possible primary processes involved in the photolysis of I: (A) homolytic cleavage of the Se-Se bond, leading to benzylselenyl radicals (eq 2); (B) formation of benzyl and benzylselenoselenyl radicals through photoinduced cleavage of C-Se bonds (eq 3).

$$\underset{\text{I}}{\text{RSeSeR}} \overset{h\nu}{\rightleftharpoons} 2\text{RSe}\cdot \quad (\text{R} = \text{PhCH}_2) \tag{2}$$

$$\text{I} \overset{h\nu}{\rightleftharpoons} \text{R}\cdot + \text{RSeSe}\cdot \tag{3}$$

An ESR study on uv-irradiated phenyl diselenide by Schmidt et al.[13] indicated the formation of phenylselenyl and phenylselenosenyl radicals. Both S-S and C-S cleavages have been shown to be the important processes for photolysis of benzyl disulfide.[4,13] Therefore, it is reasonable to propose that both Se-Se (i.e., eq 2) and C-Se (i.e., eq 3) scissions are operative in the photolysis of I. The longest wavelength maximum in I at 310 nm corresponds to about 92 kcal/mol which is greater than the bond energies for Se-Se (44 kcal/mol)[14] and benzyl C-Se (57 kcal/mol).[15] There is, then, sufficient energy to cause the rupture of both Se-Se and C-Se bonds by wavelength up to 500 nm.

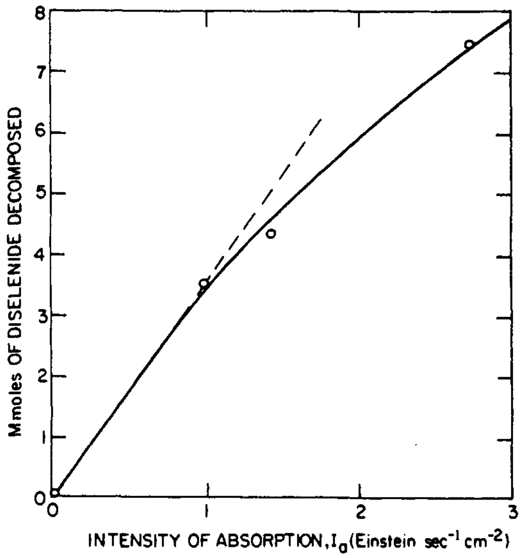

Figure 2. Photolysis of benzyl diselenide in CH_3CN, 0.034 *M*, as a function of absorbed light intensity I_a (einstein sec^{-1} cm^{-2}).

Scheme I

$$\text{RSeSeR} \xrightarrow{h\nu} \text{RSeSeR}^* \tag{4}$$

$$\text{RSeSeR}^* \xrightarrow{k_5} \text{RSeSeR} \tag{5}$$

$$\text{RSeSeR}^* \xrightarrow{k_6} 2\text{RSe}\cdot \tag{6}$$

$$\text{RSeSeR}^* \xrightarrow{k_7} \text{R}\cdot + \text{RSeSe}\cdot \tag{7}$$

$$\text{RSeSe}\cdot \xrightarrow{k_8} \text{RSe}\cdot + \text{Se} \tag{8}$$

$$\text{R}\cdot + \text{RSeSeR} \xrightarrow{k_9} \text{RSe}\cdot + \text{RSeR} \tag{9}$$

$$\text{R}\cdot + \text{RSe}\cdot \xrightarrow{k_{10}} \text{RSeR} \tag{10}$$

$$2\text{RSe}\cdot \xrightarrow{k_{11}} \text{RSeSeR} \tag{11}$$

Initially formed benzylselenyl radicals (eq 2) may combine or attack the weak Se-Se linkage leading to radical displacement and re-formation of I. Neither of these reactions results in the observed photoproducts. A possible hydrogen abstraction by the benzylselenyl radical, as observed for phenylselenyl radical in the presence of *trans*-stilbene,[16] does not appear to be operative here. Therefore, eq 3 is the most probable step leading to the formation of the observed photolysis products. Scheme I satisfactorily accounts for the experimental observations.

In this scheme R is the benzyl moiety. Assuming steady-state conditions for all reaction intermediates, the following rate expression may be derived

$$-\text{d}[\text{RSeSeR}]/\text{d}t = I_a k_7/(k_5 + k_6 + k_7)$$

where I_a is the rate of absorption of light by I. The rate constants refer to the above steps, respectively. The results are in agreement with the zero-order dependence for I found experimentally. Furthermore, the dependence on light intensity shown in Figure 2 is entirely consistent with the mechanism. In our suggested mechanism, most of the excited molecules return to the ground state through various deactivation processes. Since the C-Se bond energy of I is low, photochemically produced benzyl radicals should possess sufficient kinetic energy to diffuse away from the solvent cage to undergo secondary radical reactions (eq 9 and 10). However, the possibility of producing monoselenide (II) and selenium by a cage process cannot definitely be ruled out. Reported observations on benzylic species[17,18] indicate that both cage and noncage reactions may occur when benzyl radicals are generated photochemically or thermally, although noncage processes are likely to be favored, particularly in photoreactions.

The presence of benzyl in our photolysis mixture is substantiated by the formation of benzyl chloride upon irradiation of I in carbon tetrachloride. Furthermore, irradiation of a solution of I in oxygenated acetonitrile gives benzaldehyde. These results confirm the importance of C-Se cleavage and the formation of benzyl radicals.

The generation of benzyl radicals further indicates the concomitant formation of the benzylselenoselenyl radical (eq 7) as an essential step leading to deposition of elemental selenium.

Photosensitization and quenching experiments as well as various scavenging reactions on the intermediate organoselenyl radicals are in progress and will be reported in full.

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Photochemistry of Metal-Metal Bonded Complexes. IV. Generation of d^5 and d^7 Mononuclear Fragments via Homolytic Cleavage in Heterodinuclear Metal Carbonyls

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Abstract: The flash photolysis of $(OC)_5M'-M(CO)_3(\eta^5-C_5H_5)$ in degassed isooctane solution yields $M'_2(CO)_{10}$ and $[(\eta^5-C_5H_5)M(CO)_3]_2$ in nearly a 1:1 ratio with high chemical yield ($\geq$65%) for M = W, Mo and M′ = Mn, Re. Photolysis at 366 nm of the $(OC)_5M'-M(CO)_3(\eta^5-C_5H_5)$ complexes in degassed CCl_4 yields $M'(CO)_5Cl$ and $(\eta^5-C_5H_5)M(CO)_3Cl$ with a M-M′ disappearance quantum yield in the range of 0.23-0.56. Photolysis at 436 nm gives the same products, but the quantum yields are substantially less. The electronic spectra of the M-M′ species exhibit absorptions which can be ascribed to transitions resulting in population of a σ-antibonding orbital with respect to the M-M′ bond. Such transitions apparently result in efficient homolytic cleavage despite the fact that heterolytic cleavage to yield $M'(CO)_5^+$ and $(\eta^5-C_5H_5)M(CO)_3^-$ would give diamagnetic fragments of the stable d^6 electronic configuration.

The photochemistry of metal carbonyls containing metal-metal bonds has involved complexes where the metals are the same, or at least of the same formal d^n configuration. In every case to date the chemistry following photoexcitation is consistent with homolytic cleavage of the metal-metal bond as the primary excited state decay path. Specific examples are $M_2(CO)_{10}$ (M = Mn, Re),[1-3] $MnRe(CO)_{10}$,[2] $Mn_2(CO)_n(PPh_3)_{10-n}$[2] (n = 9, 8), $[Mn(CO)_3(phen)]_2$,[4] $(OC)_5Mn-Re(CO)_3(phen)$,[4] and $[(\eta^5-C_5H_5)M(CO)_3]_2$ (M = Mo, W).[5] Phenomenologically, at least, it may also be said that the $Re_2Cl_8^{2-}$ undergoes $Re\equiv Re$ homolysis upon photoexcitation in CH_3CN,[6] and $Ru_3(CO)_{12}$ undergoes Ru-Ru homolysis upon photolysis in the presence of CO to quantitatively yield $Ru(CO)_5$.[7]

Heterodinuclear complexes having metals of differing d^n configuration seemingly have the best a priori chance of yielding efficient photoinduced heterolytic cleavage. This would be especially true if the resulting cations and anions could have stable electronic configurations. Such a series of heterodinuclear compounds are the $(OC)_5M'-M(CO)_3(\eta^5-C_5H_5)$ (M′ = Mn, Re; M = Mo, W) complexes which are thermally stable, well-characterized species.[8] Here heterolytic splitting could yield $(OC)_5M'^+$ and $(\eta^5-C_5H_5)M(CO)_3^-$ which are both of the d^6 electronic configuration. Homolytic cleavage would give the metal radicals which can be photogenerated from appropriate homodinuclear metal carbonyls.[1-3,5] In this short paper we report electronic spectral properties and photochemistry of the $(OC)_5M'-M(CO)_3(\eta^5-C_5H_5)$ complexes.

Results

a. Spectra of the Complexes. The $(OC)_5M'-M(CO)_3(\eta^5-$