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UV laser-induced photolysis of diethyl selenium and diethyl tellurium: extrusion of selenium and tellurium via molecular elimination of ethene

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Abstract

KrF laser-induced photolysis of gaseous $(C_2H_5)_2M$ (M = Se, Te) compounds is shown to be a one-photon process controlled by the cleavage of both C–M bonds. It is dominated by the molecular elimination of ethene and yields elemental selenium and tellurium. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diethyl selenium; Diethyl tellurium; Laser photolysis; Molecular mechanism

1. Introduction

The gas-phase photolysis of diethyl ether [1] and diethyl sulfide [2] has been examined to elucidate the mechanism of these reactions. It has been shown that the primary process is the fission of the C–O (C–S) bond to yield $C_2H_5^\bullet$ and $C_2H_5O^\bullet$ ($C_2H_5S^\bullet$) radicals, and that final photolytic products are accounted for mostly by radical and not molecular steps. The C1–C4 hydrocarbons, ethanol, acetaldehyde and ethoxybutanes were produced from diethyl ether, and C2, C4 hydrocarbons, ethanethiol, 4-methyl-3-thiahexane and methyl-3,5-dithiaheptane were obtained from diethyl sulfide. The O- and S-containing products are compatible with the perseverance of the ethoxyl and ethylthiyl radicals and confirm the cleavage of only one of the carbon–heteroatom bonds.

$$(C_2H_5)_2Te \xrightarrow[-\,C_2H_4]{} H\text{-}Te\text{-}C_2H_5 \xrightarrow[-\,C_2H_4]{} H_2Te \xrightarrow[-\,H_2]{} Te$$

Scheme 1.

Less attention has been paid to the photolysis of the congener $(C_2H_5)_2M$ molecules with M = Se, Te. Thus, the photolysis of diethyl selenium has not been studied at all and that of diethyl tellurium, although examined, is poorly understood as to the mechanism. It was shown that laser photodissociation of $(C_2H_5)_2Te$ through a one-photon absorption at 193 and 248 nm [3] and through a multiphoton absorption at 358–395 nm [4] yields ground-state Te atoms; these were presumed to originate via the homolysis of the Te–C bond (Eq. (1)).

$$(C_2H_5)_2Te \rightarrow Te(^3P_2) + 2C_2H_5^\bullet \qquad (1)$$

A more complicated photochemical scheme involving C_2H_5Te transient was surmised for mercury–xenon lamp-induced photodeposition of Te [5]. No Te-containing short-lived species were, however, detected by dye-laser mass spectroscopy [6], despite that a very high sensitivity of this technique was proved with other alkyl metals [6,7]. The formation of the observed Te photoproduct can be, in principle, rationalised in terms of two different mechanisms: (a) the assumed Te–C homolysis (Eq. (1)) and (b) a sequence of a two-fold β-elimination of ethene [8] and elimination of H_2 from unstable hydrogen telluride (Scheme 1). Until now, neither transient nor final stable hydrocarbon products

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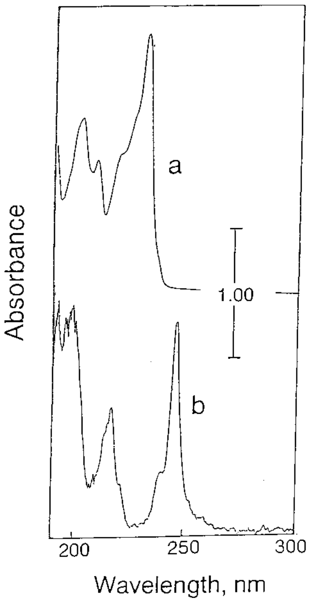


Fig. 1. UV absorption spectrum of (a) $(C_2H_5)_2Se$ and (b) $(C_2H_5)_2Te$. Conditions: 1 Torr, pathlength 9 cm.

of the gas-phase $(C_2H_5)_2Te$ photolysis have been identified, despite that the differentiation between these two pathways can be made on the basis of the determined yields of hydrocarbon products and consideration of relative rate constants for combination and disproportionation of the $C_2H_5^{\bullet}$ radical [9].

In conjunction with our previous studies on the gas-phase UV laser photolysis of ketones [10], organosilicon [11], organogermanium [12] compounds and selenophene and tellurophene [13], we explored in this work KrF laser photolysis of diethyl selenium and diethyl tellurium. We reveal that these compounds photolytically cleave to elemental selenium and tellurium and that the heteroatom extrusion occurs mostly by a molecular elimination of ethene.

2. Experimental

Laser photolysis experiments were performed on gaseous samples of $(C_2H_5)_2M$ (M = Se, Te) by using an LPX 210i (KrF) laser operating at 248 nm with a repetition frequency 10 Hz. The samples of $(C_2H_5)_2Se$ (11 Torr) or $(C_2H_5)_2Te$ (8 Torr) in helium (total pressure 790 Torr) were irradiated in a reactor (140 ml in volume) which was equipped with a sleeve with a rubber septum and PTFE valve, and consisted of two orthogonally positioned Pyrex tubes (both 3 cm in diameter), one (9 cm long) fitted with two quartz windows and the other (13 cm long) furnished with two NaCl windows. The laser beam of different fluences (full-width at half-maximum typically 23 ns) effective on the area of 2.6 cm^2 was monitored for energy output by a Gentec ED-500 joulmeter connected to a Tektronix T912 10 MHz storage oscilloscope.

The progress of the photolysis was monitored by FTIR spectroscopy (a Shimadzu FTIR 4000 spectrometer) using absorption bands at 1233 cm^{-1} ($(C_2H_5)_2Se$) and 1198 cm^{-1} ($(C_2H_5)_2Te$), and by gas chromatography on a Gasukuro Kogyo 370 chromatograph (programmed temperature 30–150°C), a 60 m long capillary (Neutra Bond-1) and 2 m long SUS Unipak S columns. Both chromatographs were equipped with flame-ionisation detectors and connected with a Shimadzu CR 5A Chromatopac data processor. The gaseous samples were introduced by a gas-tight syringe (Dynatech Precision Sampling). The photolytic products were identified by the gas chromatography using the comparison of retention times with those of authentic samples.

For the examination of the dependence of $(C_2H_5)_2Se$ and $(C_2H_5)_2Te$ depletion on the laser fluence, the entrance reactor window was cleaned before each experiment. This helped to circumvent the data irreproducibility caused by a gradual decay of laser power within the reactor, which was due to some formation of Se and Te films on the reactor window.

The quantum yields of both processes were determined on the basis of initial depletion of $(C_2H_5)_2M$ (as measured by IR spectroscopy) and the amount of laser energy absorbed in $(C_2H_5)_2M$ (as measured by the Gentec ED-500 joulmeter).

Diethyl selenium [14] and diethyl tellurium [15] were prepared using the reported procedures and distilled as a fraction with b.p. 106°C and 82°C/100 Torr, respectively. Their purity (better than 98%) was checked by chromatography and ^1H-NMR spectroscopy.

3. Results and discussion

The absorption spectrum of diethyl selenium consists of absorption bands at 204, 210 and 230 nm and that of diethyl tellurium (almost coincident with that reported [3,16]) shows absorption bands at 201, 217 and 246 nm (Fig. 1). The absorptivity at 248 nm of diethylselenium (3×10^{-3} $Torr^{-1}$ cm^{-1}) is significantly lower than that of diethyl tellurium (1.5×10^{-1} $Torr^{-1}$ cm^{-1}).

The KrF laser photolysis of diethyl selenium results in an instant formation of a white fog and that of diethyl tellurium affords a dark fog, both of which descend onto the reactor walls when the irradiation is ceased. The white fog creates films that are initially white in colour and later pink, whereas the dark fog grows into a dark powder. XPS measurements proved that these materials correspond to elemental selenium and tellurium. Apart from these solid products, various C_1–C_4 hydrocarbons are produced. The presence of these hydrocarbons and that of elemental selenium and tellurium, but not of any Se- and Te-containing organic compounds, reveals that photolysis of $(C_2H_5)_2M$ (M = Se, Te) can be rationalised by cleavage of both C–M bonds.

3.1. Photolysis of diethyl selenium

The initial quantum yield of the laser photolysis (the number of $(C_2H_5)_2Se$ molecules decomposed by one absorbed photon) was estimated as 0.08–0.10. The slope of the initial $(C_2H_5)_2Se$ depletion versus laser fluence in a double-logarithmic plot is very close to 1 (Fig. 2), which indicates that the photolysis is a one-photon process. Apart from the white films deposited on the reactor walls, the photolysis yields hydrocarbons whose distribution (in relative mol%) — ethene (80–86), *n*-butane (8–13), ethane (4–6), propane (0.5–2.0), propene (0–1.0), methane (1–5) and ethyne (0–1) — does not noticeably change within the ca. 10–100% photolysis progress in the range of fluence, 30–210 mJ cm^{-2}.

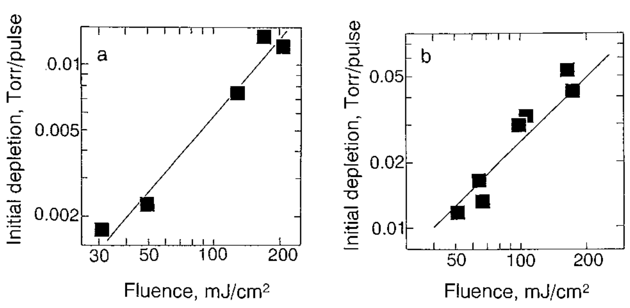


Fig. 2. Dependence of initial rate of (a) $(C_2H_5)_2Se$ and (b) $(C_2H_5)_2Te$ photolysis on laser fluence.

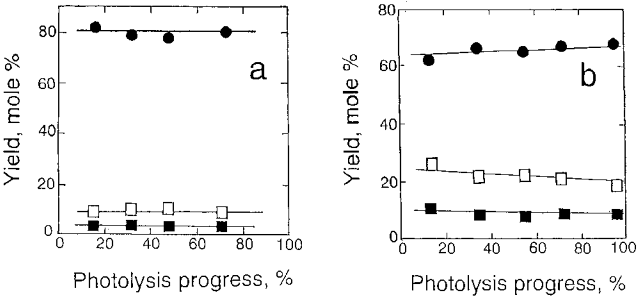
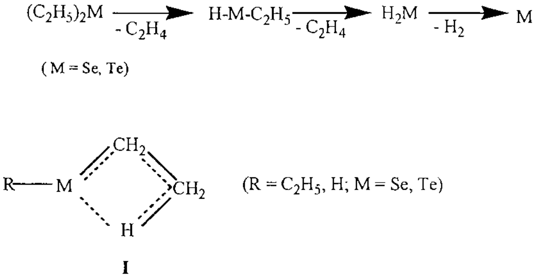


Fig. 3. Hydrocarbon product yield (in relative mole percent) at different stages of (a) $(C_2H_5)_2Se$ photolysis with fluence 127 mJ cm^{-2} and (b) of $(C_2H_5)_2Te$ photolysis with fluence 100 mJ cm^{-2}. n-C_4H_{10} (□); C_2H_6 (■); C_2H_4 (●).



Scheme 2.

3.2. Photolysis of diethyl tellurium

The initial quantum yield of the laser photolysis (the number of $(C_2H_5)_2Te$ molecules decomposed by one absorbed photon) was estimated as 0.4–0.5. The slope of the initial $(C_2H_5)_2Te$ depletion versus laser fluence in a double-logarithmic plot is very close to 1 (Fig. 2). This reveals that the photolysis is a one-photon process as assessed earlier for KrF laser photolysis of $(C_2H_5)_2Te$ in the absence and excess of hydrogen [3,4].

Apart from the dark dust collected on the reactor bottom, the photolysis yields hydrocarbons whose distribution (in relative mol%) — ethene (62–68), *n*-butane (27–20), ethane (8–10), propane (0.5–2.0), propene (0–1.0) and methane (0–2) — does not noticeably change within the ca. 10–100% photolysis progress in the range of fluence, 55–160 mJ cm^{-2}.

3.3. Photolysis mechanism

We assume that the observed high amounts of ethene, *n*-butane and ethane (and the insignificant amounts of other hydrocarbons) are consistent with the one-photon absorption process in which the energy delivered by the photons at 248 nm (corresponding to ca. 480 kJ Einstein^{-1}) is barely enough to remove both ethyl groups from Se and Te. The average bond energy for the Se–C [17] and Te–C [5,18] bonds in $(C_2H_5)_2M$ has been speculated as being ca. 250 kJ mol^{-1}. It is thus conceivable that the formed hydrocarbon fragments may possess only very small excess energy and that they are deactivated by excess helium gas. The observed small amounts of propene, propane and methane reflect an unimportant role of cleavage of the $C_2H_5^{\bullet}$ radical and of reactions of the $CH_3^{\bullet}$ radical (addition to C_2H_4, cross-disproportionation and combination with the $C_2H_5^{\bullet}$ radical).

The distribution of the most significant hydrocarbon products — ethene, ethane and *n*-butane — and their invariant ratios in different stages of the photolysis (Fig. 3) clearly show that the homolysis of $(C_2H_5)_2M$ into M atoms and two ethyl radicals (Eq. (1)) cannot be regarded as a major photolytic pathway. In accordance with the known disproportionation ($2C_2H_5^{\bullet} \rightarrow C_2H_4 + C_2H_6$)/combination ($2C_2H_5^{\bullet} \rightarrow n\text{-}C_4H_{10}$) rate ratio, k_d/k_c, for the ethyl radical (~ 0.13, [9]), the clean M–C homolysis would have yielded *n*-butane in a large excess over equal amounts of ethane and ethene.

The observed dominance of ethene over both *n*-butane and ethane thus reveals that more than 90% of ethene in both photolyses must be produced via a different channel, i.e. via the β-elimination (Scheme 2) taking place via a four-centre transition state (I).

Although the presumed intermediary species were not observed, this molecular mechanism is in keeping with the elusive nature of the RMH species [6] and with UV photolysis of the H_2M ($M = Se$ [19], Te [20]) compounds yielding selenium and tellurium.

The distribution of the final products thus reveals that the β-elimination is a dominating route and that intrusion of radical processes is small. The ascertained mechanism of the laser photolysis of the $(C_2H_5)_2M$ compounds cannot be compared to the mechanism of homogeneous thermal decomposition of these compounds, since the latter has been only studied under conditions not circumventing heterogeneous catalysis. In this process, a computer kinetics simulation revealed that the β-elimination from $(C_2H_5)_2Te$ is insufficient to describe experimental observations [18]. It was also reported that the thermolysis of diethyl tellurium catalysed by heated substrate or by deposited Te yields slightly higher amounts of ethene relative to ethane and takes place as a blend of almost equally important β-elimination of ethene from $(C_2H_5)_2Te$ and expulsion of ethane from intermediary C_2H_5TeH [21].

In conclusion, the gaseous diethyl selenium and diethyl tellurium photolytically cleave in a completely different way than do their O- and S-atom containing congeners. The photolysis of $(C_2H_5)_2M$ ($M = Se$, Te) occurs via a two-fold four-centre molecular expulsion of ethene, the paths not assumed in the photolysis of diethyl tellurium earlier [3,4]. The reaction is promising in the chemical vapour deposition of pure selenium and tellurium films and nanoparticles and can find application in microelectronics and photothermal optical recording.

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