Photodissociation of Tetramethyltin at 193 nm

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Tetramethyltin has been photodissociated in a molecular beam at 193 nm. The time-of-flight spectrum of the methyl radicals obtained is converted into the translational energy distribution. This distribution is well represented by a sum of two prior distributions with restricted number of vibrational degrees of freedom, one for two-body dissociation, $Sn(CH_3)_4 \rightarrow Sn(CH_3)_3 + CH_3$ and the other for three-body dissociation, $Sn(CH_3)_4 \rightarrow Sn(CH_3)_2 + 2CH_3$.

KEY WORDS: Photodissociation; tetramethyltin; molecular beam; time of flight; two-body dissociation; three-body dissociation.

INTRODUCTION

Tetramethyltin absorbs ultraviolet (UV) photons continuously from a long wavelength limit at ~225 nm. By analogy with an analysis of the UV spectra of a series of alkyl metal compounds, the first electronic transition of tetramethyltin weakens the Sn—C bond since an electron is removed from an Sn—C bonding orbital and placed into either a non-bonding or Sn—C antibonding orbital as discussed for $Ga(CH_3)_3$[1,2]. Then, the first electronic transition must be directly dissociative.

In the photolysis of alkyl metal compounds, three-body dissociation often occurs because of the weak carbon–metal bond. For example, Jonah et al.[3] observed asymmetric dissociation of dimethylcadmium.

Tamir *et al.*[4], Kellman *et al.*[5] and Pattengill[6] have calculated classical trajectories of collinear three-body photodissociation of dimethylcadmium. Sizun *et al.*[7] have discussed the photodissociation of small metal halides into three fragments. In this paper we will present experimental results of two-body and three-body dissociations of $Sn(CH_3)_4$.

EXPERIMENTAL

The apparatus used to measure the translational energy distribution has been described elsewhere[8,9]. In brief, for the molecular beam photolysis the axes of a pulsed molecular beam, an excimer laser, and a quadrupole mass spectrometer are mutually perpendicular. The center of the ionizer is 16 cm away from the point of the interaction region. For the photolysis of solid tetramethyltin, neat sample molecule is deposited on a quartz plate attached to a copper block that is cooled to ~ 100 K. The light beam from the ArF excimer laser was introduced into the interaction chamber so as to illuminate the whole area of the solid sample. Output pulses from a detector were accumulated in a signal averager.

RESULTS

Photolysis of molecular beam

When the molecular beam of tetramethyltin was photodissociated at 193 nm, the only fragments detectable by this mass spectrometer were those of mass 15. The distribution of times of flight of CH_3 radicals is shown in Figure 1. The time-of-flight distribution was transformed to the translational energy distribution of the methyl photofragments as shown in Figure 2.

Photolysis of neat solid

In order to measure the bond dissociation energy $D_0(C–Sn)$, the neat solid of $Sn(CH_3)_4$ on the quartz plate was photodissociated to give signals of methyl radicals as shown in the inset of Figure 1. Since the substrate has an infinite mass, the fastest photofragment can carry all the excess energy as translational energy, i.e. $D_0 = \hbar\omega - E_T^{max}$. The
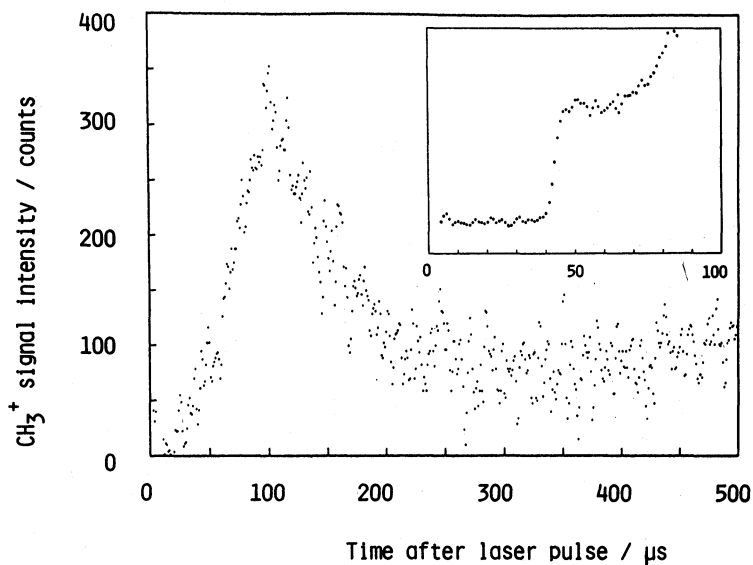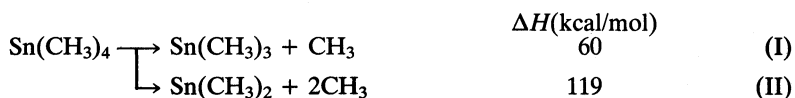
Figure 1 Time-of-flight spectra of CH_3 photofragments observed in the photolysis of a molecular beam of $Sn(CH_3)_4$ at 193 nm. The inset shows the threshold region of the time-of-flight spectrum of CH_3 photofragments generated in the photolysis of solid neat $Sn(CH_3)_4$ at 193 nm. For both cases, the drift time in the quadrupole mass filter tube is 17 μs for CH_3^+ ions.
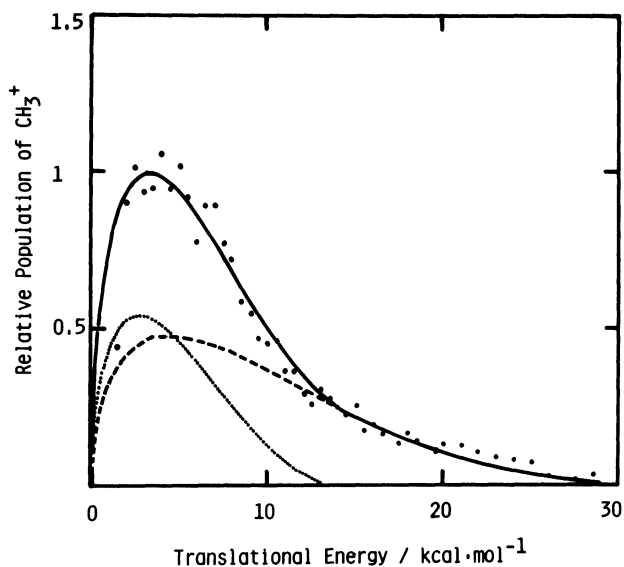
bond dissociation energy is found to be 61 kcal/mol from the threshold of the time-of-flight signal. The obtained value is in good agreement with 60 ± 2 kcal/mol reported by Lampe and Niehaus[10].

DISCUSSION

Equipartition model for translational energy of methyl photofragments with a restricted number of vibrational degrees of freedom

The following primary processes are energetically possible in the 193-nm photolysis[11]:

$$\Delta H(\text{kcal/mol})$$

$$Sn(CH_3)_4 \longrightarrow Sn(CH_3)_3 + CH_3 \qquad 60 \qquad \text{(I)}$$
$$\longrightarrow Sn(CH_3)_2 + 2CH_3 \qquad 119 \qquad \text{(II)}$$

Figure 2   Translational energy distribution $P(\varepsilon_T)$ of CH_3 photofragments generated in the photolysis of a molecular beam of $Sn(CH_3)_4$ at 193 nm. The dotted line refers to Eqn (1) for the three-body dissociation $(n = 2)$ and the broken line to Eqn (3) for the two-body dissociation $(s = 3)$. The solid line is the sum of these curves when relative intensity of the three-body dissociation to the two-body dissociation is 0.6.

The dissociation into more than three fragments is popular in the photodissociation of alkyl metals as is reported for photolysis of $Ga(CH_3)_3^2$, $Cd(CH_3)_2^3$, or $Sn(CH_3)_4^{10}$.

Assuming the statistical energy partitioning in dissociation, the available and total translational energies become[12]:

$$E_{AVL} = [3(f - 1) + R + 2V]/2\beta$$
$$E_T = 3(f - 1)/2\beta$$

where f, R, and V are the total number of the fragments, and rotational and vibrational degrees of freedom of the fragments, respectively; β is a parameter. Due to angular momentum restrictions, R and $3(f - 1)$ must be reduced by one. Concerning the vibrational degrees of freedom V, we assume that the effective number of vibrational degrees of freedom for $Sn(CH_3)_3$ fragments is two and those for $Sn(CH_3)_2$ and CH_3 are one in the following discussion. This is because vibrational frequencies are expected to be low in the ν_2 and ν_4 modes of $Sn(CH_3)_3$

and the v_2 mode of $Sn(CH_3)_2$. Although the v_1 mode of CH_3 fragments has a rather high frequency, the equilibrium structure is changed from C_{3v} in stannous compounds to D_{3h} in free methyl radicals, then the v_1 mode becomes active[13].

For two-body dissociation into $Sn(CH_3)_3 + CH_3$, the average translational energy of the methyl radicals, $\bar{\varepsilon}_T$, is found from calculation to be 12.5 kcal/mol. As shown in Figure 2, since the average value of the translational energy is much lower than 12 kcal/mol, then the contribution of another dissociation process is expected. For simultaneous dissociation into three fragments, $Sn(CH_3)_2 + CH_3 + CH_3$, $\bar{\varepsilon}_T$ is found from calculation to be 3.5 kcal/mol. Then, the simultaneous three-body dissociation occurs in the photodissociation of $Sn(CH_3)_4$ at 193 nm, in addition to the two-body dissociation.

The other possibility is the sequential three-body dissociation:

$$Sn(CH_3)_4 \longrightarrow Sn(CH_3)_3 + CH_3$$
$$Sn(CH_3)_3 \longrightarrow Sn(CH_3)_2 + CH_3.$$
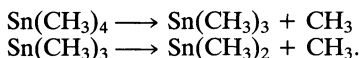
If this is the case, $\bar{\varepsilon}_T$ has two values of 3.4 and 12.4 kcal/mol. In practice the translational energy distribution of Figure 2 shows unequal intensities at 3.4 and 12.4 kcal/mol. Then, this possibility seems to be small.

Translational energy distribution functions

Next we deal with distribution functions to resolve the translational energy distribution of CH_3 fragments into two-body and three-body dissociaton contributions. Concerning the three-body dissociation, Ondrey and Bersohn[14] have previously derived an equation of translational energy of a single fragment in the three-body dissociation for three identical fragments. Equations for general cases are derived in the following way under the conditions of energy and momentum conservation:

$$P_1^2/2m_1 + P_2^2/2m_2 + P_3^2/2m_3 = E_T,$$
$$P_1 + P_2 + P_3 = 0,$$

where P_i is the momentum of the ith fragment relative to the center of mass of the parent. In the case of three-body dissociation, as shown in the Appendix, the translational energy distribution of methyl radicals is given by:

$$P^0(\varepsilon_T \mid E_{AVL}) \propto \{\varepsilon_T[(2/3)E_{AVL} - a\varepsilon_T]\}^{1/2}(E_{AVL} - 2\varepsilon_T)^n \tag{1}$$

where a is a mass factor (0.75) given in the Appendix and n is the effective number of vibrational degrees of freedom of the photo-fragments.

A prior distribution for the two-body dissociation is given by:

$$P^0(E_T \mid E_{AVL}) \propto E_T^{1/2}(E_{AVL} - 2E_T)^s \tag{2}$$

where E_T is the total translational energy. Since ε_T is $(1 - m/M)E_T$, Eqn (2) is converted to:

$$P^0(\varepsilon_T \mid E_{AVL}) \propto \varepsilon_T^{1/2}[(1 - m/M)E_{AVL} - 2\varepsilon_T]^s \tag{3}$$

where m refers to the mass of a methyl radical and M to that of a parent molecule.

In the above equations, the numbers of vibrational degrees of freedom, n and s, are parameters. The relative population of two distributions of Eqns (1) and (3) is also a parameter for simulation of the experimental results. Best-fit calculation of Figure 2 is obtained by assuming that $n = 2$, $s = 4$ and the relative contribution of the three-body to the two-body process is 0.6. When the value of s changes from 2 to 4, the shape is not so sensitive to s. These values of n and s are quite small compared to the full number of vibrational degrees of freedom of the fragments. In the previous paragraph, n and s are assumed to be three, which is close to the value obtained here in the best-fit calculation. Concerning these small values of n and s, the effect of a heavy atom has been considered, especially on the rates of intramolecular energy transfer to intepret the chemical activation experiments[15] and the overtone absorption spectra[16]. In the former experiments, it was postulated that non-RRKM (Rice-Ramsperger-Kassel-Marcus) behavior can be the result of a heavy central atom impeding energy flow from the initially activated side of the molecule through the central atom[15]. In the latter experiment the C—H overtone linewidth of $Sn(CH_3)_4$ is narrower than that of $C(CH_3)_4$. The widths decrease as a function of increasing mass of the central atom[16]. These results indicate that energy flow is impeded by heavy central atoms, or the effective vibrational degrees of freedom in energy flow are lowered in $Sn(CH_3)_4$.

In conclusion both two- and three-body dissociations are observed for the photolysis of $Sn(CH_3)_4$ at 193 nm. The three-body dissociation occurs probably because the divalent state of tin, $Sn(CH_3)_2$, is metastable while the trivalent tin compound, $Sn(CH_3)_3$, is unstable. This is the

case for Ga(CH$_3$)$_3$ photolysis, i.e. the stable monovalent gallium compound, GaCH$_3$, has been reported as products in the photolysis[2].

Acknowledgements

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Appendix

Ondrey and Bersohn[14] have derived a prior equation for single fragment energy in the three-body dissociation for three identical fragments. Here we derive the equation for the general case based on their work. The conservation of energy and momentum can be written:

$$P_1^2/2m_1 + P_2^2/2m_2 + P_3^2/2m_3 = E_T,$$
$$P_1 + P_2 + P_3 = 0,$$

where P_i is the momentum of the ith fragment relative to the center of mass of the parent molecule.

The total number of states available to the system for a given E_T is:

$$\Omega(E_T) = (V/h^3)\int dP_1 \int dP_2 \int dP_3$$
$$\times \delta(P_1^2/2m_1 + P_2^2/2m_2 + P_3^2/2m_3 - E_T)\delta(P_1 + P_2 + P_3)$$
$$= (V/h^3)\int dP_1 \int dP_2$$
$$\times \delta(P_1^2(1/2m_1 + 1/2m_3) + P_2^2(1/2m_2 + 1/2m_3)$$
$$+ 2P_1P_2/2m_3 - E_T)$$

The remaining delta function which is normalized to one on the energy scale can be expressed in terms of momenta by the substitution[17]:

$$E' - E_T = \frac{\delta[P_2 - P_2(+)]}{|\partial E/\partial P_2|_{P_2(+)}}$$

where

$$E' = P_1^2(1/2m_1 + 1/2m_3) + P_2^2(1/2m_2 + 1/2m_3) + (1/m_3)P_1P_2\cos\theta_{12}$$

and $P_2(+)$ is the positive root of the quadratic equation $E' - E_T = 0$.

It is now convenient to define the direction of P_2 with respect to P_1, i.e. to integrate over $\theta_1, \phi_1, \theta_{12}, \phi_{12}$ instead of $\theta_1, \phi_1, \theta_2, \phi_2$. θ_i, ϕ_i are the polar and azimuthal angles of P_1 and θ_{12}, ϕ_{12} are the polar and azimuthal angles of P_2 with respect to P_1. One thus obtains:

$$\Omega(E_T) = 8\pi^2(V/h^3)^3 \int_0^\infty dP_1P_1^2$$
$$\times \int_0^\pi d\theta_{12}\sin\theta_{12}\cdot[(\cos^2\theta_{12}/m_3^2)\ P_1^2 - 4M_{23}M_{13}P_1^2$$
$$+ 4M_{23}E_T]^{-1/2} \times \int_0^\infty dP_2P_2^2\delta[P_2 - P_2(+)]$$
$$= 4\sqrt{6}M_{23}^{3/2}(V/h^3)^3 \int_0^\alpha dP_1P_1^2[2E_T/3 + (M_{23}/6m_3^2$$
$$- 2/3M_{13})P_1^2]^{1/2}$$

where $1/M_{ij}$ is $1/2m_i + 1/2m_j$.

If we make the transformation from magnitude of the momentum P_1 to kinetic energy, i.e. $P_1^2 = 2m_1\varepsilon_1$, then:

$$\Omega(E_T) = 8\sqrt{3}\pi^2M_{23}^{3/2}m_1^{3/2}(V/h^3)^3 \int_0^\alpha \varepsilon_1^{1/2}[(2/3)E_T - a\varepsilon_1]^{1/2}d\varepsilon_1$$

where a is $4m_1/3M_{13} - M_{23}m_1/3m_3^2$ and α is $(2/3)E_T/a$.

The normalized distribution of translational energy of a single fragment is:

$$f(\varepsilon_T) = (9a^{3/2}/\pi E_T^2)\ \varepsilon_T^{1/2}[(2/3)E_T - a\varepsilon_T]^{1/2}$$

Next we consider the case where $Sn(CH_3)_4$ dissociates into three photofragments, $2CH_3 + Sn(CH_3)_2$. When the vibrational degrees of freedom are taken into consideration and the total translational energy E_T is approximated by $E_T = 2\varepsilon_T(CH_3)$, because of large mass difference between CH_3 and $Sn(CH_3)_2$ fragments, the prior distribution is given by:

$$P^0(E_T) \propto \{E_T[(2/3)E_{AVL} - (a/2)E_T]\}^{1/2}(E_{AVL} - E_T)^s$$

where s is the effective number of vibrational degrees of freedom of the photofragments and E_{AVL} refers to available energies in a dissociation process. For a single fragment, the above equation is converted to:

$$P^0(\varepsilon_T) \propto \{\varepsilon_T[(2/3)E_{AVL} - a\varepsilon_T]\}^{1/2}(E_{AVL} - 2\varepsilon_T)^s.$$