SECTION A
Inorganic, Physical, and Theoretical Chemistry

Flash Photolysis of $SnCl_2$ and $SnCl_4$. Dissociation Energies of $SnCl_2$ and SnCl

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$SnCl_2$ is dissociated to SnCl and Cl by absorption of light in the 320 nm region. This sets a maximum value to the dissociation energy of $SnCl_2$. Further consideration of thermochemical and spectroscopic data gives the probable values of the dissociation energies of $SnCl_2$ and SnCl as 370 ± 20 and 420 ± 20 kJ mol^{-1} respectively.

$SnCl_2$, SnCl, and Sn are observed during the flash photolysis of $SnCl_4$. $SnCl_2$ is produced by decomposition of vibrationally excited $SnCl_3$ formed in the primary photolysis. SnCl is produced by secondary photolysis of $SnCl_2$ and reacts with $SnCl_4$ at a rate approaching the encounter rate. Sn also reacts rapidly with $SnCl_4$.

TIN(II) CHLORIDE vapour absorbs u.v. radiation below 250 nm and in a region about 20 nm wide with a maximum at 322 nm.[1] The absorption in each case appears continuous. Both the 320 nm absorption and a series of bands in the visible region have been observed in emission.[2] The visible system and the 320 nm absorption have been assigned to transitions between $^3B_1$ and $^1B_1$ states and the $^1A_1$ ground state.[1] The work described here shows that absorption in the 320 nm region leads to photolysis. The maximum value of the dissociation energy of $SnCl_2$ can therefore be calculated, and the value obtained leads to a revision of the dissociation energy of SnCl.

The radicals SiBr, SiI, GeCl, $GeCl_2$, GeBr, GeI, SnCl, $SnCl_2$, SnBr, and SnI are observed following isothermal flash photolysis of the corresponding tetrahalides.[3,4] Since the primary photolysis is expected to yield larger radicals, these diatomic and triatomic species must arise from secondary processes. Investigations of the photolysis of polyhalogenomethanes[5] have shown that CCl and CBr are produced by secondary decomposition of vibrationally excited substituted methyl radicals formed in the primary photolysis. The energy of the absorbed photon is greatly in excess of that required for bond fission and a significant proportion of the excess of energy appears as vibration of one of the fragments. For example the production of CBr in the photolysis of $CHBr_3$ is explained in reactions (1) and (2).

$$CHBr_3 + h\nu \longrightarrow CHBr_2^* + Br \qquad (1)$$

$$CHBr_2^* \longrightarrow CBr + HBr \qquad (2)$$

Vibrational excitation of photolysis products would be expected to be a general phenomenon. Absorption by the tetrahalides of Group 4 generally occurs at wavelengths corresponding to energies well in excess of those required for bond fission, and vibrational excitation of the primary photolysis products is therefore possible. The diatomic and triatomic radicals observed may arise from decomposition of excited tetratomic species, but could also be produced by secondary light absorption by the primary photolysis products. By examining the flash photolysis of $SnCl_4$ we find that $SnCl_2$ is produced mainly by decomposition of vibrationally excited $SnCl_3$ and SnCl is formed principally by secondary light absorption by $SnCl_2$.

EXPERIMENTAL

The flash photolysis apparatus was conventional. The reaction vessel was 470 mm long and situated parallel to the photolysis lamp. Both were constructed of quartz and surrounded by a reflector of aluminium foil. The reflector was enclosed in a furnace which could be heated to 300 °C to vaporise $SnCl_2$. The flash energy used in most experiments was 1500 J.

Spectra were recorded on Ilford HP3 plates with a Hilger medium quartz spectrograph (E498), by use of an ' end-on ' capillary flash lamp. The densities of the plates were measured with a Joyce-Loebl Mark 3 microdensitometer. Relative SnCl concentrations were determined from the absorption of the (2,0) band of the $B^2\Sigma$–$X^2\Pi_{\frac{1}{2}}$ system at 290 nm. Experiments showed that the change in absorbance of this band was directly proportional to the length of the absorption path.

$SnCl_2$ was supplied by Dr. K. G. G. Hopkins and prepared as described by him.[6] $SnCl_4$ (Hopkin and Williams) was redistilled *in vacuo* before use. B.O.C. ' white spot ' nitrogen was used as a diluent without further purification. Greaseless stopcocks were used in those parts of the vacuum system containing $SnCl_4$.

RESULTS AND DISCUSSION

Photolysis of $SnCl_2$.—Tin dichloride is a solid which melts[7] at 247 °C and boils[8] at *ca.* 620 °C. Experiments

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[1] J. W. Hastie, R. H. Hauge, and J. L. Margrave, *J. Mol. Spectroscopy*, 1969, **29**, 152.

[2] R. K. Asundi, M. Karim, and R. Samuel, *Proc. Phys. Soc.*, 1938, **50**, 581; D. Naegeli and H. B. Palmer, *J. Mol. Spectroscopy*, 1966, **81**, 325; P. Deschamps and G. Pannetier, *J. Chim. phys.*, 1964, **61**, 1549.

[3] G. A. Oldershaw and K. Robinson, *Trans. Faraday Soc.*, 1968, **64**, 616, 2256; 1970, **66**, 532; unpublished work.

[4] G. A. Oldershaw and K. Robinson, *J. Mol. Spectroscopy*, 1969, **32**, 469.

[5] J. P. Simons and A. J. Yarwood, *Trans. Faraday Soc.*, 1961, **57**, 2167; 1963, **59**, 90.

[6] K. G. G. Hopkins, Ph.D. Thesis, University of Hull, 1970.

[7] K. K. Kelley, *U.S. Bur. Mines*, 1936, Bull. 393.

[8] K. K. Kelley, *U.S. Bur. Mines*, 1935, Bull. 383.

on the photolysis of the vapour were carried out by introducing a small quantity of solid to the reaction vessel, adding nitrogen to prevent temperature rises during photolysis, and heating the vessel to the temperature required to produce a convenient vapour pressure. The absorption of the vapour at 322 nm, the maximum of the continuous region, was calibrated by measuring its variation with the temperature of the solid and liquid in the range 230—280 °C. The concentration of the vapour was calculated from the vapour pressure of the solid or liquid at each temperature. Vapour pressures were calculated, first, by extrapolating the data of Karpenko and Novikov,[9] assuming the difference in heat capacities of liquid and vapour to be 33 J mol^{-1} K^{-1}, and, secondly, from the equation given by Kelley.[8] In both cases the enthalpy of fusion[7] was taken to be 13 kJ mol^{-1}. Dimerisation of the vapour in equilibrium with the liquid is probably small[9] and was neglected. Figure 1 shows that although, owing to the long extrapolations of pressures involved, the absolute calibration factor is uncertain, the absorption at 322 nm is proportional to the concentration.

Photolyses of $SnCl_2$ and of mixtures of $SnCl_2$ and $SnCl_4$ were carried out with the reaction vessel completely enclosed in a Pyrex sheath which cut off all radiation below 290 nm. This limited absorption by $SnCl_2$ to the 320 nm region and blank experiments showed that the filter also prevented photolysis of $SnCl_4$, which absorbs only around 220 nm. Flash photolysis of $SnCl_2$ mixed with excess of nitrogen at 260 °C resulted in the production of SnCl, the time-dependence of which is shown in Figure 2. The addition of $SnCl_4$ caused a drastic reduction in the lifetime of SnCl, as shown in Figure 2. No absorption line of atomic tin was detected in these experiments.

Absorption by $SnCl_2$ in the 320 nm region therefore results in dissociation of the molecule to SnCl and Cl. The absence of atomic tin contrasts with its observation in the photolysis of $SnCl_4$, when vessels transparent to shorter wavelengths were used. The reduction in the lifetime of SnCl caused by the addition of $SnCl_4$ is due to a rapid reaction between these two molecules which is discussed later.

Dissociation Energies of $SnCl_2$ *and* SnCl.—The fact that $SnCl_2$ is dissociated by light in the 320 nm region is relevant to the dissociation energies of both $SnCl_2$ and SnCl, since these are linked through the heat of formation of $SnCl_2$. D_0(SnCl) has been estimated by extrapolation of the vibrational levels of the $B'^2\Delta$–$X^2\Pi$ band system and it has been assumed[10] that the products of dissociation are $Cl(^2P_{3/2})$ and $Sn(^1D_2)$, which gives a value of 310 ± 20 kJ mol^{-1}. If the dissociation products are $Cl(^2P_{3/2})$ and $Sn(^3P)$ the value is considerably higher.

The maximum absorption of $SnCl_2$ occurs at 322 nm, corresponding to an energy of 371 kJ mol^{-1}, and the lowest wavelength of appreciable absorption is *ca.* 310 nm, or 386 kJ mol^{-1}. This is the maximum value of the Cl–SnCl dissociation energy.

D_0(Cl–SnCl) and D_0(SnCl) are related by the atomic heat of formation of $SnCl_2$. The standard heat of formation of solid $SnCl_2$ has recently been redetermined[6] as −378 ± 4 kJ mol^{-1}. The heat of sublimation of $SnCl_2$ is not known with precision but the value 121 kJ mol^{-1} given in Feber[11] may be used, with an error of ±25 kJ to include an earlier value[12] of 100 kJ mol^{-1}. The atomic heat of formation of gaseous $SnCl_2$ calculated from these data and the heats of formation of Cl(g)[13] and of Sn(g)[14] is −802 ± 30 kJ mol^{-1} at 298 K. If the difference between this and the corresponding quantity at 0 K is ignored, the use of $D_0(\text{Cl–SnCl}) \leqslant 386$ kJ mol^{-1} gives $D_0(\text{Sn–Cl}) \geqslant 416 \pm 30$ kJ mol^{-1}.

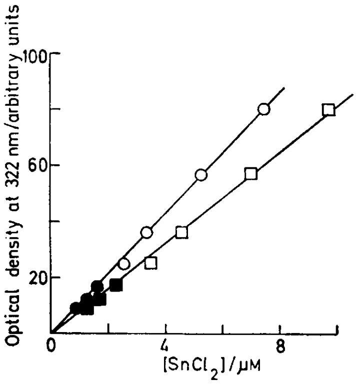

FIGURE 1 Absorbance of $SnCl_2$ as a function of concentration; concentration from data of ○, ref. 8; and □, ref. 9; filled symbols represent solid, open symbols liquid

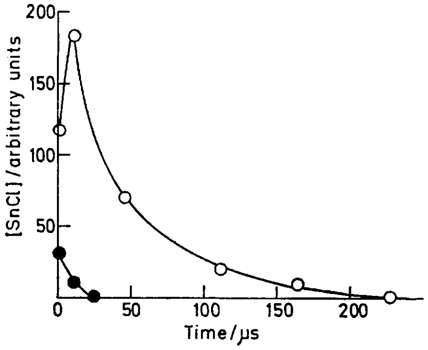

FIGURE 2 SnCl production in photolysis of $SnCl_2$; ○, 3·6µM-$SnCl_2$ + 2·2mM-N_2; ●, 3·6µM-$SnCl_2$ + 38µM-$SnCl_4$ + 2·2mM-N_2

A dissociation limit for SnCl can also be derived from a reasonably short extrapolation of the vibrational levels of the $B'^2\Delta$ state. Bands of the $B'^2\Delta$–$X^2\Pi$ system involving levels of $^2\Delta_{3/2}$ up to $v' = 4$ and levels of $^2\Delta_{5/2}$ up to $v' = 5$ are known. The parameters of

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[9] N. V. Karpenko and G. I. Novikov, *Vestnik Leningrad Univ.*, 1967, **22**, 72.

[10] A. G. Gaydon, 'Dissociation Energies,' Chapman and Hall Ltd., London, 3rd edn., 1968, p. 284.

[11] R. C. Feber, U.S. A.E.C., Report LA-3164, 1965.

[12] Nat. Bur. Stand. Circular 500, 1952.

[13] Nat. Bur. Stand. Technical Note 270—1, 1965.

[14] Nat. Bur. Stand. Technical Note 270—2, 1966.

$B'^2\Delta$ calculated by Ferguson [15] and by Sarma and Venkateswarlu [16] are listed in the Table, together with the limits derived by linear extrapolation. If the error in extrapolation is taken as 40% the value of the dissociation limit is 412 ± 30 kJ mol^{-1}, which agrees with the value 410 kJ mol^{-1} independently calculated [17] from Ferguson's data.

Dissociation limit of $B'^2\Delta$ state of SnCl

	T_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	Limit (cm^{-1})
$^2\Delta_{5/2}$	28,966 [a]	302	4·1	34,500
	28,968 [b]	303	3·7	35,200
$^2\Delta_{3/2}$	28,692 [a]	300	4·2	34,100
	28,693 [b]	301	4·0	34,400

[a] Ref. 15. [b] Ref. 16.

D_0(SnCl) can be calculated from the limit if the states of the atomic products of dissociation of $B'^2\Delta$ are known. The energies of the $^1D_2$, $^3P_2$, and $^3P_1$ levels of Sn relative to $^3P_0$ are 103, 41, and 20 kJ respectively.[18] If it is assumed that Cl($^2P_{2/3}$) is one of the dissociation products, D_0(SnCl) is 309 ± 30 kJ mol^{-1} if Sn is produced in the $^1D_2$ state. This is well below the minimum value of 416 ± 30 kJ mol^{-1} derived from the data on SnCl$_2$, and it is concluded that Sn is produced in the ^3P state. The values of D_0 corresponding to production of Sn in the $^3P_2$, $^3P_1$, and $^3P_0$ states are 371 ± 30, 392 ± 30, and 412 ± 30 kJ mol^{-1}, respectively, so that production of Sn($^3P_2$) also appears unlikely.

With the error limits assumed, combination of the data for SnCl and SnCl$_2$ brackets D_0(SnCl) between 386 and 422 kJ mol^{-1} if Sn($^3P_1$) is produced from $B'^2\Delta$, and between 386 and 442 kJ mol^{-1} if Sn($^3P_0$) is produced. A value of 420 ± 20 kJ mol^{-1} seems most probable. D_0(Cl–SnCl) lies between the maximum 386 kJ mol^{-1} already derived and a minimum value of 330 kJ mol^{-1} deduced from D_0(SnCl) and the heat of formation of SnCl$_2$. A value of 370 ± 20 kJ mol^{-1} is most likely.

Photolysis of SnCl$_4$.—Absorption by SnCl$_4$ is weak at 240 nm and increases towards shorter wavelengths. The measured absorbance of 8·8μM-SnCl$_4$ vapour in a 93 mm path length changed from 0·2 at 220 nm to 1·2 at 200 nm, and most of the radiation absorbed from the flash would lie between these two wavelengths, corresponding to energies between 540 and 600 kJ mol^{-1}. The atomic heat of formation of gaseous SnCl$_4$ at 0 K [13,14] is 1251 kJ mol^{-1}. Use of the values of D_0(SnCl) and D_0(Cl–SnCl) recommended above yields D(Cl–SnCl$_3$) ≈ D(Cl–SnCl$_2$) ≈ 230 kJ mol^{-1}, on the assumption that the first two bonds are of roughly equal strength. The energy of the absorbed photon is therefore much greater than that required to dissociate SnCl$_4$ into SnCl$_3$ and Cl.

Transient species observed in the photolysis of SnCl$_4$ were SnCl$_2$, SnCl, and atomic tin. Transitions of Sn involving the $^3P_2$, $^3P_1$, and $^3P_0$ levels were recorded and all varied in a similar manner with time. Measurements were made by use of the line at 271 nm. The lifetimes of Sn and SnCl (20—100 μs) were much shorter than that of SnCl$_2$, which persisted for several ms.

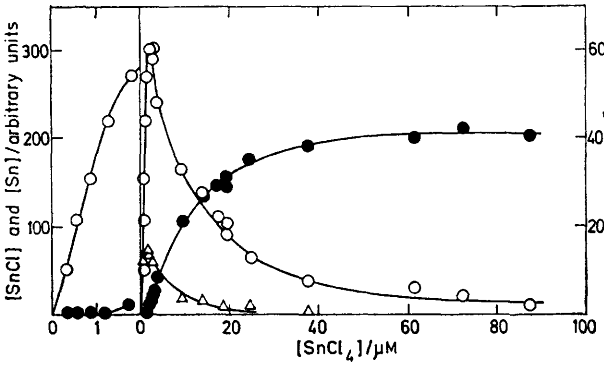

FIGURE 3 Variation of ●, [SnCl$_2$]; ○, [SnCl]; and △, [Sn] with [SnCl$_4$]

Figure 3 shows the concentrations of SnCl$_2$, SnCl, and Sn observed, at a delay time corresponding to the maximum of the photoflash, in the photolysis of various pressures of SnCl$_4$ diluted with a fixed excess (3·8mM) of nitrogen. For very low pressures of SnCl$_4$ little or no SnCl$_2$ is observed and the SnCl produced is proportional to the SnCl$_4$ used. With increasing pressures of SnCl$_4$, SnCl$_2$ is produced in increasing quantities until it reaches a limiting value, and the SnCl concentration is reduced. The variation of atomic tin is similar to that of SnCl.

Reactions removing SnCl *and* Sn.—The reduction in concentration of SnCl with increasing pressure of SnCl$_4$ indicates that SnCl is removed by a rapid reaction, probably process (3), with SnCl$_4$. This conclusion is

$$\mathrm{SnCl} + \mathrm{SnCl_4} \longrightarrow \mathrm{SnCl_2} + \mathrm{SnCl_3} \quad (3); \qquad \Delta H = -140 \text{ kJ mol}^{-1}$$

supported by the fact that, if sufficiently high pressures of SnCl$_4$ are used, the variation of SnCl with time corresponds to that of the photoflash. Figure 4 compares the decay of SnCl with the relative intensity of the

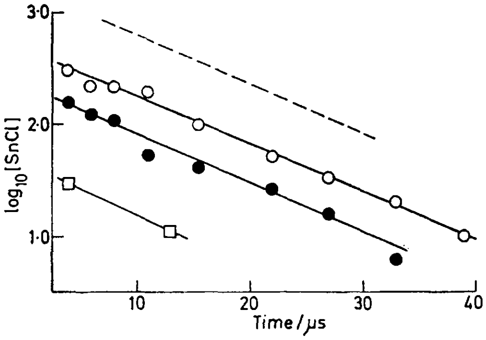

FIGURE 4 Decay of SnCl; ○, 8·1μM-SnCl$_4$ + 3·8mM-N$_2$; ●, 19μM-SnCl$_4$ + 3·8mM-N$_2$; □, 3·6μM-SnCl$_2$ + 38μM-SnCl$_4$ + 2·2mM-N$_2$; ‒ ‒ ‒ ‒ photoflash decay

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[15] W. F. C. Ferguson, *Phys. Rev.*, 1928, **32**, 607.

[16] P. R. K. Sarma and P. Venkateswarlu, *J. Mol. Spectroscopy*, 1965, **17**, 252.

[17] R. F. Barrow and A. Lagerquist, *Arkiv Fys.*, 1949, **1**, 221.

[18] C. E. Moore, Nat. Bur. Stand. Circular 467, vol. 3, 1958.

photoflash at different times determined from oscillograms. Measurements of the decay of SnCl during the photolysis of $SnCl_2$ with added $SnCl_4$ are also included. Evidence that SnCl is produced by secondary photolysis of $SnCl_2$ is presented below. Under conditions where $SnCl_2$ absorbs weakly, equation (4) applies, where I_t

$$d[SnCl]/dt = k_{12}I_t[SnCl_2] - k_3[SnCl][SnCl_4] \quad (4)$$

is the intensity of the photoflash at time t, and k_{12} includes factors allowing for the extinction coefficient of $SnCl_2$ and the effective absorbing path. If the rate of process (3) is sufficiently high, we obtain equation (5).

$$[SnCl] \approx k_{12}I_t[SnCl_2]/k_3[SnCl_4] \quad (5)$$

Since $[SnCl_2]$ and $[SnCl_4]$ change only slightly during the relevant time interval (the measured variation of log $[SnCl_2]$ was *ca.* 0·1), [SnCl] is approximately proportional to I_t.

An estimate of k_3 can be obtained from the fact that $-d[SnCl]/dt < k_3[SnCl][SnCl_4]$. The half-life of the decays shown in Figure 4 is 7 μs and the lowest $SnCl_4$ concentration 8 μM, so that $k_3 > 1{\cdot}2 \times 10^{10}$ l mol^{-1} s^{-1}. The reaction therefore occurs at a rate approaching the encounter rate. The variation of the atomic tin concentration with time was similar to that of SnCl, which indicates that it is also removed by a rapid reaction with $SnCl_4$, most probably process (6).

$$Sn + SnCl_4 \longrightarrow SnCl + SnCl_3 \quad (6); \quad \Delta H = -190 \text{ kJ mol}^{-1}$$

In contrast to Sn and SnCl, the $SnCl_2$ produced in the photolysis lasts for several ms. Figure 5 shows that after an initial reduction occupying *ca.* 500 μs, the concentration falls gradually to zero after *ca.* 20 ms. The slow removal is due to condensation of $SnCl_2$ to form a solid, since at 238 °C $[SnCl_2]$ decays to a constant value corresponding to the vapour pressure at this temperature.

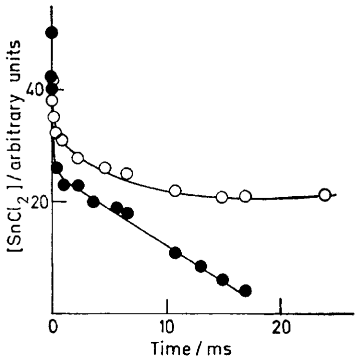

FIGURE 5 Decay of $SnCl_2$ following photolysis of 38μM-$SnCl_4$ + 2·2mM-N_2; ●, 25 °C; ○, 238 °C

Decomposition of Vibrationally Excited $SnCl_3$.—The concentrations of both $SnCl_2$ and SnCl observed at the peak of the photoflash are dependent on the pressure of nitrogen used as a diluent. This is attributed to the deactivation by N_2 of vibrationally excited $SnCl_3$ formed in the primary photolysis. Figure 6 shows that both the $SnCl_2$ and SnCl observed during the photolysis of 19μM-$SnCl_4$ increase rapidly as the pressure of nitrogen is reduced. The effect of nitrogen shows that $SnCl_2$ is not produced in the primary photolysis but results from the breakdown of excited $SnCl_3$ which contains much of the excess of energy absorbed from the photon. The major reactions involved are (7)—(9) where $SnCl_3$* represents a vibrationally excited radical.

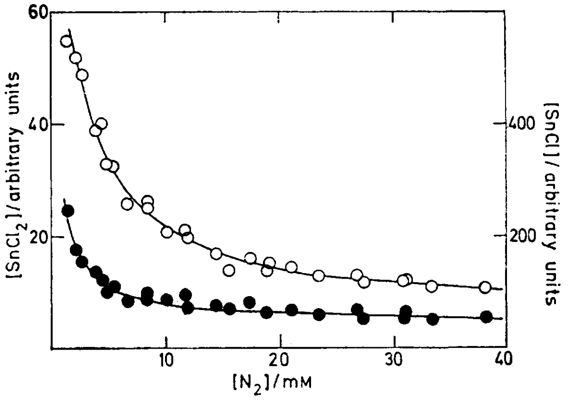

FIGURE 6 Effect of nitrogen pressure on ○, $[SnCl_2]$ and ●, [SnCl] in flash photolysis of 19·4μM-$SnCl_4$

$$SnCl_4 + h\nu \longrightarrow SnCl_3^* + Cl \quad (7); \quad \Delta H \approx 230 \text{ kJ mol}^{-1}$$

$$SnCl_3^* \longrightarrow SnCl_2 + Cl \quad (8); \quad \Delta H \approx 230 \text{ kJ mol}^{-1}$$

$$SnCl_3^* + N_2 \longrightarrow SnCl_3 + N_2 \quad (9)$$

Since removal of $SnCl_2$ is relatively slow, the concentration observed at the maximum of the photoflash is a measure of the $SnCl_2$ produced up to this time. If processes (8) and (9) were the only ones involved, a plot of $[SnCl_2]^{-1}$ against $[N_2]$ would be linear and $[SnCl_2]$ would tend to zero at very high $[N_2]$. In fact the plot is curved and $[SnCl_2]$ tends to a small finite value at large $[N_2]$. A minor additional process yielding $SnCl_2$ therefore exists. This might be the direct production of $SnCl_2 + Cl_2$ in the primary photolysis, but is more probably the secondary photolysis of a small proportion of the $SnCl_3$. The curve drawn through the $SnCl_2$ concentrations in Figure 6 was calculated by use of $k_9/k_8 = 460$ l mol^{-1} and taking the proportion of $SnCl_3$ photolysed in step (10) as 5%. If deactivation of $SnCl_3$* occurs at every collision with N_2 and the relevant collision diameter is about 40 pm, the value of k_9/k_8 implies that the lifetime of $SnCl_3$* is about 3 ns.

$$SnCl_3 + h\nu \longrightarrow SnCl_2 + Cl \quad (10); \quad \Delta H = 230 \text{ kJ mol}^{-1}$$

The products of decomposition of $SnCl_3$* are determined energetically. Thus process (8), which is endothermic by 230 kJ mol^{-1}, is preferred to process (11), which requires at least 357 kJ mol^{-1}. Step (11) is only

$$SnCl_3^* \longrightarrow SnCl + Cl_2 \quad (11); \quad \Delta H \approx 357 \text{ kJ mol}^{-1}$$

just energetically feasible and is unlikely to occur. The energy of the absorbed photon in excess of that required for step (7) is between 310 and 370 kJ mol^{-1}. The occurrence of process (8) shows that in some cases at least 60% of this energy appears as vibration of $SnCl_3$*.

Production of SnCl *and* Sn.—The similarity of the variations with pressure of [SnCl] and [$SnCl_2$] in Figure 6 suggests that $SnCl_2$ is the precursor of SnCl. It has already been demonstrated that photolysis of $SnCl_2$ produces SnCl. The production of SnCl by secondary

$$SnCl_2 + h\nu \longrightarrow SnCl + Cl \quad (12); \quad \Delta H = 370 \text{ kJ mol}^{-1}$$

photolysis of $SnCl_2$ is supported by the fact that, as illustrated in Figure 7, the concentration of SnCl at the peak of the photoflash is roughly proportional to the square of the flash energy, provided that sufficiently high pressures of $SnCl_4$ are used.

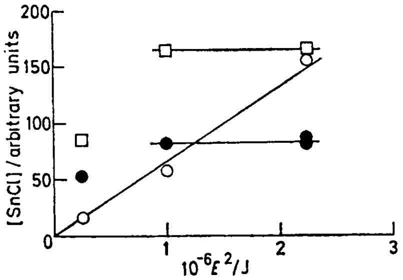

FIGURE 7 Effect of flash energy on [SnCl]; ○, 25μM-$SnCl_4$; □, 1·1μM-$SnCl_4$; ●, 0·5μM-$SnCl_4$; 3·8mM-N_2 in each case

Atomic tin probably results from the photolysis of a small proportion of the SnCl produced during the flash. Absorption by SnCl occurs [4] in the *B–X* system between 280 and 300 nm and in the *C–X* and *D–X* systems between 220 and 250 nm. The absence of Sn from the experiments on $SnCl_2$ carried out with a Pyrex vessel, when some absorption by part of the *B–X* system probably occurred, indicates that dissociation probably occurs as a result of absorption in the *C–X*, *D–X*, or lower-wavelength systems rather than in the *B–X* system.

Results obtained with Low Pressures of $SnCl_4$.—Figure 3 shows that the dependence of the concentration of SnCl observed on the pressure of $SnCl_4$ used is markedly different for high and for low pressures of $SnCl_4$, and a similar difference exists in the dependence of [SnCl] on flash energy, as shown in Figure 7. If very low pressures of $SnCl_4$ are employed most of the $SnCl_4$ is decomposed by the flash, and most of the $SnCl_2$ produced is further photolysed to SnCl. Under these conditions the SnCl produced is limited by the $SnCl_4$ concentration used, so that [SnCl] is proportional to [$SnCl_4$] and independent of flash energy. The lifetimes of SnCl and Sn are also longer, of the order of 100 μs, since rapid removal by reactions (3) and (6) is precluded.

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