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ENTHALPIES OF FORMATION OF PhSeBr AND PhSeBr$_3$

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ABSTRACT

Enthalpies of formation $\Delta H_f^{\ominus}$(298 K) have been determined calorimetrically as PhSeBr(c) +(34.1±4.6) kJ mol^{-1}, and PhSeBr$_3$(c)+(7.7±5.2) kJ mol^{-1}. Enthalpies of sublimation have been found as PhSeBr+(78.4±1.3) kJ mol^{-1} (304–324 K) and PhSeBr$_3$ +(71.0±1.3) kJ mol^{-1} (298–321 K). Values for Se–Br bond dissociation energies are given.

INTRODUCTION

Previously, [3] we have measured the enthalpy of formation of diphenyldiselenide, PhSeSePh by rotating bomb combustion calorimetry. This opens the way to a determination of the enthalpies of formation of phenylselenium bromide, PhSeBr, and phenylselenium tribromide by solution calorimetry.

Diphenyl diselenide reacts quantitatively at room temperature with one mole of bromine to yield phenylselenium bromide [1] and with two moles of bromine to yield phenylselenium tribromide [2]. We have determined the enthalpies, $\Delta H(1)$ and $\Delta H(2)$ of reactions (1) and (2) (below) by measurement of the enthalpies of reactions (3)–(8). Whereas PhSeBr is soluble in CCl$_4$, PhSeBr$_3$ is almost insoluble in this solvent, so that we have used 1,2,4-trichlorobenzene, C$_6$H$_3$Cl$_3$ as solvent for reactions involving PhSeBr$_3$.

$$\mathrm{Ph_2Se_2(c) + Br_2(l) \rightarrow 2PhSeBr(c)} \tag{1}$$

$$\mathrm{Ph_2Se_2(c) + 3Br_2(l) \rightarrow 2PhSeBr_3(c)} \tag{2}$$

$$\mathrm{Br_2(l) + [3Ph_2Se_2 + 260CCl_4](l) \rightarrow [2PhSeBr + 2Ph_2Se_2 + 260CCl_4(l)} \tag{3}$$

$$\mathrm{Ph_2Se_2(c) + [2Ph_2Se_2 + 260CCl_4](l) \rightarrow [3Ph_2Se_2 + 260CCl_4](l)} \tag{4}$$

$$\mathrm{2PhSeBr(c) + [2Ph_2Se_2 + 260CCl_4](l) \rightarrow [2PhSeBr + 2Ph_2Se_2 + 260CCl_4](l)} \tag{5}$$

$$\mathrm{Ph_2Se_2(c) + [6Br_2 + 450C_6H_3Cl_3](l) \rightarrow [2PhSeBr_3 + 3Br_2 + 450C_6H_3Cl_3](l)} \tag{6}$$

$$\mathrm{3Br_2(l) + [3Br_2 + 450C_6H_3Cl_3](l) \rightarrow [6Br_2 + 450C_6H_3Cl_3](l)} \tag{7}$$

$$\mathrm{2PhSeBr_3(c) + [3Br_2 + 450C_6H_3Cl_3](l) \rightarrow [2PhSeBr_3 + 3Br_2 + 450C_6H_3Cl_3](l)} \tag{8}$$

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RESULTS AND DISCUSSION

The following values, which refer to 298 K, were obtained $\Delta H(3) = -(28\ 75 \pm 0\ 23)$ kJ mol^{-1}, $\Delta H(4) = +(27\ 83 \pm 0\ 08)$ kJ mol^{-1}, $\Delta H(5) = +(51\ 50 \pm 0\ 76)$ kJ for 2 mole PhSeBr, $\Delta H(6) = -(12\ 94 \pm 0\ 09)$ kJ mol^{-1}, $\Delta H(7) = +(3\ 67 \pm 0\ 12)$ kJ for 3 mole Br_2, $\Delta H(8) = +(95\ 90 \pm 2\ 00)$ kJ for 2 mole $PhSeBr_3$ Using these values and the relationships $\Delta H(1) = \Delta H(3) + \Delta H(4) - \Delta H(5)$ and $\Delta H(2) = \Delta H(6) + \Delta H(7) - \Delta H(8)$, we obtain the values $\Delta H(1) = -(52\ 42 \pm 1\ 07)$ kJ mol^{-1} and $\Delta H(2) = -(105\ 2 \pm 2\ 2)$ kJ mol^{-1}

By incorporating the value $\Delta H_f^{\ominus}(298\ K)(Ph_2Se_2,\ c) = +(120\ 6 \pm 8\ 2)$ kJ mol^{-1} [3], we obtain $\Delta H_f^{\ominus}(298\ K)(PhSeBr,\ c) = +(34\ 1 \pm 4\ 6)$ kJ mol^{-1} and $\Delta H_f^{\ominus}(298\ K)(PhSeBr_3,\ c) = +(7\ 7 \pm 5\ 2)$ kJ mol^{-1} Enthalpies of sublimation have been measured as $\Delta H_{sub}(PhSeBr) = +(78\ 4 \pm 1\ 3)$ kJ mol^{-1}, over the range 304–324 K, and $\Delta H_{sub}(PhSeBr_3) = +(71\ 0 \pm 1\ 3)$ kJ mol^{-1}, over the range 298–321 K Assuming these to be the values at 298 K, within the limits of experimental uncertainty, we write $\Delta H_f^{\ominus}(298\ K)(PhSeBr,\ g) = +(112\ 5 \pm 5\ 9)$ kJ mol^{-1} and $\Delta H_f^{\ominus}(298\ K)(PhSeBr,\ g) = +(78\ 7 \pm 6\ 5)$ kJ mol^{-1}

The sum of the bond dissociation energies $D_1(PhSe{-}Br) + D_2(PhSe{-}Br)$, which corresponds to the sum of the enthalpies of reactions (9) and (10), may be calculated from the enthalpy, $\Delta H(11)$, of reaction (11)

$$PhSeBr_3(g) \rightarrow PhSeBr_2(g) + Br(g) \tag{9}$$

$$PhSeBr_2(g) \rightarrow PhSeBr(g) + Br(g) \tag{10}$$

$$PhSeBr_3(g) \rightarrow PhSeBr(g) + 2Br(g) \tag{11}$$

$$PhSe{-}SePh(g) + 2Br(g) \rightarrow 2PhSeBr(g) \tag{12}$$

by use of the relationship $\Delta H(11) = \Delta H_f^{\ominus}(PhSeBr,\ g) + 2\Delta H_f^{\ominus}(Br,\ g) - \Delta H_f^{\ominus}(PhSeBr_3,\ g) = D_1(PhSe{-}Br) + D_2(PhSe{-}Br)$ Taking the value $\Delta H_f^{\ominus}(Br,\ g) = +(111\ 86 \pm 0\ 12)$ kJ mol^{-1}, (4) we obtain the sum $D_1(PhSe{-}Br) + D_2(PhSe{-}Br) = +(257\ 5 \pm 4\ 4)$ kJ mol^{-1} The bond dissociation energy, $D_3(PhSe{-}Br)$, in phenylselenium bromide may be calculated from the enthalpy, $\Delta H(12)$, of reaction (12) and the relationship $\Delta H(12) = D(PhSe{-}SePh) - 2D_3(PhSe{-}Br) = 2\Delta H_f^{\ominus}(PhSeBr,\ g) - \Delta H_f^{\ominus}(Ph_2Se_2,\ g) - 2\Delta H_f^{\ominus}(Br,\ g)$ Using the value $\Delta H_f^{\ominus}(Ph_2Se_2,\ g) = +(237\ 3 \pm 10\ 7)$ kJ mol^{-1} we obtain the value $\Delta H(12) = -(236\ 0 \pm 4\ 9)$ kJ mol^{-1} Using the value $D(PhSe{-}SePh) = +(280\ 0 \pm 19\ 0)$ kJ mol^{-1} [3] leads to the value $D_3(PhSe{-}Br) = +(258\ 0 \pm 12\ 0)$ kJ mol^{-1} Thus, successive bond dissociation energies of the Se–Br bonds in $PhSeBr_3$ are

$$D_1(PhSe{-}Br) + D_2(PhSe{-}Br) = +(257\ 5 \pm 4\ 4)\ \text{kJ mol}^{-1}$$

$$D_3(PhSe{-}Br) = +(258\ 0 \pm 12\ 0)\ \text{kJ mol}^{-1}$$

$$\langle D \rangle(PhSe{-}Br) = +(171\ 8 \pm 6\ 1)\ \text{kJ mol}^{-1}$$

where $\langle D\rangle$(PhSe–Br) is the mean bond dissociation energy corresponding to one third of the enthalpy of removal of all three gaseous bromine atoms from gaseous phenylselenium tribromide

EXPERIMENTAL

Diphenylselenide (Alddrich Chemical Co) was recrystallized from methanol, fused for 5 min and stored over phosphorus pentoxide, m p 336 K (literature value [2] 336 K) The purity, determined by use of a differential scanning calorimeter technique [5], was found to be at least 99 90 ± 0 04 mol% Microanalysis gave C 46 16, H 3 19, calc for $C_{12}H_{10}Se_2$, C 46 18, H 3 23 mol% Phenylselenium bromide was prepared by mixing chloroform solutions of stoichiometric quantities of diphenyldiselenide and bromine The red crystals, recrystallised from diethyl ether, had m p 333 K (literature value [2] 335 K) Microanalysis gave C 30 43, H 2 06, calc for C_6H_5SeBr, C 30 55, H 2 12 mol% Phenylselenium tribromide was prepared by mixing carbon tetrachloride solutions of diphenyldiselenide and excess bromine The scarlet crystals, recrystallised from chloroform, had m p 373 K (literature value [2] 378 K) Microanalysis gave C 17 99, H 1 17, calc for $C_6H_5SeBr_3$ C 18 21, H 1 26 mol% Carbon tetrachloride (B D H. spectroscopic grade) was distilled b p 348 1 K, 783 5 torr (literature values [6] 349 7 K, 760 0 torr) 1,2,4-Trichlorobenzene (B D H AnalaR) was distilled b p 485 8 K, 741 4 torr (literature values [6] 486 7 K, 760 0 torr) Bromine was supplied by Hopkin and Williams

Enthalpy measurements were made at 298 15 K using the LKB 8700 Precision Calorimetry System equipped with a 25 cm^3 vessel and a polytetrafluoroethylene ampoule holder/stirrer The charged calorimeter was calibrated electrically The quoted values of ΔH are those derived from the mean of five determinations and the uncertainties are twice the standard deviations of mean values Enthalpies of sublimation were determined by measurement of the rate of effusion of a sample [3]

REFERENCES

1 O Behagel and H Seibert, Chem Ber, 65 (1932) 812
2 K W Bagnall, The Chemistry of Selenium, Tellurium and Polonium, Elsevier, Amsterdam, 1966, Chap 7
3 C T Mortimer and J Waterhouse, J Chem Thermodyn , 12 (1980) 961
4 CODATA, J Chem Thermodyn , 10 (1978) 903
5 B G Cooksey and R A W Hill, J Therm Anal , 10 (1976) 83
6 Handbook of Chemistry and Physics, 56th edn , The Chemical Rubber Co , Ohio, 1975