Thermochimica Acta, 103 (1986) 401–403
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

MASS SPECTROMETRIC DETERMINATION OF THE HEATS OF FORMATION OF $POFBr_2$ AND POF_2Br

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(Received 12 December 1985)

High temperature molecules like POCl [1,2], PSCl [3,4], POBr [5] can be generated by the reaction of phosphorusoxytrihalides (respectively, phosphorusthiotrihalides) with silver metal at temperatures of about 1000 K. Attempts to obtain POF by an analogous reaction failed. The compound POF and the knowledge of its thermodynamic stability is of particular interest, because it connects the well known molecules SiF_2 and SO_2 to an isoelectronic series. Our experiments have shown [6], that POF is formed by reaction (1) at temperatures of about 1100 K.

$$POFBr_{2(g)} + 2\,Ag_{(s)} = POF_{(g)} + 2\,AgBr_{(g)} \tag{1}$$

To evaluate the heat of formation of POF from mass spectrometric equilibrium measurements, we need the heat of formation of $POFBr_2$. The intention of this work was to determine this.

EXPERIMENTS AND EVALUATION OF DATA

The compounds $POFBr_2$, POF_2Br and POF_3 have been prepared by fluorination of $POBr_3$ using SbF_3 as fluorinating agent. The reaction products POF_3, POF_2Br and $POFBr_2$ have been purified by fractional condensation. The mass spectra and IR spectra agreed well with literature data [7].

To obtain information about the thermodynamic stability of $POFBr_2$ and POF_2Br we have studied the equilibrium between solid CaF_2 and gaseous $POBr_3$ by means of Knudsen cell measurements and mass spectrometric analysis of the equilibrium vapour. The assembly has been described earlier [8]. The reaction was carried out in a corundum Knudsen cell (diameter of the evaporation orifice 1 mm). Mass spectrometric analysis has been done by an Extranuclear Quadrupol spectrometer (ionisation by electron impact, 70 eV). The mass spectra (temperature of CaF_2: 818 K) show the formation of POF_3, $POFBr_2$ and POF_2Br. $POBr_3$ was also detectable. The fragmentation of these compounds by electron impact ionisation leads to a very com-

0040-6031/86/$03.50

plicated mass spectrum. Only the parent ions could unequivocally be attached to one of these compounds. To obtain a correct value of the equilibrium constants of reactions (2) and (3)

$$POF_3 + 2\ POBr_3 = 3\ POFBr_2 \qquad (2)$$

$$2\ POF_3 + POBr_3 = 3\ POF_2Br \qquad (3)$$

we used the sum of intensities of all ions originated by each of the four species. Therefore, we have measured the mass spectra of the pure compounds POF_3, POF_2Br, $POFBr_2$ and $POBr_3$. In these spectra the following ion intensities (arbitrary units) have been observed (intensities in brackets):

POF_3 :P (180), PO (320), PF (300), POF (84), POF_2 (5100), POF_3 (4470)

POF_2Br:P (330), PO (1200), PF (840), POF (540), POF_2 (7800), POFBr (620), $POFBr_2$ (4000)

$POFBr_2$:P (190), PO (83), POF (530), PBr (50), POFBr (1840), $POFBr_2$ (230)

$POBr_3$:P (525), PO (4155), PBr (411), POBr (1065), $POBr_2$ (2090), $POBr_3$ (398).

Using these values it was possible to calculate the sum of intensities of POF_3, POF_2Br, $POFBr_2$ and $POBr_3$ in the equilibrium mixture by multiplying the intensities of the parent ions with a factor considering the fragmentation process (fragmentation factor). The following fragmentation factors have been calculated from the intensity values given above: POF_3 (2.339), POF_2Br (3.833), $POFBr_2$ (12.709) and $POBr_3$ (21.719).

These values show that the fragmentation patterns of these very similar molecules are significantly different and have to be noted.

In the equilibrium mixture, formed by the reaction of $POBr_3$ with CaF_2 at 818 K the following ion intensities of the parent ions have been observed: POF_3^+ (500), POF_2Br^+ (426), $POFBr_2^+$ (279), $POBr_3^+$ (47). From this and the given fragmentation factors one can calculate the following sum of intensities: $\Sigma I(POF_3) = 1170$, $\Sigma I(POF_2Br) = 1633$, $\Sigma I(POFBr_2) = 3546$ and $\Sigma I(POBr_3) = 1021$. These values give equilibrium constants of reactions (2) and (3): $K_p(2) = 3546^3/1170 \cdot 1021^2 = 36.6$ and $K_p(3) = 1633^3/1170^2 \cdot 1021 = 3.1$. The entropies and change of molar heats of the considered reactions should be near 0 J K mol^{-1}. Using van't Hoff's equation one can calculate the heats of reactions (2) and (3) from the measured equilibrium constants as $\Delta H_R^0(2)_{298} = -29.9$ kJ mol^{-1} and $\Delta H_R^0(3)_{298} = -9.4$ kJ mol^{-1}. Together with literature data ($\Delta H_{298}^0(POBr_{3,g}) = -389.1$ kJ mol^{-1} [9], $\Delta H_{298}^0(POF_{3,g}) = -1236.8$ kJ mol^{-1} [9] the heats of formation of the considered compounds can be calculated: $\Delta H_{298}(POFBr_{2,g}) = -681.6$ kJ mol^{-1}, $\Delta H_{298}(POF_2Br_g) = -957.4$ kJ mol^{-1}. We estimate an error in these values of ± 15 kJ mol^{-1}.

Our results show, that the heats of formation of the mixed phosphorylhalides $POFBr_2$ and POF_2Br from the pure phosphorylhalides POF_3 and

$POBr_3$ are not far from 0 kJ mol^{-1}. A linear interpolation of the heats of formation of such mixed halides between the heats of formation of the pure halides seems to be a good approximation.

A more correct interpolation should be the linear interpolation of the heats of atomisation. Combining the values given above with literature data [9] of the heats of formation of P_1 (333.9 kJ mol^{-1}), O_1 (249.4 kJ mol^{-1}), F_1 (76.8 kJ mol^{-1}) and Br_1 (111.9 kJ mol^{-1}) the following heats of atomisation can be calculated: POF_3 (2050.5 kJ mol^{-1}), POF_2Br (1806.2 kJ mol^{-1}), $POFBr_2$ (1565.5 kJ mol^{-1}), $POBr_3$ (1308.1 kJ mol^{-1}). A linear interpolation between the heats of atomisation of POF_3 and $POBr_3$ leads to 1803.0 kJ mol^{-1} (POF_2Br) and 1555.5 kJ mol^{-1} ($POFBr_2$). The deviation of these interpolated values from the measured one is very small.

This is probably the way to calculate correct values of the thermodynamic stability of other mixed halide compounds.

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