Correlation of Crystal Structure and Vapor Composition of Metal Dihalides

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Z. Naturforsch. **48a**, 1000–1004 (1993); received July 20, 1993

The presence of dimers in the vapor of metal dihalides, as seen in electron diffraction experiments, is found to be correlated with the crystal structure of the halide and with the difference in the heat of vaporization between monomers and dimers. If the dimeric molecule cannot be recognized as a unit in the crystal, dimers are not detected in the vapor. If dimeric molecules are discernible in the crystal, they will be observed in the vapor if their heat of vaporization is not greater than that of the monomer by more than 10 kcal/mol.

Key words: Crystal structure; Vapor composition; Metal dihalides; Correlation of structure and vapor composition; Gas-phase electron diffraction.

Introduction

Comparison of gas-phase and crystal-phase structures is important for molecules which form molecular crystals. Useful information can be obtained about intermolecular forces acting in crystals from such comparisons [1–4]. The situation is different for metal halides because of their considerable ionic character. They form 3-dimensional ionic lattices with 4 to 8 coordination of the metal, and this arrangement is not directly comparable to the gas-phase molecules in which the coordination of the metal is much smaller. The formation of a gas-phase molecule from these crystals requires the disruption of a large number of bonds in the crystal, and this is one of the reasons why these molecules can be evaporated only at rather high temperatures.

This high (close to or over 1000 K) temperature is one of the difficulties of the gas-phase structural investigation of metal halide molecules. Another problem, which we may call "interpretational" difficulty, is that the vapor of metal halides may contain more species than just the monomeric molecule. In the early days of gas-phase electron diffraction, the structure of alkali metal halides was studied by this technique, and the bond lengths reported [5, 6] differed considerably from those determined later by microwave spectroscopy [7]. The reason for the discrepancy was that the large amount of dimers sometimes present in the vapor of these alkali metal halides was overlooked in the early electron diffraction studies, and thus the bond length determined was actually the weighted average of the monomer and dimer bond lengths.

Even today, with modern data analysis and more information available on these systems, the presence of small amounts of other species, such as dimers, is sometimes overlooked. It was shown before that each percent of a dimer present in the vapor beside the monomer, but ignored, may lead to an error of 0.1% in the determined monomer bond length [8]. For 5% dimer, e.g., this is an order of magnitude larger than the total experimental error of this parameter.

During the past two decades the molecular structure of several metal dihalides has been determined (see e.g. [9] and [10]). Electron diffraction was combined with a quadrupole mass spectrometric analysis in these experiments to monitor and control the vapor composition [11]. It was found that the vapors of metal dihalides often contain a small amount of dimeric molecules that is not negligible at the accuracy of state-of-the-art electron diffraction work.

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0932-0784 / 93 / 1000-1000 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. Dimer content in metal dihalide vapors found by electron diffraction experiments.

MX_2	Melting point [12] K	T [a] K	Dimer % of the vapor	Ref.
$MgCl_2$	987	1171	10.8 ± 2.1	[13]
$MgBr_2$	984	1433	7.8 ± 1.3	[14]
$CaCl_2$	1055	1433	1.9 ± 0.8	[10d]
$CaBr_2$	1033	1383	5.3 ± 1.5	[10d]
CaI_2	1057	1183	2.4 ± 0.7	[10d]
$SrBr_2$	926	1400	0	[10b]
$MnCl_2$	923	961	0	[10a]
$MnBr_2$	971	881	5.3 ± 0.8	[10a]
$FeCl_2$	950	898	5.7 ± 0.8	[10a]
$FeBr_2$	962	981	11.2 ± 2.4	[10a]
$CoCl_2$	1013	1010	3.9 ± 0.7	[10a]
$CoBr_2$	951	908	5.8 ± 0.7	[10a]
$NiCl_2$	1303	1099	0	[10a]
$NiBr_2$	1236	976	0	[10a]
$ZnCl_2$	591	656	0	[10e]
$ZnBr_2$	667	614	0	[10e]
ZnI_2	719	580	0	[10e]
$CdCl_2$	842	805	0	[15]
CdI_2	661	678	0	[10c]
$HgCl_2$	553	710	0	[16]
HgI_2	523	683	0	[17]

[a] Temperature of the electron diffraction experiment, uncertainty ±50 K.

Table 1 summarizes experimental results on the dimer content. The variation in the relative abundance of dimers seems worthy of further scrutiny. There does not seem to be any obvious explanation of why dimers appear in the vapor of one metal dihalide and not in that of another.

In this paper we try to give an at least rudimentary interpretation of the variation in the dimer content of metal dihalides. It is based on a comparison of crystal and gas-phase structures, augmented by some thermodynamic considerations. We would like to stress that our considerations apply only to a dimer content of at least a few percent of the total vapor composition. The presence of dimers or other associates of smaller concentration, often observed by mass spectrometry, is not considered here.

Comparison of Structures

According to our observations, dimeric species are only present in the vapor if the dimeric molecule can also be recognized in the crystal.

Three examples may suffice for illustration. All first row transition metal dihalides (except the fluorides) and many alkaline earth dihalides have a $CdCl_2$ or CdI_2 type crystal structure [18]. These are layer structures with octahedral coordination of the metal atoms/ions. The gas-phase dimeric molecules, according to all experimental evidence so far, have a four-membered bridged structure [9, 10, 19, 20], see Figure 1. This dimer structure is closely related to the $CdCl_2$ and CdI_2 crystal structures, as shown in Figure 2. This means that the dimer molecule can get free from the crystal directly during vaporization, and there is no need for reorganization.

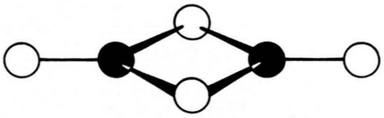

Fig. 1. The geometry of the four-membered bridged dimer of metal dihalides.

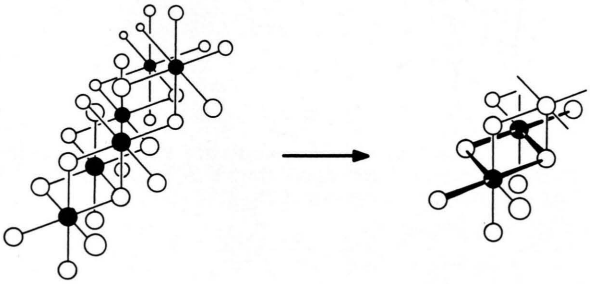

Fig. 2. Connection between the crystal structure and the structure of the dimeric molecule in the vapor phase for MX_2 type molecules with the $CdCl_2$ and CdI_2 type crystal structure. Part of the $CdCl_2$ crystal structure is drawn after [18].

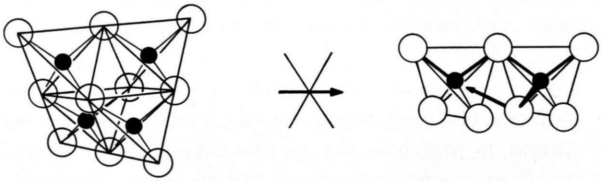

Fig. 3. Part of the ZnI_2 crystal structure after [21]. Tetrahedra connected at vertices do not give directly M_2X_4 type bridged dimeric molecules.

The other situation can be illustrated by the ZnX_2 and HgX_2 molecules. The structure of crystalline ZnI_2 [21] is shown in Figure 3. Zinc has four-coordination, and a four-membered ring dimer cannot be formed directly from this crystal; first some bonds have to be broken and new bonds have to be formed. For this type of molecules dimers were not found in the vapor at the electron diffraction experimental conditions.

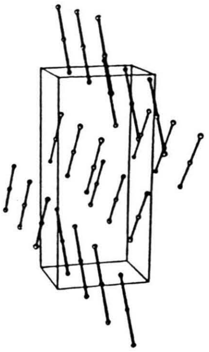

Fig. 4. The structure of $HgCl_2$ displaying monomeric molecules in the crystal. Reproduced from V. Subramanian and K. Seff, Acta Crystallographica **B 36,** 2132 (1980).

The structure of mercury dichloride [22] is shown in Figure 4. This crystal can be considered as being built from monomeric $HgCl_2$ molecules since two of the halogens are much closer to the metal than the others. The situation is similar with mercury dibromide and diiodide. Dimeric units are not present in this arrangement and, indeed, no dimers have been observed in their vapor.

For those metal dihalides whose gas-phase dimeric molecule is closely related to the crystal structure, we should, in principle, always find dimers in the vapor, based on structural consideration alone. However, according to our experience dimers do not always appear in the vapor in the electron diffraction experiment. Simple thermodynamics may be invoked to understand the situation.

Thermodynamic Considerations

From a thermodynamic point of view, the difference in the free energy of vaporization between the monomer and dimer will determine their relative abundance (their partial pressures) in the vapor phase. Since the entropy of vaporization is determined mainly by the translational entropy of the gaseous molecules, it can be taken to be about the same for the vaporization processes of monomers and dimers. This means that the relative magnitude of the free energies of vaporization for various processes (evaporation or sublimation of monomers and dimers) will be the same as that of the enthalpies of these processes. Consequently, in order to draw conclusions about the presence of dimers in the vapor phase, one should compare the enthalpy of vaporization of the dimer with that of the monomer [23, 24].

Consider the vaporization of metal dihalides to monomers and dimers

$$AX_2(c) \Rightarrow AX_2(g), \qquad \Delta H_{vap,\,m}\,,$$

$$2\,AX_2(c) \Rightarrow [AX_2]_2(g), \qquad \Delta H_{vap,\,d}\,,$$

and the dimerization reaction in the gas

$$2\,AX_2(g) \Rightarrow [AX_2]_2(g), \qquad \Delta H_{dim}\,,$$

where c and g refer to the condensed and gaseous phase, respectively; $\Delta H_{vap,\,m}$ and $\Delta H_{vap,\,d}$ are the enthalpies of vaporization of monomer and dimer, and ΔH_{dim} is the enthalpy of dimerization in the gaseous phase. It follows then that

$$\Delta H_{vap,\,d} = 2\,\Delta H_{vap,\,m} + \Delta H_{dim}\,.$$

Values for $\Delta H_{vap,\,m}$ can be calculated from the available experimental vapor pressure data [12] by the Clausius-Clapeyron equation (vide infra).

For molecular dimers of a wide range of metal halides the ratio of bridge to terminal bond dissociation energies has been found approximately constant and equal to 0.60 ± 0.04, irrespective of the absolute magnitude of the terminal bond dissociation energy, the charge of the metal ion, and the nature of the halogen [25]. In other words, bridge bonds can be considered to be about 60% as strong as terminal bonds. Assuming that the dimer terminal bonds (see Fig. 1) are about as strong as the monomer bonds [25], one has

$$\Delta H_{dim} = 2\,D_{AX} - 4 \times 0.6\,D_{AX} = -\,0.4\,D_{AX}\,,$$

where D_{AX} is the A–X bond dissociation energy for the monomer, that can be obtained from the dissociation enthalpies of the gaseous metal dihalides to gaseous atoms ($D_{AX} = 0.5\,\Delta H^0_{atom}$, see Table VII in [12]). In case of the calcium dihalides, the experimentally observed dimerization enthalpies [26] give a value of 0.37 ± 0.02 for the ratio of bridge to terminal bond dissociation energies, and for these molecules this value was used in the calculations.

Finally, the heat of vaporization obtained from vapor pressure data ($\Delta H_{vap,\,exp}$) can be taken, to a good approximation, to be equal to $\Delta H_{vap,\,m}$. Then

$$\Delta H_{vap,\,d} - \Delta H_{vap,\,m} = \Delta H_{vap,\,exp} + \Delta H_{dim}\,.$$

The calculated values of $\Delta H_{vap,\,d} - \Delta H_{vap,\,m}$ for different metal dihalides are collected in Table 2.

Table 2. Enthalpy of dimerization (ΔH_{dim}), and enthalpy of vaporization of monomers ($\Delta H_{\mathrm{vap,\,m}}$) and dimers ($\Delta H_{\mathrm{vap,\,d}}$).

	$-\Delta H_{\mathrm{dim}}$ [a] kcal/mol	$\Delta H_{\mathrm{vap,\,exp}}$ [b] kcal/mol	$\Delta H_{\mathrm{vap,\,d}} - \Delta H_{\mathrm{vap,\,m}}$ kcal/mol
$MgCl_2$	39	43 (l) [c]	4
$MgBr_2$	32	34 (l)	2
$CaCl_2$	48 [d]	56 (l)	8
$CaBr_2$	49 [d]	53 (l)	4
CaI_2	45 [d]	52 (l)	7
$SrBr_2$	39	55 (l)	16
$MnCl_2$	37	51 (s) 37 (l)	14 (s) 0 (l)
$MnBr_2$	32	50 (s) 40 (l)	18 (s) 8 (l)
$FeCl_2$	37	47 (s)	10
$FeBr_2$	33	33 (l)	0
$CoCl_2$	36	52 (s) 41 (l)	16 (s) 5 (l)
$CoBr_2$	31	51 (s) 41 (l)	20 (s) 10 (l)
$NiCl_2$	35	55 (s)	20
$NiBr_2$	30	56 (s)	26
$ZnCl_2$	31	28 (l)	−3
$ZnBr_2$	26	33 (s)	7
ZnI_2	20	28 (s)	8
$CdCl_2$	27	41 (s)	14 (s)
CdI_2	18	36 (s) 26 (l)	18 (s) 8 (l)
$HgCl_2$	21	–	–
HgI_2	14	16 (l) [e]	2

[a] $\Delta H_{\mathrm{dim}} = -0.2\,\Delta H^0_{\mathrm{atom}}$. The values of $\Delta H^0_{\mathrm{atom}}$ were taken from Table VII of [12].

[b] Calculated from the vapor pressures given in Table IX of [12], see text.

[c] l: liquid, s: solid. – [d] From [26]. – [e] From [27].

A comparison of Tables 1 and 2 shows that in those cases where the enthalpy of vaporization of the dimer is greater by at least about 10 kcal/mol than the enthalpy of vaporization of the monomer ($NiCl_2$, $NiBr_2$, $CdCl_2$, CdI_2), dimers have not been observed in the gaseous phase. This is so in spite of the fact that the dimeric molecule can be recognized as a unit present in the crystal. On the other hand, thermodynamic considerations alone would allow the presence of dimers in the vapor phase of zinc dihalides, but the direct formation of a dimer from the crystal is not possible in this case (see Figure 3), and dimers have not been detected in the gaseous phase. Similarly, although the presence of dimers in the vapor of HgX_2 would be possible from a thermodynamical point of view, since the crystals consist of monomeric units (Figure 4), dimers have not been observed in the vapor in accordance with expectations. $SrBr_2$ has a crystal structure in which the metal is partially 7- and partially 8-coordinated [28] and the direct relation of this structure to the gas-phase dimer structure is not obvious either. Both structural and thermodynamical considerations ($\Delta H_{\mathrm{vap,\,d}} - \Delta H_{\mathrm{vap,\,m}} > 10$ kcal/mol) predict that dimers will not appear in the vapor of $SrBr_2$, in accordance with the experimental findings.

If dimers can, in principle, be evaporated from the crystal, it seems that their appearance in the vapor depends on the electron diffraction experimental temperature. If the electron diffraction experimental temperature is higher than the melting point of the substance, i.e. the molecules are evaporated from the molten state, dimers are observed in the vapor phase. The magnesium and calcium dichlorides and dibromides illustrate this; the experimental temperature for all these molecules is at least 200 degrees higher than the melting point. If, however, sublimation is taking place during the electron diffraction experiment, i.e. the temperature is lower than the melting point, dimers do not appear in the vapor phase. Examples are the nickel dihalides, which where evaporated at temperatures more than 200 degrees lower than the melting point of these substances. For most of the other systems studied so far, the electron diffraction experimental temperature is very close to the melting point. Taking into consideration the fact that the experimental temperature is usually given with about 50 degrees uncertainty, the other systems may fall into either cathegory. The only example that does not follow the above general observation is $MnBr_2$, for which the experimental temperature is given as 90 degrees lower than the melting point, and yet dimers were observed in the vapor. Looking at the logbook of the electron diffraction experiment, however, we found a comment about the possibility that the uncertainty of the temperature measurement may have been larger than usual. Therefore we believe that all cases studied so far confirm our observation. Incidentally, the possibility of a larger than usual uncertainty of the electron diffraction experimental temperature in the study of $MnBr_2$ does not influence the reliability of the determined geometrical parameters for that molecule.

Conclusions

The variation of dimer-content of metal dihalide vapors has been discussed in terms of the crystal phase structure and of thermodynamic considerations of the vaporization process. It is concluded that dimers are not found in the gaseous phase if the dimeric molecule cannot be derived directly from the crystal structure and thus there is no possibility for the dimers to go over directly from one phase to the other during evaporation.

If the dimeric molecule is already present as a unit in the crystal, then the difference in the heat of vaporization between monomers and dimers determines whether dimers will be detected in the gaseous phase or not. Our detailed analysis shows that dimers appear in the vapor when their enthalpy of vaporization does not surpass that of the monomer by more than about 10 kcal/mol. According to our experience, if the temperature of the electron diffraction experiment is lower than the melting point of the metal dihalide there is no dimer in the vapor, whereas if the evaporation occurs from the molten state dimers appear in the gaseous phase.

Acknowledgement

M.H. wishes to thank the Hungarian Academic Research Fund for financial support (AKA 1-300-2-92-0-804).

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