



Review

Molecular complexes formed by halides of group 4,5,13–15 elements and the thermodynamic characteristics of their vaporization and dissociation found by the static tensimetric method

E.I. Davydova, T.N. Sevastianova, A.V. Suvorov, A.Y. Timoshkin*

Department of Chemistry, St. Petersburg State University, University pr. 26, Old Peterhof, 198504 St. Petersburg, Russia

Contents

1. Introduction	2032
2. Molecular donor–acceptor complexes of group 4,5,13–15 element halides	2033
2.1. General characteristic	2033
2.2. Structural features of adduct compounds	2035
2.2.1. Tetrahedral EX ₃ ·D adducts	2035
2.2.2. Trigonal bipyramidal EX ₃ ·2D adducts	2036
2.2.3. Octahedral EX ₃ ·3D adducts	2036
2.2.4. Trigonal bipyramidal EX ₄ ·D adducts	2041
2.2.5. Dimeric octahedral [EX ₄ ·D] ₂ adducts	2042
2.2.6. Octahedral EX ₄ ·2D adducts	2043
2.2.7. Octahedral EX ₅ ·D adducts	2043
2.2.8. Use of the structural characteristics of adducts in tensimetry studies	2043
3. Description of the experimental method	2048
3.1. Tensimetric methods and their capabilities	2048
3.2. Static method	2049
3.3. Static method with membrane null-manometer	2049
4. Primary processes upon vaporization of the complex	2050
4.1. General considerations	2050
4.2. Concurrence between vaporization and dissociation on the example of the adduct of 1:1 composition	2051
5. Illustrative examples	2053
5.1. Vaporization without dissociation and subsequent thermal dissociation and pyrolysis of the AlI ₃ ·Py complex	2053
5.2. Vaporization of the complex which is accompanied by the partial gas phase dissociation. GaCl ₃ ·NH ₃ complex	2054
5.2.1. Unsaturated vapor range	2054
5.2.2. Saturated vapor range	2055
5.3. Vaporization of complex which is accompanied by the significant dissociation in the gas phase. Vaporization and equilibrium dissociation of GaI ₃ ·Py adduct	2056
5.3.1. Unsaturated vapor region	2056
5.3.2. Saturated vapor region	2057

Abbreviations: A, acceptor molecule (Lewis acid); AZ, alumazene [2,6-(*i*-Pr)₂C₆H₃NAIme]₃; CVD, chemical vapor deposition; cyt, cytosine; D, donor molecule (Lewis base); DA, donor–acceptor; depe, diethylphosphinoethane; detu, (1,3diethylthiourea); deu, (1,3diethylurea); DICNQ, dipyrido[f,h]quinoxaline-6,7-dicarbonitrile; DMA, dimethylacetamide O=C(Me)NMe₂; dmap, 4-NMe₂-Py; DMF, *N,N*-dimethylformamide O=CHNMe₂; dmit, 1,3-dimethyl-2(3H)-imidazoethione; dmpe, dimethylphosphinoethane; DMSO, Me₂SO; DO, dioxane C₄H₈O₂; dpm, dipivaloylmethanate (2,2,6,6-tetramethylheptane-3,5-dionate); dpmpy, 2-Ph₂CH-Py; dppe, diphenylphosphinoethane; dppeN, Ph₂P(CH₂)₂PPH₂; dppeS₂, SP(Ph₂)CH₂CH₂P(Ph₂)S; dppm, diphenylphosphinomethane; Hbta, bezotriazole; LSM, least squares method; *m*, mass of the sample; *M*, molecular mass; mcyt, 1-methylcytosine; Me₃[9]aneN₃, 1,4,7-trimethyl-1,4,7-triazacyclononane; morph, morpholine: NH(C₄H₈)O (coordination via N); mpy, 2-Me-Py; NTMSI, *N*-trimethylsilylimidazol; *P*, pressure; *P*^{*}, hypothetical pressure of the compound, which is computed on assumptions that (1) full amount of the compound exists in the system in the gaseous state, (2) any reactions of the compound are neglected; PhA, *N*-phenylacetamide; phen, 1,10-phenanthroline; pic, 4-methylpyridine; pip, piperidine C₅H₁₁N; *P*_{total}, total pressure (usually this quantity is measured experimentally); py, pyridine C₅H₅N; pyz, pyrazine C₄H₄N₂; quin, quinuclidine; *R*, universal gas constant (8.314 J mol^{−1} K^{−1}, 0.0821 atm K^{−1}, 62.400 Torr ml K^{−1}); S(pz)₂, bis(pyrazolyl)sulfane; *T*, temperature, K; terpy, 2,2′,2″-terpyridil (2,6-di-2-pyridylpyridine); TEU, tetraethylurea; THF, tetrahydrofuran; tmeda, tetramethylethylenediamide; tmpH, 2,2,6,6-tetramethylpiperidine; tmtu, *N,N,N',N'*-tetramethylthiourea; tmu, *N,N,N',N'*-tetramethylurea; tu, thiourea; *V*, volume of the system.

* Corresponding author. Tel.: +7 812 428 4071; fax: +7 812 428 6939.

E-mail address: alextim@AT11692.spb.edu (A.Y. Timoshkin).

5.4.	Vaporization with congruent dissociation of the solid adduct into gaseous products. System SnCl_4 –dioxan.....	2058
5.5.	Subsequent ligand dissociation from the solid adduct. Alumazene–pyridine system	2061
5.6.	System ZrCl_4 – POCl_3	2063
6.	Summary of the studied systems and obtained thermodynamic characteristics	2065
7.	Estimation of the sublimation enthalpies for Donor–acceptor complexes	2067
7.1.	A critical note about the widely used approach toward estimation of vaporization enthalpies of the donor–acceptor complexes	2067
7.2.	Estimation of the sublimation enthalpies based on structural data	2071
8.	Conclusions	2071
	Acknowledgements	2072
	References	2072

ARTICLE INFO

Article history:

Received 20 July 2009

Accepted 2 April 2010

Available online 10 April 2010

Keywords:

Donor–acceptor complexes

Adducts

Structure

Thermodynamics

Vaporization

Dissociation

Tensimetry

Static method

ABSTRACT

Donor–acceptor molecular complexes (adducts AD_x) play important role in modern technology. They are prospective single-source precursors for the synthesis of solid phases by the chemical vapor deposition (CVD) method. Stability of the complex in the gas phase is an important issue for many practical applications. High-temperature thermodynamic data for adducts are not readily available, which underlines the fundamental need for the systematic study of processes which adducts undergo upon heating. Such processes are: the congruent or incongruent vaporization (sublimation), the reversible dissociation in the gas phase into the components and the irreversible thermal destruction (pyrolysis).

The static tensimetric method with membrane null-manometer is unique method for studying donor–acceptor interactions both in gaseous and condensed phases. It is a useful method for: (1) the evaluation of the complex composition AD_x ; (2) characterization of the nature of the main process which the complex undergoes upon heating; (3) determination of the thermodynamic characteristics of such processes. The static method allows to achieve the true equilibrium state, it is applicable both to the heterogeneous and homogeneous systems and allows one to measure the vapor pressure–temperature dependence for the pressure range 1–1000 Torr and temperatures up to 1100 °C. For the homogeneous systems (processes in the gas phase), the vapor composition and the vapor density can be determined, which allows to calculate partial pressures of three molecular forms in vapors and determine the equilibrium constant at a given temperature. From the temperature dependence of the equilibrium constant, the enthalpies and entropies of the respective process can be evaluated.

In the present review the application of the static tensimetry method for the determination of the nature of the process, vapor composition and thermodynamic characteristics is illustrated on the following examples:

- Sublimation (vaporization) of the adduct without decomposition.
- Reversible gas phase dissociation of the adduct into components.
- Sublimation (vaporization) of the adduct accompanied by its reversible dissociation into components.
- Complete congruent dissociation of the adduct into gaseous components upon heating.
- Incongruent dissociation of the adduct (subsequent dissociation of the solid AD_x adducts into solid AD_{x-1} and gaseous D).
- Appearance of the upper temperature limit due to the irreversible thermal destruction (pyrolysis) of one of the components.

Our results on systematic studies of the thermal decomposition of adducts of group 4,5,13,14,15 element halides (chlorides, bromides and iodides) with group 15, 16 element-containing donors are presented. Experimentally obtained thermodynamic characteristics of vaporization and dissociation for more than 50 adducts are summarized for the first time.

Current approaches towards estimation of the sublimation enthalpies of donor–acceptor complexes are critically evaluated. It is shown, that the widely used approximation (sublimation enthalpy of the complex equals the sublimation enthalpy of 1 mol of the ligand) generally performs very poor and may result in large (about 70 kJ mol^{−1}) errors. Its application is not recommended. Moreover, reported values for the gas-phase metal–ligand bond dissociation energies, based on such approximation, are incorrect and should not be trusted. Approaches based on the structural information appear to be more perspective.

The structural features of the DA complexes of group 4,5,13,14,15 element halides both in gaseous and solid states are also summarized for the first time.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

High-temperature gas phase chemistry plays an important role in modern technology. In particular, the chemical vapor deposition (CVD) method [1–4] is widely used for the production of binary and composite materials, such as semiconductors and refractory nitrides and oxides. Donor–acceptor (DA) molecular complexes AD_x (also called adducts) [5] formed by Lewis acids A and Lewis bases D are prospective single-source precursors for the synthesis of the solid phases [6–14]. Donor–acceptor interactions often stabi-

lize unusual structures. For example, inorganic heterocycles of the N_3P_2 , N_4As , N_4P series have been stabilized by Shulz [15–17].

Saturated vapor pressure of the single-source precursor and its stability in the gas phase are the two most important issues for its practical application. Thus, there is a fundamental need for the systematic study of processes which adducts undergo upon heating. Such processes are: congruent or incongruent vaporization (sublimation), reversible dissociation in the gas phase (into donor and acceptor components) and irreversible thermal destruction (pyrolysis). Homogeneous gas-phase dissociation of the DA complexes is

Download English Version:

<https://daneshyari.com/en/article/1300634>

Download Persian Version:

<https://daneshyari.com/article/1300634>

[Daneshyari.com](https://daneshyari.com)