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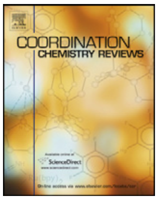

Review

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

Abbreviations: A, acceptor molecule (Lewis acid); AZ, alumazene $[2,6\text{-}(i\text{-}Pr)_2C_6H_3NAlMe]_3$; 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 $O{=}C(Me)NMe_2$; dmap, 4-NMe_2-Py; DMF, *N,N*,dimethylformamide $O{=}CHNMe_2$; dmit, 1,3-dimethyl-2(3H)-imidazolethione.; dmpe, dimethylphosphinoethane; DMSO, Me_2SO; DO, dioxane $C_4H_8O_2$; dpm, dipivaloylmethanate (2,2,6,6-tetramethylheptane-3,5,-dionate); dpmpy, 2-Ph_2CH-Py; dppe, diphenylphosphinoethane; dppen, $Ph_2P(CH)_2PPh_2$; dppeS_2, $SP(Ph_2)CH_2CH_2P(Ph_2)S$; dppm, diphenylphosphinomethane; Hbta, bezotriazole; LSM, least squares method; *m*, mass of the sample; M, molecular mass; mcyt, 1-methylcytosine; Me_3[9]aneN_3, 1,4,7-trimethyl-1,4,7-triazacyclononane; morph, morpholine: $NH(C_4H_8)O$ (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-phenantroline; pic, 4-methylpyridine; pip, piperidine $C_5H_{11}N$; P_{total}, total pressure (usually this quantity is measured experimentally); py, pyridine C_5H_5N; pyz, pyrazine $C_4H_4N_2$; quin, quinuclidine; *R*, universal gas constant (8.314 J mol^{-1} K^{-1}, 0.082 l 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).

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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.

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 stabilize 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