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Title: Enthalpy and free energy of Formation of Diamido and monoamido phosphoric acid.

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Abstract

Diamidophosphate has been identified as a possible prebiotic compound used in the precursor membranes of the first 'life'. Compounds such as these will be helpful in developing novel biomimetic approaches in synthetic chemistry. Thermochemical data for this type of compounds are not available. Hess' law and estimates from calorimetric measurements used by Wakefield in the 1970s for other amido phosphates have been used to estimate the thermochemical values for the diamido and monoamido-phosphoric acid. Enthalpy of formation at 298.15 ^{o}C is calculated as – 821.9 kJ/mol and the free energy of formation calculated as -813.5 kJ/mol for the diamidophosphoric acid. The calculated enthalpy of formation of monoamidic phosphoric acid is -1117.1 kJ/mol and its free energy of formation is -1105 kJ/mol.

Keywords: amidophosphoric acid, diamidophosphate, prebiotic phosphoryl compound, phosphonitrogen glass, enthalpy, Gibbs Free energy, biomimetic nitrogen fixation .

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1. Introduction

Initial preparations of the amidophosphoryl compounds by Stokes in 1893 to 1898 were by a variety of methods. Diamidophosphoric acid and its compounds have been known for 125 years since Stokes preparedsome of the amido phosphoryl compounds [1, 2], and described by Klement in the 1960's [3]. These diamido chemicals have been used in variety of applications such as specialty fertilizers, low temperature inorganic glasses, pharmaceutical drugs, etc., over the years, and have come to the fore recently in the studies of how the components for the 'first cell' of life may have occurred by the near room temperature aqueous polymerization - made possible using the diamido phosphoric acid as demonstrated by Krishnamurthy and his group at Scripps Institute [4, 5]..

Thermochemical data developed mostly by computer analyzed methods following some experimental studies shown by Pedley [6]. is a valuable tool for giving the best estimates for the enthalpy and free energy of formation of organic functional groups belonging to the CHNOS and halogen elements and requires updating to include the important bio-element P – phosphorus and its biogeo organic functional groups. Estimates and methods shown in this study along with references can be adapted in adding data for phosphoryl compounds.

2. Methods

2.1.Prior thermodynamic Data on amidophosphates

The thermodynamic property – enthalpy of formation of ammonium hydrogen monoamido phosphate,NH4HPO3NH2, was published in 1970 by Zachary T Wakefield, Basil Luff and Robert Reed from the TVA Division of Chemical Development [7].. The same group published in 1972,.the enthalpy of formation of Phosphoryl triamide, PO(NH2)3 and its heat capacity, entropy S^o, and the Gibbs function $[\Delta G^o - \Delta H^o]/T$ [8,9]. They provided the methodology, an extension of Hess's Law for computing heat of formation of an unknown component from heats of reaction and heats of formation of known components. and Kirchoff's laws of estimating the specific heat from the enthalpy variation with temperature of these phosphoryl amido compounds. Hess's law states that the change of enthalpy in a chemical reaction (i.e. the heat of reaction at constant pressure) is independent of the pathway between the initial and final states.

A simple reaction [1] with reactants A and B giving a product AB can be written as follows:

$$A \ + B \ = \ AB \quad ------ (1)$$

From Hess's law, the enthalpy changes are additive. The Heat of formation of AB - Heat of Formation of A + Heat of Formation of B equals the Heat of Reaction. Heat of

Formation is written as ΔH_f and the heat of reaction is written as ΔH_r. When the heats of formation of AB, $\Delta H_{f[AB]}$, $\Delta H_{f[B]}$ and the heats of reaction [such as solution, dilution, combustion, etc] ΔH_r are known, one can compute the heat of formation of the unknown compound, A, ΔHf[A].

The unit for enthalpy is kJ/mole, and the values shown in older references in kcal/mole are converted to kJ/mole in this article for consistency and to avoid confusion. The values are shown to one significant digit after decimal. Conventional reporting of enthalpy and entropy values are usually shown depicting experimental errors in calorimetric procedures. In this paper experimental error variations are not shown.

Wakefield prepared the ammonium hydrogen mono amidophosphate [NH4HPO3NH2] in 1970 using phosphoryl chloride in ice cold aqueous ammonia solution and separated the compound from diamido compound using acetone into two layers, neutralized and crystallized. The pure compound was then mixed with phosphoric acid in forming an ammonium dihydrogen phosphate for the calorimetric methods to define the enthalpy of formation [7]. The enthalpy of formation ΔH_f of NH4HPO3NH2, was shown to be -1222.4 kJ/mol. This calorimetric method measured temperature changes of the reaction,

NH4HPO3NH2 (c) + H3PO4 +H2O (l) = 2 NH4.H2PO4 (c) …..(2)

Calorimetric measurements defined the values for the heat of reaction, followed by computing the enthalpy of formation. From Hess' law we get the enthalpy of formation of NH4HPO3NH2 (c) as equal to

2(ΔH_f of NH4.H2PO4 (c)) - ΔH_f H3PO4 - ΔH_f H2O (l) $\Delta H_{r(1)}$.

Wakefield's calorimetric methods gave a heat of solution or heat of reaction , $\Delta H_{r(1)}$, component of -106.34 kJ/mol while using a heat of formation of -1273.1 kJ/mol for H3PO4.0.915 H2O. This value for phosphoric acid hydrolysis reaction involving one mole of water per mole of H3PO4 would change to -113.7 kJ/mol using a heat of formation for H3PO4 (l) at -1265.7 kJ/mol.

Wakefield's group later defined the enthalpy of formation of phosphoryl -triamide prepared from phosphoryl chloride and liquid ammonia in chloroform in a dry ice –acetone cooled bath where the ammonium chloride formed was separated using diethylamine. The enthalpy of formation was determined from the reaction (3) below [8].

2 H3PO4 (l) + 3 H2O) (l) + PO(NH2)3 (c) = 3 NH4.H2PO4 (c) …….. (3)

The heat of formation of the triamide was determined from published values of the enthalpies of formation [2] H3PO4 (l) -1265.7 kJ/mol, H2O (l) -285.6 kJ/mol and NH4H2PO4 (c) -1443.7 kcal/mol adjusting for the heat of reaction for 2(H3PO4.1.5H2O). The computed enthalpy of formation of the phosphoryl -triamide was -598.6 kJ/mol after adjusting for the measured heat of reaction and heat of solution for the 3 moles of water per mole of H_3PO_4 in the phosphoric acid hydrolysis of -344.3 kJ/mol. This is about 3 times the heat of reaction of the one mole of water hydrolysis for Reaction (2).

Wakefield's measurements of specific heats, entropy and free energy functions give a free energy of formation, $\Delta G_{f,}$ of the triamide to be -581.9 kJ/mol [9]. Here, the difference between the enthalpy of formation and the free energy of formation was only 16.7 kJ/mol.

3. Results & Discussion

3.1. Thermodynamic Data for diamido phosphoric acid

Kowalczyk noted that the phosphorodiamidic acid when heated to 110 °C condenses into P, P' diamido diimido phosphoric acid with a heat of condensation of -3.6 kJ/mol [10].

The enthalpy of formation of the phosphorodiamidate compound which is in between the monoamido and triamido phosphate could not be found in literature. For the studies involving minimization of Gibbs Free energy using chemical thermodynamics, it is essential to get the thermochemical properties of diamidophosphoric acid and related compounds. The open source thermochemical software by Dick Jeffrey at Berkeley called CHNOPSZ [11]. a leading software discussing mineral, protein, and soil chemical reactions can add properties for additional species to facilitate a thermochemical study of prebiotic reaction plausibility to augment experimental studies. The present study attempts to fill some of this information. Other thermochemical software such as HSC Chemistry, etc. which do not have the properties of the amidophosphates can also benefit from these data. Wakefield's methodology which follows the fundamental Hess' principle of additive heats of reaction method is then used to arrive at the following values. The formation of ammonium hydrogen phosphates from the monoamido and triamido phoshates provides an estimate for the following reaction

$$(NH_2)_2PO_2H\ (c) + H_3PO_4(l) + 2H_2O\ (l) = 2\ NH_4.H_2PO_4\ (c) \quad \ldots\ldots.. \quad (4)$$

$$\Delta H_{f\,[(NH2)2PO2H]} = 2\ \Delta H_{f[NH4H2PO4]} - \Delta H_{f[H3PO4]} - 2\ \Delta H_{f[H2O]} - \Delta H_{r(4)}$$

Using standard enthalpies of Formation of H_3PO_4 -1265.7 kJ/mol*, H_2O (l) -285.4 kJ/mol and $NH_4.H_2PO_4$ (c) -1443.7 kJ/mol gives -1050.9 – $\Delta H_{r\,(4)}$ kJ/mol

The unknown is the heat of reaction $\Delta H_{r\,(4)}$, is estimated to be between that for reactions (2) and (3) measured by Wakefield as the hydrolysis involves 2 moles of H_2O per mole of H_3PO_4 for reaction (4) compared to that of 1 mole water per mole of H_3PO_4 for reaction (2)] and that of 3 moles of water per mole of H_3PO_4 for reaction (3). This is considered 2/3rd proportionality for the diamido group compared to triamido group. Using $\Delta H_{r\,(4)}$ 229 kJ/mol [average of 113.7 and 344.3 kJ/mol], the heat of formation for diamidophosphoric acid is -821.9 kJ/mol. {* for consistency in calculations we used the value -1265.7 kJ/mol used by Wakefield in 1972 instead of the value of -1288 kJ/mol shown in 1982 NBS data book page 82 for H_3PO_4 [12]}.

The free energy of formation of diamido phosphoric acid, $(NH_2)_2POH$, is calculated as

-804.0 kJ/mol - $\Delta G_{r(4)}$ using free energy formations at 298.15 K of H_3PO_4 (l) -1142.5 kJ/mol, $NH_4H_2PO_4$ (c) -1210.4 kJ/mol, H_2O (l) -237.1 kJ/mol. The Gibbs function adjustment, -(G-H), for the triamide is 16.7 kJ/mol [9]; by using the 2/3 proportionality noted earlier, the Gibbs function adjustment gives $\Delta G_{r(4)}$ for the diamido group as -11.2 kJ/mol. When this correction is applied to the enthalpy of formation the value for ΔG_f for $(NH_2)_2POH$, is determined as -813.5 kJ/mol.

3.2. Thermodynamic data for monoamidic phosphoric acid

The thermodynamic values for monoamidic phosphoric acid can be arrived at from reaction (5)

$NH_2\,PO_3\,H$ (c) + H_2O (l) = $NH_4\,H_2PO_4$ (c) …….. (5)

$\Delta H_{f[NH2PO3H]} = \Delta H_{f[NH4H2PO4]} - \Delta H_{f[H2O]} - \Delta H_{r(5)}$

The calculated enthalpy of formation of monoamidic phosphoric acid is -1117.1 kJ/mol using a $\Delta H_{r(5)}$ -42.6 kJ/mol for the of hydration reaction. The heat of reaction value 42.6 kJ/mol for hydration is chosen from the value known for metaphosphoric acid hydration to orthophosphoric acid, from published values of enthalpies of formation from Wagman, [12], for the reaction (6) below.

HPO_3 + H_2O (l) = H_3PO_4 ……… (6)

Guthrie reported a value of 131.7 kJ/mol for the free energy dehydration of orthophosphoric acid to metal phosphoric acid – which is the reverse of reaction (6) [13]. Using the value of -131.7 kJ/mol for hydration reaction with water and the free energies of formation of $NH_42H_2PO_4$ and H_2O in[13] reaction (5) the calculated free energy of formation of monoamidic phosphate, NH_2PO_3H, is -1105 kJ/mol.

4. Conclusion

Reactions (4) and (5) are thermodynamically feasible at 298 K, with negative free energies of reaction, provided the exothermic heat of reaction can be controlled by cooling; otherwise competing reactions such as intermediate polymerizations or decomposition of the mono- ammonium hydrogen phosphate can occur. Krishnamurthy notes that -Amidophosphates (based on its chemistry) should be expected to be better in condensing and form polyphosphates (thermodynamically and kinetically) than ammonium phosphate. We see this to be true in water when the pH is lowered to around 6. Ammonium phosphate is completely inert while diamidphosphate forms the dimer, trimer and cyclotriphosphate [14].

. The enthalpy of diamido phosphoric acid is calculated to be -821.9 kJ/mol , and found that reaction (4) is exergonic. This shows that processs of nitrogen containing phosphate inorganic glasses noted in the ceramic industry and the recently demonstrated ‘prebiotic’ membranes instrumental in the creation of life using the phosphoryl-amidates. are possible. In natural surroundings the exergonic heats of reaction energy can be used for other endergonic reactions, involved in related nano-chemical and biomimetic synthesis. Many of the computational thermochemistry publications also do not have the basic properties of some of the subgroups involved with the phosphoryl amido groups. Most of the studies are on synthesis by experimentation and analysis of products formed than of a predictive chemistry usable in biomemtic approaches. Thermochemical data such as developed here may shed newer light in the biomimetic development of dinitrogen fixation which has been a challenge for chemists The use of Gibbs free energy minimization software can only be useful by supplying data for all the possible products that may come out from input reactants. . The present paper is helpful in providing some answers.

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