

STABILITY OF CHLOROPHYLL METALLANALS IN SOLUTIONS

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ABSTRACT:

The study of the stability characteristics of porphyrin complexes, the increase in the stability of metalloporphyrins, the decrease in porphyrin-ligand basis, the effect of this interaction, the kinetics of solvoprotolytic dissociation of metalloporphyrins and the dissociation kinetics of perennial and numerous metalloporphyrins and metallophthalocyanins.

KEYWORDS: Porphyrin, compound, chlorophyll, dissociation kinetics, metalloporphyrin, ethanol vinegar.

INTRODUCTION:

The stability of metalloporphyrins in different environments is one of the decisive factors in the practical application of these compounds. There is a lot of work devoted to the study of the stability of complex compounds of porphyrins in different protonodonor environments [1, 2]. Although the study of sustainability initially began with chlorophylls, attention to these compounds has now declined significantly. This is because knowing the economic inefficiency and labor-intensive nature of separating them from plants is one of the main factors that prevents them from being applied in practice.

A new prospect of obtaining these compounds is that the study of their stability in this or that solvent rises to the level of priority tasks in connection with the creation of the raw material base. In this paper, we summarize and study the data on the stability of chlorophyll and its analogues in various solvents necessary for the use of this group of porphyrins for model tests and practical purposes.

The study of the stability of chlorophyll in solution, the qualitative indicators of the decomposition of porphyrin complexes from the time it was first obtained in pure form, showed that most complexes dissociate rapidly with alkali and alkaline-earth metals under the influence of water: Ag^{2+} , Zn^{2+} , Cd^{2+} , Mg^{2+} porphyrins dissociate well in dilute acid solutions, as well: Cu^{2+} , Ni^{2+} , Co^{2+} , Pd^{2+} , Fe^{3+} and Mn^{3+} concentrated sulfuric acid or metal sulfates are required for extraction [3,4].

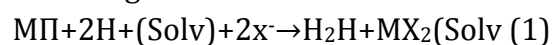
Quantitative study of the dissociation kinetics of a solution of chlorophyll in 90% aqueous acetone with the addition of $\text{H}_2\text{C}_2\text{O}_4$, H_2SO_4 and HCl , J. McKineem and D.J. Johnson [5-7] were unable to obtain reliable kinetic parameters. This is due to the inability to select an appropriate protogenic solvent, which may include side effects and cases of partial protonation and aggregation of pheophytin.

However, at the same time, α -chlorophyll was found to dissociate 7 times faster than ν -chlorophyll. Further similar work on the stability of chlorophyll and similar compounds in 82% solution of aqueous acetone with the addition of NSI was carried out by S. Shanderl and colleagues [8]. They found that at the same activation energy (43.9kJ / mol) the dissociation rate of α -chlorophyll was 5.5 times greater than that of ν -chlorophyll. Replacing the phytol residue in chlorophylls with C_2H_5 -, CH_3 - or H slightly accelerates the dissociation reactions of magnesium-porphyrins. Dissociation of structural analogues of A-line chlorophylls 0.00017; 0.00021; 0.00026 and 0.00029 are equal to C-1. Suitable for chlorophyll, ethylpheophorbide, methylpheophorbide and phosphorbides, respectively. In this case, the activation energy of the reaction does not change.

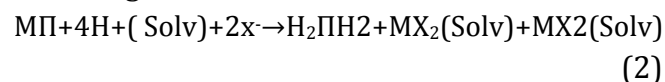
Only many years of systematic experimental work by Professor B.D. Berezin allowed to reveal the laws of stability of these compounds and the mechanisms of dissociation reactions. The generalized conclusion of these studies showed that these compounds exhibit phenol stability in some unusual cases. Ionic-type labile complexes are formed only by alkali and alkaline-earth metals. Metals bonded to the macro ring through a covalent bond: Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Cr^{2+} , Al^{3+} , Ti^{4+} , Pd^{4+} , Pt^{4+} and others form stable complexes.

Because metalloporphyrins bind highly stable substances, their formation reactions cannot be supported by the commonly used thermodynamic approach, which studies the formation of complex compounds. When studying the stability characteristics of porphyrin complexes, their kinetic stability is often studied. That is, the free activation energy is used in the dissociation of solvoprotolytic reactions [1]. Dissociation of

metalloporphyrins of average size takes place as a protolytic process according to the following scheme:



in highly acidic environments it follows the following scheme



Chlorophyll and its labile metalloanalogs are irreversibly dissociated in ethanol-acetic acid media according to equation [1]. From the dissociation concentrations of these substances shown in Table 1, it can be seen that the stable chlorophyll within this group is several times lower under these conditions.

At the same time, it was found that the stability of chlorophyll a is much lower under such conditions.

Table 1. The dissociation rate constants of pheoditin labile complexes in ethanol acetic acid medium.

$C^0, \text{mol/l, ZnCl}_2$	$k_{\text{ef}} \cdot 10^3, \text{s}^{-1}$	$k_v, \text{l/e} \cdot \text{mol}$
$1 \cdot 10^{-2}$	$3,430 \pm 0,070$	$0,343 \pm 0,007$
$1 \cdot 10^{-3}$	$0,646 \pm 0,097$	$0,646 \pm 0,010$
$1 \cdot 10^{-4}$	$0,047 \pm 0,014$	$0,470 \pm 0,140$

It is clear from the kinetic characteristics of the stable metalloanalogs of chlorophyll in Table 2 that the Fe^{3+} , Ni^{2+} , Cu^{2+} , Pd^{2+} complexes dissociate only in the protonodonor medium (solution of H_2SO_4 monohydrate in glacial acetic acid). Zn^{2+} , Co^{2+} Ag^{2+} complexes are also decomposed in weak protodonodonor media (ethanol-acetic acid). Complexes of nickel and copper with α -pheophytin dissociate in glacial acetic acid at high temperatures. Iron, zinc, and silver complexes proceed according to the equations given in (1) or (2). The copper, palladium, nickel, and cobalt complexes of the A-chlorophyll analogs are accompanied by the formation of semi-dyed substances as a result of the destruction of theophytine [9].

Table 2. kinetics of dissociation characteristics
of stable metallogues of α -chlorophyll in
glacial acetic acid

Complex	C _{nas} , mol/l	T/K	k _{ef} , °10 ⁴ , c ⁻¹
MgF a	2,0	298	0,036
		313	0,106
		323	0,211
		333	0,394
	4,0	298	0,944
	8,0	298	9,17
	10,0	298	115,3
CdF a	0,02	298	1,89
		308	1,78
		318	1,72
	0,04	298	5,17
	0,06	298	10,56
	0,10	298	38,33
	0,20	298	230,0
HgF a	0,02	298	very fast

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