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Abstract

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CHEMISTRY

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ON METHODS FOR STUDYING THE STABILITY OF COMPLEX COMPOUNDS OF PHTHALOCYANINE

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The currently known methods for studying complex compounds (^{1}) are successfully applied only to the study of comparatively low-stability complex compounds, i.e., those in whose solutions dissociation into their constituent ions is clearly expressed:

$$MA_n \rightleftarrows M^{n+} + nA^-. \quad (1)$$

With increasing degree of covalency in the M—A bonds, the ions constituting the complex approach more and more closely the state of neutral atoms (^{2}); the bond loses its ionogenic character, and with it the tendency to decompose into ions, acquiring the ability to dissociate into electroneutral particles. For this reason, the stability in solution of especially strong complex compounds formed, for example, by ions of typical complex-formers such as Co^{3+}, Pt, Pd with a wide range of addends, and also by many cations with such important addends as porphyrins, pentadienyl, carbonyl, and phthalocyanine, becomes impossible to characterize by an instability constant. In addition to negligibly small dissociation into ions, there is still another reason that does not allow the concept of an instability constant to be applied to a number of complex compounds. This concerns complexes with unstable dissociation products, for which an apparent irreversibility of the dissociation process is characteristic.

The metal phthalocyanines discussed in the present work dissociate appreciably only in a medium of protonic acids*:

$$MPc_t + 2H^+ = M^{2+} + H_2Pc_t; \quad (2)$$

$$MPcH^+ + 2H^+ = H_2PcH^+ + M^{2+}. \quad (2a)$$

Process (2) proceeds in the solid phase, process (2a) in H_2SO_4 with a concentration above 8 mol/l. Our investigations have shown that processes (2) and (2a) proceed rapidly and irreversibly for labile phthalocyanines formed by cations of alkali and alkaline-earth metals, and also Hg^{2+}, Cd^{2+}, Pb^{2+}, Mg^{2+}, Be^{2+}, Ag^{+}, Fe^{2+}. To these should be added the phthalocyanines Sb^{3+}, Mn^{2+}, Sn^{2+}.

Stable phthalocyanines formed by Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pt^{2+}, Pd^{2+}, V^{4+}, $AlCl^{2+}$, and partially $SnCl_2^{2+}$, undergo transformations according to schemes (2) and (2a) to a just noticeable extent (^{3}). The absence in H_2SO_4 solutions of isotopic exchange between $MPcH^+$ and Co^{2+}-60, which should proceed according to scheme (2a), as well as the study of reaction (2) with the participation of radioactive *CoPc and *ZnPc, showed that in aqueous acidic media stable phthalocyanines dissociate according to schemes (2) and (2a) irreversibly. Thus, phthalocyanines, despite the presence of appreciably expressed ionic dissociation in an acidic medium, cannot be characterized by the equilibrium constant (2) or (2a), owing to the irreversibility of the dissociation process in aqueous acidic media. However, the question of the order of stability of superstrong complex compou—

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* Pc is a conventional designation for the doubly charged anion of tetrabenzotetrazaporphin (phthalocyanine). M^{2+} is a metal ion.

of compounds is of exceptional value for the chemistry of complexes (2). It is also of interest for metal phthalocyanines, since, first, phthalocyanine as a ligand is extremely specific, and, second, phthalocyanines are related to a group of important physiologically active porphyrin derivatives (4,5). At present, methods that make it possible to characterize the stability of very strong complexes are only beginning to be developed. In those cases where it is impossible or difficult to determine the instability constant or to carry out thermochemical measurements of the bond energy of the metal with the ligand, the following methods are used to characterize the strength of the complex: 1) isotope exchange (6), 2) shift of the long-wavelength band corresponding to the electronic transition in the ligand (7), 3) shift of bands in the IR spectrum (8), 4) proton magnetic resonance (9), 5) rates of metal elimination under the action of acids (10). The last two methods are the least known.

Using phthalocyanine complexes as an example, we investigated the possibilities of method (5), having first studied the forms in which phthalocyanines exist in H_2SO_4 at different temperatures and certain properties of sulfuric acid as a solvent. It had previously been shown (11–13) that phthalocyanines in concentrated H_2SO_4 at ordinary temperature behave as monoacid bases:

Table 1

Exponents of the equilibrium constants pK for the dissolution reaction in H_2SO_4 of stable phthalocyanines at 25°

Phthalocyanine	$pK = -\lg K$	Phthalocyanine	$pK = -\lg K$
H_2Pc	1.65 ± 0.02	CuPc	1.64 ± 0.03
NiPcCl	1.46 ± 0.03	$CuPcCl_{15}$	2.82 ± 0.04
PdPcCl	1.52 ± 0.05	ZnPc	2.31 ± 0.04
PtPcCl	1.50 ± 0.06	$(SO_4)VPc$	1.92
CoPcCl	2.06 ± 0.04	$(HSO_4)AlPc$	2.60
		$(HSO_4)_2SnPc$	3.52

$$MPc_\tau + H_2SO_4 \rightleftarrows MPcH^+ + HSO_4^-. \tag{3}$$

The equilibrium constants of reaction (3) at 25°, calculated by the method $^{(11)}$, are given in Table 1. For phthalocyanines important from the industrial point of view, the constants were measured at different temperatures (Table 2). From a review of the values of the constants two important conclusions follow. The constants remain constant at all temperatures. This is yet another confirmation that concentrated H_2SO_4 exhibits the properties of an ideal solvent $^{(14–16)}$, owing to which the constancy of the ratio of the activity coefficients of the participants in reaction (3) is preserved and complete dissociation of the reaction product $(MPcH)HSO_4$ is achieved. The constancy of the constants proves the validity of scheme (3) and, together with spectral data $^{(12)}$, confirms the predominance in H_2SO_4 solutions of the $MPcH^+$ particle. The dependence of the exponents of the equilibrium constants (pK) of reaction (3) on the nature of the metal is determined, in our opinion $^{(11)}$, mainly by the nature of the chemical bonds of the metal with the ligand and their strength. The pK values make it possible to judge the formation and strength of σ- and π-bonds, and consequently also the stabil— of MPc, the presence of excess charge on the central ion, and the induction effect of substituents in the benzene ring (^{13}). Calculation of the change in thermodynamic functions (Table 3) in reaction (3) shows the presence of an endothermic

Table 2

Temperature dependence of pK of phthalocyanines in H_2SO_4

Temp., °C	CuPc	$CuPcCl_{15}$	ZnPcCl	ZnPc	CoPcCl
20	1.75 ± 0.04	–	–	2.31 ± 0.01	–
25	1.64 ± 0.03	–	–	–	2.07 ± 0.01
30	1.52 ± 0.02	2.81 ± 0.04	1.52 ± 0.05	–	–
40	1.43 ± 0.04	2.70 ± 0.03	1.45 ± 0.04	–	1.78 ± 0.01
50	1.29 ± 0.06	2.65 ± 0.03	1.40 ± 0.02	1.95 ± 0.03	1.66 ± 0.06
70	1.54 ± 0.02	2.70 ± 0.01	1.60 ± 0.03	–	1.72 ± 0.01

effect, which decreases as the solvating ability of phthalocyanine increases owing to the ability of the central ion to undergo additional coordination (ZnPc, ZnPcCl) (^{17}), owing to the presence of charge on the central ion ($^+$AlPcCl), or as a result of bond polarization (^{13}) upon chlorination of the benzene rings ($CuPcCl_{15}$). These assumptions are also confirmed by the magnitude of the entropy change in reaction (3).

Table 3

Change in thermodynamic functions upon dissolution of phthalocyanines in sulfuric acid

Phthalocyanine	ΔH°_{298}, cal/mol	ΔZ°_{298}, cal/mol	ΔS°_{298}, entropy units
CuPc	5700 ± 600	2235 ± 40	11.6 ± 2.1
CoPcCl	6810	2820	13.4
ZnPcCl	2930	2110	2.76
ZnPc	5230	3060	7.28
$^+$AlPcCl	4220	3542	2.26
$CuPcCl_{15}$	3660	3790	−0.44

As noted in the literature (^{5}), phthalocyanine is destroyed in H_2SO_4 solutions. The process is accompanied by complete hydrolysis at the macrocycle:

$$[H_2(C_8H_4N_2)_4H^+] + 8H_2O + 3H^+ \rightarrow 4C_8H_6O_2N + 4NH_4^+ + H_2. \qquad (4)$$

The coloration of $MPcH^+$ and H_2PcH^+ then disappears. We carried out a detailed study of the hydrolysis process of the macrocycle of free phthalocyanine (H_2PcH^+) and studied the influence of the nature of the central ion on hydrolysis. It was found that all labile phthalocyanines hydrolyze according to the hydrolysis scheme for free phthalocyanine.

Table 4

Rate constants of hydrolysis k_{op} of labile phthalocyanines at 25°

Phthalocyanine	Conc. H_2SO_4, mol/l	k_{op}, h^{-1}	Phthalocyanine	Conc. H_2SO_4, mol/l	k_{op}, h^{-1}
H_2Pc	17.65	0.137 ± 0.008	PbPc	17.65	0.109 ± 0.008
H_2Pc	15.40	5.30 ± 0.14	PbPc	15.40	5.08 ± 0.23
MgPc	17.65	0.113 ± 0.011	SnPc	17.65	0.145 ± 0.024
MgPc	15.40	3.40 ± 0.26	SnPc	15.40	2.26 ± 0.42

Phthalocyanine	Conc. H_2SO_4, mol/l	k_{op}, h^{-1}	Phthalocyanine	Conc. H_2SO_4, mol/l	k_{op}, h^{-1}
CdPc	17.65	0.103 ± 0.007	ClFePc	17.65	0.198 ± 0.014
CdPc	15.40	4.60 ± 0.13	ClFePc	15.40	0.566 ± 0.018 (light)
AgPc	17.65	0.170 ± 0.010	ClFePc	15.40	0.550 ± 0.025 (dark)
AgPc	15.40	0.78 ± 0.20	Cl_2SnPc	17.65	0.0155 ± 0.0014
			Cl_2SnPc	15.40	0.160 ± 0.018

Reaction (2a) proceeds rapidly; the rate-limiting stage is hydrolysis of the macrocycle H_2PcH^+ according to reaction (4), which is described by a first-order kinetic equation:

$$-\frac{dC_{\text{MPc}}}{dt} = k_{\text{op}} \cdot C_{\text{MPc}}.$$

k_{op} depends on the concentration $[H_3O^+]$ and is related to $[H_3O^+]$ by the equation

$$k_{\text{op}} = k_{\text{ist}} \cdot [H_3O^+]^4.$$

Tables 4-6 give the values of k_{op}, from which, using Brand' s equation (^{18}), one can find k_{ist}, independent of the concentration of H_2SO_4. The high order of the reaction with respect to $[H_3O^+]$, also characteristic of the cleavage of etioporphyrins in H_2SO_4 (^{10}), indicates a complex mechanism of hydrolysis of H_2PcH^+. A study of the mechanism of hydrolysis of stable metallophthalocyanines, using the least robust $(HSO_4)_2SnPc$ as an example (Table 6), showed that they also obey equation (1), but the rate-limiting stage of hydrolysis is the detachment of the metal (2a), proceeding with rupture of che-

Table 5

Hydrolysis rate constants (k_{op} $h^{-1} \cdot 1000$) of stable phthalocyanines

Phthalocyanine	18.2 M H_2SO_4, 100°	18.2 M H_2SO_4, 120°	16.20 M H_2SO_4, 100°	16.20 M H_2SO_4, 120°
CuPc	10,4$±0, 4|185±12|—|815±57||*ZnPc*|280±20|3930±130|—|—||(*SO*_{4})*VPc*|—|—|2200±60|—|			

Table 6

Dependence of the hydrolysis rate constant of Cl_2SnPc at 40° on H_2SO_4 concentration

H_2SO_4, mol/l	$k_{op} \cdot h^{-1}$	H_2SO_4, mol/l	$k_{op} \cdot h^{-1}$	H_2SO_4, mol/l	$k_{op} \cdot h^{-1}$
14,10	0,328$±0, 035|16, 05|0, 287±0, 025|17, 25|0, 102±0, 005||15, 08|0, 326±0, 018|17, 00|0, 160±0, 008|17				

of three metal–nitrogen coordination bonds; in this case $k_{op} = k_{ist}[H_3O^+]^2$. Stable phthalocyanines undergo noticeable hydrolysis only at high temperatures (Table 5). In terms of the ease of detachment of the central ion in phthalocyanines, the metals are arranged in the series:

$$V^{4+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Pd^{2+} > Pt^{2+},$$

in which the ions are arranged in the order of strengthening of the coordination bonds M–N, accompanied by increasing neutralization of the basic properties of the four intracyclic nitrogen atoms ([11]), responsible for reactions (2) and (2a). Phthalocyanine Pt^{2+} possesses the greatest strength; $(HSO_4)AlPc$ has extremely high strength. The series given above completely reproduces the series of the strength of the metal bond in porphyrin complexes: $Ba^{2+} > Mg^{2+} > Mn^{2+} > Fe^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Pd^{2+}$, established from the shift of λ_{max} in absorption spectra ([7]) and from the rate of metal detachment ([10]). This circumstance serves as weighty evidence in favor of the fact that, in a series of complexes of the same type, the rate of detachment of the central ion under proton attack may be a reliable method for characterizing the strength of the metal bond with the addend.

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