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Complex compounds of titanium(IV) and methylphenols in concentrated aqueous sulfuric acid solutions

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The formation of the complexes of Ti(IV) and 2-, 3- and 4-methylphenol (MePh) have been investigated. The composition and the stability constants of the complexes formed were determined, both immediately after contact of the reactants as well as after a stabilization period after which the absorbance of the solution was no longer time-dependent. Ti(IV) and methylphenol complex compounds in 85% and 96% sulfuric acid have wide absorption bands in the visible part of the spectrum, with absorption maxima in the region of 410-480 nm. The composition of the Ti(IV) and 2-, 3- and 4-MePh complexes in 85% sulfuric acid was determined by the Job method immediately after mixing the reactants. The components ratio was 1:1 in all the investigated cases. The obtained constants are: $\log K = 3.05$ (Ti-2-MePh), $\log K = 2.64$ (Ti-3-MePh), and $\log K = 3.12$ (Ti-4-MePh). The components ratio of Ti-2-MePh in 96% sulfuric acid, as determined by the Job method, 2 h after mixing the reactants, was also 1:1. The corresponding stability constant was: $\log K = 2.51$.

Many data can be found in the literature on the complex formation of some transition metals with hydroxybenzenes in concentrated aqueous solution of mineral acids.[1-15] Titanium was found to form colored complexes with monohydroxybenzene,[14] 1,2-dihydroxybenzene,[1], 1,3- and 1,4-dihydroxybenzene,[12-16] and 1,3,5-trihydroxybenzene,[16] mostly with a 1:1 mole ratio. A general characteristic of all these complexes is the considerable time-dependent change in the visible region of their absorption spectra, as well as a noticeable effect of the acid concentration on the color intensity and its perseverance. This is ascribed to the complex reaction between the acid and hydroxybenzene resulting not only in protonation,[17-19] but also in sulfonation and disulfonation,[19-21] *i.e.*, also to the formation of sulfonic and disulfonic acids.

In some earlier works, it was proposed that these colored reactions form the basis for the analytical determination of metals, firstly Nb, Ti and W.[2,3,5] The practical application of these reactions has lost its importance after the development of new methods. However, many questions, concerning the type of reaction in the system, the nature and the site of bonding, the composition and the stability of complexes still have to be answered. In this paper, the results of an investigation of the composition and stability of Ti and methylphenol complexes, along with some suggestions on the possible type of bonding in these compounds, are presented.

EXPERIMENTAL

All spectrophotometric measurements were performed on a spectrophotometer Carry 17D with 1 cm quartz cells. Aqueous solutions of sulfuric acid with concentrations less than 96% were prepared diluting concentrated acid with distilled water. The solution concentrations were determined by measuring the conductivity.[22] A titanium standard solution (0.01 mol/dm^3) was prepared from an exactly weighed quantity of TiO_2 that was melted in a platinum crucible with $K_2S_2O_7$, before being dissolved in 96% sulfuric acid. Methylphenols (Merck *p.a.*) were redistilled before use. Methylphenols stock solutions (0.1 mol/dm^3) were prepared by dissolving exact quantities of the corresponding substances in distilled water. All working solutions were made by diluting small volumes of the stock solution in sulfuric acid of the appropriate concentration. All experiments were performed at ambient temperature. The time dependent spectral changes of methylphenols dissolved in sulfuric acid have been described elsewhere.[23] The composition of the methylphenol and titanium complexes in sulfuric acid was determined after various intervals. Measurements were performed 1 min after mixing the reactants and after stabilization of the system, *i.e.*, after the end of the absorbance changes. All measurements were recorded with respect to a reference solution of the corresponding concentration.

RESULTS

The absorption spectrum of the 2-MePh-Ti complex in 85% sulfuric acid has a wide band in the visible region, with a maximum at about 460 nm (Fig. 1). The position of the absorption maximum, as well as its absorbance, changes with time and is shifted, after 7 h, to 480 nm. The complex compound 3-MePh-Ti has an absorption maximum at 450 nm. After stabilization of the complex, the absorbance at the maximum is considerably lower whereas the maximum shifts batochromically to approx. 480 nm. The absorption spectrum of the complex 4-Me-Ph-Ti has a maximum at 470 nm. After 4 h this maximum shifts to 450 nm. The time dependent absorbance diminution is also evident here. The composition of the complex was determined by the Job method (Table I). The total concentration of the reactants was constant: $c_{tot}=0.001$ mol/dm^3.

TABLE I. Composition and log *K* values of methylphenol and titanium complexes in 85% sulfuric acid

Methylphenol	Composition of the complex with titanium after 1 min	Composition of the complex with titanium after 20 h	Mol. abs. [mol^{-1}cm^{-1}]	λ [nm]	log *K*
2-Methylphenol	1:1	--	5480	460	3.05
3-Methylphenol	1:1	--	4840	450	2.64
4-Methylphenol	1:1	1:1	6280	470	3.12

The molar absorptivity, ε, was determined at constant titanium concentration by varying the concentration of the methylphenols from 9.0×10^{-4} to 9.8×10^{-2} mol/dm^3 until a constant absorptivity value was achieved. Knowing ε, the reactants ratio and initial concentrations of the reactants, after checking the validity of the Beer law, the stability constant of the complex was determined from the equation: $K_s = \frac{M_m L_n}{M^m L^n}$ where: M and L are the metal and ligand equilibrium concentration, respectively; $M_m L_m$ is the concentration of the complex, and m and n represent the number of metal atoms and the ligand molecules involved in the reaction, respectively.

The composition and log K value for titanium 3-MePh and 4-MePh complexes were determined by the same procedure. To investigate the posible effect of ageing on the composition of the formed complexes, the ratio of metal and ligand for 4-MePh-Ti complex in 85% sulfuric acid was determined 20 hours after mixing the reactants. The results obtained by the Job method point to the formation of a 1:1 molar complex. Titanium and 2-, 3- and 4-methylphenol complexes were also investigated in 96% sulfuric acid. Due to the time dependent absorbance changes being more rapid than in 85% acid, the composition of the complex was determined only after the period needed for stabilization of the absorbance. The composition of the Ti-2-MePh complex was determined by the Job method 120 min after mixing the reactants. The obtained ratio was 1:1, the same as in 85% acid, and log $K = 2.51$. the molar absorption coefficient, 4440 $\mathrm{mol}^{-1}\mathrm{cm}^{-1}$, was determined at 420 nm. The composition of the complexes of titanium with 2- and 3-methyl phenol in 96% H_2SO_4 were also studied by the Job method. After 150 and 300 min complexes having a 1:1 composition were obtained. We were not able to determine the pK values of these complexes. (For the determination of the pK the molar absorptivity, ε, must be known, which is not possible because of the constant rise in the absorbance upon the addition of excessive concentration of titanium ions.) For all the investigated titanium-methylphenol complexes in 85% and 96% sulfuric acid, maxima of the Job curves were observed at a metal ligand ratio of

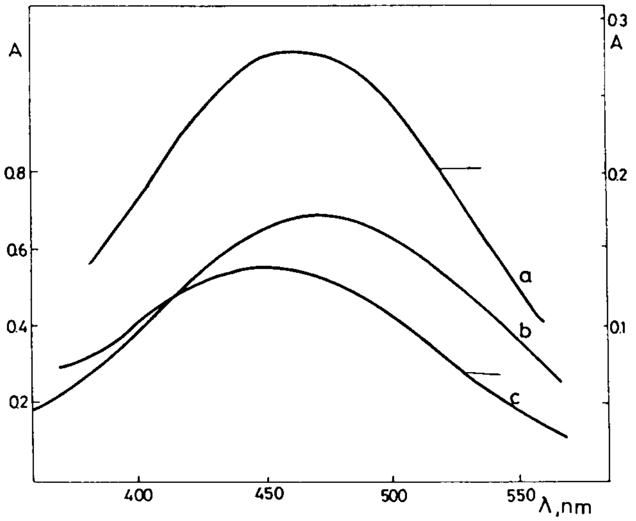


Fig. 1. Absorption spectra of Ti-methylphenol complexes in 85% H_2SO_4 taken 1 min after mixing the components;the concentrations were: a) Titanuim 9 × 10^{-4} mol/dm^3,2-methylphenol 1 × 10^{-4} mol/dm^3; b) Titanium 8 × 10^{-4} mol/dm^3, 4-methylphenol 2 × 10^{-4} mol/dm^3; c) Titanium 9 × 10^{-4}mol/dm^3, 3-methylphenol 1 × 10^{-4} mol/dm^3.

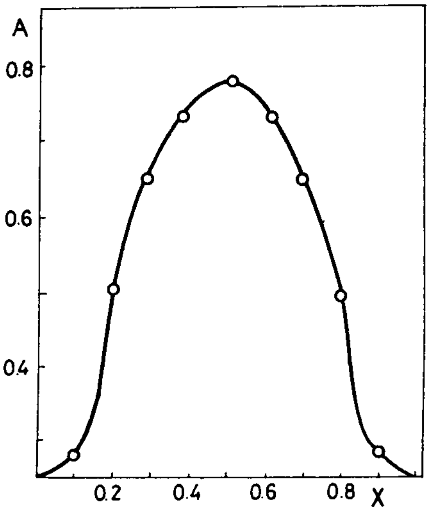


Fig. 2. Job curve for Ti : 2-methylphenol in 85% H_2SO_4.Total concentration of reactants was 10^{-3}mol dm^{-3}. $x = c_{o\text{-}c}/(c_{Ti} + c_{o\text{-}c})$

1:1. However, in most cases, the inflexion points and parabolic parts of the Job curves were observed within the range od X values ($X=L/M+L$) close to 0 and to 1 (Fig. 2). According to the literature data,[24] Job curves of this shape are indicative of the formation of a polynuclear complex with $m = n > 1$.

DISCUSSION

The literature data on metal and hydroxybenzene complexes in concentrated aqueous solutions of strong mineral acids support the conclusion that such complexes are formed mainly by some transition metal, such as Ti, V, Mo, Nb, Ta, as well as W, Sb, As, and U. No data have been found on hydroxybenzenes forming complexes in strong acid with other metals, as for example Cu, Ni, Co, Zn, Cr, Mn, Fe, *etc.*, although, it is known that these metal form complexes with other ligands in aqueous solutions,[25,26] and even in concentrated H_2SO_4 aqueous solutions. On the other hand only benzene derivatives having oxygen in the substituent group (OH, OCH_3 and similar oxygen containing groups) form colored complexes with metals in concentrated aqueous solutions of mineral acids. Such complexes can therefore be formed by all mono-, di- and trihydroxy and alkoxy benzenes, as well as the nitro, amino and halogeno derivatives of hydroxybenzenes (except some *ortho* derivatives) and other similar compounds.[1-15]

Ortho-derivatives of hydroxybenzenes without intramolecular hydrogen bond between neighboring groups, such as *o*-phenylphenol[1] or *o*-methylphenol, form colored complexes with metals in concentrated mineral acid solutions. On the contrary, no such complexes with *o*-aminophenol or *o*-nitrophenol have been observed.[1] The only exception are complexes with ligands that have an OH group in *ortho* position, such as catechol (1,2-dihydroxybenzene). However, with respect to the protonation its behavior is specific.[18] The color fading of the already formed complex compounds has been observed in subsequent substitution of phenol (for example by sulfonation) with a group in the *ortho*-position capable of intramolecular bonding.[27] Therefore, for a colored complex to be formed it is necessary to have a free oxy-group in the organic ligand. If such a group does not exist or is blocked by intramolecular bonding no complexation can take place.

In most cases, coloration of the investigated systems was observed only when the solvent acid concentration was sufficiently high. Although it depends, to some extent, on the kind of metal and ligand, generally, coloration is not possible until a relatively high acidity of the solvent used is achieved. Most of these investigations were performed in sulfuric acid solutions. Metal and phenol colored complexes are also formed in perchloric, hydrochloric and other mineral acids,[3,12] but only at H_0 values equal to or higher than that of 60% sulfuric acid.

The color intensity of the formed complex is discernible time-dependent. This has been emphasized in the majority of the papers cited, and ascribed to the transformation of the organic ligand in acid medium. More detailed explanations have been given elsewhere.[14,23,27] However, at a constant ratio of the reactant concentrations and after the same reaction time, the coloration intensity increases with increasing acidity of the medium.

The form of a metal ion in the solution can be affected by increasing the acid concentration. Although reliable data, especially for high acidity solutions, are scarce, there is no doubt that the metal ion changes its form with changes in the medium acidity.[3,7,11,13,28-35] According to literature data, in sulfuric acid solutions titanium primarily forms sulphate or aqueous complexes. Starting from 80% sulfuric acid, the SO_4^{2-} ion concentration and the water content sharply decrease with increasing acid concentration,[36] while the bisulfate ion becomes the main nucleophile in the system, probably leading to the observed change of titanium form in the solution. This should be valid for other metals (V, Mo, Nb) that may be expected to appear in many more different forms than titanium due to the changeable oxidation state of molybdenum[7,10,13] or the various degree of niobium polymerization.[29]

Although the color intensity could be affected by changes in the metal forms, the increasing acidity of the solution affects the color of the complex, no matter what kind of acid is used (H_2SO_4, $HClO_4$, HCl). Since it is hard to assume that the change of the metal ions with changing acid concentration is the same in different acid media, the increasing color intensity of the complex can hardly be ascribed to the possible change in the form of the metal ions. The fairly regular change of the color intensity with increasing solution acidity is more probably due to some, also regular, change in the system. Since this type of complexes is typical only for oxy derivatives of benzene it seems logical to ascribe the formation of such complexes to the protonation reaction of the oxygen bonded to the aromatic ring. Almost all protonation constant values of these compounds correspond to acidities exceeding 60% sulfuric acid.[17,20,23,33,37,38] Benzoic acid, for example, although it can be protonated on the oxygen, does not form this kind of complex because its oxygen atom is not directly bonded to the ring. Practically no oxygen protonated phenols or formation of colored complexes have been observed below this acidity value. It is well known that many oxy – derivatives of benzene can be protonated on the aromatic ring, but hydroquinone and *p*-

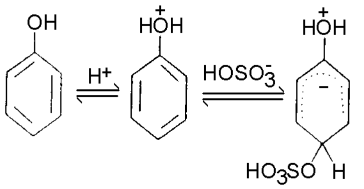
dimethoxybenzene undergo protonation exclusively on the oxygen,[17] whereas with respect to complex formation they behave as any other oxy – derivative of benzene. These facts emphasize the importance of oxygen protonation for complex formation.

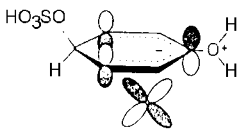
The predominant role of the oxy-group in the formation of the investigated complexes is also shown by the fact that complexes are not formed in the case when, besides the oxy-group, another substitutent capable of intramolecular bonding is present in the *ortho*-position.

Colored complexes of substituted phenols and titanium are formed in strong acid, sulfuric and/or perchloric, media. Under these conditions, a substantial concentration of protonated hydroxybenzenes ($pK[ArOH]^+ \approx -7$) is present, which is important for the formation of colored complexes.

Assuming the titanium ion in sulfuric acid solutions to be tetrahedrally complexed by highly concentrated ligand water molecules as well as by sulphate and bisulfate ions, the complex obtained should be a standard, uncolored, d^0 one. Color would appear only after new electrons were introduced into the system by some new ligand. However, protonated phenol, as an oxygen ligand, could hardly be a good electron donor. On the other hand, it is well known that phenols are coordinated by transition metals through a π-electron system.[39] Such interaction is enhanced by partial localization of the aromatic π-electrons, whereby η^5-cyclohexadienyl anion system acts as the ligand.

In protonated phenol the interaction with titanium can hardly be sufficient to stabilize the localization of electrons in a part of the molecule far from the center of the positive charge, -OH^+ group. Bearing in mind that bisulfate ions predominate in the solution, the following pattern for its reaction with the protonated phenol can be inferred:





At sufficiently high bisulfate or perchlorate ion concentrations, a σ-complex is formed by the bonding an anion to the most electrophilic atom in the ring. A kind of Wilkinson's intermediate, that can form π-complexes with transition metal atoms, is formed in this way.

The frontier orbital for p-electrons in the η^5-cyclohexadienyl intermediate has a symmetry suitable for interaction with the *d* orbital belonging to the triple degenerated group in the tetrahedral (or octahedral) symmetry group.

The C-sulfatized intermediate is enriched by new electrons introduced by the bisulfate anion and represents very suitable ligand. Positions 2,4, and 6 in a monohydroxybenzene ring are the most favorable for binding a sulphate group, especially the position 4 because the highest electron density of the anion π-system on C-1 is also stabilized by the attraction of the neighboring positive charge on the oxygen.

The efficiency of the intermediate formation can be considerably affected only by strongly electron attracting substituents in the *ortho* position, such as NH_3^+, or the NO_2 group, which decrease the reactivity towards C-sulfatization by inducing an increase in the electron density on the very same atoms that were formerly most suitable for nucleophilic attack.

ИЗВОД

КОМПЛЕКСНА ЈЕДИЊЕЊА ТИТАНА(IV) СА МЕТИЛФЕНОЛИМА У КОНЦЕНТРОВАНИМ ВОДЕНИМ РАСТВОРИМА СУМПОРНЕ КИСЕЛИНЕ

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Проучено је формирање комплекса Ti(IV) са 2-, 3- и 4-метилфенолима (MePh). Одређени су састав и константе стабилности формираних комплекса, непосредно након контакта реактаната и након периода стабилизације када се апсорбанца раствора више не мења са временом. Комплексна једињења Ti(IV) и метилфенола у 85% и 96% сумпорној киселини имају широке апсорпционе траке у видљивом делу спектра, са апсорпционим максимумима у области од 410-480 nm. Састав комплекса Ti(IV) са 2-, 3- и 4-MePh у 85% сумпорној киселини одређен је Job-овом методом непосредно након мешања реактаната. Однос компонената је у свим случајевима био 1:1. Добијене константе стабилности су: $\log K = 3{,}05$ (Ti-2-MePh), $\log K = 2{,}64$ (Ti-3-MePh), и $\log K = 3{,}12$ (Ti-4-MePh). Однос компонената у Ti-2-MePh у 96% сумпорној киселини, одређен Job-овом методом 2 сата након мешања реактаната био је такође 1:1. Одговарајућа константа стабилности је била: $\log K = 2{,}51$.

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REFERENCES

1. P.H. Caulfield, R.J. Robinson, *Anal. Chem.* **25** (1953) 982
2. L. Ikenberry, J.L. Martin, W.J. Boyer, *ibid.* **26** (1953) 1340
3. S.Ya. Shnaiderman, G.I. Khrustalev, *Zh. Obschch. Khim.* **29** (1957) 20
4. G.R. Waterbury, C.E. Bricker, *Anal. Chem.* **30** (1958) 1007
5. J.P.Mc Kaveney, *ibid.* **33** (1967) 744
6. S.Ya. Shaiderman, *Ukr. Khim. Zh.* **32** (1967) 92
7. G.El Inany, D.S. Veselinović, *J. Electroanal. Chem.* **32** (1971) 437
8. S.Ya. Shnaiderman, A.M. Pleskonos, *Ukr. Khim. Zh.* **38** (1972) 1083
9. S.Ya.Shaiderman, A.M. Pleskonos, *ibid.* **39** (1973) 641
10. D. Marković, D. Veselinović, S. Milenković, *J. Electroanal. Chem.* **73** (1976) 109
11. D. Veselinović, F. Bajraktari, D. Marković, *Z. Phys. Chemie, Leipzig* **259** (1978) 295
12. F. Bajraktari, D. Marković, D. Veselinović, *Glasnik Hem. društva Beograd* **46** (1981) 329
13. D. Marković, D. Veselinović, M. Obradović, *Can. J. Chem.* **64** (1986) 2334
14. D. Marković, D. Veselinović, *J. Serb. Chem. Soc.* **53** (1988) 29
15. M. Obradović, D. Veselinović, D. Marković, *ibid.* **56** (1991) 161
16. M. Obradović, D. Veselinović, D. Marković, *Glasnik Hem. društva Beograd* **49** (1984) 453
17. E.M. Arnett, C.Y. Wu, *J. Am. Chem. Soc.* **82** (1960) 5660
18. G.A. Olah, Y.K. Mo, *J. Org. Chem.* **38** (1973) 353
19. A. Koeberg-Telder, H.J.A. Lambrechts, H. Cerfontain, *Rec. Trav. chim.* **102** (1983) 293

20. H. Cerfontain, H.J.A. Lambrechts, Z.R.H. Schaasberg-Nienhuis, R.G. Coombes, P. Hadjigeorgiu, G.P. Tucker, *J. Chem. Soc. Perkin Trans.* **2** (1985) 659
21. H.J.A. Lambrechts, Z.R.H. Schaasberg-Hienhuis, H. Cerfontain, *ibid.* (1985) 669
22. H.E. Darling, *J. Chem. Eng. Data* **9** (1964) 421
23. D.M. Marković, D.A. Marković, D.S. Veselinović, *J. Serb. Chem. Soc.*, in press
24. C.D. Johnson, A.R. Kartritzky, B.J. Ridgewell, N. Shakir, A.M. White, *Tetrahedron* **21** (1965) 1055
25. D.S. Veselinović, D.L. Malešev, *Glasnik Hem. društva Beograd* **43** (1978) 545
26. D. Veselinović, D. Malešev, *ibid.* **48** (1983) 159
27. D.S. Veselinović, D.A. Marković, D.M. Jovanović, *ibid.* **43** (1978) 225
28. G.I. Gridtschina, *Zh. Neorg. Khim.* **11** (1966) 299
29. B.I. Nabivanec, *ibid.* **9** (1964) 1079
30. S.V. Elinson, *Spektrofotometria Niobiuma i Tantala*, Atomizdat, Moskva 1973
31. H.T.S. Button, G. Wellford, *J. Chem. Soc.* (1940) 895
32. G.A. Richnitz, H.A. Laitinen, *Anal. Chem.* **33** (1961) 1473
33. A.K. Babko, B.I. Nabivanec, *Zh. Neorg. Khim.* **2** (1957) 2085
34. D. Perrin, *Organic Complexing Reagents,* Interscience, New York 1964, p. 293
35. F. Chauveau, *Comptes rendus* **242** (1956) 2154
36. R.A. Cox, *J. Am. Chem. Soc.* **96** (1974) 1059
37. M. Liler, *Reaction Mechanisms in Sulphuric Acid*, Academic Press, London, 1971
38. C.H. Rochester, *Acidity Function*, Academic Press, London, 1970
39. D.J. Cole-Hamilton, R.J. Young, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* (1976) 1995.