

THERMOANALYTICAL STUDY OF SOME SALTS OF 3d METALS WITH d-TARTARIC ACID

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Abstract

The processes of dehydration and decomposition of the Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) salts of d-tartaric acid were studied by using TG, DTG and DTA methods in air or in argon, and also IR-spectroscopy.

The equations of thermal decomposition were established. For the dehydration processes, the kinetic parameters n , E and $\ln A$ were determined.

Keywords: d-tartaric acid salts, 3d metals, IR spectra, thermal analysis

Introduction

Tartaric acid is one of the basic components of waste products from the food and wine industries. Tartaric acid can form three kinds of optical isomers: *d*, *l* and meso. Many of its salts have interesting magnetic, optical and catalytic properties.

In a well-known study by Ablov and Popovici [1] on the salt of Cu(II) with tartaric acid, the anion structure was represented by the formula $(\text{Cu}_4\text{Tart}_3)^{3-}$, i.e. a polynuclear complex structure was advanced. Ciurikova *et al.* [2] studied the influence of *pH* on the composition of the tartrates of Co^{2+} and Ni^{2+} , and found that at $\text{pH} < 7$ the normal $\text{M}(\text{Tart})$ salts appeared, but different forms, such as $\text{M}(\text{Tart})_2$, may also be formed, depending on the metal/acid ratio and the *pH* range. Unfortunately, the authors did not mention which optical isomers were used. A short thermoanalytical study of Ca salts with the different optical isomers of tartaric acid was recently published [3].

Several papers [3–7] deal with investigation of the structure of oxyacid salts, including tartaric acid, by IR spectroscopy. As an example, Kirschner *et al.* [4] studied Seignette salt; they established from the IR spectra that the 3550 cm^{-1} absorption band is to be attributed to OH groups of the crystallization water and

the 3192 cm^{-1} band to the OH groups of the acid. For Cu(II) tartrate, they found that the splitting of the peak at 1097 cm^{-1} results from the two peaks of the secondary OH groups at 1080 cm^{-1} , while the shift in the 1750 cm^{-1} band of tartaric acid to 1654 cm^{-1} is due to the coordination process.

Pribilov *et al.* [8, 9] found that the final products of thermal decomposition of the *d*-tartrates of Co, Ni, Cu and Zn are the corresponding oxides. Only the Cu(II) salt can yield the metal.

The aim of the present study is to shed new light on the thermal properties and IR spectra of the *d*-tartrates of 3*d* metals.

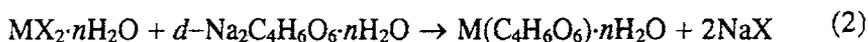
Experimental

Materials

The complexes of *d*-tartaric acid with 3*d* metals were prepared by interaction of the acid or of its sodium salts with simple salts of the 3*d* metals in aqueous medium, as follows from the equations



$M = \text{Mn, Fe, Co, Ni, Cu, Zn}$



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The results of the elementary analyses of the substances obtained are given in Table 1. The metal contents of the salts were determined by usual chemical analysis methods [10, 10a].

Methods

TG, DTG and DTA curves in air were obtained by means of a computer Derivatograph C (sample mass 50 mg; heating rate 5°C min⁻¹). A DuPont 1090 Thermal Analyzer with a 951 TGA was used for TG and DTG analysis in an Ar atmosphere (sample mass 40 mg; heating rate 5°C min⁻¹; Ar flow rate = 60 ml min⁻¹). Kinetic parameters were calculated by using the embodied Derivatograph C routine [11] and are given in Table 3. IR spectra were registered on an M-80 spectrophotometer.

Results and discussion

IR spectra

The IR spectrum of *d*-tartaric acid (No. 7 in Table 2) contains absorption band of alcoholic-OH and carboxylic-OH in the range 3100–3600 cm^{-1} ; below

Table I Elementary analysis results of the investigated substances

No.	The substance	Determined/%			Calculated/%			Residue
		M	C	H	M	C	H	
1	Mn(C ₄ H ₄ O ₆)·2H ₂ O	22.54	19.67	3.27	22.97	20.09	3.37	Mn ₃ O ₄
2	Fe(C ₄ H ₄ O ₆)·3H ₂ O	22.19	17.91	3.45	21.64	18.62	3.90	Fe ₃ O ₄
3	Co(C ₄ H ₄ O ₆)·2H ₂ O	23.87	20.18	3.86	24.24	19.76	3.32	Co ₃ O ₄
4	Ni(C ₄ H ₄ O ₆)·4H ₂ O	21.52	16.99	4.05	21.05	17.23	4.33	NiO
5	Cu(C ₄ H ₄ O ₆)	28.27	21.95	2.11	28.08	21.78	2.28	CuO
6	Zn(C ₄ H ₄ O ₆)·3H ₂ O	25.66	18.09	3.59	25.34	18.04	3.86	ZnO

1650 cm^{-1} , a few bands are observed which can be assigned to valence vibrations, $\nu(\text{CO})$, and to angular deformation, $\delta(\text{C-OH})$. These absorption bands are characteristic for *d*-tartaric acid, so that the structural changes produced by its reactions with 3*d* metals are reflected in the structure of these bands.

In the salts, the disappearance of the $\nu(\text{OH})$ (RCOOH) band in the 3600 cm^{-1} region is observed; the splitting of the 1700 cm^{-1} band in $\nu_{\text{asim}}(\text{C-O})$ and $\nu_{\text{sim}}(\text{C-O})$ points to the chelation of *d*-tartaric acid with 3*d* metals, the acid acting as a tetradentate ligand. Important changes are also observed in the range 1300–1600 cm^{-1} , indicating the formation of M–O bonds, i.e. metal complex formation.

The IR spectra of salts heated to 90°C show the complete disappearance of the $\nu(\text{OH})$ bands at 3200 and 3400 cm^{-1} . Some shifts were observed for the bands connected with hydrogen-bonding in the complexes (at 1670, 1090 and 1045 cm^{-1}). When the salts are heated until the complete elimination of water (115–117°C), the absorption bands are more pronounced, but not shifted as compared with those obtained for the substances heated to 90°C. Further, no supplementary splitting of the bands is observed, which indicates that they are simple isomers, not racemic.

In the IR spectrum of $\text{Co}(\text{Tart})\cdot 2\text{H}_2\text{O}$, for instance, two large absorption bands are found in the $\nu(\text{OH})$ (3100–3350 cm^{-1}) and $\nu_{\text{sim}}(\text{C=O})$ (1625–1650 cm^{-1}) regions, which can be attributed to crystallization water. Since the coordination number of Co^{2+} is 6, it follows that *d*-tartaric acid occupies 4 coordination sites, the remaining two being occupied by two water molecules. The frequencies $\nu(\text{OH})$ (3300 cm^{-1}) and $\delta(\text{OH})$ (1300 cm^{-1}) are no longer present (pointing to deprotonation, but with characteristic shifts for coordination: $\Delta\nu_{\text{asim}}(\text{C-O}) = -70 \text{ cm}^{-1}$ and $\Delta\nu_{\text{sim}}(\text{C-O}) = +20 \text{ cm}^{-1}$). New absorption bands characteristic of M–O bonds appear at approximately 300, 400 and 520 cm^{-1} . The frequency $\nu(\text{OH})$ (R-OH) at 3620 cm^{-1} is present, showing that the alcoholic-OH groups of tartaric acid do not take part in the coordination process or form hydrogen-bonds. However, merely from the above data it is difficult to say whether the structure of the complex is monomeric or polymeric.

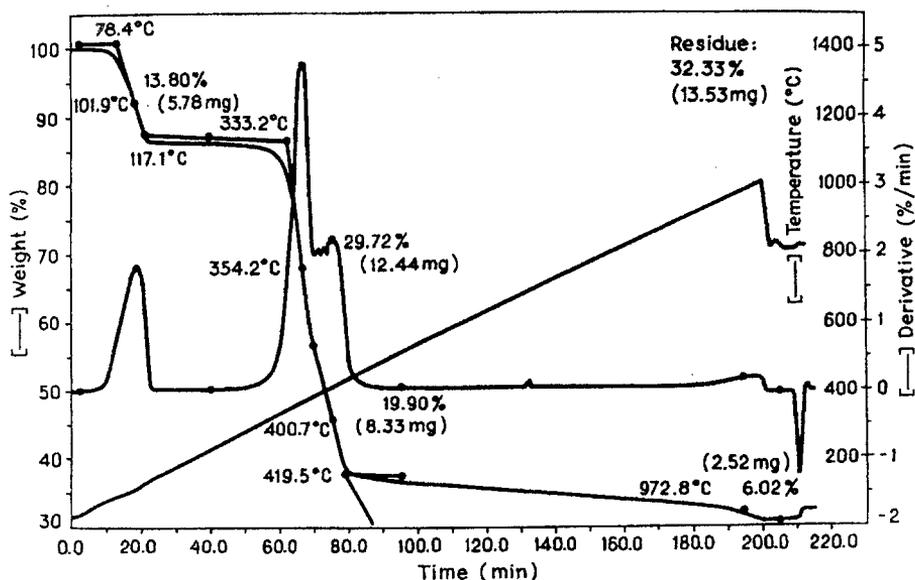
Most of the IR spectra of the 3*d* metal salts of *d*-tartaric acid are similar, indicating a presumably octahedral structure, with the acid acting as a tetradentate ligand and with two coordinated H_2O molecules. Only the data on the $\text{Cu}(\text{II})$ complex do not conform to this assumption, the latter most probably having a tetrahedral structure (Table 2).

Thermal analysis

For all the studied complexes, the thermograms are similar with respect to the dehydration step both in air and in Ar. Differences appear in the decompositions of the anhydrous salts and consequently in the natures of the residues. To

Table 3 Kinetic parameters of the dehydration steps of the $M(C_4H_4O_6) \cdot nH_2O$

No.	Reaction order	Activation energy $E/kJ M^{-1}$	Pre-exp. factor lgA
	n		
1. Mn	0.82	88.0	11.39
2. Fe	0.94	100.5	13.18
3. Co	0.95	91.0	12.03
4. Ni	2.03	42.9	4.95
5. Zn	0.86	110.3	15.76

**Fig. 1** Thermoanalytical curves of $Mn(C_4H_4O_6) \cdot (2-x) \cdot H_2O$, $x=1/12$ (argon, DuPont 1090)

illustrate this, the thermal curves of the Mn and Co salts (Figs 1 and 2) and the derivatograms of the Co and Zn salts (Figs 3 and 4) are presented. The general equation for the thermal decomposition of the studied salts can be written as:

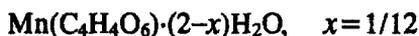


Only Zn tartrate eliminates the crystal water in two steps.

The 'moisture-free' mass obtained after dehydration and attributed to $M(\text{Tart})$ was taken as reference in the evaluation of the results obtained on both instruments. The derivative curve (DTG) was considered, where not clear-cut differences were observed between the dehydration and decomposition steps.

Manganese salt

The mass change due to water loss in Ar atmosphere (Fig. 1) corresponds to less than 2 molecules. Organic decomposition between 240 and 480°C takes place in two steps (evidenced on derivative). The residue at 480°C could be attributed to MnO₂. Up to 1000°C, this decomposes to MnO, which is stable in Ar. After cooling to 800°C and air admission, this is readily oxidized to Mn₃O₄. A similar process takes place in air. Organic decomposition steps are not separated in the DTG curve. The residue at 420°C corresponds to Mn₂O₃, which further decomposes to Mn₃O₄ as reported by Puerta and Valerta [12]. The formula of the initial complex can be assumed to be



Iron salt

Less than 3 water molecules are lost between 20 and 150°C. Two unresolved steps can be seen up to 300°C (both in air and in Ar). The residue in air at 300°C is Fe₂O₃. In Ar, at almost the same temperature, a residue corresponding to FeO(OH) is found, which subsequently decomposes to a nonstoichiometric oxide FeO_x at around 750°C. The assumed formula is

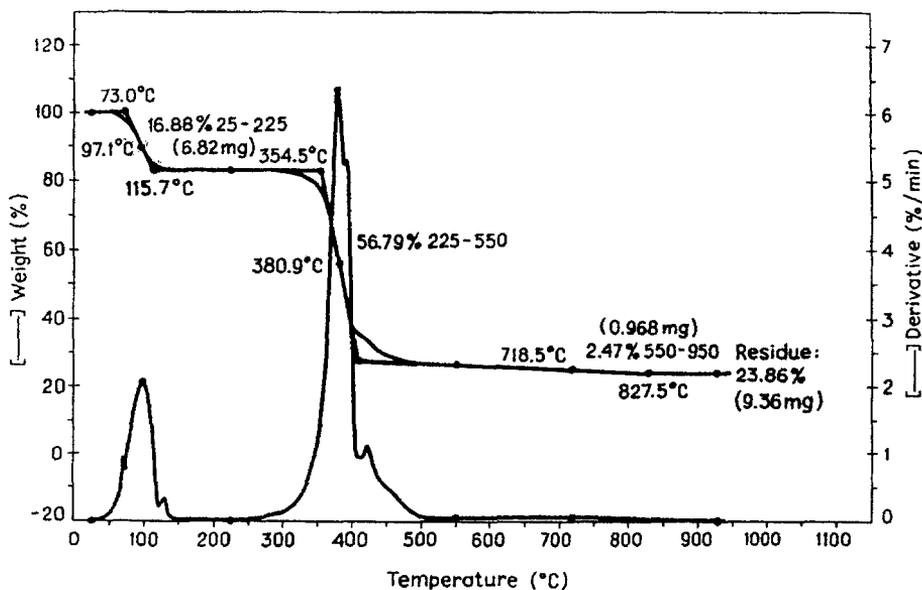
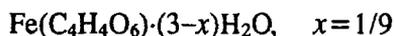


Fig. 2 Thermoanalytical curves of $\text{Co}(\text{C}_4\text{H}_4\text{O}_6) \cdot (3-x) \cdot \text{H}_2\text{O}$, $x=2/9$ (argon, DuPont 1090)

Cobalt salt (Figs 2 and 3)

The dehydration process is identical in air and in Ar, the mass loss pointing to less than 3 water molecules. The decomposition takes place at a higher rate in air, leading to Co_3O_4 , which at about 1000°C gives a residue of CoO . In Ar at 550°C , the sample mass corresponds to $\text{CoO}_{0.5}$, which further decomposes to metallic Co up to 950°C . The initial complex formula may be assumed to be

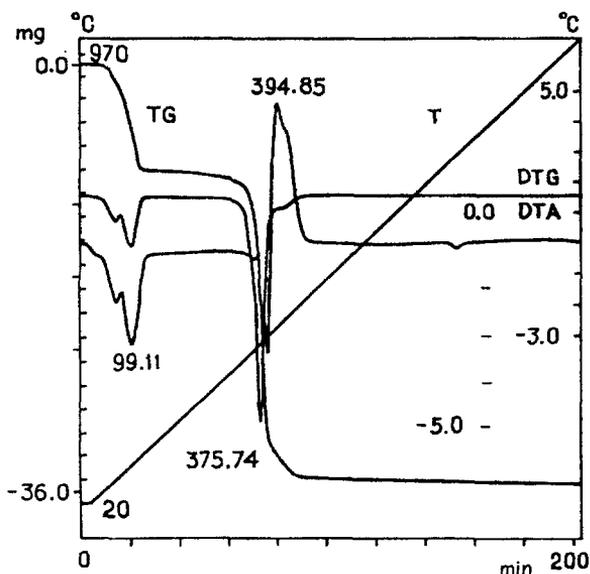
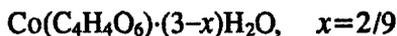


Fig. 3 TG, DTG and DTA curves of $\text{Co}(\text{C}_4\text{H}_4\text{O}_6) \cdot (3-x)\text{H}_2\text{O}$, $x=2/9$ (air, Derivatograph C)

Nickel salt

Unlike the other salts, the Ni^{2+} salt of *d*-tartaric acid is highly hygroscopic and the water loss is not well evidenced either in air or in Ar. The decomposition takes place in two well-defined steps both in air and in Ar. The mass of the 400°C sample residue in Ar corresponds to $\text{NiO}_{0.75}$, and that in air to NiO . In Ar, further heating leads to metallic Ni , while in air, a nonstoichiometric oxide results. The initial combination is assigned the formula



Copper salt

Copper forms the only anhydrous tartrate as concerns the salts we studied: up to 200°C , there is a plateau both in air and in Ar. Only one decomposition

step is observed in Ar, leading to Cu_2O , and then to Cu at about 900°C , which readily reoxidizes to Cu_2O and CuO upon air admission. In air, two steps are observed in the DTG curve, with Cu_2O formation at 280°C , which rapidly oxidizes to CuO, the stable form up to 1000°C . A simple formula is attributed to the Cu(II) salt:

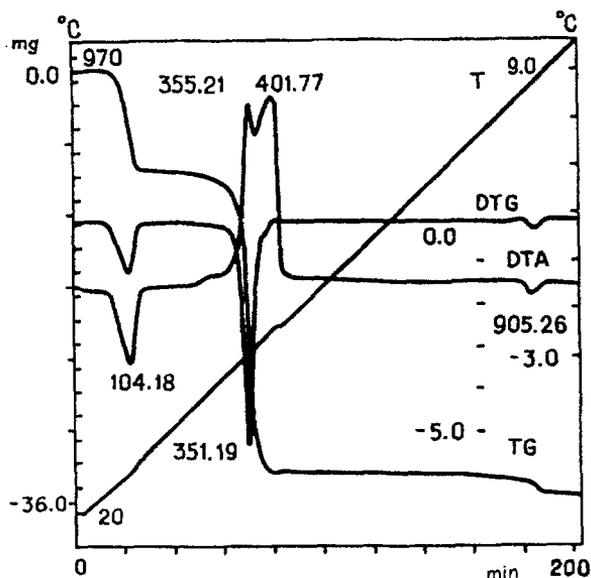
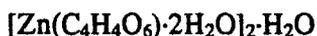


Fig. 4 TG, DTG and DTA curves of $[\text{Zn}(\text{C}_4\text{H}_4\text{O}_6)\cdot 2\text{H}_2\text{O}]_2\cdot\text{H}_2\text{O}$

Zinc salt

The Zn salt is unique (among the investigated ones), exhibiting a two-step dehydration process in both air and Ar. The first pertains to a mass loss equivalent to about half a water molecule (weakly bonded), whereas the second loss corresponds to two more strongly bonded ones. In air, the decomposition takes place in two well-defined steps, the first being endothermic and the second exothermic, leading to ZnO at 450°C and to nonstoichiometric oxide upon further heating. The decomposition steps for the other substances studied were all exothermic. In Ar, the mass loss within the range $250\text{--}450^\circ\text{C}$ is less than that observed in air. The sample mass at 450°C cannot be assigned a definite formula. Most probably a carbonaceous residue strongly held on the ZnO surface is formed (which in air readily burns). Upon further heating this slowly decomposes, the process overlapping with the sublimation of ZnO in an Ar flow (ZnO was found on the cold parts of the TG quartz tube). The initial complex formula



takes into account the existence of weakly-bonded H_2O .

Conclusions

The thermoanalytical investigation of some 3*d* metal salts of *d*-tartaric acid, $\text{M}(\text{II})(\text{C}_4\text{H}_4\text{O}_6)\cdot x\text{H}_2\text{O}$ ($\text{M}(\text{II}) = \text{Mn, Fe, Co, Ni, Cu, Zn}$) was performed in both oxidizing (air) and inert (Ar) atmospheres. The dehydration processes were practically identical in both cases, with minor instrumental differences. With the exception of Cu, the TA and IR data seem to indicate an octahedral structure, with the tartrate anion acting as a tetradentate chelating ligand and with two coordinated water molecules: $\text{M}(\text{II})(\text{C}_4\text{H}_4\text{O}_6)\cdot 2\text{H}_2\text{O}$.

However, the observed water deficit (for the Mn salt) or excess (for the Fe, Co, Ni and Zn salts) points to the formation of some macromolecular structure, which the above data alone are unable to determine definitely.

The subsequent decomposition processes, as expected, differ. In air, they take place at lower temperature and are generally exothermic, whereas the reverse is true in Ar. The final (1000°C) residues are higher oxides in air, whereas in Ar metallic phases can be obtained (for Co, Ni and Cu).

References

- 1 A. V. Ablov and G. A. Popovici, *Zh. Obshch. Khim.*, 24 (1954) 974.
- 2 I. M. Ciurokova, D. N. Glebivskii and A. S. Kreiciuk, *Vestnik Leningrad. Univ.*, 4 (1986) 126.
- 3 I. Drančă, T. Lupascu, V. Sofranski, V. Ropot and I. Haritonov, *Zh. Neorg. Khim.*, (in press).
- 4 S. Kirschner and R. Kiesling, *J. Amer. Chem. Soc.*, 82 (1960) 4174.
- 5 D. I. Alioshin, L. S. Soloviev and A. L. Iudin, *Izv. Sib. Otd. A. N. SSSR, Ser. Khim. Nauk.*, 9 (1967) 11.
- 6 V. Ropot, A. Maftuleac, V. Sofranskii and I. Drančă, *Zh. Fiz. Khim.*, 61 (1983) 1988.
- 7 K. Nakamoto, *Infrared and Raman Spectra of Inorganic Compounds (Russian translation)*, Mir, Moskova 1991, p. 257.
- 7a L. Belami 'Novie dannie po IK spectram slojnih molekul', Mir, Moskova 1971, p. 318.
- 8 K. I. Pribilov, R. I. Valiukina and R. A. Gorodnicheva, *Zh. Neorg. Khim.*, 30 (1985) 2698.
- 9 K. I. Pribilov, R. I. Valiukina and R. A. Gorodnicheva, *Zh. Neorg. Khim.*, 32 (1987) 2198.
- 10 V. A. Klimova, *Osnovnie Micrometodi Analiza Organiceskih Soedinenii, Himia, Moskova 1975*, p. 59.
- 10a C. Sharlo 'Metody analiticeskoi himii'. (in Russian) Himia, Moskova 1965, p. 975.
- 11 I. Paulik, F. Paulik and M. Arnold, *J. Thermal Anal.*, 32 (1987) 301; M. Arnold, P. Somogyvári, J. Paulik and F. Paulik, *J. Thermal Anal.*, 32 (1987) 679.
- 12 M. C. Puerta and P. Valerga, *J. Chem. Education*, 67 (1990) 344.