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THERMAL ANALYSIS OF IRON-8-QUINOLINOL COMPLEXES

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Thermal analysis studies were performed on the iron-8-quinolinol complexes $Fe(Ox)_2$, $Fe(Ox)_3$, $Fe(Ox)_2(OH)$, $Fe(Ox)(OH)_2$ and $Fe(Ox \cdot HCl)_2Cl_3$ (where Ox is 8-quinolinol). Mixtures of these complexes with $Fe(OH)_3$ and Fe_2O_3 were also investigated.

Some metal complexes of 8-quinolinol, with the general formulae $M(Ox)_2$ and $(MOx)_3$, have been investigated by differential thermal analysis [1]. The gas-chromatograms show that H_2, CH_4, CO, N_2 result during the thermal decomposition. The non-volatile product contains carbon, hydrogen, oxygen, nitrogen and sometimes free metal. In the case of trivalent metals, the elimination of Ox radicals is possible directly by dissociation. Mass-spectrometric analysis of these complexes revealed the molecular ions $[M(Ox)_3]^+$ and $(M(Ox)_2]^+$. The ions $[M(Ox)]^+$ and M^+ together with ligand fragments CO, H_2O, C_2H_2, $H^{\cdot}$ and $HO^{\cdot}$, were detected only for the metals with two valence states [2]. The purpose of the present work was to investigate $Fe(Ox)_2$, $Fe(Ox)_3$, and other iron-8-quinolinol complexes such as $Fe(Ox)_2OH$, $Fe(Ox)(OH)_2$ and $Fe(Ox \cdot HCl)_2Cl_3$. We were also interested in the investigation of $Fe(Ox)_3 + Fe(OH)_3$, $Fe(Ox)_3 + Fe_2O_3$, $Fe(Ox)_2(OH) + Fe(OH)_3$, $Fe(Ox)_2(OH) + Fe_2O_3$, $Fe(Ox)(OH)_2 + Fe(OH)_3$, $Fe(Ox)(OH)_2 + Fe_2O_3$ with regard to radioactive iron transfer between these complexes and iron hydroxide labelled with Fe-59 [3].

Experimental

Iron hydroxide and iron-8-quinolinol complexes were prepared using the methods previously described [4]. Mixture of complexes with $Fe(OH)_3$ or Fe_2O_3 in a 1: 1 molar ratio were milled in a vibratory mill and the powders were pressed into pellets at 120 Kgf/cm^2. These kind of samples were prepared in the same manner as the radioactivity transfer samples, to permit a better homogenisation and interaction between the system components, for the proposed investigations.

Thermal analysis was performed on the powder samples with a MOM Derivatograph, Paulik–Paulik–Erdey system, in a static air atmosphere, using dynamic and isothermal heating. As sample holders were used No. 2 standard and multiplate (six plates) platinum crucibles. In the study of the simple complexes, empty platinum crucible was used as reference material. For the mixed systems, Al_2O_3 calcined up to 1500° served as reference material, for the thermal compensation of the component reach in Fe_2O_3 from the mixtures.

Results and discussion

Complexes containing both 8-quinolinol and OH groups can be regarded as substituted $Fe(OH)_3$, in which the behaviour of the OH groups during heating must be nearly the same. Further, in systems to which $Fe(OH)_3$ has been added, interaction between OH groups of the complex and $Fe(OH)_3$ is possible. The TG and DTA curves of $Fe(OH)_3$ (Fig. 1) show that about 90% of the water is lost in an endothermic process. When the following 5–8% of the water is lost, the DTA curve exhibits an exothermic peak due to rearrangement of Fe_2O_3 into a compact crystalline lattice. This behaviour is general, and has been known for other metal hydroxides since the 19th century [5]. The formation of crystalline Fe_2O_3 is observed over a wide temperature range ($300 \pm 40°$), depending on the primary iron salt, the preparation of the hydroxide, the heating rate (dT/dt), the granulometric distribution of the powder, the volume and the shape of the crucible, and the thickness of the sample. The last traces of water are lost near 700°.

1) The DTG and DTA curves of $Fe(Ox)(OH)_2$ (Fig. 2) show that 0.5 molecule of water is eliminated in each of two steps, with the formation of Fe–O–Fe

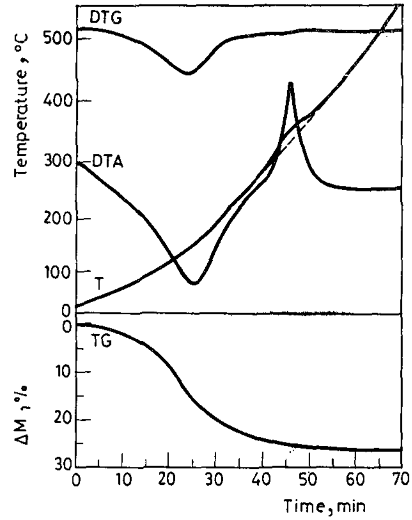

Fig. 1. TG, DTG and DTA curves of $Fe(OH)_3$. Sample weight 322 mg, heating rate ~ 10°/min

bridges [6, 7]. At 300° an exothermic peak occurs, as in the case of $Fe(OH)_3$, followed by rupture of the nitrogen containing ring of the ligand. The fragments formed during the decomposition also combine with atmospheric oxygen in exothermic processes. At 350° the second ring of the ligand is opened, with heat consumption, as evidenced by the DTA curve. The final product is Fe_2O_3. Because of the overlapping of the reactions in a normal sample crucible, multiplate sample holder for thin layers were used. In the TG, DTG and DTA curves of thin-layer sample, the splitting of the two 8-quinolinol rings are separated. From the isothermal heating of $Fe(Ox)(OH)_2$ step by step, it was verified that the first 0.5 molecule of water is eliminated at 150°, but the second 0.5 molecule only at 230° after three hours of heating. Rearrangement of the Fe–O–Fe bridges apparently took place at 280° when the temperature was subsequently increased up to 285°. During this rearrangement, the nitrogen-containing ring of the ligand is broken with elimination of nitrogen and CH_2 (possibly CH_2O) fragments. Splitting of the phenolic ring does not lead to an exothermic peak in the DTA curve, and the elimination of the different fragments (24%) is very slow. When the temperature is increased dynamically to 500°, exothermic peaks are observed at 325–330° (4% lost) and 420° (9% lost). In this final step the last CH group is eliminated, together with the excess of oxygen.

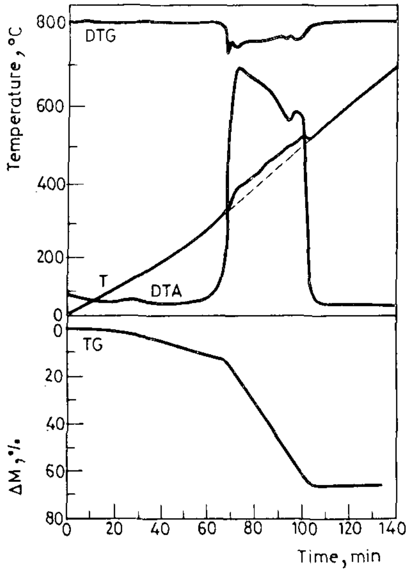

Fig. 2. TG, DTG and DTA curves of $Fe(Ox)(OH)_2$. Sample weight 102 mg, heating rate ~ 5°/min

2) The TG and DTA curves of $Fe(Ox)_2(OH)$ (Fig. 3) show the elimination of adsorbed water up to 150°, while up to 285° 0.5 mole water is eliminated from the

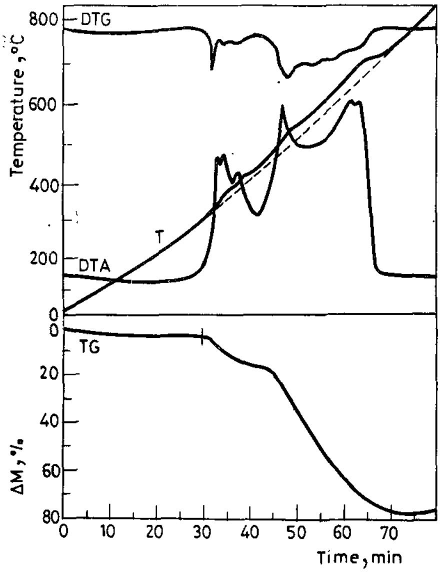

Fig. 3. TG, DTG and DTA curves of $Fe(Ox)_2(OH)$. Sample weight 99 mg heating rate ~ 10°/min

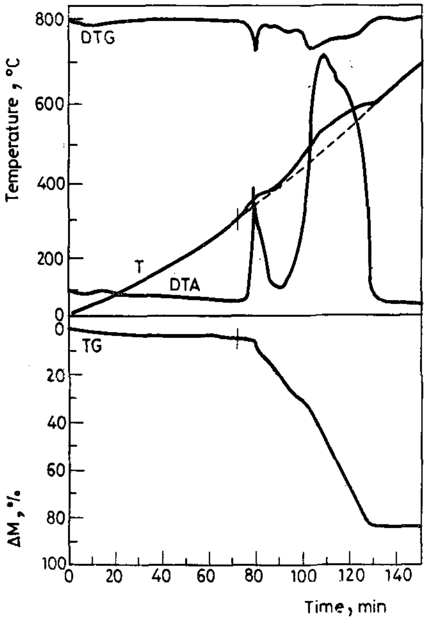

Fig. 4. TG, DTG and DTA curves of $Fe(Ox)_3$. Sample weight 85 mg, heating rate ~ 5°/min

OH groups. Rearrangement of the pseudo-oxidic structure, followed by the splitting of the first ligand ring, is revealed at 320°. The presence of oxygen in the furnace atmosphere leads to a very complex thermal degradation, with the elimination of CO, CO_2, C_2H_2 (possibly), H_2O etc. The formation of these compounds is generally an exothermic process, but their diffusion and liberation are endothermic. Accordingly, the DTA curves has a complex shape. The heat in some points of the sample leads to a temperature 80 – 100° higher than that of the reference sample (A_2O_3). In such points other reactions are initiated and a faster degradation is produced, in contrast with the normal process. The phenolic rings of the ligand are split at 450°, and the DTG and TG curves show that by 720° the sample is completely transformed to Fe_2O_3. The TG curves of the thin-layer samples confirm that at the same heating rate (10°/min), up to 400 – 450° about 50% is lost from the ligand molecules (the nitrogen rings of the 8-quinolinol). The last peak in the DTA curve is given by the oxidation of reduced iron by atmospheric oxygen. This peak is absent from the curve of thin-layer sample with a slow heating rate (1.3/min°), because the decomposition fragments are liberated from the sample before interacting with the matrix.

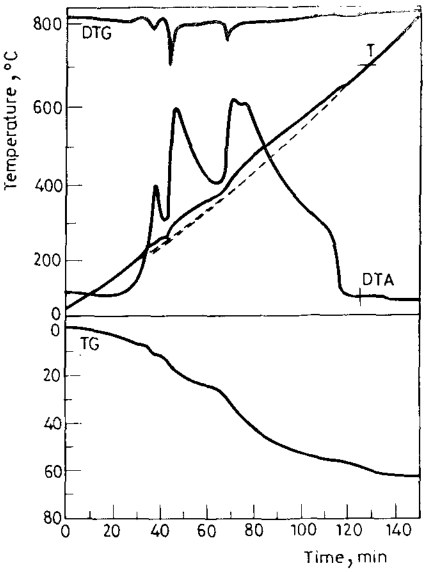

Fig. 5. TG, DTG and DTA curves of $Fe(Ox)_2$. Sample weight 231 mg heating rate ~ 5°/min

3) $Fe(Ox)_3$ loses its humidity water up to 150° (Fig. 4). The last traces of water can cause the partial hydrolysis of some complex molecules and the elimination of Ox ligand radicals up to 300°. Near 325° the DTA curve shows an exothermic

peak with a weight loss of 2.5%. A possible explanation is the splitting of one Fe-N bond, the elimination of nitrogen, and rearrangement as a Fe–O–Fe bridge with the addition of atmospheric oxygen. After this maximum in the DTA curve, some endothermic processes occur, due to the splitting of the fragments, the diffusion and the liberation, which consume energy. After 440° the thermal decomposition is very complicated, with the elimination of the ligand rings and fragments, which are oxidized in exothermic processes. Because of the exothermic effects, the decomposition reactions are superposed and it is not possible to separate the individual processes in the DTA and TG curves. At higher temperatures (near 550°) reduced iron may appear. The oxidation of iron to Fe_2O_3 is quantitative at 700°. The thermal curves of the thin-layer sample at low heating rate (1.3°/min) show that the process is over near 425°, with an exothermic peak in the DTA curve. In this case the concentration of reducing fragments is high, and enough to produce reduced iron.

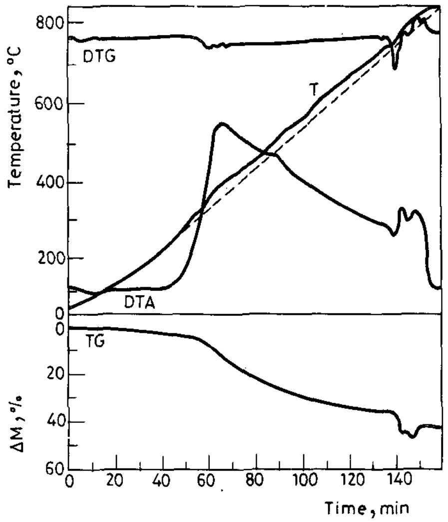

Fig. 6. TG, DTG and curves DTA of $Fe(Ox)(OH)_2 + Fe_2O_3$. Sample weight 305 mg, heating rate ~ 5°/min

4) $Fe(Ox)_2$ normally occurs as the hydrated form $Fe(Ox)_2 \cdot 2H_2O$. The TG and DTA curves in Fig. 5 show that the coordination water is lost in two steps up to 200°. At 220° the oxidation of divalent iron occurs, followed by rearrangement of the structure. The initial trans-planar configuration is broken and a possible Fe–O–Fe structure appears. The heat of this exothermic process can lead to splitting of the ligand, with the elimination of nitrogen and CH groups. After 365° the decomposition is very complicated, with the formation of different radicals which are oxidized. $Fe(Ox)_2$ is unstable, and in time is degraded to an

$Fe(Ox)_{3-n}(OH)_n$ mixture (where $n = 0$, 1 and 2). This hydrolytic oxidation was revealed by Mössbauer spectrometry [4]. The thermal curves of degraded $Fe(Ox)_2$ have roughly the same shape as that of $Fe(Ox)_2(OH)$.

5) When the $Fe(Ox)(OH)_2 + Fe_2O_3$ system is heated up to 520°, it exhibits nearly the same behaviour as $Fe(Ox)(OH)_2$, apart from the decomposition rate (Fig. 6). At 520° the radicals formed by splitting of the last ligand fragments of the complex react with the Fe_2O_3 matrix and atmospheric oxygen. This interaction is characterised by two simultaneous processes:

(a) outwards diffusion of the radicals, with the possibility of reduction of Fe^{3+} to Fe^{2+} and Fe^0;

(b) diffusion of atmospheric oxygen, with the oxidation of the reducing radicals and reduced iron.

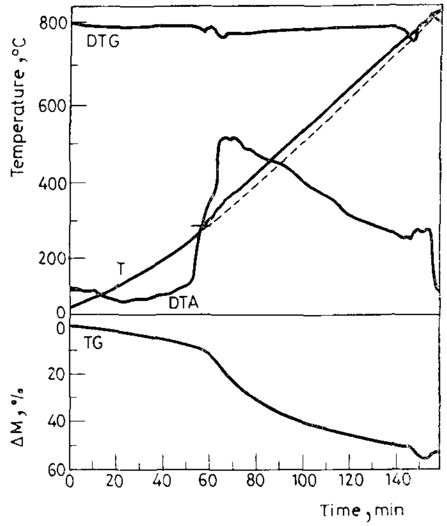

Fig. 7. TG, DTG and DTA curves of $Fe(Ox)(OH)_2 + Fe(OH)_3$. Sample weight 252 mg, heating rate ~ 5°/min

At 750° a weak endothermic process occurs with the fast decomposition of a metastable intermediate, leading to a mixture of Fe^{3+}, Fe^{2+} and Fe^0. Afterwards, the TG, DTA, and DTG curves show the oxidation of reduced iron. The addition of oxygen corresponds to 19.5% of the total Fe_2O_3. On the isothermal heating step by step, up to 250° the DTG and TG curves show the endothermic elimination of water from OH groups. At 275° the exothermic rearrangement of the structure is followed by decomposition and the oxidation of liberated fragments. The rate of decomposition decreases in time, the splitting of the next CH group being an endothermic process. The last fragments are eliminated in two steps at 300 and 375°. Iron reduction followed by oxidation is less evident than in the case of dynamic heating.

6) The DTA and TG curves for Fe(Ox)(OH)$_2$ + Fe(OH)$_3$ (Fig. 7) show the elimination of 95% of the water from the OH groups up to 300° (possibly in two steps). Fe–O–Fe bridges can be formed involving both Fe(Ox)(OH)$_2$ and Fe(OH)$_3$ molecules. When the last traces of water are lost, the exothermic rearrangement of the structure occurs, followed by splitting of the ligand nitrogen ring at 320–340°. Near 450° the second ligand ring is broken and a weak maximum is present at 470° in the DTA curve. Up to 700° the shapes of the DTA and TG curves are similar as for the Fe(Ox)(OH)$_2$ + Fe$_2$O$_3$ system. The addition of oxygen for the oxidation of the reduced iron in the last step at 750° amounts only 11% of the total Fe$_2$O$_3$. This smaller quantity is caused by the matrix differences formed during thermal decomposition. The matrix differences are greater for isothermal heating, when the exothermic character of the decomposition in the case of the Fe(Ox)(OH)$_2$ + Fe(OH)$_3$ system is less evident.

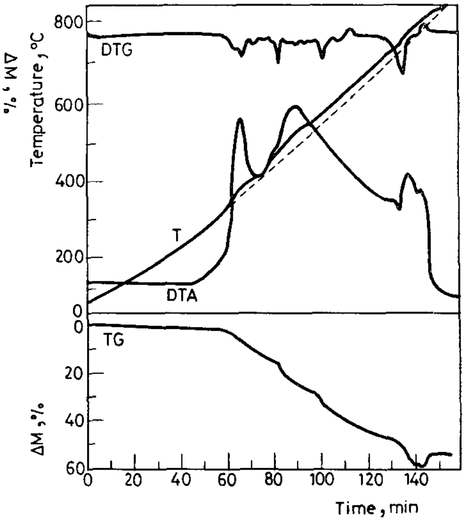

Fig. 8. TG, DTG and DTA curves of Fe(Ox)$_2$(OH) + Fe$_2$O$_3$. Sample weight 263 mg, heating rate ~ 5°/min

7) Up to 290° Fe(Ox)$_2$(OH) + Fe$_2$O$_3$ loses about 95% of the water from the OH groups, and probable rearrangement of the structure is accompanied by a weak exothermic effect. Near 360° the first ring of one ligand molecule is broken, the oxidation of the fragments being strongly exothermic as seen in the DTA curve (Fig. 8). Up to 430° elimination of the fragments occurs with small energy consumption. At 450° the other rings are broken, with elimination of a great number of fragments as the result of the different decomposition reaction. Near 700° the same metastable intermediate compound is formed as in the case of Fe(Ox)(OH)$_2$ + Fe$_2$O$_3$. The reduced iron formed by decomposition at 720° is 21% of the total Fe$_2$O$_3$.

8) The TG and DTA curves of $Fe(Ox)_2(OH) + Fe(OH)_3$ (Fig. 9) show elimination of the water up to 270° (possibly in two steps). The structural rearrangement

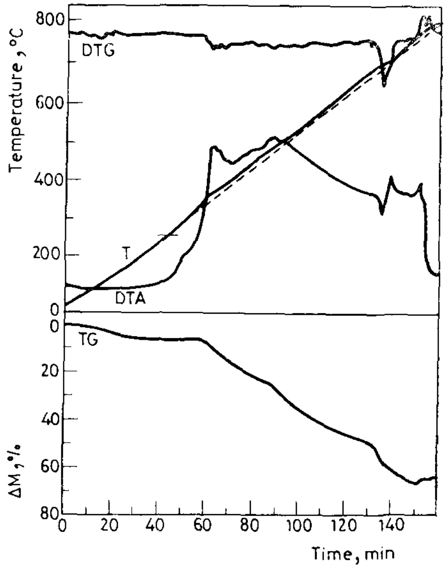

Fig. 9. TG, DTG and DTA curves of $Fe(Ox)_2(OH) + Fe(OH)_3$. Sample weight 274 mg, heating rate ~ 5°/min

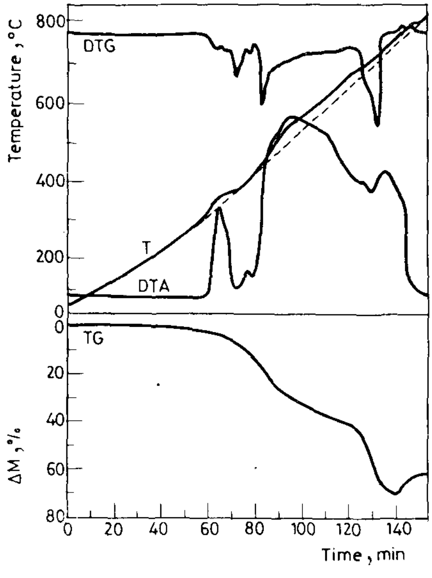

Fig. 10. TG, DTG and DTA curves of $Fe(Ox)_3 + Fe_2O_3$. Sample weight 277 mg, heating rate ~ 5°/min

is revealed at 320° in the DTA curve, followed by the splitting of one nitrogen ring of the ligand. Up to 700° the TG and DTA curves show a superposition of different reactions, the elimination of Ox radicals also being possible directly by dissociation. The metastable intermediate compound produced at 730–750° contains twice as reduced iron as the $Fe(Ox)(OH)_2 + Fe(OH)_3$ mixture. In the last part of the process at 770° some carbon traces are oxidized and the iron is transformed totally to Fe_2O_3.

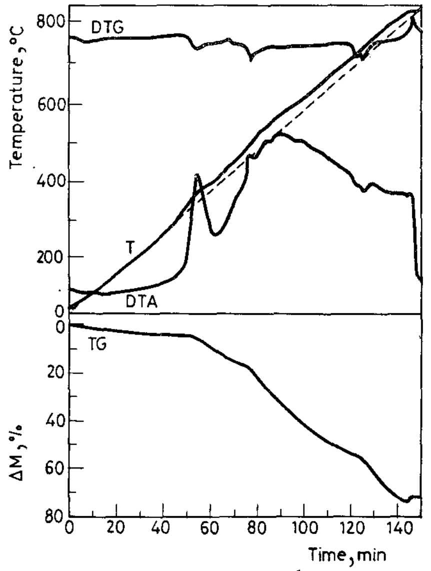

Fig. 11. TG, DTG and DTA curves of $Fe(Ox)_3 + Fe(OH)_3$. Sample weight 264 mg heating rate ∼ 5°/min

9) $Fe(Ox)_3 + Fe_2O_3$ decomposes in almost the same way as the $Fe(Ox)_2(OH) + Fe_2O_3$ mixture (Fig. 10). Because of the higher concentration of reducing fragments in the system, the reduced iron is nearly 32% of the total Fe_2O_3.

10) The $Fe(Ox)_3 + Fe(OH)_3$ system displays no evident differences from the $Fe(Ox)_3 + Fe_2O_3$ mixture (Fig. 11).

11) $Fe(Ox \cdot HCl)_2Cl_3$ contains the 8-quinolinol group bonded only by an Fe–O bond, the nitrogen being present as the $(NH)^+Cl^-$salt. The central iron atom might appear pentacoordinated, but in reality the complex is a dimer, with chlorine bridges [4]. The TG and DTA curves show the elimination of two hydrochloric acid molecules up to 260°, with a weak endothermic effect (Fig. 12). Two chlorine atoms are eliminated in two steps at 280 and 320°. When the last chlorine is lost, the iron becomes bonded to oxygen, and the structure rearranges at 380° with a slight exothermic effect. The splitting of the nitrogen ring of the ligand and the elimination of different fragments occur from 400 to 580°. For the phenolic

ring the splitting is endothermic, but oxidation of the fragments yields and exothermic peak at 630° in the DTA curve. Near 740° the thermal decomposition finishes with Fe_2O_3 as the final product. In practice the amount of Fe_2O_3 is a little smaller than the theoretical, because of some $FeCl_3$ evaporation during the chlorine elimination.

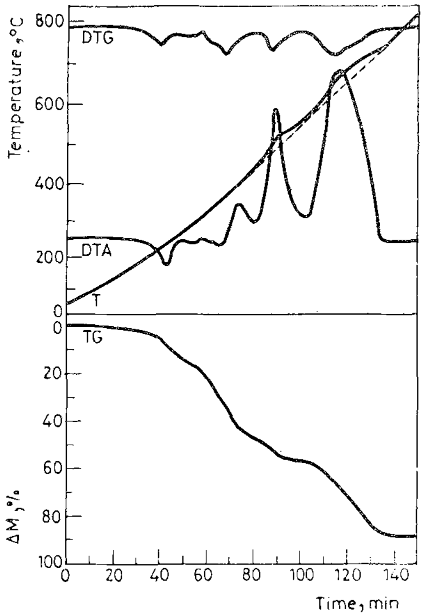

Fig. 12. TG, DTG and DTA curves of $Fe(Ox \cdot HCl)_2Cl_3$. Sample weight 100 mg, heating rate ~ 5°/min

Conclusions

In the first step of thermal decomposition $Fe(Ox)(OH)_2$ and $Fe(Ox)_2(OH)$, behave very similarly to $Fe(OH)_3$; he formation of Fe—O—Fe bridges is demonstrated by the exothermic peak in the DTA curve and by Mössbauer studies [8]. For the thin-layer samples the thermal curves show a separation in the DTA curve for the splitting of the nitrogen and phenolic rings of 8-quinolinol.

The absence of plateaux from the TG curves indicates simultaneous and successive reactions. The reasons for, and the effects of such behaviour have been analysed elsewhere [9]. Study of the compounds from $Fe(OH)_3$ to $Fe(Ox)_3$ demonstrates the roles of the ligand and of the Fe—O—Fe structure on the thermal degradation.

Thermal analysis confirms the possibility of obtaining complexes not fully saturated with ligand [10].

For the mixtures complex + Fe_2O_3, in the first stage Fe_2O_3 behaves as an inert substance. With the increase of temperature, radical formation leads to two processes: the outwards diffusion of the radicals, and the inwards diffusion of oxygen, through the Fe_2O_3 layers. During these processes the oxygen in the Fe_2O_3 has the possibility to react with a proportion of the fragments. In the final step, the decomposition of the metastable intermediate leads to reduced iron. During water elimination, the complex + $Fe(OH)_3$ mixtures form Fe–O–Fe bridges; this structure has an evident influence on the occurrence of reduced iron [10]. The degradation of the ligand is easier, but the resulting radicals and other fragments have not so many possibilities to interact with the matrix, especially for the $Fe(Ox)(OH)_2$ system. The isothermal experiments confirm the dynamic heating results.

In the case of the thermal decomposition of $Fe(Ox \cdot HCl)_2Cl_3$, the pseudo-oxidic structure is formed at higher temperature (380°), but after chlorine elimination the mechanism is similar to that of $Fe(Ox)_3$.

The thermal analysis study of these iron-8-quinolinol complexes and mixture system yields new data on the importance of diffusion processes during decomposition.

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References

1. H. A. Flaschka and A. J. Barnard Jr., Chelates in Analytical Chemistry, Marcel Dekker Inc., New York, Vol. 1, 1967.
2. J. Charalambous, M. J. Frazer, R. K. Lee, A. H. Qureshi and F. B. Taylor, Organic Mass Spectrom., 5 (1971) 1169.
3. C. N. Turcanu and R. Dragomir, Radiochem. Radioanal. Letters, 25 (1976) 153.
4. C. N. Turcanu and G. Filoti, Radiochem. Radioanal. Letters, 15 (1973) 117 and 18 (1974) 23.
5. H. Le Chatelier, Bull. Soc. Chim. France, 47 (1887) 303.
6. B. Jezowska-Trzebiatowska, Coord. Chem. Rev., 3 (1968) 255.
7. K. S. Murray, Coord. Chem. Rev., 12 (1974) 1.
8. C. N. Turcanu and G. Filoti, (Unpublished results).
9. A. Zuda, Thermochim. Acta, 8 (1974) 217.
10. G. Filoti, C. N. Turcanu and V. S. Spanu, Internat. Conf. Appl. Mössbauer Effect, Corfu, Greece, Sept. 13–17 (1976).

Résumé — Etude par analyse thermique de complexes du fer avec l'hydroxy-8 quinoléine: $Fe(Ox)_2$, $Fe(Ox)_3$, $Fe(Ox)_2(OH)$, $Fe(Ox)(OH)_2$ et $Fe(Ox \cdot HCl)_2Cl_3$ (où Ox est l'hydroxy-8 quinoléine), ainsi que de leurs mélanges avec $Fe(OH)_3$ et Fe_2O_3.

Zusammenfassung — Thermoanalytische Untersuchungen der Eisen-8-Oxy-Chinolin-komplexe wurden für $Fe(Ox)_2$, $Fe(Ox)_3$, $Fe(Ox)_2(OH)$, $Fe(Ox)(OH)_2$ und $Fe(Ox \cdot HCl)_2Cl_3$ (Ox = 8-Oxy-Chinolin) durchgeführt. Gemische dieser Komplexe mit $Fe(OH)_3$ und Fe_2O_3 wurden ebenfalls untersucht.

Резюме — Проведен термический анализ таких железо-8-хинолинол комплексов, как $Fe(Ox)_2$, $Fe(Ox)_3$, $Fe(Ox)_2(OH)$, $Fe(Ox)(OH)_2$ и $Fe(Ox \cdot HCl)_2Cl_3$, где Ox — 8-хинолинол. Исследованы также смеси этих комплексов с $Fe(OH)_3$ и Fe_2O_3.