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# A THERMOANALYTICAL STUDY ON SOME COMPOUNDS OF Zr(IV) WITH AZOPYRAZOLONIC DERIVATIVES

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Thermoanalytical data on six reagents and on their compounds with Zr(IV) are reported. Except for H acid, all reagents were azopyrazolonic derivatives obtained by synthesis. The purpose of this study was to obtain data on the thermal stabilities of the reagents and their zirconium compounds, and to establish the reagent : zirconium : water combination ratio.

The results obtained from investigations of some azopyrazolonic derivatives as reagents for the spectrophotometric [1,2] and amperometric [3] determinations of zirconium have shown that well-defined, stoichiometric compounds are formed in solution. Since these compounds could also be separated in the solid state by precipitation, we decided to pursue their study by using thermal methods of analysis; we have also taken into account that tartrazine, a reagent belonging to the same class, has been utilized in the gravimetric determination of zirconium [4]. The thermoanalytical study undertaken followed two aspects: establishment of the thermal behaviour of both the reagents and their compounds with zirconium, and determination of the reagent : zirconium : water combination ratio.

## Experimental

In order to monitor the thermal behaviour of the mentioned compounds, a Model Q-1500D derivatograph capable of the graphical recording of the DTA, DTG, TG and T curves was used, with the following experimental parameters:

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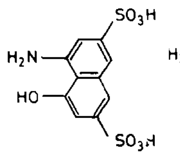
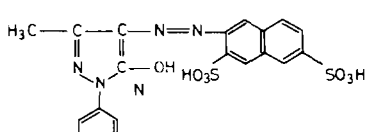
— furnace heating rate: 5 deg/min; maximum heating temperature: 1000°; paper recording speed: 2.5 mm/min;

— amount of sample measured: 50–60 mg for the reagents, 60–200 mg for their zirconium compounds;

— atmosphere in the furnace: static air.

The following reagents and compounds with Zr(IV) were investigated.





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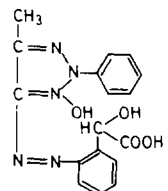

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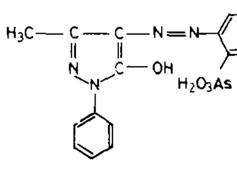

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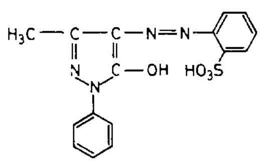

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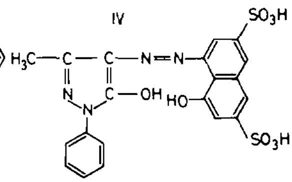

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## Results and discussion

### *1. H acid and its compound with Zr(IV)*

During heating, H acid undergoes a series of transformations (Fig. 1*a*). The first endothermic effect occurs between 90 and 130°; it is accompanied by mass loss, and it should therefore be regarded as a typical effect of moisture elimination. As the temperature is increased, the DTA curves show a series of thermal effects, the first of these being an endothermic effect at 205°, followed by two exothermic effects at 405 and 520°, all accompanied by mass losses. This sequence of effects is produced by the thermal degradation of H acid as a function of temperature. At about 550° the reagent is entirely decomposed; the white residue weighs only about 18% of the initial mass of the reagent. This residue consists mainly of $Na_2SO_4$, formation of which is probably due to the traces of NaCl in the reagent during synthesis.

The compound of this reagent with zirconium gives thermal curves which are to

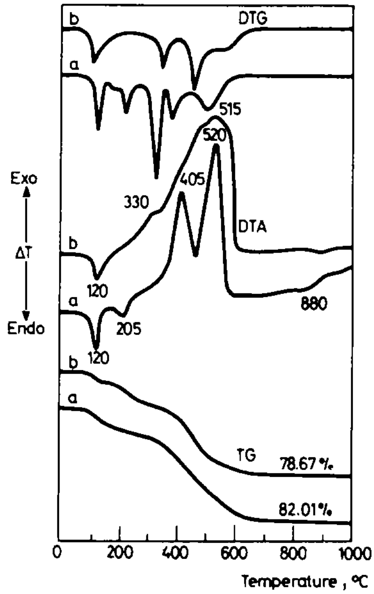


**Fig. 1** The thermal curves of *H* acid (reagent I) *(a)* and of its Zr(IV) compounds *(b)*

some extent similar to those of the reagent (Fig. 1*b*). A specific mass-loss effect occurs at around 120° and lags to about 270°. Calculation proved that the compound crystallizes with 6 water molecules. The theoretical value for these 6 water molecules is 19.63%, whereas the found experimental value was 19.96%.

As the temperature increases, the compound shows a relatively small mass loss up to about 320°. Starting from this temperature, strong decomposition of the compound begins, as demonstrated by the very pronounced exothermic effect in the DTA curve and the associated mass loss in the DTG and TG curves. The thermal decomposition of the compound is practically complete at 580°. Between 320 and 580° a mass loss of 58.71% was measured, the residue representing only 21.33% of the initial mass of the compound. Calculations on the experimental data established that the combination ratio is 1 mole of reagent to 0.94 moles of zirconium. It can therefore be assumed that the reagent : zirconium : water ratio is 1 : 1 : 6.

## *2. Reagent II and its compound with Zr(IV)*

In the thermal curves (Fig. 2*a*) obtained by heating of this reagent, a weak endothermic effect occurs first, caused by moisture loss. As the temperature increases, the reagent is thermally stable up to about 300–310°, but from about 310–390° strong thermal decomposition begins, accompanied by the high-rate ejection of some components from its mass. Afterwards, a slow degradation of the

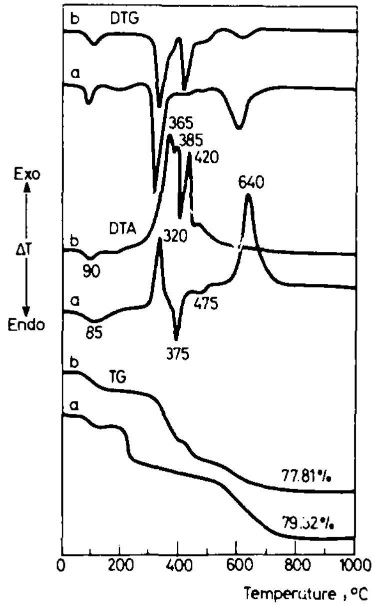


**Fig. 2** The thermal curves of reagent II *(a)* and of its Zr(IV) compound *(b)*

reagent takes place up to about 520°, when a pronounced exothermic effect again occurs following the pyrolysis of the compound; this process is completed at 670°. Finally, a white residue remains, mainly consisting of $Na_2SO_4$, which represents 20.68% of the original mass of the reagent.

The compound of this reagent with zirconium gives a typical moisture loss effect in the thermal curves (Fig. 2*b*); this extends over a larger temperature range than in the case of the reagent and reaches 260°. The mass loss produced by this effect indicates that the compound crystallizes with 16 water molecules.

A vigorous degradation of the compound begins above 260°, as evidenced by a series of pronounced exothermic effects in the DTA curves and associated mass losses in the DTG and TG curves. Finally, a white residue of zirconium oxide remains; this represents 22.19% of the initial mass of the compound. The thermoanalytical data suggested that the compound formed by zirconium with this reagent has a reagent : zirconium : crystallization water ratio of 2 : 3 : 16; the experimental value found was 2 : 2.94 : 16.41.

### *3. Reagent III and its compound with Zr(IV)*

The thermoanalytical data given in Fig. 3*a* reveal that the reagent contains some moisture. A pronounced thermal process occurs between 180 and 270° in the DTA curve; this suggests that some components are eliminated with high rate from the

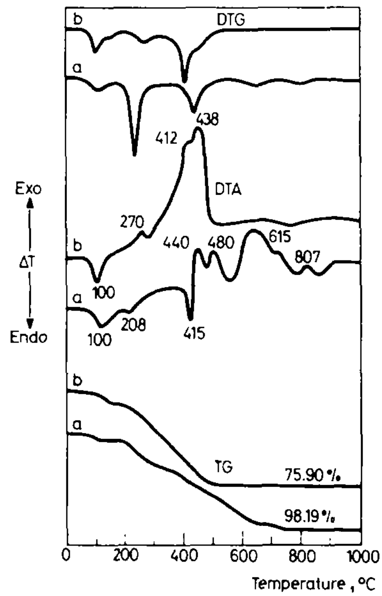


Fig. 3 The thermal curves of Mandelazo I (reagent III) *(a)* and of its Zr(IV) compound *(b)*

compound. Next, over the large temperature range between 270 and 850°, a series of thermal effects caused by degradation and pyrolysis of the reagent occur. Finally, a very small amount of residue remains, representing only 1.81% of the initial mass of the compound; we believe that this residue consists of impurities present in the reagent.

The zirconium compound of this reagent shows thermal curves which are entirely different from those of the reagent (Fig. 3*b*). An endothermic effect, accompanied by a 12.77% mass loss (corresponding to the elimination of the crystallization water), occurs between 80 and 175°. As the temperature increases, a single, very strong exothermic effect occurs between 275 and 580°; this is due to the thermal degradation of the compound. Above this temperature range, the residue is stable up to 1000° and represents 24.10% of the initial mass of the compound.

The experimental value found for the reagent: zirconium : crystallization water ratio, 1 : 1.09 : 3.96, suggested the theoretical combination ratio of 1 : 1 : 4.

### 4. *Reagent IV and its compound with Zr(IV)*

The thermal curves of this reagent (Fig. 4*a*) show that between room temperature and 200° a series of three endothermic effects occur, whose peaks are located at 70, 120 and 160°. The total mass loss accompanying these effects is 7.39%. A pronounced exothermic effect appears between 220 and 260°, associated with a fast

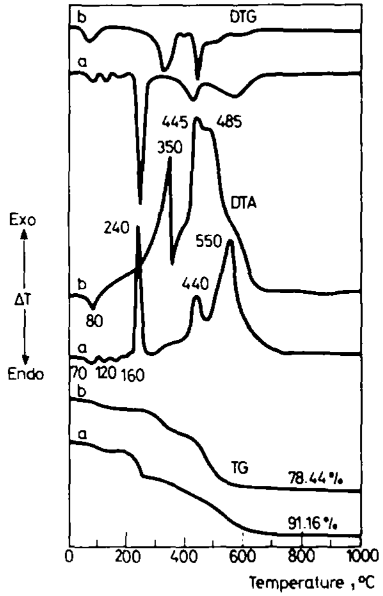


Fig. 4 The thermal curves of reagent IV *(a)* and of its Zr(IV) compound *(b)*

mass loss; this shows that the decomposition of the reagent is explosive. Between 400 and 650° a double effect, also exothermic, occurs, accompanied by mass loss, as a consequence of the pyrolysis of the constituents of the already-decomposed reagent. Finally, after complete pyrolysis, a residue remains which represents 8.84% of the initial mass.

For the compound formed by this reagent with zirconium, the thermal curves (Fig. 4*b*) first show a low-temperature endothermic effect, corresponding to a 4.46% mass loss. Afterwards, the compound is stable up to about 250°, when its thermal decomposition begins. This decomposition appears as exothermic effects in the thermal curves, the first at 350° and the second as a double effect at 445 and 485°. Above 600°, decomposition and pyrolysis are completed, and the white residue represents 21.56% of the original mass of the compound.

The experimental reagent : zirconium : crystallization water ratio 1 : 0.95 : 1.33, suggested the theoretical ratio 1 : 1 : 1.50.

*5. Reagent V and its compound with Zr(IV)*

The thermal curves (Fig. 5*a*) evidence a series of effects which are quite similar to those of the already discussed reagents. Thus, the first thermal effect is produced by moisture removal, followed immediately, at 130°, by an exothermic effect,

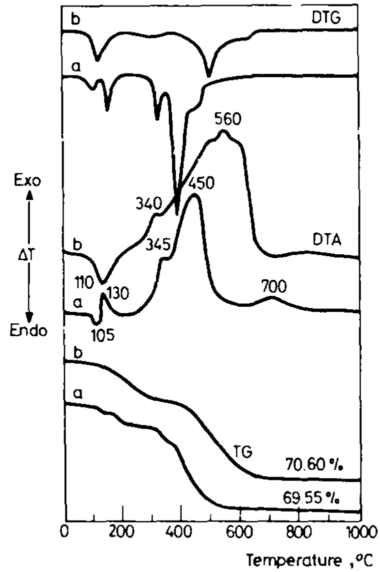


**Fig. 5** The thermal curves of reagent V *(a)* and of its Zr(IV) compound *(b)*

associated with a 4.06% mass loss. We believe this effect to be caused by the removal of a functional group from the reagent. Relative stability was then noted, up to about 300°. Above this temperature, a pronounced exothermic effect, accompanied by mass loss, was evidenced; this thermal degradation occurred between 300 and 485°. Above 485°, the remaining residue, representing 30.45% of the initial mass, is thermally stable up to 1000°, showing only a polymorphic-type anomalous transformation in the DTA curve, at 700°.

The zirconium compound of this reagent exhibits thermal curves similar to those of the reagent (Fig. 5*b*), with the only exception that the 130° exothermic effect is absent. A wide endothermic effect occurs between room temperature and 260°, associated with a 19.44% mass loss. In fact, however, this effect continues up to 360°, showing only a small inflection at 345°; over this range, a mass loss of 4.63% was measured. The two effects are produced by the elimination of crystallization water and constitution water, respectively.

On increase of the temperature from 400 to 650°, a strong exothermic effect, accompanied by mass loss, was observed, caused by the decomposition and pyrolysis of the organic constituents of the compound. The remaining residue, representing 29.40% of the initial mass of the compound, was white and stable up to 1000°. The experimental value of the reagent : zirconium : crystallization water : constitution water ratio, 1 : 1.83 : 8.25 : 1.97, is compatible with the theoretical value 1 : 2 : 8 : 2.

*6. Reagent VI and its compound with Zr(IV)*

The thermal curves recorded for this reagent (Fig. 6*a*) evidence a typical moisture effect at around 110°, corresponding to a 5.20% mass loss. Immediately following water removal, slight decomposition of the reagent sets in, and from 280° pronounced thermal degradation begins, shown in the DTA curve by a series of three exothermic effects, located at 330, 420 and 545°. The reagent appears to be

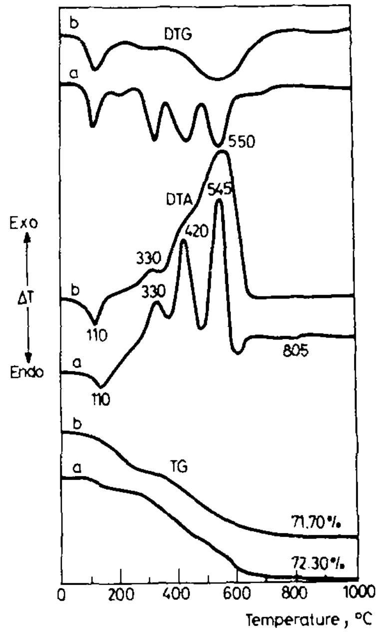


Fig. 6 The thermal curves of reagent VI (*a*) and of its Zr(IV) compound (*b*)

practically decomposed at about 600°; the white residue represents 27.70% of the initial mass and shows a small endothermic effect at 805°, due to melting of the alkali metal sulfates.

The thermal curves of the zirconium compound of this reagent (Fig. 6*b*) evidence a wide endothermic effect between 20 and 235°, due to water elimination, accompanied by a 21.36% mass loss. As concerns the nature of this thermal effect (the peak located at 110°), we tentatively believe that the compound contains both crystallization water and moisture. As the temperature is increased, the compound continuously loses mass due to the decomposition and pyrolysis of the organic constituents; such phenomena were recorded in the DTA curve as a wide exothermic effect having a peak at 550°. The thermal degradation of the compound is practically completed at 650°, when a white residue results, comprising 28.30% of the mass of the compound.

The experimental data obtained, relating particularly to the elimination of water, allow two possible interpretations of the reagent : zirconium : crystallization water ratio. The experimental value is 1 : 2.30 : 11.86, which may be regarded either as 1 : 2 : 11 or as 1 : 2 : 10 if we assume that the compound is moist.

The thermoanalytical data obtained for the six reagents and their zirconium compounds, listed in Table 1, show good agreement between the experimental values and the theoretical ones.

**Table 1** The thermoanalytical data, the value of the combination ratio and the Zr(IV) content (in %)

| Compd. No. | Amount of compd., mg | | Mass loss, mg | | R : Zr : Crystn. water ratio | | Zr, %* | |
|---|---|---|---|---|---|---|---|---|
| | Initial | $ZrO_2$ residue | Water | Org. subst. | Found | Calcd. | Found | Calcd. |
| I | 166.4 | 35.50 | 33.21 | 97.69 | 1 : 0.94 : 6 | 1 : 1 : 6 | 19.73 | 20.61 |
| II | 79.4 | 17.62 | 14.40 | 47.38 | 2 : 2.94 : 16.41 | 2 : 3 : 16 | 20.07 | 20.60 |
| III | 66.4 | 16.00 | 8.48 | 41.92 | 1 : 1.09 : 3.96 | 1 : 1 : 4 | 20.45 | 19.94 |
| IV | 111.8 | 24.10 | 4.98 | 82.72 | 1 : 0.95 : 1.33 | 1 : 1 : 1.5 | 16.71 | 17.98 |
| V | 209.5 | 61.60 | 50.43 | 97.47 | 1 : 1.83 : 8.25 | 1 : 2 : 8 | 27.01 | 28.47 |
| VI | 203.0 | 57.50 | 43.36 | 102.14 | 1 : 2.30 : 11.86 | 1 : 2 : 11<br>1 : 2 : 10 | 26.67 | 24.30 |

* The zirconium content was calculated in compounds without crystallization water.

## References


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**Zusammenfassung** — Thermoanalytische Daten von 6 Reagenzien und deren Verbindungen mit Zr(IV) werden mitgeteilt. Außer H-Säure waren alle Reagenzien durch Synthese erhaltene Azopyrazolon-Derivate. Zweck der Untersuchung war, Daten über die thermische Stabilität dieser Reagenzien und ihrer Zirkonverbindungen zu erhalten und das Verhältnis Reagens : Zirkon : Wasser festzustellen.

**Резюме** — Приведены термоаналитические данные для шести реагентов и их комплексов с четырехвалентным цирконием. Исследованные реагенты, являясь азопиразолонпроизводными, были синтезированы за исключением H-кислоты. Целью проведенного исследования являлось получение данных о термоустойчивости реагентов и их комплексов с цирконием, а также определение соотношения реагент : цирконий : вода.