

SOME OBSERVATIONS ON THE THERMOCHEMISTRY OF TELLURIC ACID

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(Received October 14, 1974; in revised form January 27, 1975)

The thermal degradation of H_6TeO_6 in air has been evaluated critically. Evidence is presented for a decomposition mechanism involving step-wise dehydration of H_6TeO_6 via non-stoichiometric amorphous solids to polymetatelluric acid and up to a composition corresponding to pyrotelluric acid. No morphological changes were observed during these structural variations and no evidence was found for the formation of allotelluric acid. Further dehydration is accompanied by reduction, which, depending upon the experimental conditions accounts for the considerable variety of results reported previously. Crystalline Te(VI)–Te(IV) oxides are obtained at about 550° from which TeO_2 is formed by additional calcination at about 620°.

Recent investigations in our laboratories concerning structure and catalytic activity of tellurium oxides on silica supports [1–3] have brought to our attention the great variety of experiences reported in the literature on the thermal decomposition of telluric acid. In particular, the results differ in the observed thermal effects and phase distribution. The partial dehydration of telluric acid to polymetatelluric acid was previously critically studied by Jander and Kienbaum, [4], the synthesis of crystalline $(H_2TeO_4)_n$ was first achieved by Glemser *et al.* [5] and its decomposition was studied by Moret and Maurin [6]. The synthesis of crystalline TeO_3 was described by Maurin [7] and Dumora [8], that of Te_2O_5 by Lindqvist [9], whereas the decomposition to tellurous oxide was investigated several times [6, 8, 10, 11], yielding in instances indications of intermediate product formation. In general it appears that thermal decomposition in air leads to amorphous or badly crystalline substances [4, 6, 10–12], whereas under hydrothermal or other specific conditions, such as very careful and slow heating, more well-defined products are obtained [5–9, 13–15].

Being nevertheless unable to give a satisfactory and unambiguous interpretation of all stages of the degradation process observed during thermal analysis of H_6TeO_6 , we have reinvestigated the system.

Experimental part

Apparatus and procedures

a) Unless otherwise indicated, thermal analyses of 100 mg samples were carried out on a Du Pont 900 Differential Thermal Analyzer, equipped with high and medium temperature cells with calibrated Pt-10% Rh and Cr-Al thermocouples in combination with an auxiliary DSC cell and a 950 Thermogravimetric Analyzer. For controlled thermal treatments requiring additional chemical and physical analyses of the samples a home-built DTA-TG system was used which permits manipulation of up to 500 mg or 2.5 cm³ of material in each of two sample holders. The system consists of a cylindrical 1.4 KWatt vertical wire wound resistance furnace programmed by a Norfa temperature programmer (temperature range up to 650°; stability ±1°; heating rates from 0.8° hr⁻¹ to -23° min⁻¹), a Sartorius balance assembly (sensitivity 2 mg) and a Leeds & Northrup temperature recorder.

b) Standard X-ray diffraction, infrared and optical reflectance equipment was used together with optical microscopy [16].

c) Analytical methods.

Determination of Te(IV). — After treatment with K₂Cr₂O₇/H₂SO₄ to transform Te(IV) into Te(VI) according to 2Cr⁶⁺ + 3Te⁴⁺ → 2Cr³⁺ + 3Te⁶⁺, excess of K₂Cr₂O₇ is back-titrated potentiometrically with a ferrous solution.

Determination of total Te-contents. — After disaggregation of the mass with a HNO₃/HF/H₂SO₄ mixture in a Pt crucible, samples are heated in 50 cm³ HCl and are then treated with a hydrazine bichlorohydrate - SO₂ solution to achieve reduction to metallic tellurium. The precipitate is subsequently taken up in nitric acid, leading to conversion into Te(IV), and the solution is evaporated to dryness in the presence of H₂SO₄. The resulting mass is then treated with a K₂Cr₂O₇/H₂SO₄ solution and Te(IV) is determined as before.

Determination of Te(VI). — Te(VI) is determined indirectly from the balance of the two analyses as above, assuming that no metallic tellurium is present.

Results

Figure 1 represents the decomposition of H₆TeO₆ (Schuchardt, 98.5 wt%), recorded at increasing temperature ($\Delta = 5^\circ \text{ min}^{-1}$); curve (i) represents the heating curve and (ii) is the registration of the percentage weight loss. The figure indicates the following sequence of events:

— Dehydration of H₆TeO₆ at atmospheric pressure, according to



between about 120° and 230°.

- Gradual decomposition of polymetate telluric acid between 230° and 550° at variable rates, leading to the formal composition $3\text{TeO}_2 \cdot \text{TeO}_3$ or $4\text{TeO}_2 \cdot \text{TeO}_3$. DTA reveals two main endothermic effects between 350–410° and 410–475° and two minor ones (480° and 490°), followed by a sharp exothermic

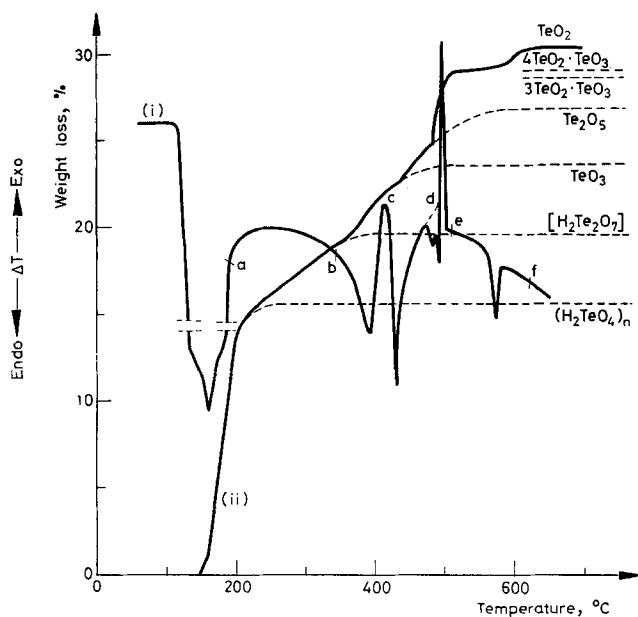


Fig. 1. Thermal degradation of H_6TeO_6 ; scanning speed 5°min^{-1} . (i) DTA; (ii) TG. Sampling points are indicated as *a* – *f*

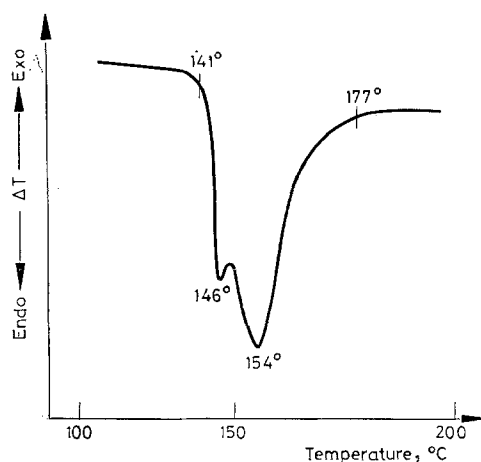
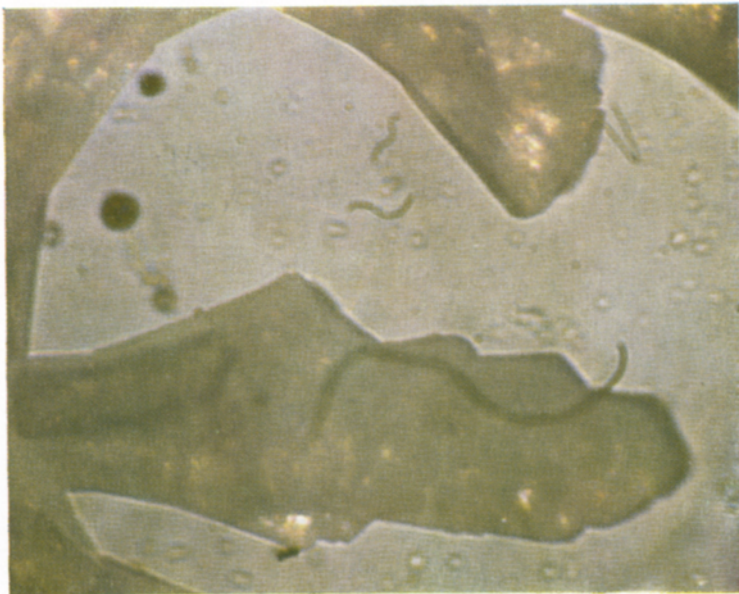


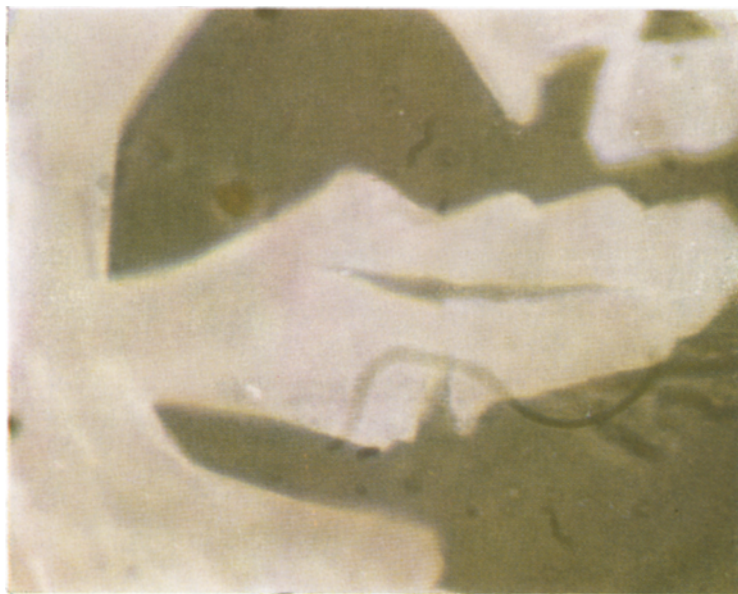
Fig. 2. Thermal degradation of H_6TeO_6 to $(\text{H}_2\text{TeO}_4)_n$ at a 5°min^{-1} heating rate



a)



b)



c)

Fig. 3. Microphotographs of degradation products of H_6TeO_6 at 145° (a), 147.5° (b), and 190° (c); $250\times$ magnification, crossed nicols

peak ($490-500^\circ$). TG indicates a maximum rate of decomposition between 480° and 500° .

— Weight loss and endothermic peak between $550-620^\circ$. The thermobalance indicates that the TeO_2 composition is reached at about 630° only.

Apart from the presence of the second endothermic effect at $350-410^\circ$ the heating curve between 20° and 500° agrees well with that reported by Jander [4]. The TG curve closely follows that given by Rosický et al. [10].

Figure 2, recorded with the thermocouple in direct contact with the sample in order to improve heat exchange, indicates that at the maximum rate of decomposition the process of depletion of most labile H_2O , leading to $(H_2TeO_4)_n$, is actually described by two endothermal effects at 146° and 154° , the first of which being particularly sharp. The same observations were made by Bayer [17], in connection to monoclinic H_6TeO_6 [18, 19], the same crystal form which was used in the present investigation. To elucidate the events in this region, samples were examined optically at a heating stage. After recrystallization from H_2O at room temperature, H_6TeO_6 exhibits both optically anisotropic and isotropic regions, the latter being due to amorphous material; at about $135^\circ-140^\circ$ the interference colours change notably until at 146° birefringence suddenly disappears completely, although the external shape of the crystals is maintained (Figs 3a, b). At higher temperatures softening of the solid and nucleation is evident, accounting for some residual birefringence. The effects of the former process are clearly illustrated

in Fig. 3c, which show a plastic deformation and development of creeps. The observed transformations are irreversible as the modified solid is stable at room temperature. The onset temperatures of the processes described above depend on the state of hydration of the solid and on the heating rate during the experiment. Quite similar observations were made for prismatic aggregates of H_6TeO_6 , both under atmospheric and controlled conditions in sealed tubes.

In order to interpret the other observed thermal effects, sampling was carried out in non-standard equipment which permits to handle quantities sufficient for various analyses (X-ray, IR, UV and visible spectroscopy). Samples were thus taken in correspondence with the main thermal effects during the 9° min^{-1} heating run: 190° , 342° , 410° , 485° , 510° and 620° (ref. *a - f* in Fig. 1); due to the relative insensitivity of the DTA cell the minor endothermic peaks at $480-490^\circ$ were not observed here (see Fig. 1). After cooling to room temperature in air the degradation products were also observed under the optical microscope and analyzed chemically. Optical microscopy performed on the samples gives indications of a sequence of solid state transformations, as the crystallites conserve the original morphology up to about 400° . In accordance with results reported above, after thermal excursion to 190° only traces of crystalline H_6TeO_6 are observed; the crystallites of the sample $(H_2TeO_4)_n$ are composed of amorphous or microcrystalline material, yellow at the borders ($n > 1.67$) and white at the center of the grains ($n < 1.67$). Chemical analyses (Table 1) suggest that differences in refractive indexes in samples collected below about 340° are presumably related to different states of hydration or polymerization rather than to different valency

Table 1

Chemical analysis of thermal degradation products of H_6TeO_6 before and after cooling to room temperature (r.t.) and ageing in air

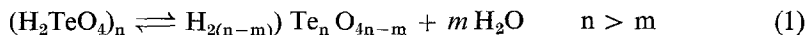
Sam- pling point ⁺	Analysis at room temperature					Analysis at <i>T</i>			
	Chemical composition, wt %					Sam- pling point ⁺	Sam- pling temp., °C	%Wt Loss (TG)	Formal Composition*
TeO ₂	TeO ₃	H ₂ O ⁺	Weight loss at <i>t</i> = ∞	Formal com- position					
b'	0.1	90.9	9.0	15.7	H ₂ TeO ₃	b	342	19.0	H _{1.16} TeO _{3.58}
c'	22.8	71.7	5.5	21.0	H _{1.10} TeO _{3.29}	c	410	22.1	H _{0.81} TeO _{3.15}
d'	63.0	35.0	2.0	26.7	H _{0.37} TeO _{2.52}	d	485	27.2	H _{0.23} TeO _{2.45}
e'	75.3	24.7	—	28.9	TeO _{2.23}	e	510	29.0	TeO _{2.23}
	100	—	—	30.5	TeO ₂	f	620	30.5	TeO ₂

⁺ Cfr. Figs 1, 4.

⁺⁺ Calculated values.

* Calculated from observed weight loss in TG, on the assumption of a Te(IV)/Te(VI) distribution as determined at r.t.

levels of tellurium, in accordance with Breusov et al. [11]. Results of Table 1 thus evidentiate that the gradual weight loss between 230° and 342° can be interpreted as a dehydration process which is probably accompanied by depolymerisation, formally as follows:



At the limit, under suitable experimental conditions, this process is expected to lead to TeO_3 ($n = m$) if no simultaneous valence change occurs. While at 342°

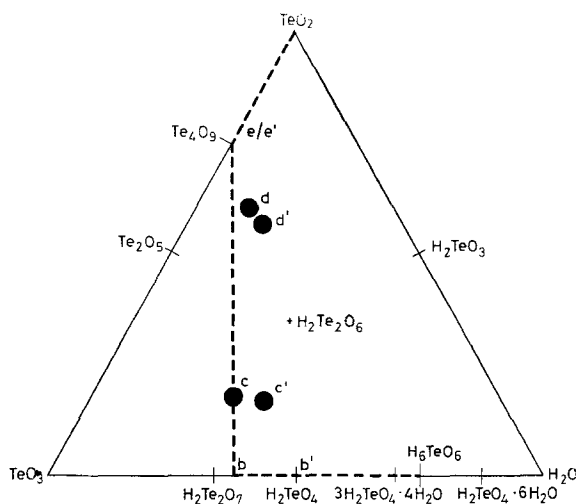


Fig. 4. Ternary system TeO_2 – TeO_3 – H_2O with overview of tellurium oxides and oxyacids. Dashed line bcde indicates degradation path of H_6TeO_6 in a 5° min^{-1} heating run; b' c' d' e' are compositions of the hygroscopical samples after long standing

the weight loss reaches about 19 wt%, after long standing (several days) at room temperature it amounts to only 15.7% (b and b', Fig. 4). In the latter sample, again with stoichiometric composition H_2TeO_4 , high refractive index material prevails. As assignment of the yellow fraction to TeO_3 does not well agree with the achieved stoichiometric composition, we suggest that the variety in optical properties of the specimen is connected to the degree of polymerization of $(\text{H}_2\text{TeO}_4)_n$. Thus, possibly the white low-index material corresponds to polymetate telluric acid with metate telluric acid, eventually arising here from hydration of TeO_3 , accounting for the higher index and yellow colouration. It thus appears that Eq. (1) is reversible. No further uptake of water to form H_6TeO_6 was observed at the conditions of our experiment. This latter hydration process is known to be quite slow [4].

Results gathered in Table 1 clearly show that the endothermic peaks between 300° and 500°, including the minor thermal effects at 480°–490°, are due to

simultaneous depletion of water and oxygen, in contrast to other interpretations [4] and indicate the hygroscopic nature of the hydrated Te(VI, IV) oxides as opposed to $(\text{H}_2\text{TeO}_4)_n$. The break of the TG curve at 360° is to be interpreted as the critical temperature at which, under given conditions, oxygen depletion sets in: it is noticed that the heating curve (Fig. 1) shows a sharp flexion in correspondence to the same temperature, leading to a pronounced endothermal effect. Optical observations of the 410° sample, after long standing at room temperature (c' , Fig. 4) show a yellow amorphous phase with residuals of the white nuclei of the granules. Local opacity of some granules, observed in polarized light, indicates transformation of yellow amorphous material into polycrystalline aggregates, not detectable by X-ray diffraction. The onset of this transformation is already evident in the 342° sample, at 485° involves all of the specimen with the exclusion of the last traces of the white phase at the nuclei of some granules. In the latter sample, a TeO_2 -like phase was also detected optically, but the sample was still X-ray amorphous. At about 510° , completion of dehydration is accompanied by an exothermic reaction which is typically due to crystal-growth phenomena. The crystalline and anhydrous specimen contains tetra- and hexavalent tellurium. The X-ray diffraction pattern is complex and consists of the contribution of three components: tetragonal TeO_2 (paratellurite), and two phases characterized by

Table 2
Observed d -spacings (\AA)

Set I		Set II	
d	I/I_0	d	I/I_0
4.91	10	7.58	65
4.63	5	5.13	65
4.19	50	4.81	33
3.565	100	3.99	65
3.436	40	3.84	100
3.342	20	3.470	100
2.912	45	2.762	33
2.886	40	2.559	33
2.762	5	2.457	90
2.457	15	2.378	100
2.444	25	1.997	25
2.265	10		
2.132	10		
2.046	10		
1.997	5		
1.948	5		
1.808	10		
1.772	5		
1.732	5		
1.608	5		
1.446	10		

d -values (Table 2a, b) which differ from those reported for TeO_3 [7, 8, 11], obtained hydrothermally, and for Te_2O_5 [6] and Te_4O_9 [15]. Finally, at about 620° stoichiometric TeO_2 is found.

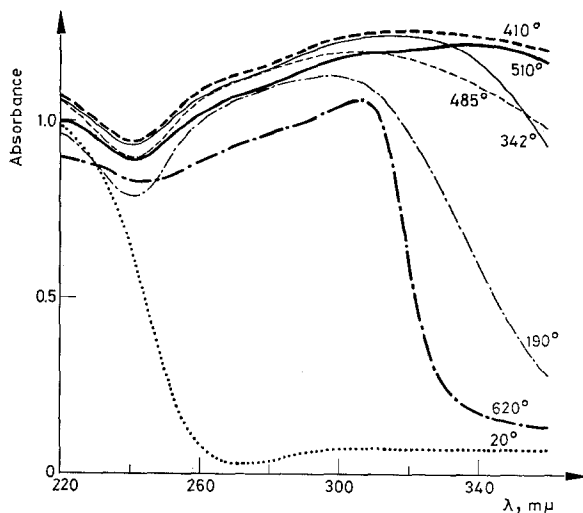


Fig. 5. U.V. reflectance spectra of the thermal degradation products of H_6TeO_6 obtained from sampling at various temperatures during DTA experiments

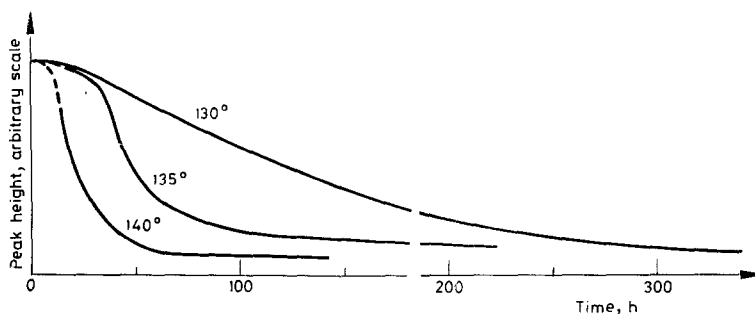


Fig. 6. Kinetics of thermal decomposition of H_6TeO_6 between 130° and 140° , as measured from decay of I (111) ($d = 4.76 \text{ \AA}$)

The degradation process of telluric acid was also followed by U.V. and visible reflectance spectroscopy performed on the same samples as described above. Figure 5 shows the various stages. We observe the striking differences between the absorbances of H_6TeO_6 with distorted octahedral symmetry [20] and the partially dehydrated product $(\text{H}_2\text{TeO}_4)_n$ at 190° ; in the polymeric acid Te is also six-coordinated [20]. Towards higher temperatures, up to about 500° , the samples are characterized by absorption in the visible region, in accordance with the observa-

tion at the microscope. This has been claimed to be related to quadri- and hexavalent Te-containing degradation products [11]. The yellow colouration reaches a maximum intensity for $\Delta w \approx -23\%$, in accordance with Breusov et al. [11]. Once TeO_2 is formed, the visible component rapidly decreases.

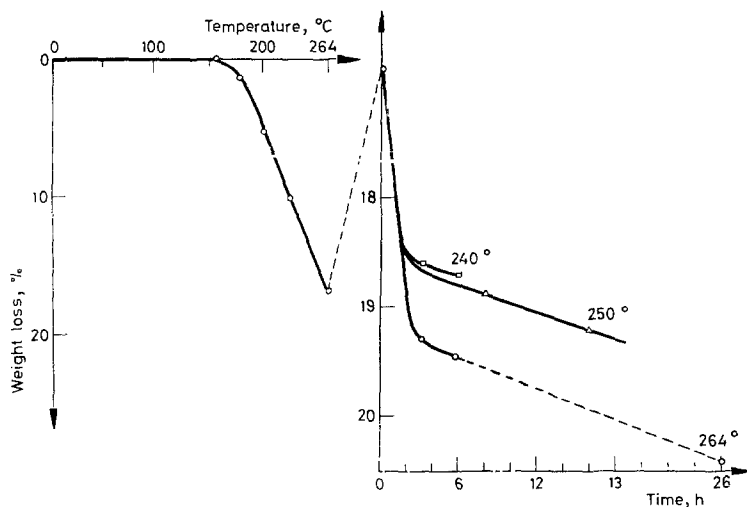


Fig. 7. Isothermal degradation of H_6TeO_6 to $\text{H}_2\text{Te}_2\text{O}_7$.

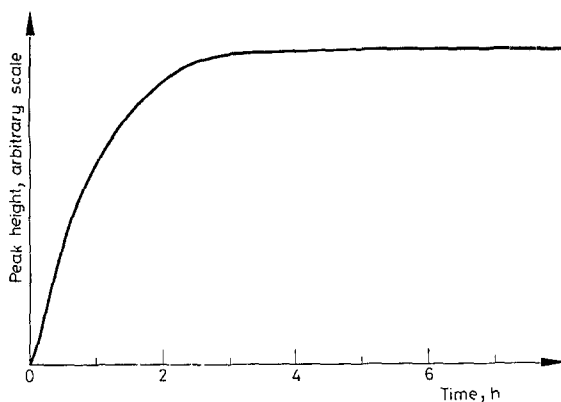


Fig. 8. Crystallization kinetics of TeO_2 as measured from I(102) at 550°

TG and X-ray diffraction studies of isothermally conditioned samples were made to confirm the results of the thermal analysis during the heating run. Figure 6 shows the decomposition of H_6TeO_6 at 130° – 140° , as observed in a high-temperature X-ray camera. In 3.5 h at 160° H_6TeO_6 settles for the theoretical weight loss expected for $(\text{H}_2\text{TeO}_4)_n$ (Table 3), in 3h at 264° for that corresponding

to $\text{H}_2\text{Te}_2\text{O}_7$ (Fig. 7). TG analysis of the latter specimen shows no further weight loss from room temperature up to about 325° ; afterwards the degradation closely follows the TG curve reported in Fig. 1. Prolonged calcination in air at 270° (Tab. 3) causes depletion of oxygen. A H_6TeO_6 sample treated at 300° for 17 h contains a considerable fraction of Te(IV), even though residual weight loss of 9.15% formally corresponds to the decomposition of TeO_3 to TeO_2 . X-ray diffraction indicates that the degradation process leads via amorphous to crystalline sub-

Table 3
Results of isothermal heat-treatments of telluric acid in air

Activation conditions		Chemical analysis, wt%			Phase distribution	Ref.
Temp, $^\circ\text{C}$	Time, h	Te ⁴⁺	Te ⁶⁺	Σ Te		
110	20	—	55.5	55.5	H_6TeO_6	a
120	25	—	—	65.9	amorphous $(\text{H}_2\text{TeO}_4)_n$	10
150	1	—	—	—	$\text{H}_2\text{TeO}_4 \cdot 0.36\text{H}_2\text{O}$	4
160	3.5	—	—	—	$(\text{H}_2\text{TeO}_4)_n$	a
250	20	—	—	—	αTeO_3	18
250	> 24	—	—	—	$(\text{H}_2\text{TeO}_4)_n$	6
270	8	0.76	65.7	66.5	$(\text{H}_2\text{TeO}_4)_n$	a
270	24	1.8	65.0	66.8	amorphous	a
300	17	20.7	48.9	69.6	amorphous	a
310	25	—	—	72.6	amorphous $\alpha\text{-TeO}_3$	10
310	20 ⁺	—	0	—	crystn. Te(IV) containing product	10
330	weeks	—	—	—	amorphous; $\text{TeO}_3\text{-B}$	6
350	18	24.4	45.6	70.0	—	a
360	40	—	—	—	crystn. TeO_3	17
400	25	61.0	15.8	76.8	amorphous + TeO_2	a
406	25	—	—	76.0	crystn. Te_2O_5	10
410	weeks	—	—	76.1	crystn. Te_2O_5	6
420+440	60	—	—	—	crystn. Te_2O_5	17
450	8	—	—	—	Phase I + TeO_2	a
450/500	8	—	—	—	Phases I, II + TeO_2	a
485	25	—	—	79.9	TeO_2	a
500	8	70.7	7.0	77.7	Phase II + TeO_2	a
500	20	—	—	—	Phase II + TeO_2	a

^a This work.

⁺ Closed tube reaction.

stances, the sequence of formation of the latter being that of the phases of Table 2 a and b, and finally TeO_2 . As to this end-product of the degradation process, prolonged heating at 400° leads to its partial formation and crystallization. From the isothermal experiments it appears that TeO_2 (paratellurite) can be obtained at 500° only after relatively long periods of heating. The results differ from other indications [11]. Above 550° the thermal decomposition leading to TeO_2 is rapid (Fig. 8).

Discussion

Literature information concerning product formation during thermal decomposition of orthotelluric acid differs considerably, especially with regard to the stability ranges of the phases, partly as a consequence of varying experimental conditions. The first overall step, formation of stoichiometric amorphous [4, 10] or crystalline [5, 7] polymetate telluric acid, $(\text{H}_2\text{TeO}_4)_n$, where $n = 11 \pm 1$ [21], through loss of two moles of H_2O of constitution, is commonly agreed on by all authors. The next sequence of events however appears to be more complex. The composite nature of the first step in the degradation process (Fig. 2) may be described as a superposition of a sharp endothermic effect with maximum at 146° onto a slower process (max. at 154°). As to the former, the corresponding sudden attenuation of birefringence appears to indicate order-disorder phenomena, such as a transition of a well-defined crystal-structure (H_6TeO_6) into a more disordered material; this may be compared to similar sharp exothermal effects during disorder-order transitions (*e.g.* crystallisation). The slower process may be understood on the basis of chemical rather than structural variations, thus degradation to chemically badly defined compositions. At 146° a partially dehydrated product is thus present and it would be of interest to establish its relation to a substance described in the literature [4], namely the metastable hydrate of polymetate telluric acid (allotelluric acid). This product however, obtained by thermal degradation of H_6TeO_6 in a sealed tube at about 136° , after loss of $2/3$ moles H_2O , is described as being a colourless syrupy mass. The microphotographs (Figs 3), illustrating the structural and chemical variations in the temperature range of Fig. 2, show pseudomorphism of the samples H_6TeO_6 and $(\text{H}_2\text{TeO}_4)_n$, thus excluding any intermediate phase transition. Consequently, this consideration casts doubt on the presence of allotelluric acid under the conditions of our experiment. The existence of this compound could not be confirmed even by approaching the conditions of ref. [4]. After the loss of the chemically weakest bonded H_2O from the ordered crystal-lattice of H_6TeO_6 the process appears to proceed via various more or less well-defined stages to yield $(\text{H}_2\text{TeO}_4)_n$.

Depolymerization and dehydration of polymetate telluric acid then continues till the formal composition $\text{H}_2\text{Te}_2\text{O}_7$ is reached, in correspondence to the break in the TG curve at 360° (Fig. 1; *cfr.* also Fig. 1 in ref. 10). Optical microscopy indicates solid state transformations from $(\text{H}_2\text{TeO}_4)_n$ to $\text{H}_2\text{Te}_2\text{O}_7$ without any morphological changes. Figure 7 reports the formation of pyrotelluric acid by isothermal dehydration of a H_6TeO_6 sample in TG equipment ($\Delta w_{\text{theor.}} = -19.6\%$). After cooling to room temperature, the X-ray amorphous solid with stoichiometry $\text{H}_2\text{Te}_2\text{O}_7$ appears as optically heterogeneous with onset of crystallization phenomena at the borders of the crystals; refractive index measurements indicate lower degrees of hydration at the external surface of the crystals than in the bulk. It thus appears that the $\text{H}_2\text{Te}_2\text{O}_7$ sample obtained here consists of a weighted mixture of various hydrated states. In spite of this, the reported behaviour of the

sample up to 325° during TG analysis seems to be indicative of a certain stability of the H_2TeO_7 composition, suggesting compound formation.

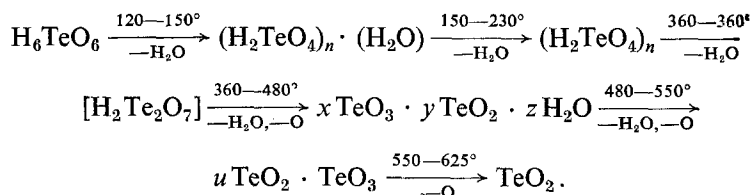
Further experiments indicate that the sample is quite easily partially rehydrated (cfr. also Tab. 1), with the crystalline fraction being more resistant.

Degradation of pyrotelluric acid, under the conditions of our experiment, proceeds as indicated in Fig. 4, thus by dehydration and depletion of oxygen (see Table 1; cfr. Fig. 1 with Figs 2 and 3 in ref. 10). Competition between the two processes can lead to oxyacids as $H_2Te_2O_6$ [15] and/or anhydrous mixed oxides as Te_2O_5 and Te_4O_9 . Indeed, it has been observed previously that thermal decomposition of H_6TeO_6 in air yields products of complex composition containing chemically combined tellurium (VI, IV)-oxides and H_2O ; this is the case of Breusov et al. [11] and of Rosický's orange-coloured X-ray amorphous α - TeO_3 [10]. The observed discontinuity in the TG curve (Fig. 1) at 430° probably stands for the onset of the decomposition of TeO_3 , known from similar experiments [8] to occur at this temperature. Our finding of loss of oxygen in isothermal runs at 270° agrees with the fact that oxygen is given off by TeO_3 at temperatures as low as 305° [11]. The apparent rate of decomposition of TeO_3 depends on the mode of preparation, particle size and temperature of decomposition [12].

Rosický [10] has presented convincing evidence for the successful synthesis of the yellow Te_2O_5 by heating H_6TeO_6 at constant T (406°) in air (Table 3 and Figs 4, 5 in ref. 10) even though the X-ray spectrum differs from that reported elsewhere [6]. The compound, not reported by Breusov et al. [11], is probably present in our specimen sampled at 485° in the DTA experiment (compare Fig. 4). Starting from crystalline β - TeO_3 , Dumora [8] registers Te_2O_5 in a DTA experiment at about 525°. The compound deoxygenates at 570° [15].

Evidence for the formation of compounds $xTeO_2 \cdot TeO_3$ stems from decomposition curves of H_6TeO_6 in air, where a phase of formal composition $Te_{2.1}$ was first ignored [10], while later a double oxide of variable composition $TeO_2 : TeO_3 = (5 - 3) : 1$, thus containing both quadri- and hexavalent tellurium, was described [11]. However, in more recent work [6, 8], no such double oxides were noticed, although $3TeO_2 \cdot TeO_3$ was synthesized in hydrothermal conditions [15]. Figure 1 clearly confirms the formation of Te(IV)-rich mixed oxides, as the weight loss in the TG experiment slows down in correspondence with the composition $3TeO_2 \cdot TeO_3$ and speeds up at $5TeO_2 \cdot TeO_3$. X-ray diffraction experiments (Table 3) have given evidence for two sets of d -spacings, one of which (set II, Table 2) was always observed together with the characteristic diffraction bands of TeO_2 and could represent superstructure reflections of a TeO_2 -like structure; instead, set I characterizes a single phase, although not identifiable with any of the (mixed) tellurium oxides described so far. Finally, decomposition to TeO_2 at increasing temperature is achieved only at about 625°, in good accordance with other work [8, 15]. The analytical results are qualitatively in agreement with the indications of optical reflectance spectra (Fig. 5).

At the scanning speed of 5° min^{-1} , DTA and TG data thus indicate the following decomposition sequence of pure H_6TeO_6 (Figs 1 and 2):



At a lower heating rate (1.6°) qualitatively the same results are obtained, but at slightly lower temperatures. Our results differ significantly from the observations of similar DTA experiments by Moret and Maurin [6] who, starting from crystalline compounds $(\text{TeO}_3 \cdot \text{H}_2\text{O})_n$, $\text{TeO}_3 \cdot A$, $\text{TeO}_3 \cdot B$ and $\text{TeO}_3 \cdot \text{TeO}_2$, failed to observe Te(IV)-rich double oxides. It is possible that the reported different chemical nature of crystalline and amorphous polymetatelluric acid, namely $\text{TeO}_2(\text{OH})_2$ as opposed to a compound containing both $\text{H}_3\text{O}-$ and $\text{OH}-$ groups [5], leads to distinct degradation paths.

The influence of the partial oxygen pressure on the thermal decomposition of telluric acid, implicit in the present work, is sustained by the observation [11] that in vacuo the oxygen depletion starts already at 200° and is completed at 430° . On the other hand, at higher pressure in hydrothermal conditions complete dehydration can be achieved before reduction sets in, thus permitting synthesis of various intermediate compounds. So is crystalline $(\text{H}_2\text{TeO}_4)_n$ obtained after 24 h at 300° in closed tubes [5], while in similar conditions in air Te(IV) is formed (Table 3). Attempts to further clear up the existence of $\text{H}_2\text{Te}_2\text{O}_7$ will probably benefit from an increased p_{O_2} .

Conclusions

The results reported warn against the dangers of careless assumptions on the nature of thermal reactions during complex degradation processes. It was shown that in the decomposition of H_6TeO_6 oxygen is lost from tellurium trioxide before the last of the water is driven off. At instances oxygen is depleted more readily than water and with a different temperature dependence. Thus weight loss data alone are not enough for the study of the thermal degradation process.

The authors are indebted to Dr. A. Marzi for the optical observations and for preparation of the microphotographs.

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RÉSUMÉ — On a réexaminé la dégradation thermique de l'acide orthotellurique. L'absence de variations morphologiques dans l'intervalle de 120°—200° exclut la formation de l'acide allotellurique. Ensuite, l'analyse thermique différentielle conduit par décomposition progressive à l'acide polymétatellurique et à l'acide pyrotellurique. La déshydratation à l'air donne lieu à des substances amorphes et est accompagnée simultanément de perte d'oxygène. On obtient des anhydrides cristallins contenant Te(IV) et Te(VI) à 550° et TeO₂ à 620°.

ZUSAMMENFASSUNG — Es wird über hydratisierte Zwischenstufen während der thermischen Abbau von Orthotellursäure berichtet. Die Abwesenheit morphologischer Änderungen und die beobachtete plastische Deformationen im 120°—200° Bereich schliessen die Bildung metastabiles Allotellursäure aus. Dagegen führen partielle Entwässerungsversuche an der Luft zu der Annahme von Pyrotellursäure. Abhängend von den Versuchsbedingungen werden DTA und TG Kurven produziert deren Verlauf nicht charakteristisch ist für separate Wasser oder Sauerstoffabgabe. Kristallinische Tellurium(VI, IV) Oxyden entstehen bei 550° und die Übergang zum Telluriumdioxid ist vollendet bei 620°.

Резюме — Была проведена критическая оценка термического разложения H₆TeO₆ в атмосфере воздуха. Представлены доказательства механизма разложения, заключающийся в ступенчатой дегидратации H₆TeO₆ до полиметателлуровой кислоты с образованием промежуточных нестехиометрически аморфных тел и с дальнейшим превращением до пиротеллуровой кислоты. В процессе структурных превращений не наблюдалось каких-либо морфологических изменений и не было обнаружено доказательств образования аллотеллуровой кислоты. Дальнейшая дегидратация сопровождается восстановлением, которое зависит от экспериментальных условий. Этим и объясняется значительное разнообразие приведенных ранее результатов. При температуре около 550° были получены кристаллические Te(VI)—Te(IV) окислы, из которых затем при дополнительном прокаливании около 620° образуется TeO₂.