Journal of Thermal Analysis, Vol. 24 (1982) 95–100

A STUDY OF THE THERMAL DECOMPOSITIONS OF ORTHOTELLURIC ACID, UREA AND THE ORTHOTELLURIC ACID ADDUCT WITH UREA

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(Received November 19, 1981)

The thermal decompositions of $Te(OH)_6$, $CO(NH_2)_2$ and the adduct $Te(OH)_6 \,.\, 2\,CO(NH_2)_2$ in air and in an inert atmosphere were studied using TG, DTG, DTA and GC methods in the interval between laboratory temperature and 750°. The first gaseous product of the decomposition of urea is water vapour; the decomposition yields first cyanamide, and then biuret in four steps. The adduct is primarily decomposed to diammonium metatellurate and urea, with liberation of H_2O and CO_2. Diammonium metatellurate is decomposed to α-TeO_3 as intermediate-product.

The present paper deals with the thermal decomposition of the adduct of orthotelluric acid with urea, $Te(OH)_6 \,.\, 2\,CO(NH_2)_2$. To facilitate the interpretation of the decomposition, the decompositions of the adduct components, i.e. orthotelluric acid and urea, were also studied. The thermal decomposition of orthotelluric acid in air has already been studied [1–5] and the formation of the solid products can be described by the scheme

$$Te(OH)_6 \xrightarrow{140-200^\circ} (H_2TeO_4)_n \xrightarrow{250-400^\circ} \alpha\text{-}TeO_3 \xrightarrow{420-485^\circ} Te_2O_5 \xrightarrow{560-600^\circ} TeO_2 \qquad (1)$$

The basis of α-TeO_3 is described in [6]. The final product is tellurium dioxide. Gaseous products of the decomposition have not yet been studied.

The thermal decomposition of urea has been studied often [7]. It is evident that it proceeds in very different ways, depending on the experimental conditions. According to ref. [8], the solid products found at 130° involve urea (I), ammonium cyanate (II) and ammonium carbonate (III); at 200° (I), biuret (IV), (II), cyanuric acid (V) and (III); at 250° (I), (II), ammeline (VI), ammelide (VII), (V), (III) and melamine cyanurate; and at 400° melamine (VIII) and (III). According to refs [9, 10], the solid products are (I), (IV) and (V) at 130°; (I), (IV), (V), guanidine, (VI) and (VII) at 160°; (I), (V), (VI) and (VII) at 200°; and cyanuric bases and (VIII) at 300°. The thermal curves of urea above 230° are virtually identical with those of biuret above this temperature [11].

As regards the urea adducts with oxoacids, the decomposition of urea phosphate has been studied [12], during which decomposition to the initial components

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occurs at the melting point of the adduct and the final solid product is predominantly polymetaphosphoric acid, $(HPO_3)_n$. The gaseous products of the decomposition of urea nitrate (N_2O, CO_2, H_2O) are known with relative certainty, but the solid products found by various authors differ considerably [13]. The thermal decomposition of urea perchlorate probably proceeds through the formation of ammonium perchlorate and cyanuric acid [14]. Some conclusions concerning the structure of the urea-orthoboric acid complex have been drawn [15] on the basis of the course of its thermal study and the infrared spectra.

Experimental

The adduct $Te(OH)_6 \cdot 2\,CO(NH_2)_2$ was prepared by crystallization from a concentrated aqueous solution of orthotelluric acid and urea in a molar ratio of 1 : 3, clear large crystals being obtained [16]. Orthotelluric acid and urea were commercial chemicals of p.a. purity. The substances and the decomposition products were stored in a desiccator at laboratory temperature.

The thermal decompositions were followed using a derivatograph (MOM, Hungary) which allows simultaneous recording of the TG, DTG, DTA and T curves, in ceramic crucibles with 200–300 mg of sample, employing a Pt–PtRh thermocouple, a temperature increase of 5 degree/min, from laboratory temperature to 750°, and using Al_2O_3 as reference material in the air and in a nitrogen atmosphere.

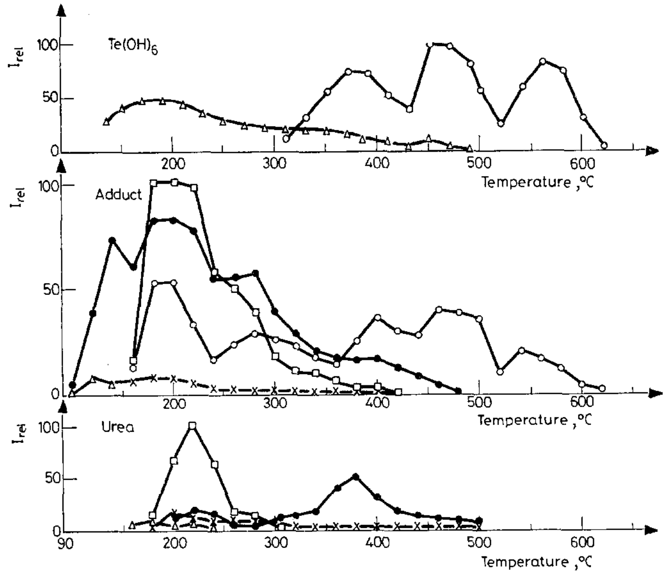

Fig. 1. Relative intensities of gas elution during the thermal decompositions of orthotelluric acid, the adduct and urea. △ H_2O, ○ O_2, ● CO_2, □ NH_3 × ×

Gas chromatographic measurements were carried out on a Fractovap C instrument (Carlo Erba, Italy) with a thermal conductivity detector. The gaseous decomposition products were separated in a glass column 80 cm long, 3 mm in I.D., packed with Porapak R (100–120 mesh), at a temperature of 80°. Helium carrier gas was used at a flow rate of 25 cm^3/min. The examples were decomposed in a Supremax glass tube in an oven, with the temperature increasing at a rate of 2 degree/min. The gaseous decomposition products were injected after 10 min, i.e. after a temperature increase of 20°, through a six-way stop-cock connected to the decomposition tube.

For some X-ray and magnetic measurements, 200 mg samples were decomposed by heating in a crucible placed in an oven for 2 hours at a given temperature, maintained with a precision of 2°. The samples were then allowed to cool to laboratory temperature in a desiccator.

X-ray studies were performed by the Debye–Scherrer method, in a chamber with a diameter of 57.3 mm, using CuK_α radiation filtered by a nickel filter. The magnetic susceptibilities were measured on a Faraday magnetic torsion balance.

The values given are averages of at least three experimental values and the last digit is rounded to 0 or 5.

Results and discussion

The TG and DTA results are given in Table 1 and the GC results in Fig. 1. It can be seen from the Table that the decompositions in air are practically the same as those in the inert atmosphere.

Orthotelluric acid (monoclinic modification) begins to decompose at 140° with liberation of water, the last portion of which escapes as late as immediately before the crystallization of the product to form Te_2O_5. Oxygen begins to escape at 305° and is liberated in three waves, with maxima at 370, 455 and 560°. The first two waves correspond to oxygen loss with the formation of Te_2O_5 and the third wave corresponds to the formation of tellurium dioxide (tetragonal modification), which melts to yield amorphous tellurium dioxide. The minimum oxygen liberation at 520° corresponds to the formation of Te_2O_5.

Urea first melts and then decomposes in a single wave with a slight inflexion at 240°. According to the DTA measurement, the decomposition above 240° is simpler in nitrogen than in air. The GC measurement has proved unambiguously that the first gaseous product is water, thus indicating that in urea decomposition an unstable intermediate, cyanamide ($CNNH_2$), is formed:

$$CO(NH_2)_2 \rightarrow CNNH_2 + H_2O \qquad (2)$$

Further gaseous products are ammonia and a basic substance with a retention time somewhat longer than that for ammonia, which is denoted by symbol X in Fig. 1. Carbon dioxide is formed at temperatures above 180°. The maximum ammonia liberation occurs at 220°. This fact can be explained by urea decomposi-

Table 1

TG and DTA data for orthotelluric acid, adduct and urea. The temperatures of the effect beginning are given in °C; symbol *E* with DTA denotes an exothermic effect

Atmosphere	$Te(OH)_6$		Adduct		$CO(NH_2)_2$		Interpretation
	TG	DTA	TG	DTA	TG	DTA	
air				90		130	melting
	140	145	90		155		beginning of decomposition
				135		180	decomposition
				205	240	230	
				305		305	
	420	335				330	
	460	420				405	
						440*E*	
		485*E*		480*E*			crystallization
	560	565		585			decomposition
	625		620		500		end of decomposition
		695		680			melting
nitrogen				100		125	melting
	140	130	100		145		beginning of decomposition
	340	330		145	240	180	decomposition
	470	415		395		330	
		460					
		480*E*		480*E*			crystallization
	590	565		580			decomposition
	600		595		520		end of decomposition
		690		685			melting

tion to an unstable intermediate, isocyanic acid (CONH), whose decomposition yields biuret, $HN(CONH_2)_2$, according to the scheme

$$\begin{gathered} CO(NH_2)_2 \rightarrow CONH + NH_3 \\ CONH + H_2O \rightarrow NH_3 + CO_2 \\ CO(NH_2)_2 + H_2O \rightarrow 2\,NH_3 + CO_2 \\ CO(NH_2)_2 + CONH \rightarrow HN(CONH_2)_2 \end{gathered} \tag{3}$$

Hence, schemes (2) and (3) represent urea decomposition better than the scheme often encountered in the literature [7], which assumes direct formation of biuret:

$$2\,CO(NH_2)_2 \rightarrow NH(CONH_2)_2 + NH_3$$

The mass loss observed at the inflexion point at 240° corresponds to possible formation of cyanuric acid, $(CONH)_3$. Both the solid intermediate formed at this temperature and the other studied solid intermediates were X-ray amorphous. This indicates that the intermediates are mixtures of substances that would require a longer time for crystallization.

The adduct begins to decompose immediately after melting, with liberation of water and a large amount of carbon dioxide, probably according to the scheme

$$Te(OH)_6 \,.\, 2\,CO(NH_2)_2 \rightarrow (NH_4)_2TeO_4 + CO(NH_2)_2 + H_2O + CO_2 \qquad (4)$$

The further stages of the decomposition are the same as those for diammonium metatellurate and urea, as indicated by the gaseous products formed from 160° and corresponding to schemes (3) and

$$2\,(NH_4)_2TeO_4 \rightarrow 2\alpha\text{-}TeO_3 + 4\,NH_3 + O_2 \qquad (5)$$

Above 360° the liberation of oxygen is similar to that with telluric acid. The solid products formed below 480° were X-ray amorphous and those formed above this temperature were identical with the products of the decomposition of telluric acid (see scheme (1)). The products obtained at 150–225° are yellowish to orange and diamagnetic. The analogously coloured products obtained in the decomposition of orthotelluric acid are paramagnetic, their paramagnetism being caused by the sorption of oxygen, O_2, or by the presence of products with the superoxide ion, O_2^- [3, 6]. Therefore, the colouration of the present products must be ascribed to the grain size.

It was impossible to carry out an analogous study of the decomposition of the urea adduct with orthoperiodic acid, $H_5IO_6 \,.\, CO(NH_2)_2$ [17], as the adduct decomposed explosively at 160°.

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ZUSAMMENFASSUNG — Die thermische Zersetzung von $Te(OH)_6$, $CO(NH_2)_2$ und des Adduktes $Te(OH)_6 \cdot 2\,CO(NH_2)_2$ wurde in Luft und in einer inerten Atmosphäre durch TG, DTG, DTA und GC-Methoden im Bereich zwischen Raumtemperatur und 750° untersucht. Das erste gasförmige Produkt der Zersetzung von Karbamid ist Wasserdampf, die Zersetzung verläuft über Cyanamid und Biuret in vier Stufen. Das Addukt wird zu Diammonium-Metatellurat und Karbamid zersetzt, unter Freisetzung von H_2O und CO_2. Das Diammonium-Metatellurat wird zu α-TeO_3 als Endprodukt zersetzt.

Резюме — Методами ТГ, ДТГ, ДТА и газовой хроматографии изучено термическое разложение $Te(OH)_6$, $CO(NH_2)_2$ и их продукта присоединения $Te(OH)_6 \cdot 2CO(NH_2)_2$ в воздушной и инертной атмосферах в интервале температур от комнатной до 750°. Пары воды являются первым газообразным продуктом разложения мочевины, а последующим продуктом разложения является первоначально цианамид и затем следует четырехстадийное образование биурета. Аддукт первоначально разлагается до метателлурат аммония и мочевины с выделением CO_2 и H_2O. Метателлурат аммония в свою очередь разлагается до α-TeO_3 как конечного продукта.