Thermal Decomposition of (BaTi) Citrates into Barium Titanate

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From aqueous solutions of barium and titanium citrates two different (BaTi) citrate salts can be precipitated, depending on the pH of the solution. The ratio of barium to titanium in the salts is either 1 : 1 or 2 : 1. The thermal decomposition of the salts was investigated by means of DTA, TGA, infrared spectroscopy, and X-ray diffraction. At about 550°C, all specimens having a barium to titanium ratio of 1 : 1 showed the overall composition $TiO_2 \cdot BaCO_3$. Prior to the formation of $BaTiO_3$, recrystallization and separation of small amounts of $BaCO_3$ and of an intermediate phase was observed. The formation of $BaTiO_3$ is completed already at 600 to 700°C. Complete mixing of the Ba and Ti on an atomic scale seems doubtful.

1. Introduction

In addition to the classical preparation method of barium titanate by mixing and calcining of $BaCO_3$ and TiO_2 the wet chemical methods of preparation are becoming increasingly important.

The wet chemical methods start with dissolved compounds of barium and titanium which are converted by coprecipitation into largely insoluble hydroxides (1) or complex compounds (2, 3) and, by subsequent heating, into barium titanate. The advantage of these techniques is that the homogeneous distribution of the barium and titanium on an almost atomic scale in the solution is largely maintained also on precipitation. The immediately adjacent ions of barium and titanium can therefore react with each other at relatively low temperatures already, 600 to 700°C, to form homogeneous, stoichiometric barium titanate. By contrast in the classical method the calcination temperature of barium carbonate and titania to form barium titanate depends on the particle size and the extent of mixing and still lies above 1000°C even after intense grinding of the raw materials (4). A further disadvantage of the mixed oxide method is the contamination of the specimens by abrasion of the grinding balls.

A question of decisive importance concerning the mechanism of formation of the barium titanate is whether the thermal decomposition of the (BaTi) citrates or polyester resins into the final product, $BaTiO_3$, takes place in practically one single step, i.e., in a very narrow temperature region, or whether the pyrolysis takes place via a series of intermediate compounds of barium and titanium which can recrystallize and separate.

Recent investigations of the thermal decomposition of barium titanyl oxalates (5) revealed that prior to the formation of $BaTiO_3$ highly reactive barium carbonate and titanium(IV) oxide were formed. In two subsequent papers, Gopalakrishnamurthy et al (6, 7) denied the appearance of $BaCO_3$ and TiO_2 as intermediate phases and assured the formation of an intermediate compound of composition $Ba_2Ti_2O_5CO_3 \cdot CO_2$. The thermal decom-

position of (BaTi) citrates must therefore be expected to lead to the occurrence of similar phases. The point to be clarified then is whether the homogeneous distribution of the barium and titanium is still maintained in the expected intermediate phases.

Another method of producing barium titanate is represented by the thermal decomposition of (BaTi) citrate polyester resins (8). The partial separation and precipitation of arbitrary mixtures of dissolved (BaTi) citrates can be prevented by esterification of the three carboxyl groups of citric acid with a polyalcohol, e.g., ethylene glycol. During evaporation of the water the solution becomes highly viscous and is converted into a transparent glass. The thermal decomposition of such (BaTi) resins also poses the question of whether the homogeneous mixing of barium and titanium on an atomic scale is maintained throughout the entire course of the pyrolysis.

2. Experimental

2.1. Preparation and Analyses

To prepare the (BaTi) citrates high-purity titanium tetrabutylate (TBT) (Dynamit Nobel Troisdorf), citric acid (purest, DAB 7, Merck, Darmstadt), and barium carbonate (Selectipur, Merck, Darmstadt) were used. In accordance with a method worked out by Mulder (9), an aqueous titanyl citrate solution was prepared from TBT and citric acid, and this remained stable for several weeks after the addition of ammonia to pH 5. The titanium content of the solution was determined gravimetrically as TiO_2 by careful incineration in a porcelain crucible at 1000 to 1100°C of a low-ash filter paper previously impregnated with a titanium citrate solution. The barium citrate solution had been prepared by dissolution of an accurately weighed quantity of barium carbonate in a 2.5 M aqueous solution of citric acid. The barium content was determined volumetrically to ±0.1% with ethylenediaminetetraacetic acid (EDTA).

TABLE I

No.	Ba/Ti molar ratio in the solution	pH	Ba/Ti molar ratio in the salt
1	1:1	0.5	0.995 ± 0.005
2	1:1	1.2	0.995 ± 0.005
3	1:1	2.0	0.995 ± 0.005
4	1:1	2.6	0.995 ± 0.005
5	1:1	3.2	1.99 ± 0.01
6	1.5:1	1.2	0.99 ± 0.005
7	1.5:1	3.2	1.98 ± 0.01

The solutions of barium and titanium citrate were mixed to a ratio of Ba:Ti = 1.000 and 1.500 and adjusted by the addition of conc. HCl to various pH values. After about 2 h the (BaTi) citrates precipitated in the form of white crystals. Irrespective of the mixing ratio of the barium and titanium solutions but depending on the pH of the solution two different salts were formed: At pH ≤ 2.6 salt I was formed, having the Ba/Ti ratio of 1:1 and at pH ≥ 3.2 salt II having the Ba/Ti ratio of 2:1. The analytical results are shown in Table I. After drying in air both salts showed X-ray diffraction spectra rich in lines, yet different. The titanium content of the citrates was determined by precipitation with cupferron from a solution acidified with 6 N HCl, followed by incineration to TiO_2 in accordance with a method described by Claasen (10). Barium was determined gravimetrically as $BaSO_4$. The composition of the two citrate salts was determined from ignition losses and by means of C, H combustion analyses as well as by potentiometric titration of the citric acid. The empirical formulas of the two salts represent the probable composition after the performance of all analyses: Salt I:BaTi $(C_6H_6O_7)_3 \cdot 6H_2O$, salt II:$Ba_2Ti(C_6H_5O_7)_2 (C_6H_6O_7) \cdot 7H_2O$.

(BaTi) polyester resins were prepared in accordance with a patent specification of Pecchini (8).

2.2. Investigations of the Thermal Decomposition

The thermal decomposition of air-dried (BaTi) citrate I in air and in N_2 was studied by

means of TGA (Sartorius, Type 4201) and DTA (Linseis, Selb) at heating rates of 2 to 5°K/min.

The decomposition was performed also with somewhat bigger specimens (about 1 g) on a sand bath at heating rates of about 1°K/min as a destructive distillation. The distillation was stopped at various temperatures between 100 and 600°C for examination of the residues. The volatile decomposition products were, as far as possible, fractionated and then examined with respect to their composition, functional groups, and melting points by means of infrared spectroscopy (Beckman ir. 20A-x) and by chemical analytical methods. The residues of the decomposition were examined by means of ir spectroscopy and of a Norelco X-ray diffractometer with CuKα radiation. The ir spectra were measured on samples in KBr pellets. All the samples of salt I investigated had the Ba:Ti ratio of 0.955 ± 0.005 and a content of citric acid and crystal water as described above in Section 2.1.

3. Results

The TGA, DTG, and DTA of the decomposition of salt I (Figs. 1 and 2) show that the thermal decomposition takes place as a series of distinctly separable steps. The individual steps of the decomposition take place either exothermally or endothermally. While decomposition of salt I is completed already at 700°C, the end of the reaction in the case of salt II is reached only at about 1000°C.

In the following, the thermal decomposition of salt II in the various temperature regions will be only discussed with respect to the special features. Figure 2c shows also the DTA of an equimolar mixture of Ba and Ti citrate and Fig. 2e shows the DTA of (BaTi) citrate ethylene glycol polyester in air.

3.1.1. Salt I between 20 and 200°C

The TGA shows that up to 80°C there is a loss in weight of about 8% (all % figures are in weight %) (first DTG peak in Fig. 1) which
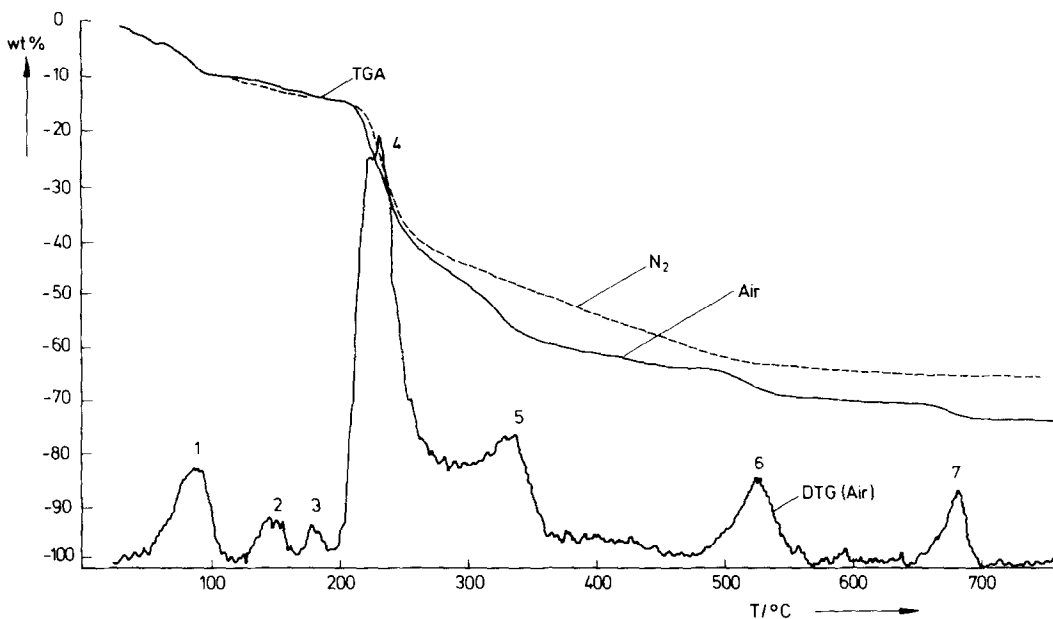

FIG. 1. TGA of the decomposition of salt I (BaTi($C_6H_6O_7$)$_3 \cdot 6H_2O$) in air and in N_2 (0.1 vol% O_2), and DTG of salt I in air. (DTG in arbitrary units)
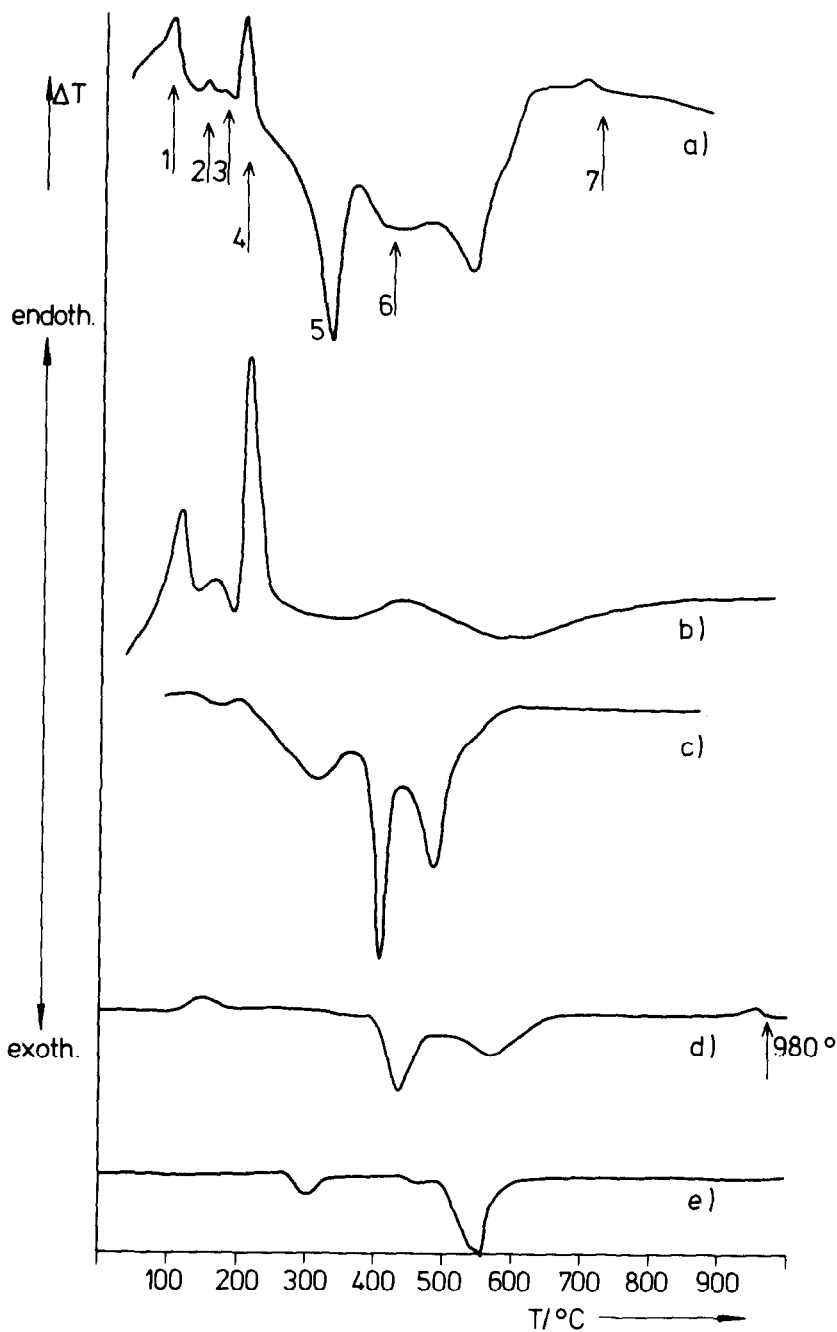
FIG. 2. DTA of the thermal decomposition of (a) salt I in air; (b) salt I in N_2 (0.1 vol% O_2); (c) equimolar mixture of Ba and Ti Citrate in air; (d) salt II $(Ba_2Ti(C_6H_5O_7)_2 \, (C_6H_6O_7) \cdot 7H_2O)$ in air; (e) (BaTi) citrate ethylene glycol polyester in air.

according to analysis of the volatile products is due exclusively to loss of water. On the basis of a molecular weight of about 863 with respect to salt I the evolution of water corresponds to about 4 H_2O/mole. The two remaining molecules of crystal water are

evolved between 150 and 200°C. The DTA (Fig. 2) shows endothermal peaks (second and third arrows) at the corresponding temperature.

3.1.2. Between 200 and 250°C

Above 200°C the evolution of water increases, accompanied above about 220°C by a vigorous evolution of carbon dioxide. The ir spectrum of the residue of decomposition at 205°C corresponded largely to the reference spectrum of the barium salt of propene tricarboxylic acid (1.2.3) (aconitic acid). This leads to the conclusion that after the liberation of crystal water, dehydration of citric acid to aconitic acid takes place at temperatures of about 200°C. The evolution of carbon dioxide observed above 210°C reaches its peak in DTG at about 220°C. The DTA (fourth arrow) shows that the evolution of carbon dioxide is a strongly endothermal process. The loss in weight of altogether about 36% corresponds to an evolution of $3CO_2$/mole of salt I, or $1CO_2$/mole aconitic acid (theoretical loss in weight 34%). Decarboxylation of the aconitic acid leads to propene (2) dicarboxylic acid (1.2) (itaconic acid). Itaconic acid was proved to be present in the volatile products of decomposition formed during further raising of the temperature. Up to this temperature no marked difference between thermal decomposition in N_2 atmosphere or air can be observed.

3.1.3. Between 250 and 400°C

Between 250 and 360°C further marked losses of weight occurred, the result of the evolution of a yellowish oil. The oil dissolved
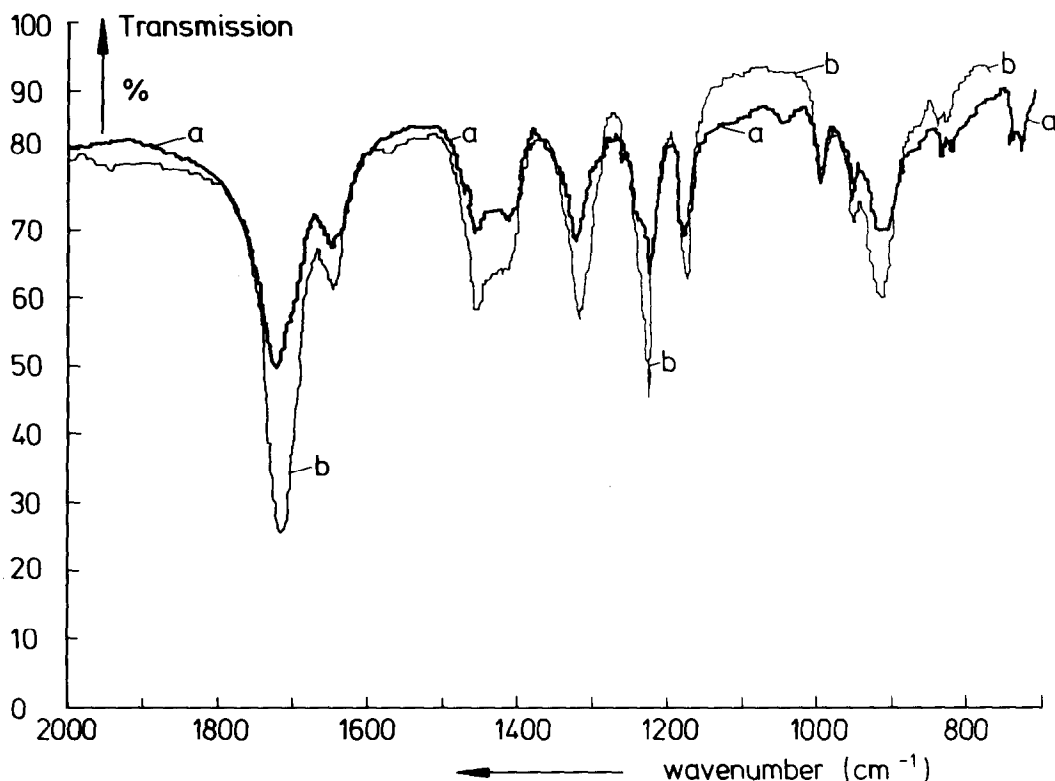

Fig. 3. Infrared spectra of products of decomposition, volatile at 250–360°C, of salt I separated from aqueous solutions (a), and reference spectrum of propene (2) dicarboxylic acid (1.2) (itaconic acid) (b).

after boiling in water. The strongly acid reaction of the aqueous solution (pH $\simeq$ 1) and the decolorization of a KMnO$_4$ solution indicated that the oil was the anhydride of an unsaturated carboxylic acid. The ir spectrum (Fig. 3) of this carboxylic acid separated from the aqueous solution was identical with the reference spectrum of propene (2) dicarboxylic acid (1.2) (itaconic acid). Furthermore the measured melting point of 162°C of the acid agreed very well with the melting point of itaconic acid (163°C).

The strongly exothermal process in air registered in the DTA at 360°C is most probably due to the combustion of itaconic anhydride in air. In contrast to the DTA in air the DTA in N$_2$ shows at 360°C a broad endothermic peak. The loss in weight of 59% recorded up to 360°C in air (fifth arrow), corresponds fairly exactly to the evolution of two parts of the anhydride of the propene (2) dicarboxylic acid (1.2) (itaconic anhydride) per molecule of salt I (theoretical loss 60%). In N$_2$ atmosphere the weight loss at 360°C is considerably lower, due to partial carbonization of the sample.

In this stage of the decomposition in all probability a double (BaTi) carboxylic salt is no longer present. According to the losses in weight at 400°C in air, one Ba and one Ti together correspond to only one part itaconic acid. The ir spectrum of the residue of decomposition at 400°C (Fig. 4) shows the typical bands of the antisymmetrical and symmetrical stretching vibrations of the carboxylate ion (—COO$^-$) at 1560 and 1410 cm^{-1}. The residues of decomposition therefore still contain a carboxylic salt. X-ray diffraction of the residues of decomposition at 400°C yielded no reflections at all. Because barium in comparison with titanium is appreciably more basic in character, the assumption is justified that the products of decomposition at 400°C contain barium salts of itaconic acid and amorphous oxides of titanium. Therefore the following course of reactions can be assumed to take place in the temperature region between 200 and 400°C in air:
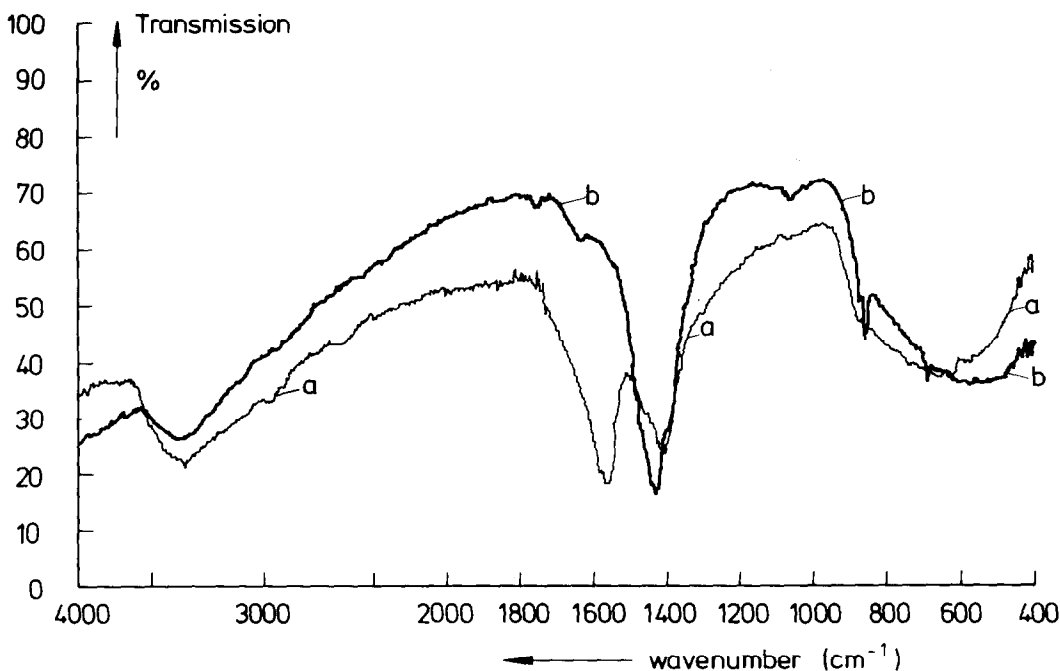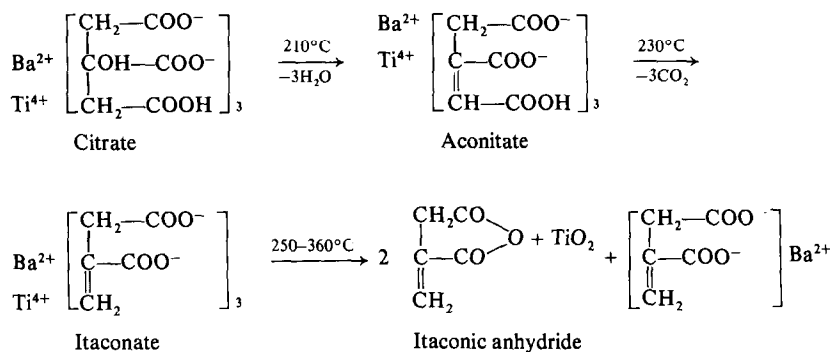

FIG. 4. Thermal decomposition of salt I in air. Infrared spectrum of the residue at (a) 400°C; (b) 500°C.

$$Ba^{2+} \begin{bmatrix} CH_2\!-\!COO^- \\ | \\ COH\!-\!COO^- \\ | \\ CH_2\!-\!COOH \end{bmatrix}_3 \xrightarrow[-3H_2O]{210°C} \begin{matrix} Ba^{2+} \\ Ti^{4+} \end{matrix} \begin{bmatrix} CH_2\!-\!COO^- \\ | \\ C\!-\!COO^- \\ \| \\ CH\!-\!COOH \end{bmatrix}_3 \xrightarrow[-3CO_2]{230°C}$$

Citrate   Aconitate

$$Ba^{2+} \begin{bmatrix} CH_2\!-\!COO^- \\ | \\ C\!-\!COO^- \\ \| \\ CH_2 \end{bmatrix}_3 \xrightarrow{250-360°C} 2 \begin{matrix} CH_2CO \\ | \quad\quad\searrow \\ C\!-\!CO \\ | \\ CH_2 \end{matrix} O + TiO_2 + \begin{bmatrix} CH_2\!-\!COO \\ | \\ C\!-\!COO^- \\ | \\ CH_2 \end{bmatrix} Ba^{2+}$$

Itaconate   Itaconic anhydride

3.1.4. Between 400 and 700°C

Above 450°C (sixth arrow) the losses in weight became greater again; they were related with the vaporization of brownish tarry products.

The ir spectrum of the residue of decomposition at 500°C (Fig. 4) shows the typical absorption bands of the carbonate ion at 1460, 1060, 860, and 690 cm^{-1}, which are nearly identical to those of BaCO$_3$ (12) having a
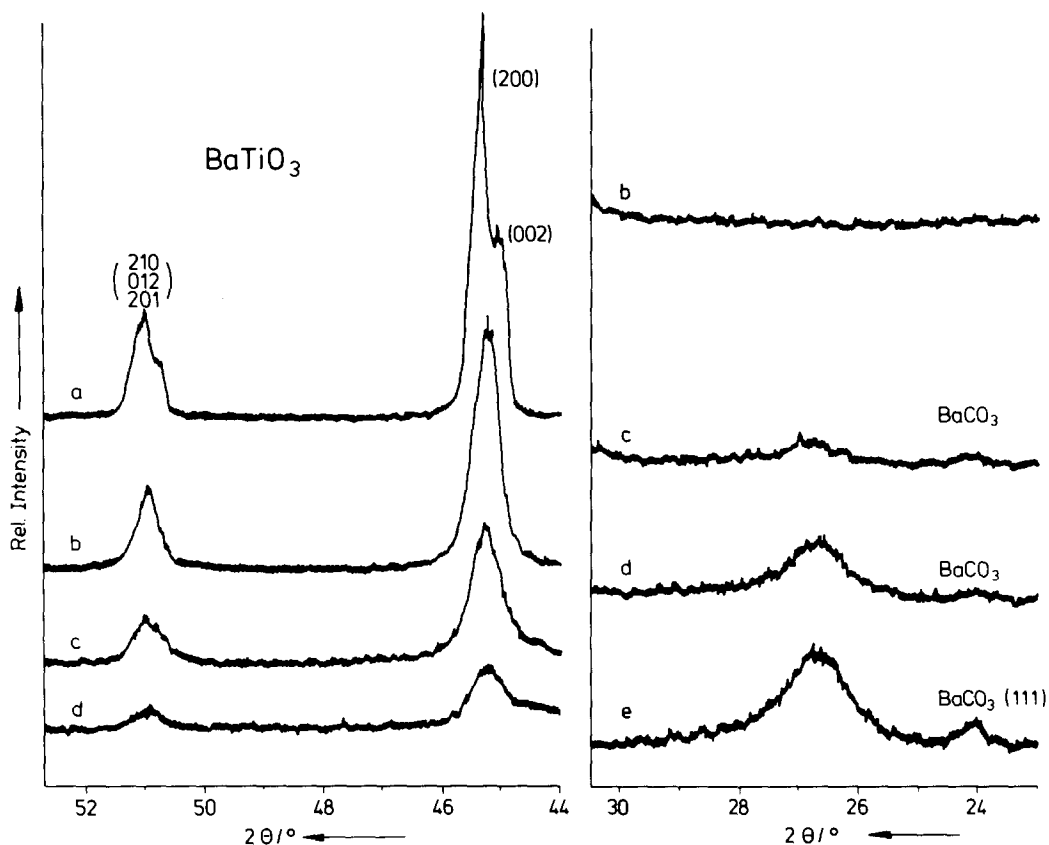

FIG. 5. Thermal decomposition of salt I in air. X-ray diffraction diagrams of the residues at (a) 1000°C; (b) 700°C; (c) 600°C; (d) 550°C; and (e) 500°C (Cu-K_α-radiation).

strong absorption at 1460 cm^{-1} and weaker absorptions at 1060, 860, and 695 cm^{-1}. The absorption band of free CO_2 at 2350 cm^{-1} as observed in the decomposition products of bariumtitanyloxalate (6) was not detected. The existence of the compound $Ba_2Ti_2O_5CO_3$-(CO_2) was therefore not confirmed. The X-ray diffraction diagram of the residue of decomposition (Fig. 5) shows in this stage weak reflections of $BaCO_3$ and of $BaTiO_3$. The only reflection which could not be assigned to any known modification of the TiO_2 (rutil or anatas) $BaCO_3$ or Ba_2TiO_4 (12) and $Ba_6Ti_{17}O_{40}$ (13) was found at $2\theta = 26.6°$ (Fig. 5) according to a spacing $d = 3.35$ Å. The same reflection accompanied by a second one according to $d = 4.11$ Å we observed in the decomposition products of barium titanyl oxalate at 550°C. With respect to the results of Gopalakrishnamurthy (6) it seems possible that these reflections belong to an intermediate compound between $BaCO_3$ and TiO_2.

Above 450°C the experimental results obtained from TGA, DTA, ir spectroscopy, and X-ray diffraction give only reduced information on the further course of the decomposition reaction. Moreover, the simultaneous presence of $BaCO_3$, $BaTiO_3$, and of an unknown intermediate compound strongly suggests the occurrence of side reactions in this temperature region. It was impossible to analyze the brownish tarry products on account of the small amount in which they were produced, and incipient combustion. DTA in air revealed an extensive exothermal region at about 530°C because of the combustion reactions.

At 540°C the loss of weight in air has attained about 67%, corresponding roughly to an empirical composition of $BaCO_3 \cdot TiO_2$ (arrow 6) (theoretical loss of weight 68%). Above 600°C the only volatile product of the reaction was CO_2. The diffraction diagram of the residues of the decomposition at 600°C (Fig. 5) shows only very weak intensities of reflections of $BaCO_3$ and of the unknown intermediate compound and a corresponding

increase of the $BaTiO_3$ reflections. Therefore from 600°C upward the only reaction still taking place is the formation of $BaTiO_3$ (DTG peak 7 and arrow 7).

According to TGA the loss of weight ceases at 700°C, at which point the weight has been reduced by 73%. Theoretically the loss of weight in the case of complete conversion to $BaTiO_3$ ought to be 72.9%. Above 700°C X-ray diffraction of the products of decomposition exhibited only the reflections of $BaTiO_3$. DTA also indicated no further reactions above that temperature. The weight losses in N_2 atmosphere were only 65% due to residues of carbon in the samples. It is interesting to note that equimolar mixtures of Ba and Ti citrates react to $BaTiO_3$ at nearly the same temperature (Fig. 2c) as the (BaTi) citrate double salt.

3.2. Decomposition of Citrate Salt II and of (BaTi) Polyester Resins

The decomposition of salt II and of (BaTi) citrate polyester resins was only cursorily treated.
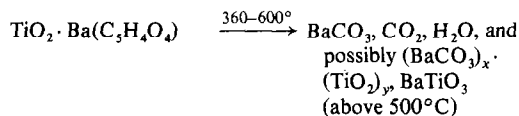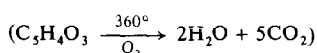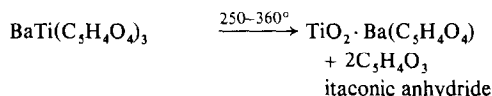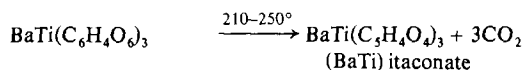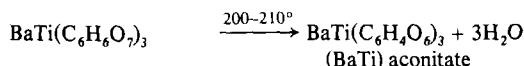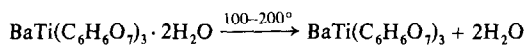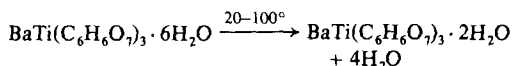
As revealed by DTA (Fig. 2) the end of decomposition of salt II occurs above 900°C. X-ray diffraction analysis of the residues of decomposition showed that salt II decomposed at about 700°C into $BaTiO_3$ and $BaCO_3$ which reacted at 980°C to Ba_2TiO_4. At the decomposition of (BaTi) citrate polyester resins traces of $BaCO_3$, TiO_2, and the intermediate compound appeared. The formation of $BaTiO_3$ by decomposition of polyester resins in air was completed at about 700°C.

4. Discussion

Investigation of the reaction of thermal decomposition of the citrate salt BaTi-$(C_6H_6O_7)_3 \cdot 6H_2O$, led to clarification of the important steps in the thermal decomposition in air.

The following scheme represents the probable course of the decomposition reactions of

$BaTi(C_6H_6O_7)_3 \cdot 6H_2O$ in the range of temperatures from 20 to 700°C in air.

$$BaTi(C_6H_6O_7)_3 \cdot 6H_2O \xrightarrow{20-100°} BaTi(C_6H_6O_7)_3 \cdot 2H_2O + 4H_2O$$

$$BaTi(C_6H_6O_7)_3 \cdot 2H_2O \xrightarrow{100-200°} BaTi(C_6H_6O_7)_3 + 2H_2O$$

$$BaTi(C_6H_6O_7)_3 \xrightarrow{200-210°} BaTi(C_6H_4O_6)_3 + 3H_2O$$
(BaTi) aconitate

$$BaTi(C_6H_4O_6)_3 \xrightarrow{210-250°} BaTi(C_5H_4O_4)_3 + 3CO_2$$
(BaTi) itaconate

$$BaTi(C_5H_4O_4)_3 \xrightarrow{250-360°} TiO_2 \cdot Ba(C_5H_4O_4) + 2C_5H_4O_3$$
itaconic anhydride

$$(C_5H_4O_3 \xrightarrow[O_2]{360°} 2H_2O + 5CO_2)$$

$$TiO_2 \cdot Ba(C_5H_4O_4) \xrightarrow{360-600°} BaCO_3, CO_2, H_2O, \text{ and}$$
possibly $(BaCO_3)_x \cdot$
$(TiO_2)_y$, $BaTiO_3$
(above 500°C)

$$\xrightarrow{600-700°} BaTiO_3, CO_2$$

A remarkable feature is that the formation of $BaTiO_3$ occurs, at least in part, via a reaction of the solid phase $BaCO_3$. The clearly demonstrable X-ray reflections of $BaCO_3$ thus provide unambiguous proof of the fact that $BaCO_3$ produced during the pyrolysis has a pronounced crystal lattice and particle sizes $\geqslant 50$ Å. With respect to the rather imperfect crystal lattice of $BaCO_3$, formed at low temperature, the concentration of the $BaCO_3$ in the sample should be higher than 5 mole% to give rise to detectable X-ray reflections. Such a high amount of $BaCO_3$, however, can be only produced by side reactions. The Ba excess of the sample, determined analytically in the double salt, is really much lower.

The experimental results point in the direction of partial recrystallization of intermediate compounds and of side reactions occurring above 400°C. It is interesting to note that $BaCO_3$ and similar intermediate compounds are also observed at the thermal decomposition of (BaTi) polyester resins. Whether the phase of overall composition $BaCO_3 \cdot TiO_2$

occurring in the course of decomposition at about 540°C represents a "genuine" phase seems doubtful. It is quite probable that phases of such composition are in fact merely an extremely divided mixture of $BaCO_3$ and TiO_2. This assumption is confirmed by the fact that thoroughly mixed equimolar samples of Ba and Ti citrates react to $BaTiO_3$ also at the rather low temperature of 700°C. The very much lower temperature of formation of $BaTiO_3$ during thermal decomposition of (BaTi) citrate double salts as well as of equimolar mixtures of Ba and Ti citrates is explained by the greater reactivity of the fine particles.

According to the results here found, complete mixing of the barium and titanium particles on an atomic scale up to the time of formation of $BaTiO_3$ is not very probable. From this point of view the difference between the classical mixed-oxide method and the formation of $BaTiO_3$ by thermal decomposition of citrates should be considered to be only a matter of degree. The real difference between the two methods is that very much smaller particles of $BaCO_3$ and of TiO_2 result from thermal decomposition than from the conventional grinding techniques.

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