Journal of Thermal Analysis, Vol. 17 (1979) 45—56

THERMAL ANALYSIS OF AMMONIUM COPPER CHROMATE*

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(Received July 13, 1978)

The thermal decomposition of ammonium copper chromate was studied by TG, DTG and DTA in the temperature range 30° to 1100°. It was found to occur in four stages. The solid decomposition products in these stages were characterized by chemical, X-ray and IR analysis. Based on the results, a probable mechanism for the overall decomposition of ammonium copper chromate in the above temperature range is discussed.

The decomposition of γ-irradiated ammonium copper chromate was also found to occur in four stages, very similarly as for ammonium copper chromate. However, γ-irradiation shifted the total weight losses and the temperatures corresponding to the DTG and DTA peaks to higher values for all decomposition stages.

The thermal decomposition of ammonium copper chromate is one of the most important steps in the preparation of active copper chromite catalyst by the co-precipitation method [1]. Copper chromite is an industrially important catalyst because of its ability to hydrogenate functional groups in aliphatic and aromatic compounds selectively. It is employed in both vapour-phase (e.g. hydrogenation of nitrobenzene and nitrotoluenes to their corresponding amines) and liquid-phase (e.g. hydrogenation of carbonyl group in aldehydes, ketones and esters to the corresponding alcohol) commercial processes [2]. It is also used as an oxidation catalyst for the conversion of carbon monoxide to carbon dioxide in automobile exhaust emission control [3].

The present investigation has been undertaken to study the thermal decomposition of ammonium copper chromate in the presence of air, the process by which copper chromite catalyst is usually obtained.

Experimental

Materials

Chemicals: Chemicals used for the preparation of ammonium copper chromate were copper(II) nitrate [L. R., B. D. H.), ammonium dichromate (L. R., B. D. H.) and liquor ammonia, 28 percent (L. R., B. D. H.); while those used for the chemical analysis were all of B. D. H. AnalaR grade.

* NCL Communication No. 2291.

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Ammonium copper chromate: This was prepared by a method similar to that described by Adkins and Connor [1] by coprecipitating it from a solution containing the required amounts of copper(II) nitrate and ammonium dichromate with aqueous ammonia at room temperature, at a pH of 7–7.2. The resulting precipitate was filtered and washed with distilled water until it was free from nitrate ions. The filtered cake was dried in an air-oven at 80–100° for 24 hours. The dried mass was powdered to >200 mesh size (<75 microns) and preserved in a desiccator.

γ-Irradiated ammonium copper chromate: γ-Irradiation of the ammonium copper chromate was done by irradiating the sample with γ-rays, using a Gamma Cell-220, at a dose rate of 22.65 krcel/hr for 72 hours.

TG/DTG/DTA

These studies were carried out on an automatic MOM (Hungary) derivatograph (Type 00-102B) with the following details: sample size: 200 mg; reference material: α-alumina; sample holder: platinum crucible placed on thermocouple rod; heating rate: 10°/min; temperature range: 30° to 1100°; atmosphere: in air under suction.

Solid decomposition products

The samples of solid decomposition products required for chemical, X-ray and IR analysis were obtained by decomposing ammonium copper chromate for 4 hours at the temperatures 310°, 400°, 750 and 1000°, chosen by studying the TG/DTA curves.

Chemical analysis

Free copper (as CuO) and chromium (as Cr_2O_3) in the solid products were separated [4] from the copper(II) and copper(I) chromites by leaching them with 10 percent hydrochloric acid. The leached copper and chromium and the residue (i.e. copper chromites) were analyzed for their copper and chromium contents by a procedure outlined elsewhere [5]. The error in the chemical analysis was of the order of 1–2 percent.

X-ray analysis

X-ray diffraction patterns of the solid products were obtained with the help of a Debye–Scherrer camera by using the radiation ($\lambda = 0.70926$) from a Mo K_α source with a zirconium filter, with an exposure time of 2 hours.

IR analysis

IR spectra of the solid samples were taken using a Perkin – Elmer (021 – 6318) IR spectroscope in the range 600 – 3800 cm^{-1} (phase: Nujol, and prism: NaCl + + grating).

Isothermal decomposition of ammonium copper chromate

This was carried out in a stainless steel decomposition tube closed at one end. The gas evolved during the decomposition was measured by collecting it over water, using a gas collector similar to that described elsewhere [6]. The amount of water formed in the decomposition was measured by absorbing it from the decomposition gases in a calcium chloride trap.

In order to check up on the evolution of ammonia in the decomposition, the decomposition gases were bubbled through 0.1 *N* hydrochloric acid and the change in the acid concentration was determined.

Results and discussion

Ammonium copper chromate

TG/DTG/DTA: The thermal curves of ammonium copper chromate are presented in Fig. 1. It can be seen that the decomposition occurs in four stages, of which stages I and III are very distinct. The decomposition in the first stage is

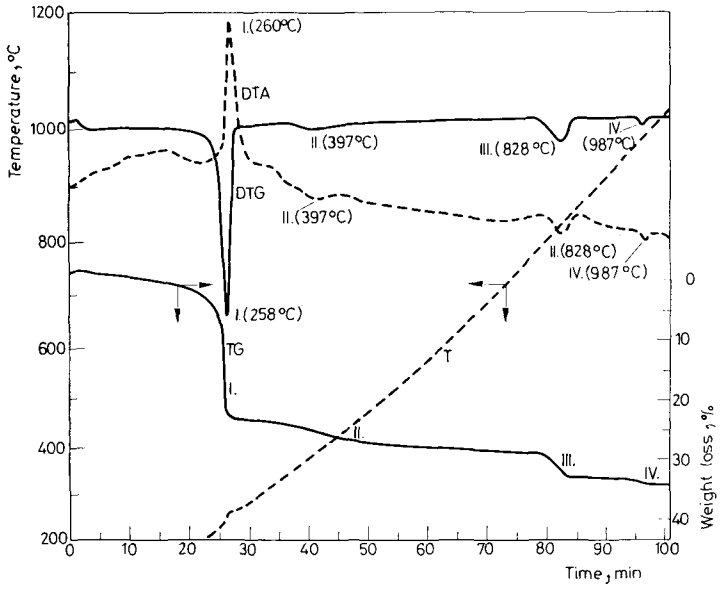

Fig. 1. TG, DTG and DTA curves for ammonium copper chromate

Table 1
Thermal decomposition data

Compound	Stage of decomposition	DTA			DTG		TG	
		Peak temp., °C	Temp. range, °C	Peak characteristics	Peak temp., °C	Temp. range, °C	% wt. loss in each of the stages of decomposition	Total % wt. loss
Ammonium copper chromate	I	260	260–290	Exothermic (very sharp and strong)	258	180–260	24.5	24.5
	II	397	360–415	Endothermic (broad and weak)	397	340–415	5.3	28.5
	III	828	780–850	Endothermic (sharp but weak)	828	780–850	7.0	33.5
	IV	987	980–1000	Endothermic (sharp but very weak)	987	980–1000	1.1	34.5
γ-Irradiated ammonium copper chromate	I	302	240–320	Exothermic (very sharp and strong)	295	220–300	26.5	26.5
	II	455	400–480	Endothermic (broad and weak)	455	400–490	8.2	32.5
	III	942	900–980	Endothermic (sharp but weak)	942	900–980	7.4	37.5
	IV	1127	1115–1140	Endothermic (sharp but very weak)	1127	1115–1140	1.2	38.2

exothermic (as indicated by a maximum in the DTA curve), while in the other stages it is endothermic. The thermal decomposition data are given in Table 1.

Chemical analysis of the solid products

The results of chemical analysis of the solid decomposition products at different temperatures are presented in Table 2.

The results showed that the free copper (as CuO) in the solid product decreases slowly up to 750° and sharply from 750° to 1000°, while the copper combined with chromium in the form of copper chromite displays exactly the opposite trend. These sharp changes in the copper content of the solid products and the Cu/Cr atomic ratio in the residue indicate a phase transition between 750° and 1000°.

Table 2

Results of chemical analysis of solid decomposition products

Decomposition temperature, °C	Residue (i.e. copper chromite), wt %	Copper (wt. %)		Chromium (wt. %)		Cu/Cr in residue (atomic ratio)
		Leachable (mostly as CuO)	Unleachable (combined with Cr as copper chromite)	Leachable (mostly as Cr_2O_3)	Unleachable (combined with Cu as copper chromite)	
310	67.5	25.1	15.5	2.5	28.8	0.44
400	71.4	22.3	17.2	2.0	30.0	0.47
500	73.5	19.9	21.3	4.4	29.1	0.60
750	75.5	17.5	22.3	5.7	27.8	0.66
1000	95.8	1.3	38.9	3.4	30.1	1.05
$CuO.CuCr_2O_4$	74.4	20.4	20.4	0.00	33.4	0.5
$Cu_2Cr_2O_4$	100	0.00	43.0	0.00	35.2	1.0

X-ray analysis

X-ray diffraction data on the solid decomposition product at different temperatures are given in Table 3. The results show that at 310° the solid product is more or less amorphous, and the single line in the diffraction pattern may be due to copper(II) oxide. The crystallization started at and above 400°, as evidenced by more and more lines in the diffraction pattern. From a comparison of the observed *d* values with the standard *d* values of copper(II) oxide, copper(II) chromite and copper(I) chromite, it can be concluded that up to 750° the solid decomposition product contained copper(II) oxide and copper(II) chromite, while at 1000° it was copper(I) chromite. Thus, a transition from copper(II) chromite to copper(I) chromite occured between 750° and 1000°.

IR analysis

The IR spectra of the solid products obtained from 310° to 750° were very similar, except for a weak absorption band at 935 cm^{-1} for the solid product obtained at 750°. On the other hand, the spectrum of the solid obtained at 1000° was quite different from the other spectra, thus showing a probable phase transition.

Table 3

X-ray powder diffraction data on solid decomposition products ammonium copper chromate

Temp. at which solid product obtained, °C	Observed *d*-spacing, Å	Standard *d*-spacing, Å			Probable crystalline phases present
		Copper(II) oxide	Copper(II) chromite	Copper(I) chromite	
310	2.511 (W)	2.52 (100)	—	—	CuO
400	2.342 (W)	2.323 (96)	2.401 (60)	—	CuO and
	2.545 (W)	2.523 (100)	2.556 (100)	—	$CuCr_2O_4$
	2.961 (W)	—	3.01 (15)		
500	1.442 (V.W)	1.505 (20)	1.442 (40)	—	
	1.516 (V.W)	—	1.505 (30)	—	CuO and
	1.631 (V.W)	—	—	—	$CuCr_2O_4$
	2.292 (W)	2.373 (96)	1.629 (40)	—	
	2.567 (S)	—	2.556 (100)	—	
	2.909 (V.W)	—	2.874 (35)	—	
750	1.269 (V.W)	—	1.276 (15)	—	CuO and
	1.436 (W)	—	1.442 (40)	—	$CuCr_2O_4$
	1.510 (W)	—	1.505 (30)	—	
	1.638 (W)	—	1.629 (40)	—	
	1.724 (V.W)	—	1.706 (40)	—	
	2.344 (S)	2.321 (96)	2.401 (60)	—	
	2.561 (V.S)	—	2.556 (100)	—	
	2.922 (V.W)	—	2.874 (35)	—	
1000	1.027 (V.W)	—	—	1.030 (20)	$Cu_2Cr_2O_4$
	1.095 (V.W)	—	—	1.015 (15)	
	1.192 (V.W)	—	—	1.172 (5)	
	1.321 (V.W)	—	—	—	
	1.432 (W)	—	—	1.319 (20)	
	1.487 (W)	—	—	1.426 (30)	
	1.651 (M.S)	—	—	1.488 (35)	
	2.187 (S)	—	—	1.640 (45)	
	2.477 (V.S)	—	—	2.470 (100)	
	2.873 (S)	—	—	2.85 (40)	

The strong absorption band around 600 cm^{-1} for the solid product obtained from 310 to 750° corresponds to the strong absorption band at 615 cm^{-1} of copper(II) chromite, while the bands at 710 cm^{-1} (strong) and 935 m^{-1} (weak) of the solid product obtained at 1000° correspond to the bands of copper(I) chromite at 715 cm^{-1} (strong) and 940 cm^{-1} (weak). These facts show the presence of copper(II) chromite in the solid products in the temperature range 310° to 750°, and copper(I) chromite at 1000°. Further, the presence of a very weak band at 935 cm^{-1} for the solid obtained at 750° shows the existence of traces of copper(I) chromite.

Isothermal decomposition

Results of the isothermal decomposition at 400° are given in Table 4. Formation of ammonia was not detected in the gaseous decomposition products at 350° and 400°. However, at 275° and 300°, some traces of ammonia (0.00039 g NH_3/g of sample at 275° and 0.00072 g NH_3/g of sample at 300°) were detected.

Table 4

Results of decomposition of ammonium copper chromate at 400°

Observation	Experimental	Theoretical [according to reaction (1)]
% wt. loss in the decomposition	26.4	27.5
Nitrogen evolved in the decomposition, ml (at NTP)/g	55.0	52.3
Formation of water in the decomposition, g/g	0.195	0.21
Formation of ammonia in the decomposition	Nil	Nil

γ-Irradiated ammonium copper chromate

The TG, DTG and DTA curves of γ-irradiated ammonium copper chromate are presented in Fig. 2. The decomposition of γ-irradiated ammonium copper

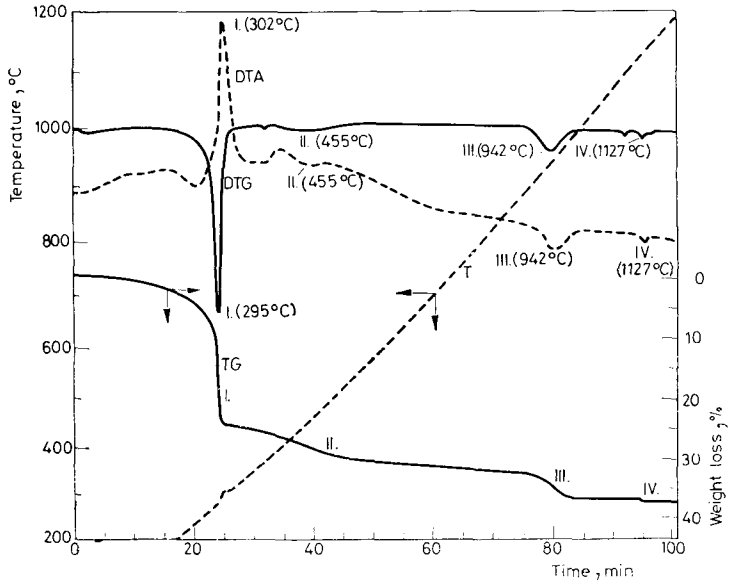

Fig. 2. TG, DTG and DTA curves for γ-irradiated ammonium copper chromate

chromate also occurs in four stages, of which stages I and III are quite distinct. The decomposition in the first stage is exothermic, while in the other three stages it is endothermic. The thermal decomposition data are given in Table 1.

Comparison of the results (Table 1) shows that for γ-irradiated ammonium copper chromate the total weight loss in every stage of decomposition is higher than that of the corresponding stage in the decomposition of ammonium copper chromate. It is also interesting to note that the temperature corresponding to the DTA or DTG peak has shifted to higher values for all stages of the decomposition following the γ-irradiation of ammonium copper chromate. Thus, γ-irradiation increases the thermal stabilities of ammonium copper chromate and its solid decomposition products. The high weight losses may be due to the creation of additional active centers in ammonium copper chromate due to γ-irradiation.

Reactions involved in the decomposition

Stage I: Decomposition in this stage is exothermic and occurs in the temperature range 200°–290° (DTG peak at 258° and DTA peak at 260°), with a weight loss of 24.5 percent. The probable reactions occurring in this stage are as follows:

Mechanism I

$$2\,Cu(OH)NH_4CrO_4 \rightarrow CuO.CuCr_2O_4 + N_2\uparrow + 5\,H_2O\uparrow \quad (1)$$
(% wt. loss = 27.5)

Mechanism II

$$Cu(OH)NH_4CrO_4 \rightarrow CuCrO_4 + NH_3\uparrow + H_2O\uparrow \quad (2a)$$
(% wt. loss = 16.3)

$$2\,CuCrO_4 \rightarrow CuO.CuCr_2O_4 + 3\,[O]\uparrow \quad (2b)$$
(% wt. loss = 13.4)

or, by combining reactions (2a) and (2b), we obtain

$$2\,Cu(OH)NH_4CrO_4 \rightarrow CuO.CuCr_2O_4 + 2\,NH_3\uparrow + 2\,H_2O\uparrow + 3\,[O]\uparrow \quad (2c)$$
(% wt. loss = 27.5)

Mechanism II may be discarded because it involves reactions (2a) and (2b) in series, whereas only one reaction occurs as evidenced by the presence of a single DTG peak. Further, reaction (2a), or the overall reaction (2c), involves the formation of ammonia. The isothermal decomposition studies at 350° and 400° did not indicate the formation of ammonia. At lower temperatures (275° and 300°), the evolution of ammonia accounts for only about 0.5 to 0.9 percent decomposition according to reaction (2a).

Reaction (1) is the most probable reaction for the decomposition at this stage because the observed weight loss (24.5 %) is very close to the theoretical weight

loss (27.5%), and also the results of the isothermal decomposition at 400° (Table 4) give a very close material balance for the products of the decomposition as required by reaction (1). A somewhat lower value of the weight loss and the evolution of traces of ammonia in the decomposition may be due to the occurrence of reaction (2a) to a small extent.

Stage II: The endothermic decomposition in this stage occurs between 340° and 415° (both DTG and DTA peaks at 397°) with a weight loss of 5.3 percent. It is most probably due to the decomposition of copper chromate, formed in small quantities by reaction (2a) in the first stage of the decomposition, according to reaction (2b). This is supported by the fact that the overall weight loss (28.5%) in this stage of the decomposition is very close to the value (27.5%) expected for the complete decomposition of ammonium copper chromate to copper(II) oxide and copper(II) chromite according to reaction (1) or (2c). X-ray and IR analysis of the solid decomposition products at 400° and 500° also indicated that the major phases present in the solid products are copper(II) oxide and copper(II) chromite, while chemical analysis indicated that these exist in nearly equimolar quantities, as expected according to reaction (1) or (2c).

Stage III: The endothermic decomposition in the third stage occurs between 780° and 850° (both DTG and DTA peaks at 828°) with a weight loss of 7.0 percent. It is mostly due to the phase transition of copper(II) oxide + copper(II) chromite to copper(I) chromite, according to the reaction.

$$CuO + CuCr_2O_4 \rightarrow Cu_2Cr_2O_4 + [O]\uparrow \quad (3)$$
$$(\%\ \text{wt. loss} = 5.1)$$

This was confirmed by chemical, X-ray and IR analysis of the solid decomposition products at 750° and 1000°. At 750°, the major phases present in the solid product were copper(II) oxide and copper(II) chromite, while at 1000° copper(II) chromite was the only important solid phase.

Stage IV: The decomposition in this stage is also endothermic and occurs between 980° and 1000° (both DTG and DTA peaks at 987°). The small weight loss (1.1%) in this stage of decomposition may be due to the decomposition of unconverted $CuCr_2O_4$, according to the reaction

$$2\,CuCr_2O_4 \rightarrow Cu_2Cr_2O_4 + Cr_2O_3 + [O]\uparrow \quad (4)$$
$$(\%\ \text{wt. loss} = 3.5)$$

and/or by the reaction between the free copper and chromium oxides present in the solid product

$$2\,CuO + Cr_2O_3 \rightarrow Cu_2Cr_2O_4 + [O]\uparrow \quad (5)$$

Keely and Mathes [7] have observed that reaction (5) occurs at about 870°. It appears to be the most probable reaction that can account for the small weight loss in this stage of decomposition.

Side-reactions: Since free copper and chromium oxides are observed in the solid decomposition product (Table 2), the reaction

$$CuO + Cr_2O_3 \xrightarrow{>480^\circ} CuCr_2O_4 \quad (6)$$

which occurs [7] at and above 480° may be taking place during the course of heating.

The decomposition of copper(II) chromite to copper(I) chromite according to reaction (4) may also account for the presence of free chromium oxide in the solid decomposition products at higher temperatures.

Conclusions

TG, DTG and DTA studies on ammonium copper chromate, supplemented by chemical, X-ray and IR analyses of the solid decomposition products and isothermal decomposition studies in the temperature range 275–400°, lead to the conclusion that the decomposition in the temperature range 100°–1000° occurs in four stages and involves the following reactions.

Decomposition in stage I

Major reaction:

$$2\,Cu(OH)NH_4CrO_4 \xrightarrow{200-290^\circ} CuO \cdot CuCr_2O_4 + 5\,H_2O + N_2\uparrow$$

Minor reaction:

$$Cu(OH)NH_4CrO_4 \xrightarrow{200-290^\circ} CuCrO_4 + H_2O + NH_3\uparrow$$

Decomposition in stage II

$$2\,CuCrO_4 \xrightarrow{340-415^\circ} CuO + CuCr_2O_4 + 3\,[O]\uparrow$$

Decomposition in stage III

$$CuO + CuCr_2O_4 \xrightarrow{780-850^\circ} Cu_2Cr_2O_4 + [O]$$

Decomposition in stage IV

$$2\,CuO + Cr_2O_3 \xrightarrow{980-1000^\circ} Cu_2Cr_2O_4 + [O]$$

Other probable side-reactions

$$CuO + Cr_2O_3 \xrightarrow{<480^\circ} CuCr_2O_4$$

$$2\,CuCr_2O_4 \xrightarrow{\text{at high temp.}} Cu_2Cr_2O_4 + Cr_2O_3 + [O]$$

γ-Irradiation increases the thermal stabilities of ammonium copper chromate and its decomposition products, and also its total weight losses in all four stages of decomposition. The increase in the decomposition (i.e. weight loss) may be due to the creation of additional active centers (or defects) for nuclear growth.

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The authors are grateful to Dr. L. K. Doraiswamy, Deputy Director, National Chemical Laboratory, Poona, for his encouragement throughout this investigation, and to Dr. (Miss) S. B. Kulkarni, Mrs. Nalini Jacob, Mr. J. S. Gujral and Dr. C. I. Jose for their cooperation in preparing TG/DTA curves, IR spectra and X-ray diffractions patterns.

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RÉSUME — On a étudié, par TG, TGD et ATD dans l'intervalle de températures compris entre 30° et 1100°, la décomposition du chromate de cuivre-ammonium. On a trouvé que celle-ci s'accomplit en quatre étapes. On a caractérisé les produits solides de la décomposition par analyse chimique, par rayons X et IR. A partir de ces résultats on discute un mécanisme probable pour la décomposition globale du chromate de cuivre-ammonium dans l'intervalle de températures indiqué.

On a également trouvé que la décomposition du chromate de cuivre-ammonium irradié aux rayons γ se réalise en quatre étapes très similaires à celles du chromate de cuivre-ammonium. Cependant, l'irradiation γ déplace les pertes de poids totales et les températures correspondant aux pics de TGD et d'ATD, pour toutes les étapes de décomposition, dans la direction des valeurs plus élevées.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Ammoniumkupferchromat wurde durch TG, DTG und DTA im Temperaturbereich zwischen 30° und 1100° untersucht. Vier Zersetzungsstufen wurden beobachtet. Die festen Zersetzungsprodukte der einzelnen Stufen wurden durch chemische, Röntgen- und IR-Analyse charakterisiert. Anhand dieser Ergebnisse wird ein möglicher Mechanismus für die Gesamtzersetzung von Ammoniumkupferchromat im o.a. Temperaturbereich diskutiert. Es wurde gefunden, daß die Zersetzung von γ-bestrahltem Ammoniumkupferchromat ebenfalls in vier Stufen erfolgt, ähnlich wie bei Ammoniumkupferchromat. Durch die γ-Bestrahlung wurden jedoch die den DTG- und DTA-Peaks entsprechenden Gesamtgewichtsverluste und Temperaturen für alle Zersetzungsstufen in Richtung höherer Werte verschoben.

Резюме — Термическое разложение двойной соли хромата меди и хромата аммония было изучено методами ТГ, ДТГ и ДТА в области температур 30—1100°. Найдено, что это разложение происходит в четыре стадии. Твердые продукты разложения охарактеризованы химическими методами, рентгенографическим анализом и ИК спектроскопией. Обсужден возможный механизм полного разложения этой соли в указанном интервале температур. Найдено, что разложение γ-облученной соли также протекает в четыре стадии, подобно разложению необлученной соли. Однако, γ-облучение вызывает смещение потери общего веса и температуры соответствующих ДТГ и ДТА пиков в более высокую сторону при всех стадиях разложения.