Journal of Thermal Analysis, Vol. 32 (1987) 601–612

A STUDY OF SOLID STATE THERMAL DECOMPOSITION CHARACTERISTICS OF SOME METALLO-ORGANIC COMPOUNDS. IV

Dehydration and decarboxylation of the hydrated calcium and some first row transition metal salts of furan-2-carboxylic acid

S. Ghosh, S. K. Ray, P. K. Ray and *S. K. Chatterjee*

DEPARTMENT OF INORGANIC CHEMISTRY, INDIAN ASSOCIATION
FOR THE CULTIVATION OF SCIENCE,
CALCUTTA 700032, INDIA

(Received October 31, 1985; in revised form May 2, 1986)

Solid state dehydration of the hydrated Ca(II), Co(II), Ni(II) and Cu(II) salts of furan-2-carboxylic acid (furoic acid) and subsequent decarboxylation of the corresponding anhydrous salts have been studied by simultaneous TG, DTA and DTG techniques. The order of thermal stability of the hydrated and the anhydrous compounds have been determined from the analysis of the TG, DTA and DTG traces for the dehydration of the hydrated salts and for the decarboxylation of the anhydrous compounds. Thermal parameters such as activation energy, enthalpy change and order of reaction for the different stages of each process have been computed by standard methods. An attempt has been made to account for the observed trend in the thermal stability of the anhydrous salts towards decarboxylation. A mechanism of thermal decarboxylation of calcium furoate has also been proposed.

Kinetic and mechanistic aspects of thermal decarboxylation in the solid state is a scantily studied area though the corresponding aspects of similar processes occurring in solution have been investigated in great details. Again, many organic and metalloorganic compounds with partial ionic character, on being gradually heated, undergo definite chemical changes prior to melting and yield products which are very difficult to obtain through conventional synthetic procedures. An interesting class of metallo-organic compounds with pronounced ionic character are the metal carboxylates. Thermal decomposition study of such compounds become particularly interesting when such species contain different types of bonds with varying thermal stability. In these compounds the difference in bond energies originate from electron shifting, difference in electronegativity or due to steric factor. Because of the difference in the temperature co-efficients of the different

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

types of bonds present in such compounds when they are graduallyheated, the bond with lowest energy is first broken while the stabler bonds are broken subsequently often generating products of varied and interesting character.

All the above considerations led us to undertake a systematic study of solid state thermal decarboxylation of metal carboxylates emphasizing its kinetic, mechanistic and product isolation aspects. Some very interesting results, which justify our contention, have already been obtained and were described elsewhere [1, 2, 16].

Experimental

Preparation of the compounds

Furoic acid (fur H_2) used was of L.R.B.D.H. grade which was recrystallized twice from hot water. The Ca(II), Co(II), Ni(II) and Cu(II) salts of furoic acid were prepared by reacting a slight excess of the respective carbonates or basic carbonates

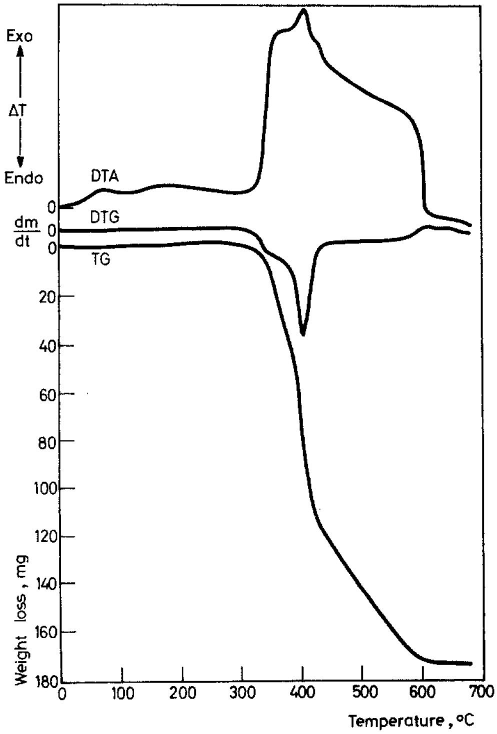

Fig. 1.1 Thermal curves of $Ca(fur)_2 \cdot H_2O$

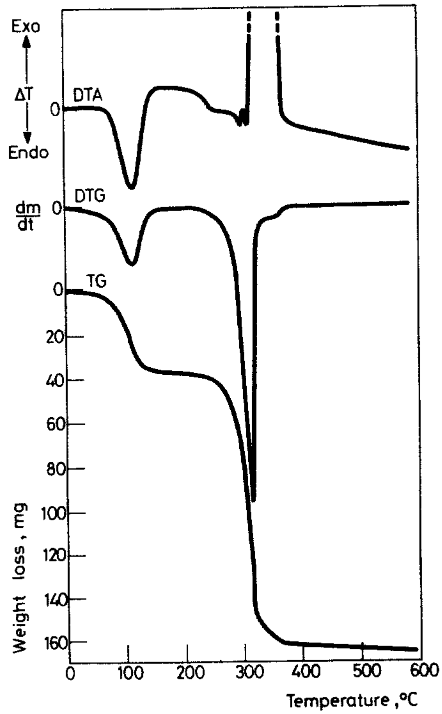

Fig. 1.2 Thermal curves of $Co(fur)_2 \cdot 3H_2O$

with a hot aqueous solution of the acid, filtering off the excess carbonate and evaporating the solution to crystallisation. The solids were filtered off, washed with cold water and dried over fused calcium chloride for seventy two hours.

Measurements and calculations

Simultaneous TG, DTG and DTA determinations of the hydrated salts were carried out with a Paulik–Paulik–Erdey type MOM derivatograph with dry air as the atmospheric gas. These TG, DTG and DTA traces are presented in Figs 1.1–1.4. Details of thermal and other measurements (such as IR, elemental analysis etc.) and procedures adopted for the evaluation of kinetic parameters such as, order of reaction, activation energy and enthalpy change accompanying the dehydration and decarboxylation processes have been described elsewhere [1, 2]. Results of elemental analysis are given in Table 1.

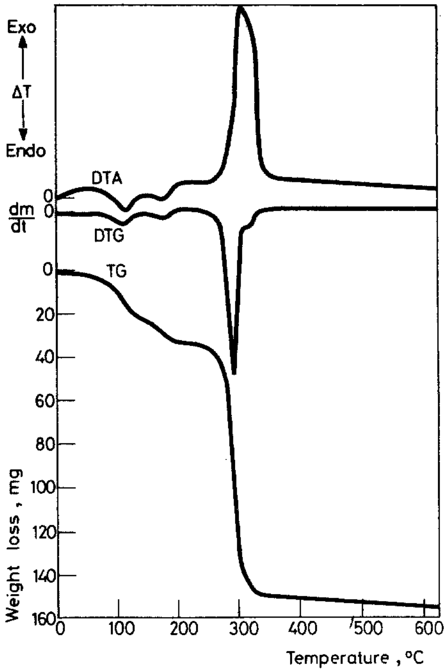

Fig. 1.3 Thermal curves of $Ni(fur)_2 \cdot 2.5H_2O$

Table 1 Results of elemental analysis

Compound	Found (Calcd.), %		
	M	C	H
$Ca(fur)_2 \cdot H_2O$	14.35 (14.28)	42.73 (42.85)	2.80 (2.85)
$Co(fur)_2 \cdot 3H_2O$	17.40 (17.58)	35.80 (35.83)	3.62 (3.58)
$Ni(fur)_2 \cdot 2.5H_2O$	18.53 (18.02)	36.79 (36.84)	3.30 (3.37)
$Cu(fur)_2 \cdot H_2O$	20.10 (20.92)	39.19 (39.53)	2.59 (2.63)

Results and discussion

Dehydration processes

The compounds ($Co(fur)_2 \cdot 3H_2O$ (B), $Ni(Fur)_2 \cdot 2.5H_2O$ (C) and $Cu(fur)_2 \cdot H_2O$ (D) are completely dehydrated within the temperature range of 70–200°, while $Ca(fur)_2 \cdot H_2O$ (A) requires a much higher temperature range (314–364°) for its complete dehydration. Careful analysis of the TG and DTA traces of the

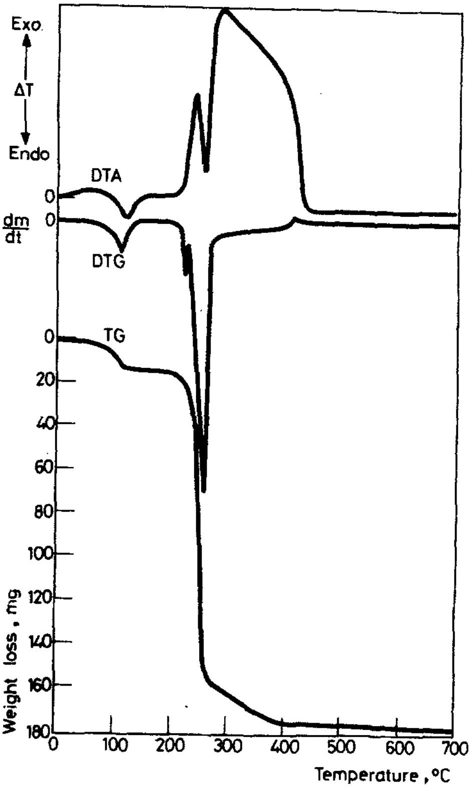

Fig. 1.4 Thermal curves of $Cu(fur)_2 \cdot H_2O$

dehydration stage indicated that compounds (A), (B) and (D) lost their water molecules in a single step, while (C) lost its water molecules in two separate steps. These dehydration reactions are presented in Table 2.

Initiation (t_i), peak (t_p) and completion (t_c) temperatures of the dehydraton of each compound were obtained from the relevant DTG traces and are given in Table 2 along with the corresponding weight losses calculated from the TG curves. Enthalpy change (ΔH) accompanying dehydration of each species [3], order of reaction for each dehydration reaction [4, 5] and activation energy (E_{Act}) of each such process [4] were determined by standard methods and the $\ln\ln\frac{w_0 - w_t^f}{w - w_t^f}$ *vs.* θ plots are presented in Fig. 2. The results obtained are included in Table 2.

In most cases the anhydrous species generated after complete dehydration of the hydrated compounds were isolated and the IR spectra of these compounds as well as those of the corresponding hydrated varieties were recorded as halocarbon mulls. Completion of the dehydration process was ascertained by the disappearance of the

Table 2 Characterization of dehydration reactions

Reaction	Initiation temp., °C	Peak temp., °C	Completion temp., °C	Loss in Wt.%		E_{Act} kcal/mole	ΔH, kcal/mole	Order of reaction
				calcd.	found.			
1 $Ca(fur)_2 \cdot H_2O \rightarrow Ca(fur)_2 + H_2O$	314	352	364	6.42	5.91	82.50	2.15	1
2 $Co(fur)_2 \cdot 3H_2O \rightarrow Co(fur)_2 + 3H_2O$	70	120	170	16.12	16.36	18.54	81.93	1
3 $Ni(fur)_2 \cdot 2.5H_2O \rightarrow Ni(fur)_2 \cdot H_2O + 1.5H_2O$	88	123	135	8.28	8.16	28.06	18.90	1
$Ni(fur)_2 \cdot H_2O \rightarrow Ni(fur)_2 + H_2O$	135	185	200	6.02	6.11	21.68	6.98	1
4 $Cu(fur)_2 \cdot H_2O \rightarrow Cu(fur)_2 + H_2O$	70	110	137	5.93	5.83	18.28	6.73	1

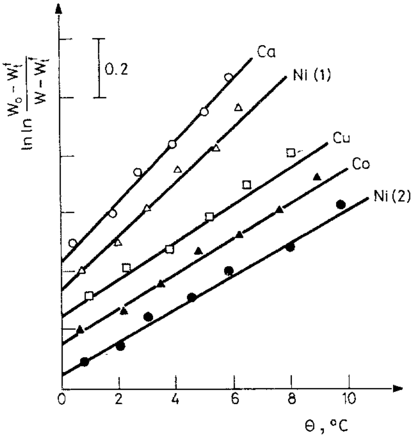

Fig. 2 Plot of $\ln\ln\frac{w_0 - w_t^f}{w - w_t^f}$ vs. θ for the dehydration stage. Dehydration stage: $Ca(fur)_2 \cdot H_2O$; $Co(fur)_2 \cdot 3H_2O$; $Ni(fur)_2 \cdot 2.5H_2O$; $Cu(fur)_2 \cdot H_2O$

3550–3300 cm^{-1} band [due to ν(O—H)] in the IR spectra of the dehydrated varieties.

Decarboxylation processes

All the anhydrous furoates exhibit considerable thermal stability and undergo decarboxylation within the temperature range 222–617°. The TG traces exhibit a two-stage decarboxylation process in which the first break in each case corresponds to an unusual composition. The first break is followed by the second and final break leading to the oxide end product. This observation is also reflected in the corresponding DTA traces which exhibit two distinctly separate stages in the cases of cobalt and copper furoates. Cobalt furoate exhibits a small endotherm followed by a large exotherm (Fig. 1.2) while the DTA of copper furoate (Fig. 1.4) shows a small exotherm followed by a large exotherm. Calcium and nickel furoates show a single exotherm in their respective DTA traces (Figs 1.1, 1.3). The corresponding DTG traces for calcium, cobalt and nickel furoates (Figs 1.2, 1.3) are of similar nature—a large endotherm followed by a rather flat plateau. The DTG trace for copper furoate (Fig. 1.4) exhibits a very small endotherm followed by a big endotherm and a plateau. The small endotherm or exotherm in the DTA traces corresponding to the first decarboxylation stage of cobalt and copper furoates respectively may be due to absorption or evolution of heat during the first stage of the decarboxylation process leading to the formation of the unstable intermediate product. The large exotherm may be attributed to the net heat change involved in the second stage of decarboxylation (for cobalt and copper furoates) comprising of the heat evolved due to the decomposition of the intermediate product into the

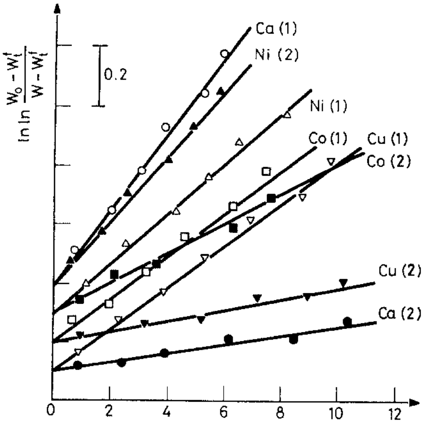

Fig. 3 Plot of $\ln\ln\frac{w_0-w_t^f}{w-w_t^f}$ *vs.* θ for the decarboxylation stage. Decarboxylation stage: M(fur)$_2$; M(1) = First stage; M(2) = Second stage

metal oxide and other gaseous products as well as the heat change due to secondary reactions amongst the different gaseous products. The single large exotherm observed in the DTA traces of the decarboxylation stage of calcium and nickel furoates may, however, be attributed to the net heat change involved in the overall decarboxylation process. That both the stages of thermal decomposition taking place after dehydration are manifestations of the decarboxylation process is indicated by the evolution of carbon dioxide through the entire course of reaction. Initiation, peak and completion temperatures for the two-stage decarboxylation processes of the anhydrous furoates along with the corresponding weight losses are given in Table 3. The final products left in the crucible were found to be mainly the oxides of the metals for cobalt, nickel and copper furoates and carbonate for the calcium salt. All these end products were identified by chemical analysis and recording of their X-ray diffraction patterns. The order of reaction for the decarboxylation processes was found to be unity. Applying the same methods used in the dehydration process, activation energy of the decarboxylation processes for both the stages were evaluated from the $\ln\ln\frac{w_0-w_t^f}{w-w_t^f}$ *vs.* θ plots given in Fig. 3. Enthalpy change accompanying each decarboxylation process was measured from the corresponding DTA traces and these are presented in Table 3. Initiation (t_i), peak (t_p) and completion temperatures (t_c) of the first-stage of thermal decarboxylation of the metal furoates and the negative heat of formation ($-\Delta H_f^0$) of the corresponding metal oxides [6] are given in Table 4.

The variation of initiation, peak and completion temperatures of thermal decomposition with the negative heat of formation of the metal oxides, which

Table 3 Characterization of decarboxylation processes

Compound undergoing decarboxylation	States of decarboxylation	Initiation temp., °C	Peak temp., °C	Completion temp., °C	Loss in wt.%		E_{Act}, kcal/mole	ΔH, kcal/mole	Order of reaction
					calcd.	found.			
1 Ca(fur)$_2$	Stage–I	365	430	448	—	37.99	70.00	369.39**	1
	Stage–II	449	—*	617	38.72	37.50	19.97		
2 Co(fur)$_2$	Stage–I	254	340	368	—	62.08	52.72	11.40	1
	Stage–II	368	—*	404	22.15	21.73	43.68	267.14	1
3 Ni(fur)$_2$	Stage–I	238	309	331	—	62.27	55.87	150.78**	1
	Stage–II	331	—*	361	29.07	30.15	83.33		1
4 Cu(fur)$_2$	Stage–I	222	275	288	—	62.50	72.05	29.59	1
	Stage–II	288	—*	460	26.32	26.19	14.50	356.48	1

* No peak but a plateau in the DTG trace could be found.

** Overall enthalpy changes.

Table 4

Compound	Initiation temp., °C	Peak temp., °C	Completion temp., °C	ΔH_f^0 of oxides [14] kcal/mole
$Co(fur)_2$	254	340	368	−57.2
$Ni(fur)_2$	238	309	331	−58.4
$Cu(fur)_2$	222	275	288	−37.1

provides a relative measure of the strength of M—O bond in the metal furoates (the metal oxides being the stable end-products in all the cases studied), is very close to the expected behaviour of gradual increase from Cu(II) to Ni(II).

Values of initiation temperatures of the different metal furoates along with the $1/r$ values [7] for the corresponding metal ions are included in Table 5. This behaviour is close to the general behaviour of gradual decrease of the stability of metal salts from Co(II) to Cu(II) with the decrease in ionic radii, the Ni(II) salt showing a departure from this general trend.

The single-step dehydration of cobalt furoate trihydrate indicate that all the water molecules in the compound are similarly bound. A single endotherm in each of the DTA and DTG traces definitely points to the same conclusion. A two-step dehydration of nickel furoate, $2.5H_2O$ is indicative of the fact that 1.5 molecules of water are bound rather loosely and are lost in the first stage of dehydration and the last water molecule, which is bound more strongly, is lost in the second stage at a higher temperature. In the single-stage dehydration of calcium furoate monohydrate, cobalt furoate trihydrate and copper furoate monohydrate and the first-stage dehydration of nickel furoate, $2.5H_2O$ represented by the equations in Table 2, the activation energies are in the order: Ca(II) > Ni(II) > Co(II) > Cu(II). The enthalpy change in the dehydration processes for the corresponding stages follow the order: Co(II) > Ni(II) > Cu(II) > Ca(II). It may be concluded from the DTG peak tem-

Table 5

Compound	Initiation temp., °C	$1/r$ Å^{-1} [15]
$Co(fur)_2$	254	1.351
$Ni(fur)_2$	238	1.428
$Cu(fur)_2$	222	1.369

peratures that the thermal stabilities of the hydrates follow the order Ca(II) > Ni(II) > Co(II) > Cu(II).

In the first stage of decarboxylation of the anhydrous metal furoates (Table 3), the activation energies follow the order: Cu(II) > Ca(II) > Ni(II) > Co(II). The overall enthalpy change for the decarboxylation processes, however, follow the order Cu(II) > Ca(II) > Co(II) > Ni(II). From DTG peak temueratυre it may be concluded that the thermal stabilities of the anhydrous metal furoates follow the order Ca(II) > Co(II) > Ni(II) > Cu(II).

Earlier workers [8–12] examining the thermal stability of other compounds of the same metal ions in the solid state noticed the stability order Co(II) > Ni(II) > Cu(II) which was just the reverse of the Irging-Williams order, Cu(II) > Ni(II) > Co(II), for the stability of metal complexes in solution [13]. Thus the thermal stability order found in our study is in conformity with the observations made by other workers. Such a reversal of the stability order on switching over from solution to the solid state probably occurs due to the interplay of high magnitude intramolecular bonds which becomes operative only in the solid state [14, 15]. It is quite possible that the observed stability order reflects the order of variation of the intermolecular forces operative in the solid compounds due to the close packing of the constituents in their crystal lattices.

Probable mechanism of decarboxylation

Solid and gaseous products of decarboxylation of the anhydrous salts were collected and characterized by a method described in details elsewhere [2]. The experiment was performed separately in dry air and dry nitrogen atmospheres and same products were identified in both the cases. Apart from the solid residue of oxide or carbonate, another solid substance was obtained as a white sublimate. 2-2′-bifuran was found to be the major constituent of this white residue which contained a small amount of 2-4′-bifuran. Among the gaseous products we were able to detect the presence of furan, carbon dioxide and carbon monoxide. Unavailability of a GC-Mass instrument did not allow us to identify and estimate each and every product. However, from the nature of the products we have identified, it appears that under the experimental conditions used in this study, the reaction proceeds through a free radical mechanism in which a furan-free radical is generated by the homolytic fission of the furan ring carbon-carboxyl-carbon bond leading to the subsequent formation of bifuran by the coupling of the two free radicals and generation of furan by abstraction of a hydrogen by one furan free radical from another.

References

1 S. Ghosh, S. K. Ray, P. K. Ray and T. K. Banerjee, J. Indian Chem. Soc., 59 (1982) 1034.

2 S. Ghosh, B. Sur, S. K. Ray and P. K. Ray, J. Thermal Anal., 30 (1985) 353.

3 K. Sano, Sci. Rep. Tohuku, 24 (1936) 719.

4 H. H. Horowitz and G. M. Metzger, Anal. Chem., 35 (1963) 1464.

5 A. W. Coates and J. P. Redfern, Nature, 201 (1964) 68.

6 Hiroko Yokobayashi, Kenzo Nagase and Kazuo Muraishi, Bull. Chem. Soc. (Japan), 48 (10) (1975) 2789.

7 Kenzo Nagase, Katsuya Sato and Nobuyuki Tanaka, Bull. Chem. Soc. Japan, 48 (1975) 439.

8 E. Cardarelli, G. D'Ascenzo, A. D. Magri and A. Pupella, Thermochim. Acta, 33 (1979) 267.

9 W. W. Wendlandt and G. R. Horton, Anal. Chem., 34 (1962) 1098.

10 W. W. Wendlandt, J. H. Van Tossel and G. R. Horton, Anal. Chim. Acta, 23 (1960) 332.

11 G. D'Ascenzo and W. W. Wendlandt, Anal. Chim. Acta, 50 (1970) 79.

12 G. D'Ascenzo, U. Baider Ceipidor and G. De Angelis, Anal. Chim. Acta, 58 (1972) 175.

13 H. Irving and R. J. P. Williams, J. Chem. Soc., 3192 (1953).

14 Norbert Adolph Lange, Handbook of Chemistry, Handbook Publishers, Inc., Sandusky, Ohio 1956, p. 1590.

15 A. F. Wells, Structural Inorganic Chemistry, Clarendon Press, Oxford 1975, p. 259.

16 S. Ghosh, P. K. Ray, S. K. Ray and T. K. Banerjee, J. Indian Chem. Soc., 61 (1984) 850.

Zusammenfassung — Die Dehydratisierung in fester Phase der hydratisierten Salze von Ca(II), Co(II), Ni(II) und Cu(II) mit Furan-2-carboxylsäure und die darauffolgende Decarboxylierung der entsprechenden wasserfreien Salze wurde mittels simultan ausgeführter TG, DTA and DTG untersucht. Die Reihenfolge der thermischen Stabilität der hydratisierten und wasserfreien Verbindungen wurde aus dem Verlauf der TG-, DTA- und DTG-Kurven ermittelt. Die thermischen Parameter (Aktivierungsenergie, Enthalpieveränderung, Reaktionsordnung) wurden für die verschiedenen Schritte eines jeden Prozesses nach Standardmethoden berechnet. Es wurde ein Versuch zur Erklärung des beobachteten Trends in der Thermostabilität der wasserfreien Salze gegenüber Decarboxylierung unternommen und ein Mechanismus für die themische Decarboxylierung von Calciumfuorat in Vorschlag gebracht.

Резюме — Совмещенным методом ТГ, ДТА и ДТГ изучена твердотельная дегидратация гидратов солей 2-фуранкарбоновой кислоты с двухвалентными кальцием, кобальтом, никелем и меди, а также декарбоксилирование их безводных солей. На основе проведенного исследования установлен порядок термоустойчивости как гидратов, так и безводных солей. Для различных стадий каждого процесса общепринятыми методами были вычислены энергия активации, изменение энтальпии и порядок реакции. Предпринята попытка объяснить наблюдаемую тенденцию термоустойчивости безводных солей с их декарбоксилированием. Для кальциевой соли 2-фуранкарбоновой кислоты предложен механизм термического декарбоксилирования.