

## INVESTIGATION OF THE THERMAL DECOMPOSITION OF POTASSIUM BENZOATE IN THE PRESENCE OF CADMIUM AND ZINC COMPOUNDS

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It was established by thermogravimetric measurements that the thermal decomposition of potassium benzoate in the presence of inorganic cadmium or zinc salts results in the formation of the easily decomposing cadmium or zinc benzoate. These carboxylates are presumably the catalysts of the transcarboxylation of potassium benzoate to terephthalate.

Raecke [1] has found that the thermal rearrangement of the potassium salts of benzene carboxylic acids in the presence of cadmium and zinc compounds gives terephthalic acid in excellent yield. Ogata [2] and Furuyama [3] examined the effect of several inorganic compounds on the terephthalic acid production. Except for the cadmium and zinc salts the catalytic effect is doubtful, because a considerable yield can be obtained even without additives [4].

Regarding the catalytic effect of cadmium and zinc compounds, Raecke has assumed that the reaction is catalyzed by cadmium or zinc metal, presumably produced by reduction during the process. These metals, however, could never be observed in the mixture [5]. According to Ogata [6] the cadmium cation forms a sandwich-type complex with the aromatic rings to facilitate the transcarboxylation. According to another assumption, cadmium and zinc oxides formed in the process from the cadmium or zinc compounds are the agents that have catalytic activity [3].

McNellis [7] found that the salts of naphthoic acid in the presence of cadmium salts decompose with  $\text{CO}_2$  evolution around  $300^\circ$ , although this kind of decomposition does not occur if no cadmium salt has been added. This observation provided the starting point of our work presented here.

The decomposition of potassium benzoate with or without additives was followed by thermogravimetry. The studies were carried out in a nitrogen atmosphere (rate of flow: 15 l/hour) using a Paulik–Paulik–Erdey MOM Derivatograph [8]. The samples (approximately 100 mg) were weighed into a platinum crucible. The heating rate was  $6^\circ/\text{min}$  up to  $600^\circ$ . The TG curves, presented in Fig. 1, show two decomposition steps in the presence of cadmium or zinc salts (a, b, c). The first, around  $300^\circ$ , corresponds to the decomposition of cadmium or zinc benzoate (d, e), the second, around  $430^\circ$ , to that of potassium benzo-

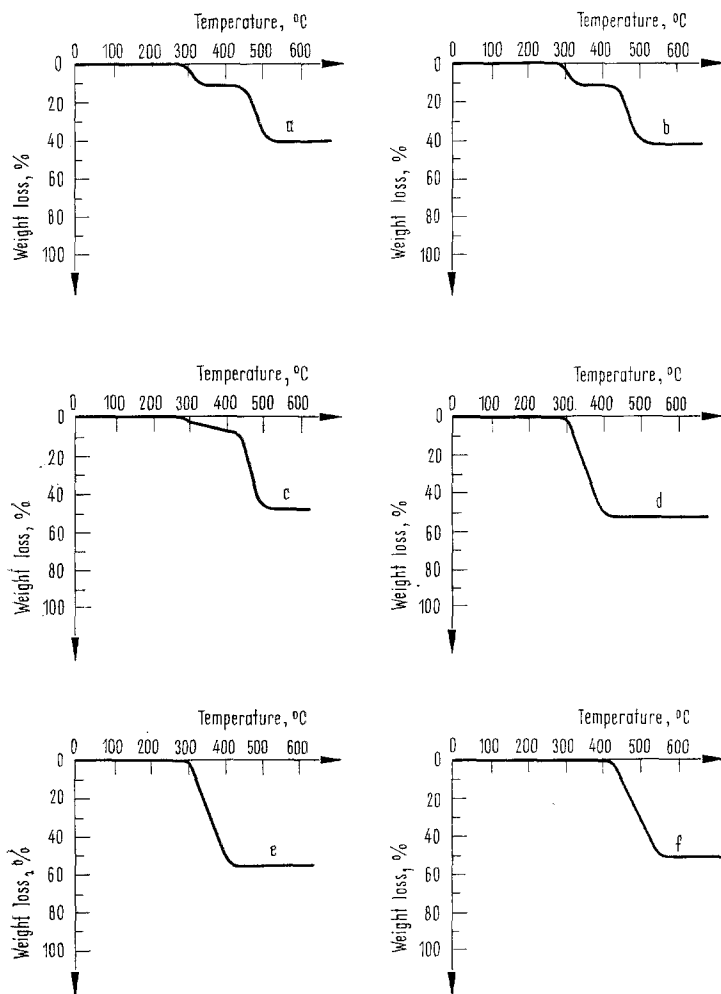


Fig. 1. Thermogravimetric curves. a: potassium benzoate with cadmium iodide (10 mole %), b: potassium benzoate with cadmium benzoate (10 mole %), c: potassium benzoate with zinc chloride (10 mole %), d: cadmium benzoate, e: zinc benzoate, f: potassium benzoate

ate (f). No weight loss can be observed around 300° using cadmium oxide, zinc oxide or zinc metal as additive.

The data of Table 1 show that the extent of the weight loss in the first stage increases with an increasing ratio of  $\text{Cd}^{++}/\text{ArCOO}^-$ . Nearly the entire potassium benzoate decomposes in the first stage when the above ratio reaches a value of 0.25. In this decomposition step significant quantities of terephthalic acid, benzene and  $\text{CO}_2$  are formed.

Table 1

Cd <sup>++</sup> /ArCOO <sup>-</sup>		% weight loss in the stage	
KB+CdI <sub>2</sub>	KB+CdB <sub>2</sub> *	1	2
0.027	—	4.0	39.0
—	0.025	4.0	39.0
0.052	—	7.2	32.0
—	0.050	7.8	31.0
0.100	—	11.0	28.5
—	0.102	13.0	26.0
0.150	—	14.5	21.0
—	0.154	17.8	17.0
0.201	—	20.0	10.0
—	0.203	22.0	7.0
0.250	—	24.0	3.0
—	0.250	27.0	1.0

\* KB: potassium benzoate  
CdB<sub>2</sub>: cadmium benzoate

On the other hand, cadmium oxide, zinc oxide and zinc metal have no measurable effect on the decomposition of potassium benzoate. The results summarized in Table 2 were obtained from an investigation of the decomposition with these additives at 450° on a home-made thermobalance in a nitrogen atmosphere (15 l/hour).

Table 2

Starting mixture	Half time (min)	Terephthalic acid yield %*
KB	40.5	19
KB + CdO	38.0	23
KB + ZnO	39.0	21
KB + Zn	40.0	18

\* Measured by an isotope-dilution method

The data of Table 2 indicate that these additives do not affect either the rate of decomposition or the production of terephthalic acid. This means that under the experimental conditions applied they cannot be considered as the catalysts of decomposition. The catalytic activity of oxides observed under CO<sub>2</sub> pressure may be attributed to the presence of the corresponding carbonates.

According to the experimental facts, the inorganic cadmium and zinc salts mixed with potassium benzoate are converted to the easily decomposing cadmium

and zinc carboxylates. Presumably these carboxylates are the catalysts of the thermal transcarboxylation of potassium benzoate in spite of the fact that the decomposition of cadmium or zinc benzoate does not produce dicarboxylates. Their catalytic activity is presumably connected with the formation of an intermediate that has the ability to react with potassium benzoate.

### References

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RÉSUMÉ — L'étude thermogravimétrique de la décomposition thermique du benzoate de potassium en présence de sels minéraux de zinc ou de cadmium montre la formation de benzoates de cadmium ou de zinc facilement dissociables. Ces carboxylates sont probablement les catalyseurs de la transcarboxylation du benzoate de potassium en téréphthalate.

ZUSAMMENFASSUNG — Es wurde durch thermogravimetrische Messungen festgestellt, daß die thermische Zersetzung von Kaliumbenzoat in Gegenwart von anorganischen Kadmium- oder Zinksalzen zur Bildung des leicht zersetzbaren Zink- oder Kadmiumbenzoats führt. Diese Carboxylate spielen möglicherweise eine katalytische Rolle bei der Transcarboxylierung von Kaliumbenzoat zu Terephthalat.

Резюме — Термогравиметрическими измерениями установлено, что термическое разложение бензоата калия в присутствии неорганических солей кадмия или цинка происходит с образованием легко разлагаемого бензоата калия или цинка. Эти карбоксилаты, по-видимому, являются катализаторами транскарбоксилирования бензоата калия до терефталата.