

THE THERMAL DECOMPOSITION OF ALKALI METAL FORMATES

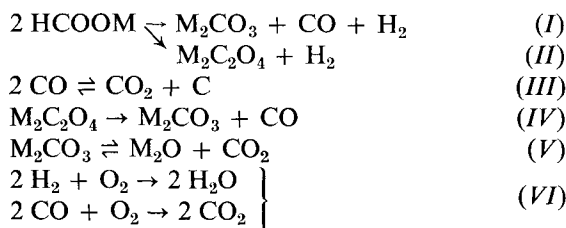
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The thermal decompositions of lithium, sodium, potassium, rubidium and caesium formates were investigated by a complex dynamic thermoanalytical method. The ratio of the products in reactions resulting in alkali metal carbonates and oxalates depended variously on the atmosphere used. Differences were found compared to isothermal investigations, in that the catalytic effects of bases could not be observed and the oxalate-conversion was lower. The formation of oxalate did not occur in the cases of lithium and caesium formates; the order for the other salts was sodium formate < potassium formate > rubidium formate.

The thermal decomposition of an alkali metal formate is a complex process, the following reactions being possible:



Reactions *I* and *II* proceed simultaneously. The ratio of the products depends considerably on the experimental conditions, primarily the nature of the atmosphere of reaction space. Processes *IV* and *V* appear separately and independently from both each other and processes *I* and *II*. In the presence of air or oxygen the carbon monoxide formed is oxidized exothermally to carbon dioxide and the hydrogen to water.

Reaction *III*, the formation of crack-carbon, depends on the temperature and is influenced by the nature of the atmosphere.

The following literature data are known relating to the thermal decomposition of the alkali metal formates, primarily under isothermal experimental conditions:

1. At about 300° mainly reaction *I* takes place, while at 350–400° reaction *II* dominates [1, 2].

2. The nature of the applied atmosphere is a very important factor. In a nitrogen or an inert gas flow the product of the first period of decomposition is primarily oxalate, but in oxygen or air it is carbonate [3].

3. The conversion to oxalate can be increased by adding catalysts. The catalytic effects of the alkali metals, alkali metal hydroxides, sodium amide, alkali metal carbonates and copper metal have been studied [1, 2, 4, 5, 6].

4. Both ionic and radical mechanism have been proposed for the decompositions [2, 3, 6–12].

5. In earlier studies the reactions was followed via the pressure of the evolved gases and by permanganometric titration of the oxalates formed. In the cases of sodium and potassium formates, Sabbah et al. determined the ratio of the end-products by the quantitative evaluation of the thermogravimetric curves [3].

The extension of the use of dynamic investigation methods to all the alkali metal formates seemed to be obvious and reasonable. In this way comparative data can be obtained and at the same time it is possible to verify whether the individual part-reactions can be followed quantitatively by the evaluation of complex thermoanalytical curves.

Experimental

The alkali metal formates were obtained by reaction of analytical grade formic acid and alkali metal carbonates. The alkali metal oxalates were in part prepared in our laboratory and in part commercial products. The compositions of the compounds were checked by chemical analysis.

Results and discussion

The complex thermoanalytical curves for lithium, sodium, potassium, rubidium and caesium formates, measured in air and nitrogen atmospheres, are shown in Figs 1–5.

Table 1

		HCOOLi		HCOONa	
		in N ₂	in air	in N ₂	in air
1st stage	t _{in.}	325	290	315	250
	t _{max.}	390	380	405	400
	t _{fin.}	430	420	440	425
2nd stage	t _{in.}	— (450)	— (450)	480 (500)	450 (470)
	t _{max.}	— (535)	— (525)	520 (545)	485 (560)
	t _{fin.}	— (575)	— (540)	540 (565)	510 (580)

The characteristic decomposition temperatures of these compounds and the corresponding oxalates are listed in Table I. In the cases of the oxalates only the data of reaction IV are summarized: it was considered unnecessary to report the

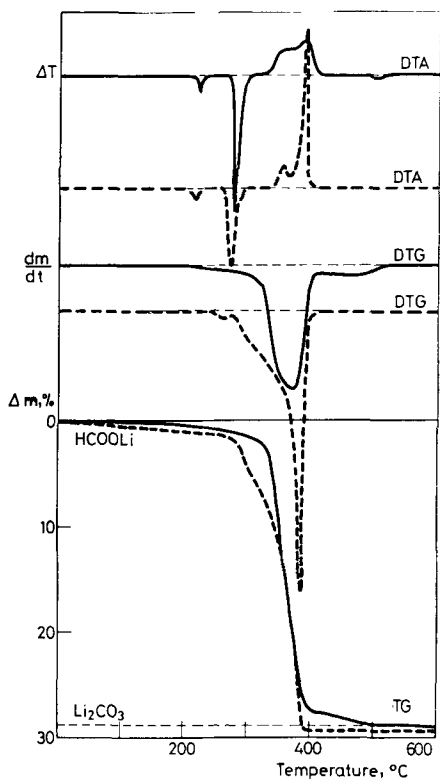


Fig. 1. Complex thermoanalytical curves of lithium formate; Full line: in nitrogen, Broken line: in air

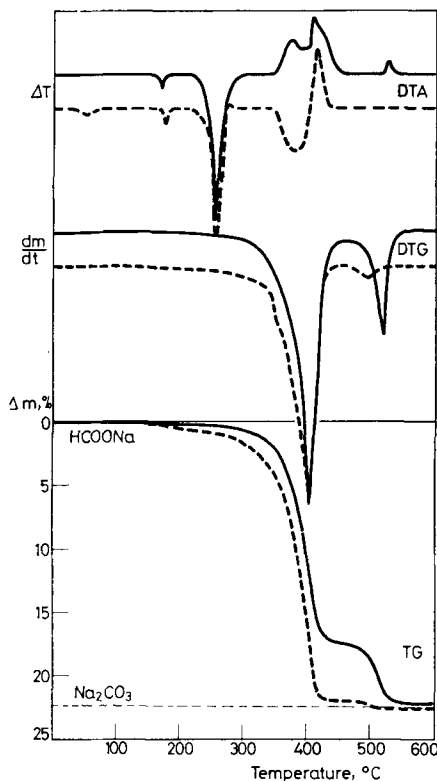


Fig. 2. Sodium formate; Full line: in nitrogen; Broken line: in air

HCOOK		HCOORb		HCOOCs	
in N ₂	in air	in N ₂	in air	in N ₂	in air
300	275	300	250	290	250
420	435	415	390	345	405
465	470	480	415	490	430
495 (475)	500 (450)	480 (500)	— (400)	— (500)	— (450)
555 (570)	520 (560)	530 (565)	— (535)	— (560)	— (520)
595 (595)	560 (575)	560 (595)	— (550)	— (590)	— (550)

data regarding their dehydrations and the decompositions of the alkali metal carbonates.

It can be seen from the shape of the curves, that reaction *IV* is sharply separated from the first-step reactions (*I* and *II*) if oxalates are formed and so the curves are very suitable for determining the ratio of products formed in reactions *I* and *II* using the stoichiometric equations.

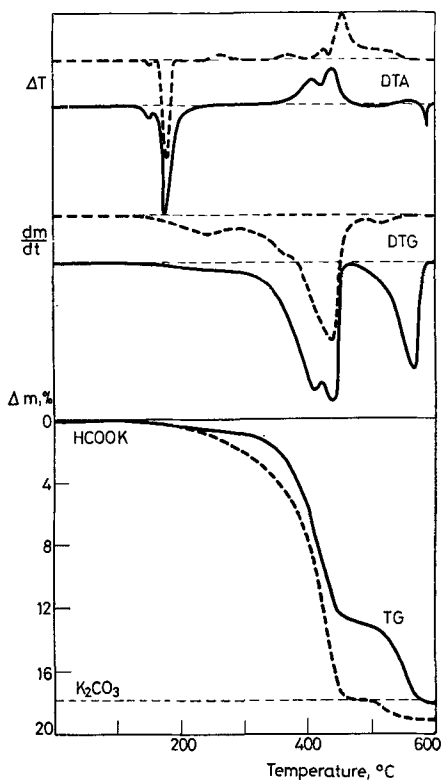


Fig. 3. Potassium formate; Full line: in nitrogen; Broken line: in air

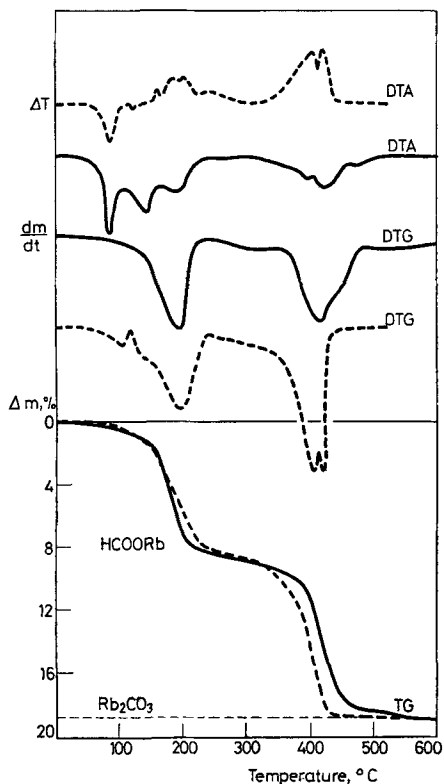


Fig. 4. Rubidium formate. xH_2O ; Full line: in nitrogen; Broken line: in air

To reach the decomposition temperatures of the alkali metal carbonates was not necessary because they formed in both reactions *I* and *II* + *IV*, and their amounts did not give any more information relating to this problem. In addition, the alkali metal oxides have a very corrosive effects on the platinum sample holder.

It is well-known in thermoanalytical practice that the characteristic temperature of a sample diluted with an inert material is lower than that of the undiluted, pure substance. In the event of the formation of oxalate in small amount, it could be

expected that the decomposition of the oxalate finely dispersed in the carbonate matrix would take place at a lower temperature, and so its TG curve would be unverifiably overlapped with that of the former process. We have determined experimentally that this effect caused a shift of the decomposition temperature of only $8 - 10^\circ$ in a sample containing 10% of oxalate, and this still allowed a good evaluation of the separated steps of the TG curves. It was also probable that the elemental carbon arising in reaction *III* could affect the results obtained from the TG curves.

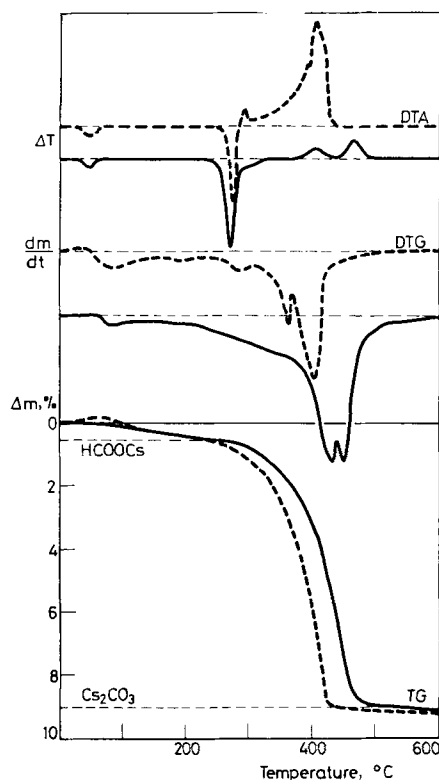


Fig. 5. Caesium formate; Full line: in nitrogen; Broken line: in air

The carbon in many residues of alkali metal formate decomposition was weighed after extraction with water and found to be 0.01–0.2%. This amount was a source of negligible error.

The relative amounts of oxalates obtained from the different alkali metal formates were compared. The oxalate-conversion is plotted in Fig. 6 against increasing size of the alkali metal ion on an arbitrary scale. It can be seen that the formation of oxalate from lithium and caesium formates was negligible in both nitrogen and

air atmospheres. It was formed in the cases of sodium, potassium and rubidium formates, but to a higher degree in nitrogen than in air.

The change of conversion was investigated as functions of linear and programmed non-linear heating rates. These parameters influenced the degree of conversion only within the limit of error. However, a multi-plate platinum large-surface sample holder caused a significant decrease in the oxalate-conversion, even when all the other experimental conditions were kept the same.

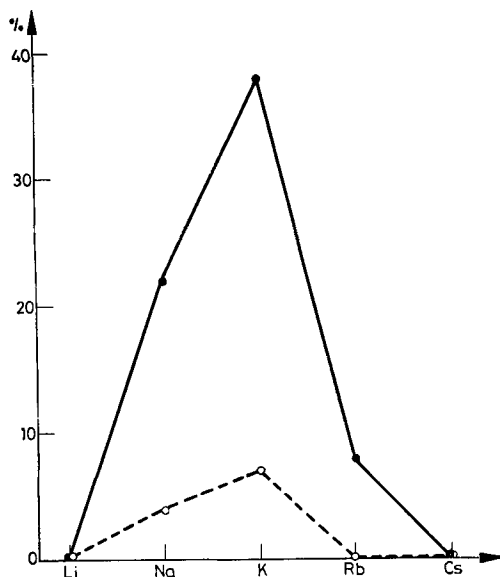


Fig. 6. The oxalate-conversions of the different alkali formates given in weight per cent. Full line: in nitrogen; Broken line: in air

The catalytic effects were also investigated. 2–5 wt. % of the corresponding alkali metal hydroxides were added to the alkali metal formates. The thermal behaviours of the bases had been previously investigated and were used to explain the thermoanalytical curves of such formate samples.

The effects of sodium amide and finely-powdered copper metal on the oxalate-conversion were also investigated. No change of conversion was found except when copper metal was used, the conversion of oxalate then increased by about 8–10%. Not only the shape of the sample holder but also its material had an effect on the conversion to oxalate. Different results were obtained using a fire-shrunk, slightly porous corundum crucible because of the reaction between alkali metal carbonate and aluminium oxide involving evolution of carbon dioxide. A sample holder made from glass was used too and the oxalate-conversion of potassium formate was found 60% instead of the 38% measured in the platinum

sample holder. If platinum metal with a large surface was mixed with the sample contained in the glass holder, the oxalate-conversion fell back to 50%. In contrast with corundum, the weight of the glass sample holder did not change during the measurements. It seemed that the glass had a catalytic effect on reaction *II*, while the platinum promoted reaction *I*, or otherwise hindered reaction *II*.

It turned out that the oxalate-conversion reported in the literature could not be attained even for optimum experimental conditions using dynamic measuring methods. This can be explained by Sabbah's data [3], according to which, using dynamic heating, the formation of oxalate reached an optimum as a function of the pressure. Our measurements were carried out at ambient pressure.

The following conclusions could be drawn from our experimental results.

1. The complex thermoanalytical method was suitable for investigating the decomposition reactions of the alkali metal formates, through the joint evaluation of thermal curves and the appropriate stoichiometric equations.

2. The method revealed the differences in thermal behaviour of the salts, depending on the nature of the metal ions. The fact that the formation of oxalate was the largest for sodium and potassium formates and negligible for the lithium and caesium salts in a given experimental series allowed the conclusion that the covalent character of the metal ion – carboxyl bond and the increasing radius of the metal ion had effects leading to the decrease of the formation of oxalate.

3. The application of programmed dynamic heating decreased the yield of reaction *II* as compared to the isothermal experiments.

4. The catalytic effects of bases could not be observed, but the use of a glass sample holder increased the conversion of reaction *II* significantly.

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RÉSUMÉ — On a étudié, avec une méthode d'analyse thermique complexe et dynamique, la décomposition thermique des formiates du lithium, du sodium, du potassium, du rubidium et du caesium. Les proportions des produits des réactions donnant des carbonates et oxalates

alcalins dépendaient de manières différentes de l'atmosphère utilisée dans les conditions données des expériences. En comparant les résultats avec ceux des examens isothermiques on trouvait des différences à l'égard de ce qu'on n'a pas pu observé des effets catalytiques chez les catalyseurs basiques et que les conversions en oxalates étaient plus faibles. Dans les cas du lithium et du caesium il n'y avait pas de formation d'oxalate, l'ordre était, cependant, formiate de sodium < formiate de potassium > formiate de rubidium.

ZUSAMMENFASSUNG — Die thermische Zersetzung der Lithium-, Natrium-, Kalium-, Rubidium- und Caesiumformiate wurde mittels einer komplexen dynamischen thermoanalytischen Methode geprüft. Das Verhältnis der Reaktionsprodukte Alkalicarbonat und -oxalat zeigte unter den gegebenen Versuchsbedingungen eine unterschiedliche Abhängigkeit von der angewandten Atmosphäre. Im Vergleich zu isothermen Untersuchungen wurden Unterschiede in der Hinsicht gefunden, daß bei basischen Katalysatoren keine katalytischen Effekte beobachtet werden konnten und die Oxalatkonversionen niedriger lagen. Bei Caesium- und Lithiumformiaten erfolgte keine Oxalatbildung, die Reihenfolge jedoch war Natriumformiat < Kaliumformiat > Rubidiumformiat.

Резюме — Исследован термораспад формиатов лития, натрия, калия, рубидия и цезия термоаналитическим комплексным динамическим методом.

Доля продукта в реакциях, происходящих с образованием карбонатов и оксалатов щелочных металлов, в значительной степени зависит от условий эксперимента. Различие, сравнительно с изотермическими условиями, в том, что каталитические эффекты щелочного катализа не наблюдалось и оксалат-переход был более низкий.

В случае формиатов лития и цезия образование оксалата не происходило, для других солей наблюдался следующий порядок: формиат натрия < формиат калия > формиат рубидия.