

INFLUENCE OF THE CATION ON THE FORMATION OF FREE HYDROGEN AND FORMALDEHYDE IN THE THERMAL DECOMPOSITION OF FORMATES

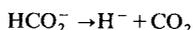
A. Górski and A. D. Kraśnicka

DEPARTMENT OF CHEMISTRY, INSTITUTE OF BASIC CHEMISTRY,
WARSAW TECHNICAL UNIVERSITY, WARSAW, POLAND

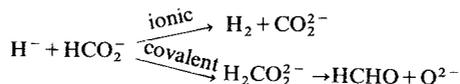
(Received January 13, 1986; in revised form December 20, 1986)

Three stages have been distinguished in the thermal decomposition of formates:

It was found that in the first stage carbon dioxide is evolved, leaving structural elements of the respective cation hydride in the reaction system:



The second stage depends on the character of the bond in the intermediately formed hydride:



The third stage is connected with formaldehyde transformation into different organic compounds, depending on the character of the metal oxide formed in the thermal decomposition of the formate. This explains the formation of free hydrogen and organic compounds identified as thermal decomposition products of various formates.

In the numerous publications concerning the mechanism of thermal decomposition of formates with different cations, no uniform concept has been proposed to account for the variety of phenomena observed. Both radical and ionic mechanisms can be found in the literature.

Homolytic cleavage of the H—C bond has been assumed to be the reason for free hydrogen formation in the case of radical mechanisms [1, 2], with homolytic cleavage of other bonds (C=O and C—O) as the reason for the formation of various organic products of thermal decomposition [3]. The possibility of the homolytic scission of particular bonds as a function of the ionization potential of the cation present in the formate has been analysed [4–6].

Among the ionic mechanisms, the concept of H—C bond cleavage has been considered [7]. A separate group of ionic mechanisms is based on the assumption of the formation of a two-molecule active complex, which then decomposes to

formaldehyde and carbonate [8, 9]. The isotopic effect observed for deuterated salts indicates the cleavage of the weakest bond of the formate anion in the transition state, i.e. the H—C bond. The negative results of ESR studies (in which no CO_2^- radicals were detected) exclude the possibility of homolytic cleavage of the H—C bond. (The presence of these radicals has been observed only in the thermal decomposition of previously irradiated sodium formate [10, 17].)

The search for a uniform mechanism for the thermal decompositions of formates with different cations is the subject of the present work. Hypotheses relating to the origin of gaseous organic products in the thermal decompositions of formates were verified previously [12]:

(a) It was shown that synthesis gas is inactive towards the solid-phase metal oxides formed in the thermal decompositions. It cannot be a precursor of organic compounds obtained from the thermal decompositions of formates.

(b) It was shown that organic compounds (methanol, formic acid, methyl formate and methane) may result from the transformation of the intermediate formaldehyde in the presence of metal oxides formed in the reaction medium.

(c) The Canizzaro and Tishchenko reaction mechanisms applied to interpret formaldehyde transformations in the presence of different metal oxides give a satisfactorily uniform explanation of the origin of the organic compounds identified in the thermal decompositions of formates.

(d) It was found that the ratios of the yield of organic compounds to the yield of inorganic ones in the final product varies within very wide ranges for particular salts.

However, it is possible to distinguish two extreme types of thermal decomposition of formates. The decomposition proceeds either via the formaldehyde stage with subsequent hydrogen evolution in the form of organic compounds (tin(II) formate) or via a mechanism leading to the evolution of free hydrogen (alkali metal formates).

The occurrence of two different types of thermal decomposition of formates, depending on the nature of the cation, will be explained in this paper.

Experimental

Reagents

NaBH_4 (p.a., BDH), HCO_2Na and $(\text{HCO}_2)_2\text{Sn}$ were used for the investigations; the latter two compounds were prepared as described in [12].

Procedure

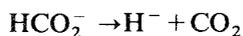
The reaction of an equimolar mixture of HCO_2Na and NaBH_4 was carried out in a nitrogen atmosphere. The reaction conditions and the apparatus were the same as described in [12]. Quantitative analysis of hydrogen was performed with a quadrupole mass spectrometer by separating other products through freezing.

Results and discussion

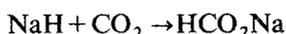
Data relating to the quantitative and qualitative composition of the gaseous products of thermal decomposition of the formates were presented in detail previously [12]. They gave rise to the assumption that in the thermal decompositions of formates two modes of hydrogen liberation co-exist; it is released either in the form of free hydrogen (H_2), or bonded in formaldehyde or its transformation products (methanol, formic acid, methyl formate and methane).

The molar fractions $n_{\text{Horg}}/(n_{\text{Horg}} + n_{\text{H}_2})$ of hydrogen contained in volatile organic compounds obtained from the thermal decompositions of particular formates are presented in Fig. 1 in a decreasing sequence, in order to illustrate the quantitative relations concerning the gaseous product. These data reveal some regularities as regards the influence of counter-ions on the mode of hydrogen liberation in the thermal decompositions of the formates. The greatest amount of hydrogen bonded in different organic compounds is obtained in the thermal decompositions of formates of metals in lower periods in the sp block (Sn, Hg, Zn, Pb, Tl and Bi) and of lanthanum and neodymium. Much less such hydrogen is obtained from the decompositions of transition element formates, magnesium and alkaline earth metals, and the least from alkali metal formates. These observations lead to the discovery of a relation not described in the literature, between the mode of hydrogen liberation in the thermal decompositions of formates of particular cations and the properties and reactivities of the respective cation hydrides.

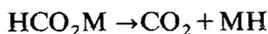
Thus, it should be presumed that a hydride is formed in the early stage of the thermal decomposition of the formate. Depending on the nature of the cation in the starting salt, this hydride reacts in the next stage either with the evolution of molecular hydrogen or with formaldehyde formation, which is then transformed into different organic compounds. According to this conception, the heterolytic cleavage of the H—C bond of the formate anion is the first stage in the thermal decomposition. This causes the formation of carbon dioxide and a hydride anion as follows:



The proposition corresponding to this assumption, that the thermal decomposition of the formate should start with the cleavage of the weakest bond (i.e. the H—C bond), is in agreement with the occurrence of the isotopic effect in deuterated formates [8, 9]. The first stage is confirmed by the deformation of the formate anion upon heating [8, 9]. This deformation causes a lengthening of the H—C bond and widening of the OCO angle in the formate anion, which in an extreme case leads to the formation of a linear carbon dioxide molecule and a hydride anion. A heterophase reaction is also known to proceed at about 80° between alkali metal hydrides and carbon dioxide, leading to the formation of an alkali metal formate [13], e.g.:

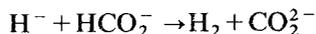


If the reversibility of this reaction is assumed, carbon dioxide and a metal hydride would be formed from the formate at elevated temperatures. The assumption that the thermal decomposition of the formate is initiated by carbon dioxide evolution and that the structural elements of the respective cation hydride are formed in the reaction system seems to be justified:



This first stage in the thermal decomposition of the formate is confirmed by the course of thermal decomposition of other carboxylic acids or their salts with different cations, where carbon dioxide is always found among the products. The hydrocarbons or carbonyl compounds obtained in these processes correspond to the hydrogen or formaldehyde produced in the thermal decomposition of the formate [14]. Thus, it seems that the first stage in the thermal decomposition of the formate, consisting in carbon dioxide evolution and hydride formation, proceeds irrespective of the nature of the cation, and hence is mutual for both types of hydrogen liberation (both in the molecular and in the bonded form).

The difference in the further course of the process results from the dissimilarity in the character of the metal—hydrogen bond in the intermediately formed hydride. If the proportion of ionic bonding in the hydride is high (e.g. alkali metal hydrides), then the almost free hydride anion reacts as a Lewis base, abstracting a proton from the non-decomposed anion and forming molecular hydrogen by a hydride-proton mechanism:



This process should proceed with a high yield, since the H—C bond is weaker than the H—H bond, which is indicated by a high amount of molecular hydrogen in the thermal decomposition products of alkali metal formates [Fig. 1]. Decomposition of the CO_2^{2-} anion takes place in the next stage, which consists in carbon oxide

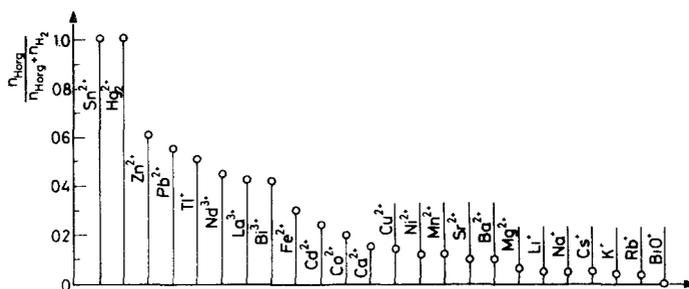
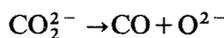


Fig. 1 The molar fraction $n_{Horg}/(n_{Horg} + n_{H_2})$ for the volatile organic compounds obtained in the thermal decompositions of formates

evolution (as justified in [15]):



Carbon dioxide and carbon originating from the disproportionation of carbon monoxide are the successive thermal decomposition products of alkali metal formates. The presence of methanol and methane resulting for the transformation of formaldehyde has also been found. The low content of the latter two organic compounds in the gases indicates that formaldehyde is formed in a side-reaction in this case [12].

The reaction of an equimolar mixture of sodium formate and sodium borohydride (see Fig. 2) provides additional evidence of a hydride-proton mechanism of molecular hydrogen formation. The broad exothermic peak (with an endo overlap due to formate melting at about 250°) follows the first local mass loss rate maximum. Determination of hydrogen up to 278° revealed that about 40% of the hydrogen present in the substrates is evolved, which corresponds to the removal of all the hydrogen from the formate. NaBH₄ which is well known as a one hydride anion donor, here causes the elimination of a proton from the formate anion, with quantitative generation of molecular hydrogen and a CO₂²⁻ anion. Since there is a possibility for stabilization of the CO₂²⁻ anion in the intermediately formed adduct (BH₃CO₂)²⁻ [13], the initial step in the reaction can be expressed by the following equation:



The further course of the reaction involves the decomposition of the adduct, with the formation of sodium metaborate and carbon compounds in low oxidation states (elemental carbon, tar, carbon monoxide, methanol and methane). The presence of oxalate was excluded throughout the temperature range of the reaction, in contrast to sodium formate and sodium borohydride mixtures with a molar ratio larger than one.

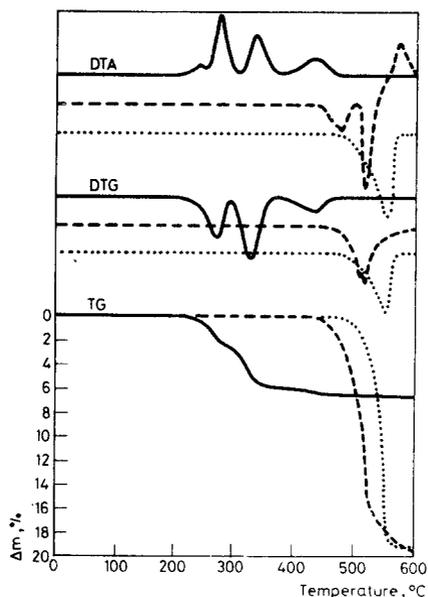


Fig. 2 TG, DTG and DTA curves for the reaction of an equimolar mixture of HCO_2Na and NaBH_4 under a nitrogen atmosphere (full line).

TG, DTG and DTA curves for the thermal decomposition of NaBH_4 under a nitrogen atmosphere (dashed line).

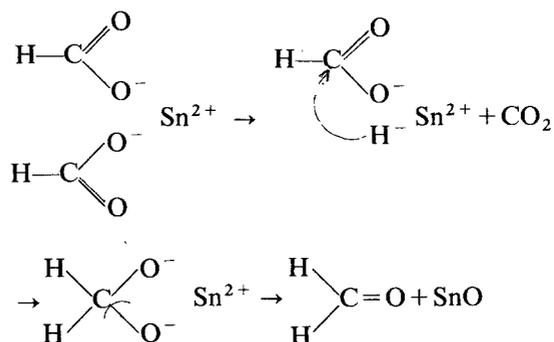
TG, DTG and DTA curves for the thermal decomposition of $\text{Na}_2\text{C}_2\text{O}_4$ under a nitrogen atmosphere (dotted line)

The second stage in the thermal decomposition of the formate proceeds differently when the proportion of the ionic bond in the intermediately formed hydride is small. This occurs in the case of formates with cations of greater polarizability, i.e. elements lying after zinc, cadmium and mercury, which have 18-electron outer shells. A rise in the proportion of the covalent bond in the intermediately formed hydride may preclude hydrogen formation according to the hydride-proton mechanism in favour of a nucleophilic type substitution:

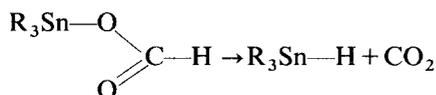


This reaction probably proceeds via a tetrahedral intermediate, $\text{H}_2\text{CO}_2^{2-}$ (preferred for carbon compounds in which a double bond occurs with a heteroatom such as O, N or S), which spontaneously decomposes with the formation of metal oxide and formaldehyde [14]. The formation of a covalent metal-hydrogen bond therefore causes a different course of thermal decomposition, which in the case of tin(II)

formate is described by the following equations:

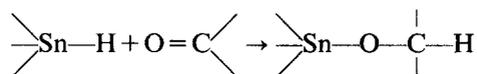


All the products mentioned above (carbon dioxide, formaldehyde and tin(II) oxide) were identified in the thermal decomposition of tin(II) formate under vacuum [16]. The presence of methyl formate was additionally found when the process was carried out under normal pressure of an inert gas. As shown in the previous paper, methyl formate is a product of the catalytic transformation of formaldehyde in the presence of tin(II) oxide according to the Tishchenko reaction mechanism [17, 18]. The reactions corresponding to the particular stages of the mechanism are known. When trialkyltin formate is heated at 160–180°, carbon dioxide is eliminated with the formation of the corresponding hydride [13]:



where R = *n*-C₃H₇ or *n*-C₄H₉

Moreover, organotin hydrides undergo addition to the carbonyl bond [13] according to the equation



The assumed mechanism of the reactions between the hydride anion and non-decomposed formate anion, leading to the formation of molecular hydrogen or formaldehyde, are consistent with the experimental results on the influence of a carbon dioxide atmosphere. It was found that the use of a carbon dioxide atmosphere in place of an inert gas atmosphere does not noticeably change the initial mass loss temperature, either in the thermal decomposition of sodium formate (316° in nitrogen and 318° in carbon dioxide atmosphere) or in that of tin(II) formate (130° in both atmospheres). However, an influence of the carbon

dioxide atmosphere was observed in the thermal decompositions of alkali metal, alkaline earth metal, lanthanum and neodymium oxalates, where carbon dioxide is also a product of the first stage. The increase in thermal stability of the above oxalates in a carbon dioxide atmosphere was explained by the reversible character of the reaction initiating the decomposition [15]:

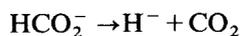


The lack of a noticeable influence of carbon dioxide on the thermal stability of the formates results from the fact that decomposition of the formate anion to carbon dioxide and a hydride anion becomes practically non-reversible, for the hydride anion immediately reacts with a non-decomposed formate anion.

The mechanisms of hydrogen liberation either in the molecular form or as formaldehyde (or its transformation products) are representative for the thermal decompositions of formates with cations which form sufficiently ionic or covalent hydrides in the first stage. However, a majority of the cations considered do not form such hydrides. Hydrides usually reveal a complex character, which consists in the participation of all three basic types of bonds, i.e. ionic, covalent and metallic. Thus, the reactivity of the hydride formed in the first stage of the thermal decomposition of the formate appears to depend on the proportions of these types of bonds. A decrease in the proportion of the covalent bond in the hydride, resulting from an increase in the proportion of either the ionic or the metallic bond, causes a drop in reactivity of the hydride in the nucleophilic substitution. This is expressed by a decrease in the yield of organic compounds derived from the thermal decomposition of the formate, with a corresponding simultaneous increase in the yield of molecular hydrogen; however, the influence of the ionic bond is stronger here.

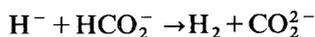
The considerations presented in this paper lead to a uniform conception of the formation of gaseous products in the thermal decomposition of formation, which can be described by the following scheme:

Stage I, independent of the nature of the cation:



Stage II, dependent on the nature of the cation:

a) for cations forming strongly polarized bonds (largely ionic) with the hydride anion:



b) for cations forming weakly polarized bonds (largely covalent) with the

hydride anion:



c) for cations forming complex types of bonds (a combination of the three basic types) with the hydride anion, reactions a) and b) occurring together.

Stage III, dependent on the character of the metal oxide formed in the thermal decomposition of the formate; formaldehyde undergoes transformations:

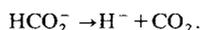
a) in the Cannizzaro reaction, yielding methanol in the presence of strongly basic oxides,

b) in the Tishchenko reaction, yielding methyl formate in the presence of weakly basic oxides.

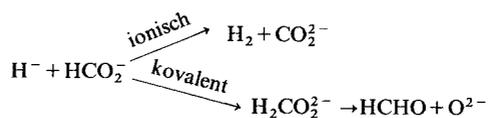
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Zusammenfassung — Bei der thermischen Zersetzung von Formiaten konnten drei Schritte unterschieden werden. Im ersten Schritt wird Kohlendioxid unter Verbleib von Strukturelementen des betreffenden Kationhydrids in Freiheit gesetzt:

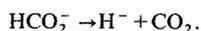


Der zweite Schritt hängt vom Charakter der Bindung in dem als Intermediärverbindung gebildeten Hydrids ab:

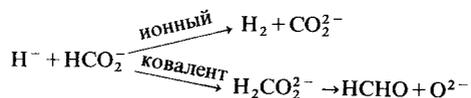


Der dritte Schritt betrifft die Überführung von Formaldehyd in verschiedene organische Verbindungen, die abhängig vom Charakter des bei der thermischen Zersetzung des Formiats gebildeten Metalloxids ist. Dadurch findet die Bildung von freiem Wasserstoff und der als Zersetzungsprodukte der verschiedenen Formiate identifizierten organischen Verbindungen ihre Erklärung.

Резюме — Разделены три стадии термического разложения формиатов. Найдено, что на первой стадии разложения образуется гидрид-ион и двуокись углерода по следующей схеме:



Вторая стадия зависит от характера взаимодействия образующегося гидрид-иона:



Третья стадия связана с дальнейшим превращением формальдегида до различных органических соединений, природа которых зависит от характера окиси металла, образующейся при термическом разложении формиата. Приведенные реакции объясняют образование водорода и органических соединений, найденных в продуктах термического разложения формиатов.