

ORIGIN OF ORGANIC GASEOUS PRODUCTS FORMED IN THE THERMAL DECOMPOSITION OF FORMATES

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The gaseous products of the thermal decomposition of formates have been investigated and compared with the products of formaldehyde and synthesis gas transformation under analogous conditions in the presence of the solids formed in the thermal decomposition of particular formates. It was found that formaldehyde transformation leads to organic compounds identical to those obtained in the thermal decomposition of the respective formates, while synthesis gas does not react under such conditions. This fact substantiates the hypothesis that formaldehyde is a precursor of the organic compounds identified in the thermal decomposition of formates. The nature of the organic compounds obtained in the thermal decomposition of formates indicates that the formaldehyde formed in the initial stages is then transformed in the Cannizzaro or Tishchenko reactions.

Various gaseous compounds, both inorganic (H_2 , CO, CO_2 and H_2O) and organic (HCHO [1-7], CH_4 [1-3, 8], HCO_2CH_3 [1, 2, 8], CH_3CH [1, 2], HCO_2H [9, 10], CH_3CHO [1], C_2H_4 , C_2H_6 and CH_3OCH_3 [2]), have been identified among the products of thermal decomposition of different formates. The yield of inorganic products is usually greater than that of organic ones [1], and only inorganic compounds were found in some studies of the thermal decompositions of alkali metal formates [11] and transition metal formates [7, 12, 13].

The reported mechanisms of formation of organic products can be divided into two groups. In the first group of mechanisms it is accepted that synthesis gas ($H_2 + CO$) is the precursor of the organic products [1, 4, 5, 11], whereas in the second group the precursor is formaldehyde [2, 3, 7]. It is assumed in both mechanisms that these precursors of the organic products are formed in the initial stages of thermal decomposition of the formates, and are then transformed in secondary reactions catalyzed by solid phases produced in the thermal decomposition of the formates.

In order to verify the above hypotheses, the gaseous products of thermal decomposition of formate have been studied in this work and compared with the

products of the formaldehyde and synthesis gas reactions proceeding in the presence of the solids resulting in the thermal decompositions of the formates. Formaldehyde reactions were carried out with fourteen metal oxides, two hydroxides and two carbonates. In the case of synthesis gas, negative results were obtained. Thus, only the experiments with two chosen metal oxides (SnO and ZnO) are presented here, for which the highest yields of organic compounds could be expected.

Experimental

Reactants

The following commercial formates (p.a. POCh, Poland) were used: HCO_2Na , HCO_2K , $(\text{HCO}_2)_2\text{Ca} \cdot \text{H}_2\text{O}$, $(\text{HCO}_2)_2\text{Zn} \cdot 2\text{H}_2\text{O}$, $(\text{HCO}_2)_2\text{Cd} \cdot 2\text{H}_2\text{O}$, $(\text{HCO}_2)_2\text{Ni} \cdot 2\text{H}_2\text{O}$ and $(\text{HCO}_2)_2\text{Cu} \cdot 2\text{H}_2\text{O}$. Other formates were prepared from the respective carbonates (p.a. POCh, Poland): $\text{HCO}_2\text{Li} \cdot x\text{H}_2\text{O}$, $\text{HCO}_2\text{Rb} \cdot x\text{H}_2\text{O}$, $\text{HCO}_2\text{Cs} \cdot x\text{H}_2\text{O}$, $(\text{HCO}_2)_2\text{Sr} \cdot 2\text{H}_2\text{O}$, $(\text{HCO}_2)_2\text{Ba}$, $(\text{HCO}_2)_2\text{Mn} \cdot 2\text{H}_2\text{O}$, HCO_2Tl and $(\text{HCO}_2)_2\text{Pb}$, from the oxides (p.a. Merck): $(\text{HCO}_2)_2\text{Mg} \cdot 2\text{H}_2\text{O}$ and $(\text{HCO}_2)_3\text{Bi}$, or from the lanthanide oxides (p.a. BDH): $(\text{HCO}_2)_3\text{La}$ and $(\text{HCO}_2)_3\text{Nd}$, and formic acid (p.a. POCh, Poland). Anhydrous bismuthyl formate $\text{HCO}_2(\text{BiO})$ was precipitated from an excess of ethanol treated with a hot solution of $(\text{HCO}_2)_3\text{Bi}$ in formic acid [14]. $(\text{HCO}_2)_2\text{Fe} \cdot 2\text{H}_2\text{O}$ and $(\text{HCO}_2)_2\text{Sn}$ were obtained through the exchange reactions of barium formate with the corresponding sulphates (p.a. POCh, Poland). $(\text{HCO}_2)_2\text{Hg}_2$ was obtained by treating freshly prepared HgO (from $\text{Hg}(\text{NO}_3)_2$ and NaOH ; p.a. POCh, Poland) with a 20% solution of formic acid. Freely soluble salts were purified by recrystallization from water or alcohol solutions.

Gaseous formaldehyde was obtained from the depolymerization of para-formaldehyde (p.a. POCh, Poland). In place of the solid products obtained directly from the thermal decompositions of the respective formates, the following anhydrous compounds were used (p.a. POCh, Poland and SERVA): Li_2CO_3 , Na_2CO_3 , NaOH , $\text{Ba}(\text{OH})_2$, Li_2O , Na_2O , CaO , SrO and BaO . The oxides ZnO , CdO , PbO , NiO and CuO were obtained from the thermal decompositions of the respective formates in an air atmosphere, and SnO from the decomposition of $(\text{HCO}_2)_2\text{Sn}$ in a nitrogen atmosphere. CoO was obtained from the thermal decomposition of $\text{CoCO}_3\text{Co}(\text{OH})_2$ (p.a. POCh, Poland) under nitrogen.

Procedure

The thermal decompositions of the formates were carried out on a derivatograph under a constant nitrogen flow (100 ml/min) (Fig. 1). Samples containing 2 mmol of formate anion were placed in a platinum crucible (height 7 mm, diameter 8 mm), with alumina as the reference material. Moreover, the thermal decompositions of the formates, and the reactions of gaseous formaldehyde and of an equimolar hydrogen and carbon monoxide mixture, in the presence of the corresponding anhydrous solids, were carried out in a quartz tube furnace with a control system permitting a similar heating performance as in the derivatograph. An excess of the solid reactant with respect to formaldehyde (2:1 on a molar basis) was applied in all reaction systems. The reactions were carried out within 200–250°; at these temperatures, most formates decompose but formaldehyde is still thermally stable. Water was removed from hydrated formates before examination of their thermal decomposition. In all cases, samples of gaseous product were transported by a nitrogen stream directly from the furnace to a gas cell placed in the measuring chamber of a Specord-75 spectrophotometer (GDR). For identification of the solid-phase substances, X-ray phase analysis was applied by means of a TUR-M-62 apparatus (GDR) with Cu K_α rays, and infrared spectroscopy was carried out as above. Samples were prepared as suspensions in paraffin oil or hexachlorobutadiene-1,3.

Results and discussion

The compositions of the gaseous and solid products obtained from the thermal decompositions of the formates are presented in Table 1. Besides carbon dioxide and carbon monoxide, the gaseous product contained at least one of the following organic compounds: formaldehyde, methanol, formic acid, methyl formate and methane (in all cases except bismuthyl formate). In no case was acetaldehyde, dimethyl ether, ethylene or ethane found, which have been reported as side-products of the thermal dissociation of the formates of the alkali metals, magnesium, the alkaline earth metals, manganese(II) and zinc [1, 2].

Table 2 shows the products obtained in the reactions of formaldehyde and synthesis gas with chosen solids formed in the thermal decompositions of the formates. The results indicate that the carbonates of the alkali metals and the alkaline earth metals are inactive towards formaldehyde within the temperature range studied. However, formaldehyde undergoes a reaction, yielding methanol and a formate in the presence of alkali metal oxides or hydroxides. The observed drop in the yield of organic products derived from the formaldehyde transformation indicates a decrease in the catalytic activity of the alkaline earth oxides

Table 1 Products of the thermal decomposition of formates

Substrate	Solid products					Gaseous products ^a , %						
	oxalate	carbonate	metal oxide	metal	carbon	HCHO	CH ₃ OH	HCO ₂ H	HCO ₂ CH ₃	CH ₄	CO	CO ₂
HCO ₂ Li		+			+		2.5		0.5		80.0	17.0
HCO ₂ Na	+	+			tr		3.0		tr	1.5	91.0	4.5
HCO ₂ K	+	+			tr		3.0			1.0	95.0	1.0
HCO ₂ Rb	+	+			tr		0.5			2.0	96.5	1.0
HCO ₂ Cs	+	+			tr		tr		tr	2.5	96.0	1.5
(HCO ₂) ₂ Mg			+		tr		1.0			tr	49.0	50.0
(HCO ₂) ₂ Ca		+			+		3.5		3.5	2.0	76.0	15.0
(HCO ₂) ₂ Sr		+			+		2.0		tr	3.0	88.0	7.0
(HCO ₂) ₂ Ba		+			+		5.0			1.0	84.0	10.0
(HCO ₂) ₂ Zn			+		tr						22.0	60.0
(HCO ₂) ₂ Cd		+		+			6.0		1.0		15.0	78.0
(HCO ₂) ₂ Hg ₂				+				50.0				50.0
HCO ₂ Tl		+		+	+		8.0		10.0		11.0	71.0
(HCO ₂) ₂ Sn			+		tr	6.5	tr		29.0			64.5
(HCO ₂) ₂ Pb		+		+		1.0	1.0		16.0		1.0	81.0
(HCO ₂) ₃ Bi		+	+	+				17.0				80.0
(HCO ₂)BiO		+	+	+			2.0				1.0	100.0
(HCO ₂) ₂ Mn			+				2.0		1.0		48.0	49.0
(HCO ₂) ₂ Fe			+				1.0		6.0	1.0	36.0	56.0
(HCO ₂) ₂ Co			+	+						5.0	24.0	71.0
(HCO ₂) ₂ Ni			+	+					1.5	1.5	16.0	81.0
(HCO ₂) ₂ Cu			+	+				7.0			1.0	92.0
(HCO ₂) ₃ La		+			+		2.0		13.0	tr	37.0	48.0
(HCO ₂) ₃ Nd		+			+		2.0		14.0	tr	40.0	44.0

^a Presented results evaluate the molar ratio of particular products (excluding hydrogen, which is undetectable in IR). The sum of moles of identified products was taken as 100%. Accuracy $\pm 1\%$.

from barium to calcium. The composition of the organic compounds changes too: besides methanol, methyl formate and methane appear.

The highest yields of methyl formate, and hence the highest total yields of organic compounds (side-products: methanol and methane), were found for the formaldehyde reactions in the presence of tin(II) and zinc oxides. However, only trace amounts of methyl formate were detected in the synthesis gas reaction in the presence of the same oxides. The remaining oxides of the main group elements showed high activity, transforming formaldehyde to methyl formate, methanol and formic acid. Oxides with oxidative properties caused the oxidation of part of the

Table 2 Reaction products of formaldehyde and equimolar mixture of hydrogen and carbon oxide with solid substances formed in the thermal decomposition of formates

Solid substrate	Gaseous substrate	Solid product					Gaseous product, ^a %							
		formate	carbonate	metal oxide	metal	carbon	HCHO	CH ₃ OH	HCO ₂ H	HCO ₂ CH ₃	CH ₄	CO	CO ₂	
Li ₂ CO ₃	HCHO		+				100.0							
Li ₂ O	HCHO	+	+	+		+		98.0				2.0		
Na ₂ CO ₃	HCHO		+				100.0							
Na ₂ O	HCHO	+	+	+		+		99.0				1.0		
NaOH	HCHO	+	+					100.0						
CaO	HCHO	+	+	+			50.0	6.0		2.0		16.0	26.0	
SrO	HCHO	+	+	+		+		96.0		tr		4.0		
BaO	HCHO	+	+			+		99.0				1.0		
Ba(OH) ₂	HCHO	+	+					100.0						
ZnO	HCHO			+				5.0		95.0	tr	tr	tr	
ZnO	H ₂ + CO			+						3.0		97.0	tr	
SnO	HCHO			+				16.0		72.0	1.0	3.0	8.0	
SnO	H ₂ + CO			+				tr		2.0		94.0	4.0	
CdO	HCHO		+	+	+			17.0		61.0		3.0	19.0	
PbO	HCHO		+	+	+			28.0		23.0		1.0	48.0	
Bi ₂ O ₃	HCHO		+	+	+			14.0	6.0	3.0		10.0	67.0	
CoO	HCHO			+	+	+		6.0				14.0	19.0	61.0
NiO	HCHO			+	+	+		7.0		21.0	3.0	25.0	44.0	
CuO	HCHO			+	+		tr	3.0	2.0			2.0	93.0	
Nd ₂ O ₃	HCHO	+	+	+		+	70.0	4.0		3.0		10.0	13.0	

^a presented results evaluate the molar ratio of particular products (excluding hydrogen, which is undetectable in IR). The sum of moles of identified products was taken as 100%. Accuracy $\pm 1\%$

formaldehyde to carbon dioxide, at the same time undergoing reduction to the free metals. The non-reacted residues of the oxides (used in the experiments in a two-fold excess with respect to formaldehyde) underwent transformation to carbonates or basic carbonates (CdCO₃, PbCO₃ · 2PbO and (BiO)₂CO₃) in the presence of the carbon dioxide formed in the reaction system.

As can be seen from Table 2, all the transition metal oxides investigated underwent reduction to the respective metal in the presence of formaldehyde. Besides the carbon dioxide formed in a majority yield, carbon monoxide and the organic compound: methanol, methane, methyl formate and formic acid were also present in the gaseous product.

Neodymium oxide displayed a similar catalytic effect towards formaldehyde to that of calcium oxide.

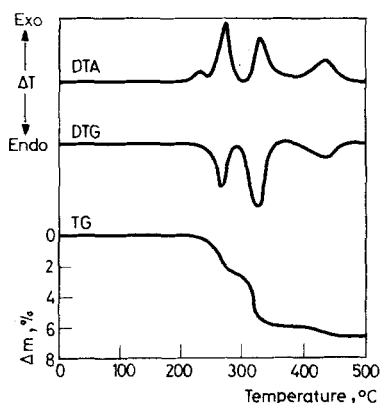
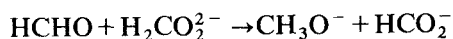
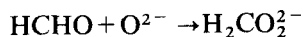


Fig. 1 TG, DTG, DTA curves for reaction of equimolar mixture of HCO_2Na and NaBH_4

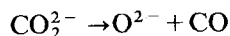
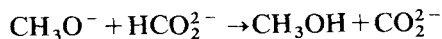
A comparison of the results in Tables 1 and 2 reveals a satisfactory conformability of the nature of the gaseous products obtained in the thermal decompositions of the formates and in the reactions of formaldehyde in the presence of the respective metal oxides. However, such a conformability of the products is not observed for the analogous reactions of synthesis gas.

These results favour the hypothesis that formaldehyde is a precursor of the organic products formed in the thermal decomposition of formates.

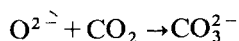
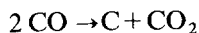
The products of formaldehyde transformation in the presence of lithium, sodium, barium and strontium oxides indicate that it undergoes the Cannizzaro reaction in these cases:



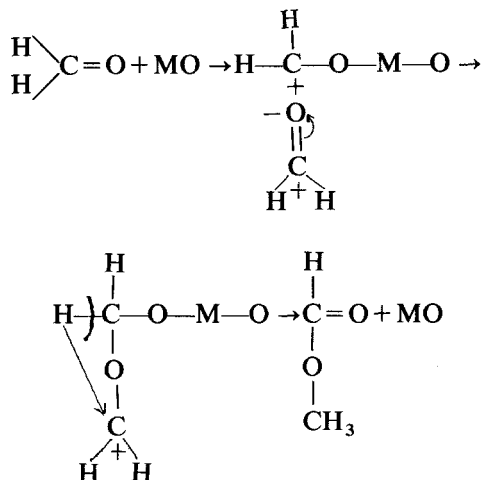
The methanolate anion, as a strong base, can abstract a proton from the formate anion, transforming it to an unstable CO_2^{2-} anion [15], which decomposes to an oxide anion and carbon monoxide:



The disproportionation of carbon monoxide occurs in the presence of alkali metal oxide, resulting in carbon and carbon dioxide. For the second time, a carbonate is formed in accordance with the experimental results:



Methyl formate, another product of the formaldehyde transformation, appears to be formed in a Tishchenko reaction (related to the Cannizzaro reaction), which also consists in a hydrogen anion transfer:

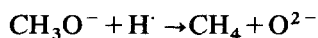


Aldehydes are known to undergo these reactions in the presence of ZnCl_2 and Al(OR)_3 [16, 17]. No other catalysts have been mentioned in the literature for use in the described case. The results of our present investigations, where methyl formate is formed in the formaldehyde reactions in the presence of different metal oxides (CaO , Nd_2O_3 , SnO , ZnO , PbO , CdO and NiO), indicate that the Tishchenko reaction can also be catalyzed by a number of metal oxides with weaker basic properties.

The reasons for methane formation during the thermal decomposition of formates and formaldehyde transformation could not be explained on the basis of the known reaction mechanisms. It is known, however, that methane results from the reaction of calcium hydride with carbon monoxide [18]:



If the participation of the hydride anion is assumed in this process, the following nucleophilic substitution reaction can be proposed:

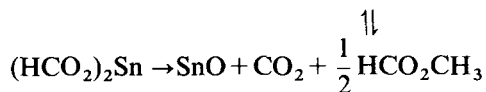


Some observations concerning the quantitative composition of the gaseous products are also essential for the explanation of the origin of the organic compounds. The identification of methyl formate, carbon dioxide and tin(II) oxide (in the absence of carbon monoxide and hydrogen) in the products of thermal

decomposition of tin(II) formate indicates that the thermal decomposition can be described by the following equations:

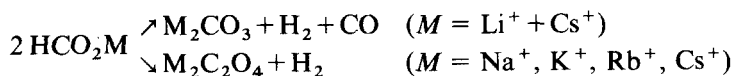


or



The type of organic compound depends here only on the conditions of the process: under vacuum formaldehyde is obtained [6], while in a static nitrogen atmosphere the product is mainly methyl formate (Table 1). These results are confirmed by the course of the reaction between formaldehyde and tin(II) oxide, where the same ester is the main product. The comparably high yields of organic compounds obtained in the case of tin(II) formate and of other main element formates indicate that formaldehyde formation is the main reaction in the thermal decomposition mechanism.

A different situation arises in the thermal decomposition of alkali metal formates, where the yield of organic compounds is minimal in comparison to that of inorganic compounds—mainly hydrogen and carbon monoxide. As the alkali metalcarbonates formed during the thermal decomposition of formates are inactive towards formaldehyde, and since formaldehyde displays good thermal stability within the temperature range studied [19], it should be detectable in the reaction products. The lack of formaldehyde among the final products and the very low yield of organic compounds indicate that formaldehyde, as an intermediate precursor of organic compounds, is formed only in a side-reaction in this case. Thus, the thermal decomposition can be described to a reasonable approximation by the following equations:



The reasons for the formation of free hydrogen or formaldehyde in the thermal decompositions of different formates will be described in a separate paper.

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Zusammenfassung — Die gasförmigen Produkte der thermischen Zersetzung von Formiaten wurden untersucht und mit den Produkten verglichen, die bei der Umwandlung von Formaldehyd und Synthesegas unter analogen Bedingungen in Gegenwart von bei der thermischen Zersetzung von speziellen Formiaten gebildeten Feststoffen entstehen. Formaldehydumwandlungen führen zu organischen Verbindungen, die identisch mit denen sind, die bei der thermischen Zersetzung des betreffenden Formiats gebildet werden, während Synthesegas unter solchen Bedingungen nicht reagiert. Dies erhärtet die Hypothese, daß Formaldehyd eine Vorstufe der bei der thermischen Zersetzung von Formiaten identifizierten organischen Verbindungen ist. Die Natur der bei der thermischen Zersetzung von Formiaten auftretenden organischen Verbindungen weist darauf hin, daß das in den ersten Reaktionsschritten gebildete Formaldehyd nach der Cannizzaro- oder Tishchenko-Reaktion weiterreagiert.

Резюме — Исследованы газообразные продукты термического разложения формиатов и сопоставлены с продуктами превращения формальдегида и искусственного газа, полученных в аналогичных условиях и в присутствии тех твердых продуктов, которые образуются и при термическом разложении отдельных формиатов. Найдено, что превращение формальдегида приводит к образованию тех же самых органических соединений, как и при термическом разложении соответствующего формиата. В тоже самое время искусственный газ в таких условиях не реагирует. Этот факт подтверждает гипотезу, что формальдегид является предшественником органических соединений, найденных при термическом разложении формиатов. Тип органических соединений, образующихся при термическом разложении формиатов, указывает, что образующийся на начальных стадиях реакции формальдегид затем вступает в реакции Канницаро или Тищенко.