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THERMOCHEMICAL REACTIVITY OF TRANSITION METAL ACETATES AND OF A NOVEL DMSO SOLVATE OF IRON(II) ACETATE IN MOLECULAR HYDROGEN

K. Ehrensberger[1], *H. W. Schmalle*[1], *H.-R. Oswald*[1] *and A. Reller*[2]

[1]Institute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland
[2]Solid State Chemistry, University of Augsburg, Universitätsstrasse 1, D-86159 Augsburg Germany

Abstract

The thermal decomposition of acetates of the transition metals Fe, Co, Ni, Mn and Cu in molecular hydrogen has been investigated by means of combined thermogravimetry/mass spectrometry, X-ray diffraction, and transmission as well as scanning electron microscopy. In the context of the reproducible preparation of the parent phases, i.e. the hydrated or anhydrous metal(II) acetates, single crystalline $Fe_3(CH_3COO)_6(DMSO)_2$, a novel DMSO solvate of iron(II) acetate, has been isolated and its crystal structure has been determined by means of X-ray diffraction. For the series of metal(II) acetates it has been found that the course of the thermal degradation in molecular hydrogen, in particular the formation of the gaseous products, strongly depends on the transition metal ion present in the parent compound. The detailed characterisation of the solid products revealed, that phases exhibiting different catalytic activities and selectivities are formed as micro- or nanocrystalline metals and/or metal oxides.

Keywords: catalytic activities and selectivities, thermal decomposition, transition metal acetates

Introduction

Transition metal salts containing organic anions such as formates, acetates, oxalates, citrates, etc. are common precursor systems for the controlled synthesis of transition metal oxides or transition metals and alloys under mild conditions. In particular, the thermal decomposition of anhydrous or hydrated transition metal acetates as well as of solvates containing solvent molecules has often been investigated with respect to kinetics and mechanism. Less attention has been paid to the type of the solid and gaseous products, which are formed in dependence of the experimental conditions, under which the degradation has been performed. Crucial information on the intermediate formation of transition metal acetates has been gained by Cressely *et al.* when they characterised the conversion of acetic acid catalysed by finely dispersed metallic iron, cobalt and copper [1]. Another series of investigations has elucidated that during the thermal degradation of $Cu(NH_3)_2CO_3$ nanocrystalline metallic copper is formed, which in turn acts as *in situ* catalyst for the formation of carbon compounds as well as amines [2]. The selective reduction of acetic acid to acetalde-

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hyde on iron oxides has been studied in various pressure ranges [3]. A good selectivity could be achieved when molecular hydrogen was continuously present on a mixed catalyst containing metallic iron and oxidic iron species. In order to specify the interdependence between in situ generated catalytically active metal and/or metal oxide species, the catalytically generated gaseous products, and the experimental conditions, in particular the temperature, the acetates of Fe, Co, Ni, Mn and Cu were decomposed in pure and diluted molecular hydrogen atmospheres. The idea of this series of measurements was whether one would be able to find a handy screening procedure for the identification of the spectrum of carbon compounds, which could be obtained by the catalysed conversion of acetic acid.

Whereas the anhydrous acetates of Mn(II), Co(II), Ni(II), and Cu(II) are readily available by thermally decomposing the corresponding hydrates it turned out to be very difficult to isolate pure anhydrous Fe(II) acetate. Anhydrous iron acetate synthesised according to the methods of Hardt and Möller [4] or Dupuy and Moreau [5, 6] always contains considerable amounts of Fe(III). Therefore we searched for an alternative synthesis route and succeeded in preparing a novel DMSO solvate of iron acetate, wherein Fe(II) cations only are accommodated. This DMSO solvate could be used as precursor for the isolation of pure anhydrous iron(II) acetate.

Experimental

The following metal(II) acetates were used for the thermoanalytical experiments:

$Mn(CH_3COO)_2 \cdot 4H_2O$ (Merck p.a.)
$Fe(CH_3COO)_2$ (synthesised, see Eqs (1) and (2) below)
$Co(CH_3COO)_2 \cdot 4H_2O$ (Fluka p.a.)
$Ni(CH_3COO)_2 \cdot 4H_2O$ (Merck p.a.)
$Cu(CH_3COO)_2 \cdot H_2O$ (Fluka p.a.)

The thermal decompositions of the metal acetates were carried out using a thermobalance TGS-2 (Perkin-Elmer, USA) coupled to a mass spectrometer QMG 511 (Balzers AG, Balzers, FL) and a combined thermogravimetry/differential thermal analysis equipment TA 2000 C (Mettler AG, Greifensee, CH). Samples usually consisting of 7 mg parent material were placed in a platinum crucible and heated with a rate of 10°C min^{-1} under a constant gas flow of 40 ml min^{-1}. In the temperature range of 130°C the dehydration of the acetates was completed (for iron(II) acetate: see below) and at around 250°C the starting degradation of the acetates was registered. The dehydration of $Ni(CH_3COO)_2 \cdot 4H_2O$ leads to a simultaneous partial decomposition of the acetate, i.e. at higher temperatures small amounts of hydrate water resp. hydroxide were persisting. For $Cu(CH_3COO)_2 \cdot H_2O$, it has to be mentioned that above 260°C partial sublimation of Cu(I) acetate is observed [7]. This effect can be assigned to the different structural features of Cu(II) acetate: whereas the Fe(II), Ni(II) and Co(II) acetates are isostructural [8], Mn(II) exhibits a closely related structural framework. For the structure of Cu(II) acetate, however, dimeric structural elements have been proposed [9].

The solid products were examined X-ray powder diffraction Guinier-4 de Wolff camera FR 552, (Enraf-Nonius, Delft, NL) equipped with a Johansson-quartz monochromator and CuK$_{\alpha 1}$ radiation. For the single crystal structure determination a full set of intensities was measured on a CAD-4 diffractometer (Enraf-Nonius, Delft, NL) [10]. The electron microscopic investigations were performed using an analytical scanning electron microscope SEM 515 equipped with an EDX system Tracor Northern 5400 (Philips, Eindhoven, NL) and a transmission electron microscope JEM 200 CX (Jeol, Tokyo, J).

Synthesis and structure of the novel DMSO solvate of iron(II) acetate, hexacetyl-bis(dimethylsulfoxide)-tri-iron(II), $Fe_3(CH_3COO)_6(DMSO)_2$

As mentioned above iron(II) acetate synthesised by the method of Dupuy and Moreau [5, 6] usually contains considerable amounts of iron(III). In order to prepare pure iron(II) acetate 2.5 g iron powder (Merck, 150 μm) were reacted under permanent stirring in 50 ml of a 1:1 mixture of dry acetic acid/acetic anhydride at 100°C. The solvent was replaced and the mixture was further reacted for 24 h. A white emulsion was obtained. The reaction can be described as follows:

$$Fe^{o} + 2CH_3COOH \rightarrow Fe(CH_3COO)_2 + H_2 \qquad (1)$$

Residual iron was removed using a magnet. Subsequently the solvent was removed and the white powder could be isolated and identified as iron(II) acetate. In humid or oxidative atmospheres the product is not stable and turns brown. All procedures were therefore carried out in an inert atmosphere (dry nitrogen). In order to further purify the iron(II) acetate, the novel DMSO solvate was obtained as follows: 1.0 g of the mentioned freshly synthesised iron(II) acetate was dissolved in a 2:10 mixture of acetic anhydride/DMSO at 100°C. By slow cooling (10°C per day) colourless single crystals grew. They were isolated and the chemical analysis revealed that a single crystalline DMSO solvate, $Fe_3(CH_3COO)_6(DMSO)_2$, had formed (Fig 1).

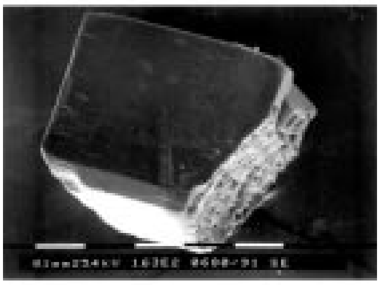

Fig. 1 Scanning electron micrograph of a single crystal of hexacetyl-bis(dimethylsulfoxide)-tri-iron(II), $Fe_3(CH_3COO)_6(DMSO)_2$

The X-ray single crystal structure determination [10] revealed a channel structure which is formed by corner- and edge sharing FeO_6 octahedron chains running along [001]. These channels are also responsible for the macroscopic striated appearance of the crystals. In Fig. 2 details of the structure are depicted: one acetate group,

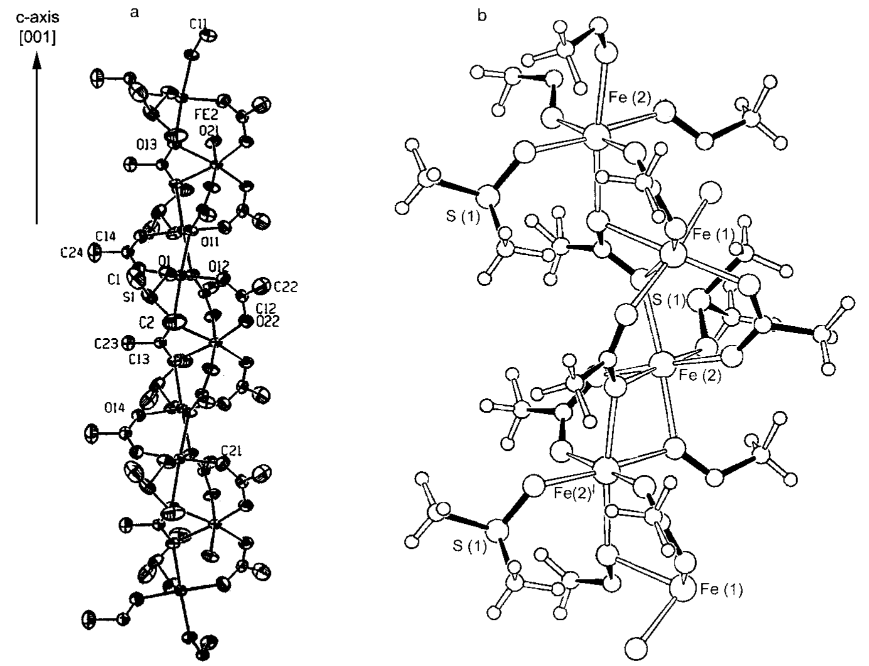

Fig. 2 Details of the single crystal structural framework of hexacetyl-bis(dimethylsulfoxide)-tri-iron(II), $Fe_3(CH_3COO)_6(DMSO)_2$. The chain of the corner and edge sharing FeO octahedra extends parallel to the crystallographic *c*-axis (Fig. 2a). The acetate anion acts as bridging element between two Fe atoms [Fe(1)·····Fe(2) or Fe(1)·····Fe(2')bridges] or even three Fe atoms [Fe(2)·····Fe(1)·····Fe(2') bridge]. The DMSO solvate molecule acts as monodentate ligand (Fig. 2b)

with its carbon atoms C(13) and C(23) lying on the crystallographic twofold axis is bidentately bound to Fe(1), which also occupies a special position on the same axis. According to this symmetry conditions, two Fe(1)·····Fe(2)/Fe(1)·····Fe(2') bridging acetate groups form corners of the strongly distorted $Fe(1)O_6$ octahedron. Fe(2) and its symmetric equivalent Fe(2') are bridged by that acetate group which is bidentately coordinated to Fe(1), i.e. this acetate group connects three Fe atoms and acts as tetradentate species. In addition, the octahedral coordination of each Fe(2) and Fe(2') contains one oxygen atom of a DMSO solvate molecule, which, in turn, is not involved in further coordinations. The 'surface' of the infinite FeO_6 octahedra chains is made up of hydrophobic methyl groups of the acetate ions and of the DMSO molecules. Thus, only Van-der-Waals forces exist between the separate chains.

Thermal degradation of the novel DMSO solvate of iron(II) acetate, hexacetyl-bis(dimethylsulfoxide)-tri-iron(II), $Fe_3(CH_3COO)_6(DMSO)_2$

In order to prepare pure iron(II) acetate the DMSO solvate has been decomposed in a 5% H_2/95% Ar atmosphere. In Fig. 3 the thermogravimetric measurement is

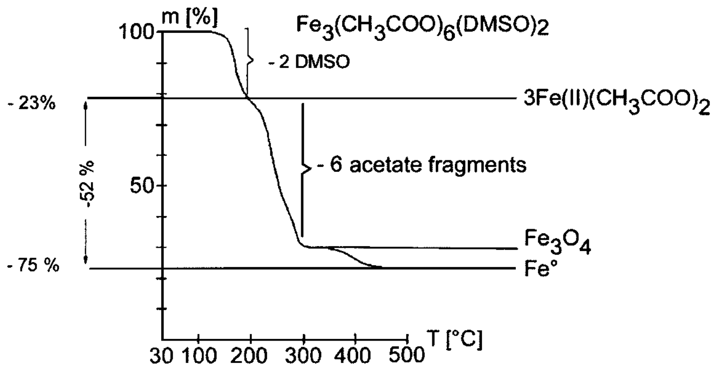

Fig. 3 Thermogravimetric measurement of the decomposition of hexacetyl-bis(dimethylsulfoxide)-tri-iron(II), $Fe_3(CH_3COO)_6(DMSO)_2$, in a 5% H_2/95% Ar atmosphere (heating rate: 10°C min^{-1})

shown. The course of the thermal degradation reveals the intermediate formation of amorphous iron(II) acetate (loss of DMSO solvate molecules), iron oxide and metallic iron according to the following equations:

$$\text{First step: } Fe_3(CH_3COO)_6(DMSO)_2 \rightarrow 3Fe(CH_3COO)_2 + 2DMSO \qquad (2)$$

$$\text{Subsequent steps: } Fe(CH_3COO)_2 \rightarrow Fe_3O_4 \rightarrow \alpha\text{–}Fe^0 \qquad (3)$$

The composition of the volatile products of the decomposition of the acetate will be described in the next chapter. Depending on the temperature and on the partial pressure of H_2 the second solid intermediate may contain different iron oxides or iron oxide/α–Fe° mixtures. The final product is always very pure, nanocrystalline α–Fe° (crystal sizes below 10 nm) as revealed by X-ray diffraction and high resolu-

Fig. 4 High resolution electron microscopic image of α–Fe° obtained from the decomposition of hexacetyl-bis(dimethylsulfoxide)-tri-iron(II), $Fe_3(CH_3COO)_6(DMSO)_2$, in a 5% H_2/95% Ar atmosphere obtained above 450°C

tion transmission electron microscopy (Fig. 4). This product acts as an in situ generated catalyst and influences directly the formation of the volatile products of the acetate degradation (see below).

Results and discussion of the *in situ* catalysed decompositions

In this chapter the experimental findings of the thermogravimetric/mass spectrometric measurements of the thermal decomposition in reducing atmospheres are summarised. It has to be mentioned that the course of the thermal degradation of the studied acetates varies pronouncedly in dependence of the compositional and structural features of the pristine compounds, but also in dependence of the redox potential of the actual transition metal and on the composition, i.e. the reduction potential of the gas atmosphere. In Table 1 the solid products are listed as they were obtained in different atmospheres.

Table 1 Main solid products formed during the decomposition of the metal(II) acetates in different atmospheres in the temperature range of 300–400°C

Atmosphere	Acetate of				
	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)
Air	Mn_2O_3	γ–Fe_2O_3	Co_3O_4	NiO	CuO
N_2	MnO	Fe_3O_4	CoO	Ni^o	Cu^o
5% H_2/95% Ar	MnO	Fe_3O_4	Co^o	Ni^o	Cu^o
100% H_2	MnO	α–Fe^o	Co^o	Ni^o	Cu^o

The findings confirm that the decomposition of the acetate creates a partially reducing atmosphere. Therefore in nitrogen atmosphere metallic nickel and copper are found. For manganese no complete reduction is observed in the temperature range up to 400°C, even by performing the degradation in 100% molecular hydrogen atmosphere. The solid products formed may influence the formation of the spectrum of volatile compounds, i.e. they represent more or less active and/or selective *in situ* catalysts. Consequently, the volatile products identified by mass spectroscopy vary from metal to metal. In addition, the reduction potential of the atmosphere, i.e. the partial pressure of hydrogen, also influences the final temperature of the decompositions as well as the composition of the solid and the volatile species. In 100% molecular hydrogen atmosphere, the end points of the decomposition are registered at lower temperature than in 5% H_2/95% Ar. The measured differences ΔT vary from 10°C for manganese(II) acetate to 90°C for iron(II) acetate to 60°C for cobalt(II) and nickel(II) acetate to 25°C for copper(II) acetate.

The following two tables show the amounts (semi-quantitative determination from mass spectrometric peak intensities) of the main volatile products obtained by the decomposition of the transition metal acetates. The numbers of a row represent the percentage of the decomposition products of the corresponding acetate.

The formation of the three main volatile decomposition products, CH_4, CO and CO_2, is subjected to the following tendencies: from weakly to strongly reducing conditions the CH_4 ratio increases remarkably. At the same time the CO and CO_2 ratios decrease. High rates of CH_4 formation are registered for the decomposition of Fe and Ni acetate under strongly reducing atmosphere. Accordingly, low amounts of CO and CO_2 are detected. For Ni(II) acetate the lowest amounts of CO_2 are measured.

Table 2 Gaseous products formed during the decomposition of the metal(II) acetates in a 5% H_2 /95% Ar atmosphere

Products	Percentages of products formed from acetate of				
	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)
CH_4	4	12	16	17	15
CO_2	64	52	48	40	51
CO	16	25	23	18	16
CH_3COCH_3	16	5	2	1	0
CH_3COOH	0	6	11	24	18

Table 3 Gaseous products formed during the decomposition of the metal(II) acetates in a 100% H_2 atmosphere

Products	Percentages of products formed from acetate of				
	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)
CH_4	29	52	42	60	40
CO_2	40	30	22	20	36
CO	4	2	7	4	4
CH_3COCH_3	27	10	4	0	0
CH_3COOH	0	6	25	16	20

The reaction enthalpies of the strongly exothermic reductions of CO and CO_2 to CH_4 and of the weakly exothermic reduction of CO_2 to CO stand face to the endothermic decomposition of the acetates. These competing forces are responsible for the different ratios of the reaction products and reaction temperatures. They are also influenced by the catalytic activity of the *in situ* formed solid species, i.e. the nanocrystalline metals.

These facts can be explained as follows: The great temperature differences and the high methane yields in the cases of Fe(II) and in Ni(II) can be explained by the high catalytic hydrogenation activity of the *in situ* generated metallic species. The largest atmosphere-dependent temperature difference for the completion of the thermal reduction is found in the Fe(II) acetate system where in 5% H_2/95% Ar Fe_3O_4 is formed as crystalline product while in 100% H_2 catalytic active α–Fe° is generated. Practically no atmosphere-dependent temperature differences are observed for the

Mn(II) system, because under both conditions the crystalline product is catalytic inactive MnO. This is also confirmed by the low methane yield. Finally, the low temperature difference between the two atmospheres and the low methane share of Cu(II) in pure H_2 means that Cu° is not a very active hydrogenation catalyst.

Mechanisms

For the decomposition of the acetates different mechanisms can be proposed. They should, however, not only explain the generation of different volatile products, but also the (at least partial) reduction of the transition metals, even in principally non-reducing, inert atmospheres (Table 1). Thus, a first mechanism suggests, that a direct disproportion of the acetate into a methyl radical and/or a O=C–CH_3 radical; the metal, however, is not reduced (Fig. 5).

This possibility is not compatible with the experimental findings, i.e. the reduction of the metal ions. A second mechanism suggests (Fig. 6) the formation of acetic anhydride and the simultaneous liberation of electrons, which in turn may reduce the transition metal ion [11]. This pathway is compatible with the qualitative findings of the experimental measurements. The quantitative or at least semi-quantitative evaluation of the yields of the formed gaseous compounds may ask for an alternative

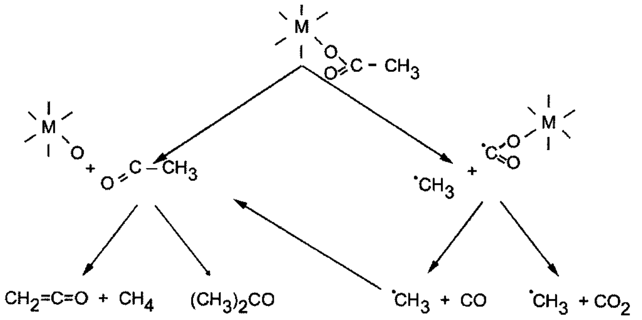

Fig. 5 Scheme of the direct radical disproportion mechanism describing the catalysed formation of different gaseous products of the decomposition of transition metal acetates. This mechanism cannot explain the *in situ* reduction of the metal ions

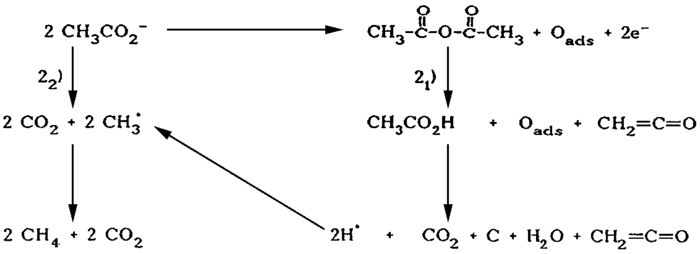

Fig. 6 Scheme of a catalysed acetate conversion mechanism describing the formation of intermediate acetic anhydride and liberation of electrons, which in turn may reduce the metal ions [11]

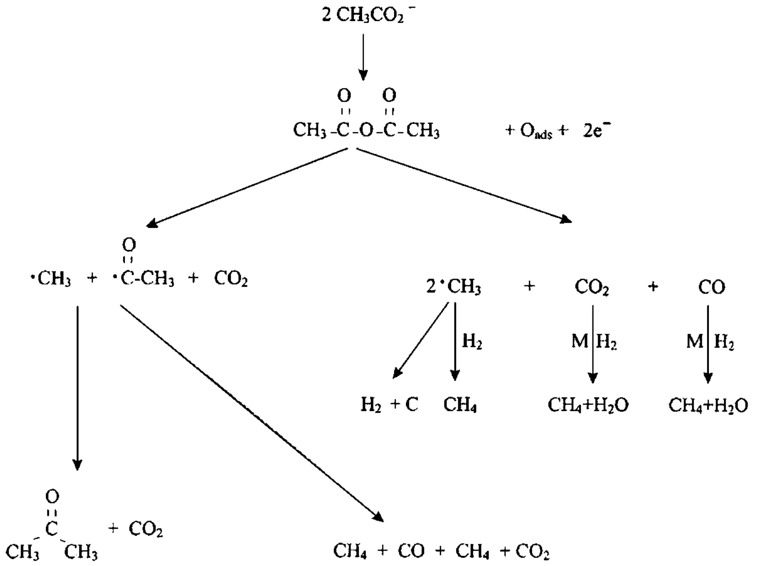

Fig. 7 Scheme of a complex catalysed acetate conversion mechanism describing the formation of intermediate acetic anhydride and liberation of electrons, which in turn may reduce the metal ions, [12]. In addition it is shown, that the complex interactions of reactive species lead to the generation of C_1, C_2 and C_3 compounds

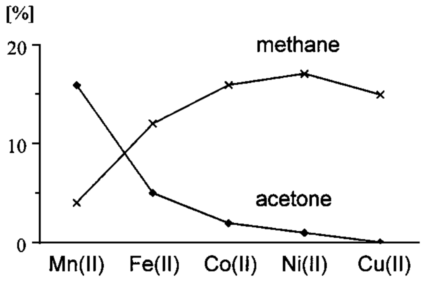

Fig. 8 Correlation depicting the relative amounts of the catalysed formation of methane and acetone during the decomposition of transition metal acetates in reducing atmosphere

mechanism (see below). A third mechanism is based on the initial formation of acetic anhydride and the subsequent indirect radical disproportion as depicted in Fig. 7 [12]. Here, the influence of the *in situ* generated catalytic metals on the different ratios of the gaseous products is obvious. The measured ratios of the evolved gaseous products, i.e. the high yields of methane and acetone suggests the so-called Kolbe mechanism, where no acetic anhydride results, but initially a methylcarboxyl radical under simultaneous liberation of an electron is formed (Eq. (4)). Subsequently, the generation of mainly methyl radicals and CO_2 is observed (Eq. (5)):

$$CH_3COO^- \rightarrow CH_3COO^{\cdot} + e^- \tag{4}$$

$$CH_3COO^{\cdot} \rightarrow {}^{\cdot}CH_3 + CO_2 \tag{5}$$

Considering the complete spectrum of the gaseous products formed during the decomposition of the acetates one finds an interesting and intriguing correlation: in a 5% H_2/95% Ar atmosphere the formation of methane competes with the one of acetone (Fig. 8). This observation supports one possible pathway found in the indirect radical disproportion mechanism (Fig. 7). Evidently, under the given dynamic conditions of the chosen experimental set up the complete frame of simultaneously occurring, competing and self-inducting catalysed processes can be registered.

Conclusions

The comprehensive mechanistic study of the thermal decomposition of transition metal acetates in reducing atmosphere revealed rather complex interrelations between thermally induced and *in situ* catalysed reaction steps. Considering the obtained solid products one would not come to this interpretation, because a comparison with the decomposition of e.g. 3d transition metal carbonates in reducing atmospheres reveals similar compositions and morphologies of the formed metals and/or metal oxides [13–15]. The examination of the qualitative and quantitative composition of the gaseous products, however, points to very complex interconnected and interdependent processes. These processes are influenced by the following factors:

– the structural and compositional features of the parent acetates,

– the kind of transition metal cation and the kind of its more or less reduced species, e.g. MnO or Cu°, which represent more or less active and selective *in situ* formed catalysts,

– the partial pressure of the reducing agent, i.e. molecular hydrogen, and

– the temperature program as well as the temperature range.

As it has been confirmed by the thermogravimetric/ mass spectrometric measurements the spectrum of carbon compounds which may be obtained is quite large, i.e. from highly oxidised C_1 species like CO_2 or CO, to C_2 and C_3 species like acetic acid or acetone, to methane. In fact, the initially chosen approach allows a screening of the possible gaseous reaction products. However, it turns out to be extremely difficult to identify defined highly selective *in situ* catalyzed processes and to define the very conditions which would lead to the production of one desired compound. As it has been shown for the decomposition of transition metal carbonates the variation of the pressure could influence the over-all process remarkably [13–15]. But the fact that in the case of the thermal degradation of carbonates only few gaseous products form, this mentioned variation of the pressure would most probably not lead to an unambiguous understanding of the interrelated ruling factors. Further leading detailed studies on the selectivity of the different metal catalysts are required. In summary the investigation of the thermochemical reactivity and the best possible specification of the reaction products gives evidence for an unexpectedly rich chemistry of the transition metal acetates – if they are allowed or forced to react.

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10 Details of the structure determination of $Fe_3(CH_3COO)_6(DMSO)_2$: space group C2, unit cell parameters: a=1266.5(3) pm, b=1246.1(1) pm, c=851.8(3) pm, β=94.68(2)°, Z=2. The intensity set was collected using an Enraf-Nonius CAD-4 diffractometer, MoK_α radiation, graphite monochromator. The data collection range was: $2^\circ<2\Theta<60^\circ$. Range of measured h, k, l: -17,17/-17,17/0,12; 48 h measuring time; number of unique reflections: 3670; number of observed reflections: 3626; number of refined parameters: 161; R=0.040, Rw=0.056, $w=1/s^2(F_o)$, GOF=1.908. Additional information to this structure can be ordered from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen, Germany. Please quote reference no. CSD 56352, the names of the authors and the title of the paper.

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