

THERMAL DECOMPOSITION STUDY OF MERCURATED HEXA- AND TRIFLUOROACETYLACETONE*

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This work presents preparation and thermal characterization of three novel organomercurials: $\text{Hg}_2(\text{CF}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-}(\text{CF}_3\text{COCCOCF}_3)_2\text{-}2(\text{CF}_3\text{C}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})_2\text{CF}_3)$ (**I**), $\text{Hg}_2(\text{CF}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-}(\text{CF}_3\text{COCCOCF}_3)$ (**II**) and $\text{Hg}_2(\text{CH}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-}(\text{CH}_3\text{COCCOCF}_3)$ (**III**) which means that they contain at least one direct mercury-to-carbon bond among the carbonyl groups of β -diketone molecules which are capable for chelating of metal ions. IR-spectra support the conclusion that mercury is most probably bound to the γ -carbon of fluorinated derivatives of acetylacetone and is not chelated through oxygen in any of the isolated compounds.

The thermal decomposition of mercurated hexafluoro- and trifluoroacetylacetone in nitrogen occurs in a few steps. Each step was identified and studied by simultaneous DTA/TG analyzer. On the basis of dynamic heating experiments by TG applying Flynn-Wall method the activation energy for each of them was determined.

Keywords: β -diketone, Flynn–Wall kinetics, mercurated hexafluoro- and trifluoroacetylacetone, thermal characterization

Introduction

β -Diketonato complexes are known for nearly every metal. In these compounds β -diketone acts as bidentate chelating ligand via both oxygen atoms forming with metal ion a six-member planar ring. But, there is a discrete class of metals (Rh, Ir, Pt, Ag, Au, Hg) that form bonds with carbon atoms among the carbonyl groups [1].

The type of mercurated β -diketones greatly depends on the reaction conditions being used [2]; e.g. the three compounds $\text{Hg}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Hg}_2(\text{C}_5\text{H}_6\text{O}_2)_2$, and $\text{Hg}_2(\text{C}_5\text{H}_6\text{O}_2)(\text{C}_5\text{H}_7\text{O}_2)_2$ were obtained as reaction products of acetylacetone and $\text{Hg}(\text{OCOCH}_3)_2$, $\text{Hg}(\text{BF}_4)_2$ and HgO , respectively. For all three compounds the existence of C–Hg bonds was proposed on the IR-spectra [3]. Crystal structure analysis of bis(dipivaloylmethyl)mercury [4, 5], dipivaloylmethylmercury acetate [6], 3,3-bis(chloromercury)-2,4-pentadione [7], and chloro(diacetylmethyl)mercury [8] revealed that in solid state mercury is bonded to carbon even if γ -carbon is hindered by bulky groups (e.g. *i*-propyl or *t*-butyl) or if one oxygen is replaced by nitrogen [9, 10]. In the case of sulphur derivatives, as thiodipivaloylmethane the mercury-to-sulphur bonds were obtained due to great affinity of

mercury(II) ion as soft Lewis acid toward soft Lewis base as sulphur atom itself [5, 9].

Hexafluoroacetylacetone (hfacH) has the strongest electron-withdrawing substituents of any β -diketone and tends to discourage the formation of metal-oxygen bond as the oxygen atoms tend to be fairly positive. Therefore, a metal-carbon bond to this ligand should be quite strong. It is well known that $(\text{CF}_3)_2\text{CO}$, undergoes nucleophilic attack at keto-carbon atom to yield the *gem*-diol hexafluoro-2,2-propanediol, which on deprotonation acts as a dianionic ligand to many metals [11–13].

By hydration of hexafluoroacetylacetone, 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol (bis(*gem*-diol), hfptH₄) is obtained [14].

Due to hydrolysis of the hfacH even by a small amount of water all reported reactions were carried out in the absence of air and water. Bouwman *et al.* [15] reported a straightforward route to high-yield of pure hfptH₄. The authors also reported its coordination abilities and in $(\text{pyH})_2[\text{Mn}_2(\text{hfpt})(\text{hfac})_4]$ ($\text{pyH}=\text{pyridinium cation}$) they established that hfpt acts as the tetradentate bridging ligand indeed. By contrast, Bouwman *et al.* [16] from an analogous reaction of $[\text{Fe}_3\text{O}(\text{Oac})_6(\text{py})_3](\text{ClO}_4)$ and hfacH obtained $(\text{pyH})[\text{Fe}(\text{hfac})_2(\text{hfptH}_2)]$ in which a bidentate chelating mode of hfptH₄ was revealed.

* Dedicated to Professor Ivan Vicković on the occasion of his 60th birthday

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From ^1H NMR studies it was established that reaction product of Me_2Hg and hfacH is the mixture of Me-Hg-C and Me-Hg-O bonded species [17].

Here we report the preparation, infrared spectroscopic identification and thermal studies (characterization and kinetics of decomposition) of $\text{Hg}_2(\text{CF}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-(CF}_3\text{COCCOCF}_3)\cdot 2(\text{CF}_3\text{C(OH)}_2\text{CH}_2\text{C(OH)}_2\text{CF}_3)$ (**I**), $\text{Hg}_2(\text{CF}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-(CF}_3\text{COCCOCF}_3)$ (**II**), $\text{Hg}_2(\text{CH}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-(CH}_3\text{COCCOCF}_3)$ (**III**).

Experimental

Preparation of compounds

$\text{Hg}_2(\text{CF}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-(CF}_3\text{COCCOCF}_3)\cdot 2(\text{CF}_3\text{C(OH)}_2\text{CH}_2\text{C(OH)}_2\text{CF}_3)$ (**I**)

(i) To the cooled hfacH (3 mL) in ice bath, solid HgO was added in small portions (0.5 g, 2.3 mmol). The white precipitate was obtained at once and left to stand for an hour, then filtered off, washed with CCl_4 and dried. Yield: 1.56 g (94.3%) Anal. Calcd. for $\text{C}_{25}\text{H}_{14}\text{F}_{30}\text{Hg}_2\text{O}_{14}$: C, 19.89, H, 0.94, Hg, 26.58. Found: C, 19.92, H, 0.84, Hg, 26.76%. Selected IR bands (cm^{-1}): 1746 (vs), 1710 (s), 1672 (vs), 1614 (s).
(ii) In acetonic suspension of HgO (0.5 g, 2.3 mmol in 1 mL) cool hfacH (3 mL) was added gradually, with constant stirring. Then CCl_4 was added very slowly in the clear solution to complete the precipitation and left to stand overnight in a cool place. The white precipitate was filtered off, washed with CCl_4 and dried. Yield: 1.5 g (90%).

$\text{Hg}_2(\text{CF}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-(CF}_3\text{COCCOCF}_3)$ (**II**)

I (0.5 g, 0.35 mmol) was heated in reaction flask in vacuum (15 mmHg) in an oil-bath (70–80 °C). **II** was obtained at 70 °C while by-products were collected in a dry-ice-acetone-cooled trap. In the reaction flask 0.36 g of **II** was left. Anal. Calcd. for $\text{C}_{15}\text{H}_2\text{F}_{18}\text{Hg}_2\text{O}_6$: C, 17.64, H, 0.20, Hg, 39.28. Found: C, 17.36, H, 0.31, Hg, 39.45%. Selected IR bands (cm^{-1}): 1752 (w), 1705 (s), 1670 (s), 1613 (s).

$\text{Hg}_2(\text{CH}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-(CH}_3\text{COCCOCF}_3)$ (**III**)

To an absolute ethanol solution of trifluoroacetylacetone (1.5 mL tfacH in 5 mL of ethanol) solid HgO (0.5 g; 2.3 mmol) was added in small portions. The reaction mixture was left for a few days in a cool place. Product was then filtered off, washed with ethanol and dried. Yield: 0.5 g (73.5%). Anal. Calcd. for $\text{C}_{15}\text{H}_{11}\text{F}_9\text{Hg}_2\text{O}_6$: C, 20.96; H, 1.29; Hg, 46.68. Found: C, 21.05; H, 1.48; Hg, 46.89%. Selected IR bands (cm^{-1}): 1729 (s), 1685 (vs), 1649 (vs, br).

Methods

IR analysis

The IR-spectra were obtained using a FTIR 1600 spectrophotometer as KBr disks in the 4000–450 cm^{-1} region.

Thermal analysis

Thermogravimetric analyses were carried out on a TA Instruments, SDT Model 2960 at different heating rates ($\beta=2, 5, 10, 15, 20 \text{ K min}^{-1}$). The TG and DTA curves were obtained by placing the samples of about 5 mg in mass, in open aluminium oxide sample pans, heated under nitrogen (purity above 99.996%) pouring at a flow rate of 50 mL min^{-1} . The SDT was calibrated with indium.

Results and discussion

Syntheses and IR spectral data

The compounds **II** and **III**, containing only mercury and hexafluoro- and trifluoroacetylacetone moieties, are obtained as reaction products of HgO and corresponding acetylacetone. These compounds with the general formula of $\text{Hg}_2\text{L}_2\text{L}'$ ($L=\text{hfac}, \text{tfac}$; $L'=\text{hfac}^-, \text{tfac}^-$) are microcrystalline substances insoluble in water and common organic solvents. Since the reaction conditions allowed hydration of hfacH an organomercurial of the formula $\text{Hg}_2\text{L}_2\text{L}'\cdot 2\text{L}''$ ($L=\text{hfac}, \text{tfac}$; $L'=\text{hfac}^-, \text{tfac}^-$; $L''=\text{hfptH}_4$) was isolated as the first reaction product. IR-spectra show that mercury is most probably bound to the γ -carbon and is not chelated through oxygen in any of the isolated compounds. The indicative observation for this statement include C=O stretching frequencies well above 1600 cm^{-1} , the absence of C-H stretching band above 3000 cm^{-1} . The characteristic C-H in plane bending absorption is difficult to assign due to overlapping with bands caused by $\nu_{\text{C-F}}$ stretching.

Thermal behavior

The samples of mercury compounds were heated from the room temperature up to 623 K. Typical TG and DTG curves of all three compounds are presented in Figs 1, 2 and 3 and the decomposition temperatures in DTG along with mass% loss are presented in Table 1.

The thermal decomposition of compound **I** is represented by two steps, Fig. 1. The first step (32.7%), the elimination of two hfptH_4 molecules is presented with a small and broad endothermic peak at 476 K. The second step, which represents the

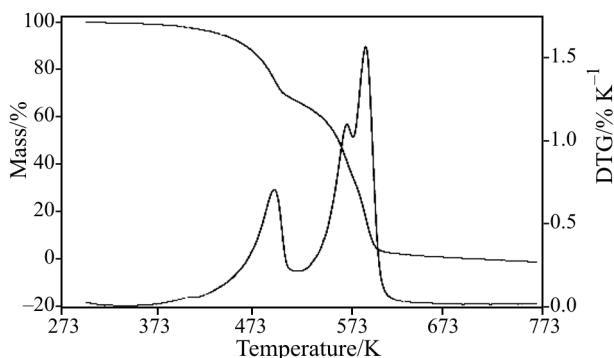


Fig. 1 TG and DTG curves of compound I

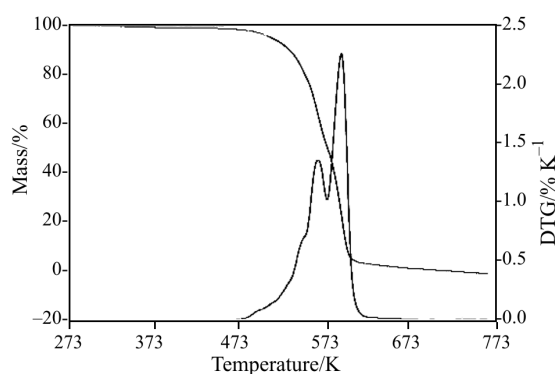


Fig. 2 TG and DTG curves of compound II

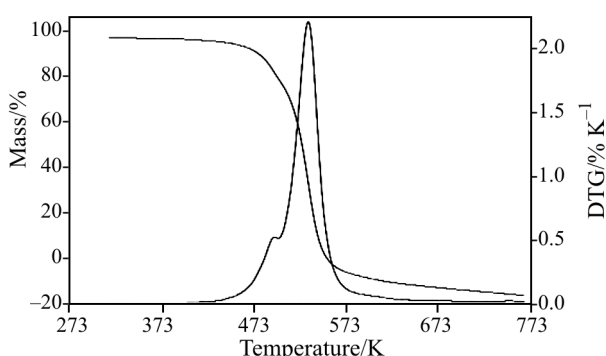


Fig. 3 TG and DTG curves of compound III

elimination of $\text{CF}_3\text{COCCOCF}_3$ (13.8%) is followed by the decomposition of $\text{Hg}_2(\text{CF}_3\text{COCHCOCF}_3)_2$ (53.5%) which is characterized by large overlapping endothermic and exothermic peaks at DTA curve. In this case DTG curve makes possible partial determination of the mass loss of partial elimination compounds.

According to the TG and DTG curve $\text{Hg}_2(\text{CF}_3\text{COCHCOCF}_3)_2$ loses its $\text{CF}_3\text{COCCOCF}_3$ (20.9%) of elimination in the first step followed by the decomposition of $\text{Hg}_2(\text{CF}_3\text{COCHCOCF}_3)_2$ (73.1%) which is characterized by a large asymmetric exothermic peak at 579–20 K, Fig. 2.

The TG and DTG curves of $\text{Hg}_2(\text{CH}_3\text{COCHCOCF}_3)_2$ - μ_2 -($\text{CH}_3\text{COCCOCF}_3$) Fig. 4, indicate that $\text{CH}_3\text{COCCOCF}_3$ -fragment is evolved in a single step (34.3%). Its elimination is characterized by broad endothermic peak at 482 K. The second step is the decomposition of $\text{Hg}_2(\text{CH}_3\text{COCHCOCF}_3)_2$ followed by a larger exothermic peak at 519 K by mass loss of 65.7%. The peaks are partially overlapped at DTG curve.

By comparison of the last stage of decomposition of all analyzed compounds we have got very interesting results which are in co-relation with their structures. In the compound I and II the decomposition temperatures of the last stages are almost the same (578 and 579 K), but in the III due to the presence of the $\text{CH}_3\text{COCHCOCF}_3$ -ligand shifted the decomposition temperature to lower temperature at 519 K. This phenomenon can be explained by electronegativity of the fluorine atoms which in the first two compounds contribute to the greater thermal stability of the compound owing to the symmetric distribution in the structure, whereas in the third case the symmetry in the structure has been destroyed. These results in the diminished thermal stability i.e. lower decomposition temperature. In favor of that speaks the fact that the enthalpy value in the third case is lower, 93.5 kJ mol^{-1} for compound III, whereas in the first case the decomposition enthalpy is $128.5 \text{ kJ mol}^{-1}$ for compound II obtained by DSC and the results are not shown.

Kinetic results

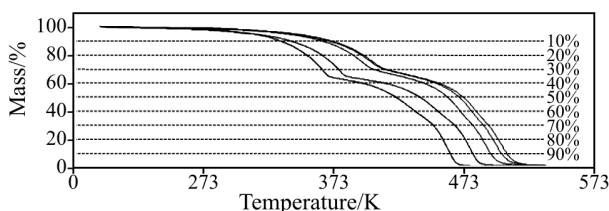
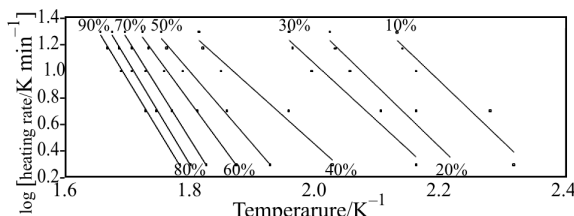
Activation energy is often used to denote the minimum energy needed for a specific to occur. The values of activation energy have been calculated using non-isothermal method. The method established by Flynn–Wall is an integral method for determining the activation energies in the dynamic heating experiments [18]. In this case with Flynn–Wall method it is not necessary to know the reaction mechanism.

With the aim to determine the activation energies of decomposition process of these synthesized compounds, the samples are thermally treated under different heating rates 2, 5, 10, 15 and 20 K min^{-1} . For each of the samples the temperature is determined at which the conversion degree in interval between 0.1 and 0.9 with the step of 0.05 is achieved, Fig. 4. The activation energy is obtained from a plot of logarithms of heating rate ($\log\beta$), as the function of the inverse temperature ($1/T$) for different conversion, Fig. 5.

The calculated activation energy is discussed on the basis of determined thermal processes which occur in particular region of conversion, (Table 1).

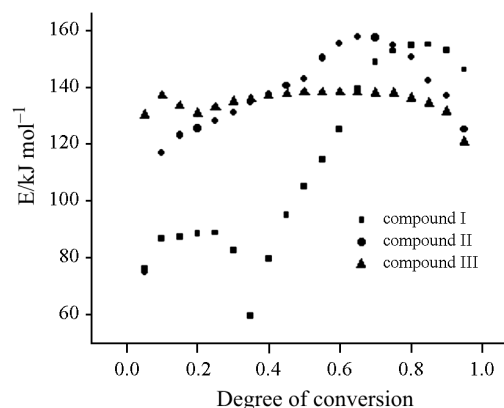
Table 1 Thermal data of **I**, **II** and **III** compounds

Compounds	Process (nature of peak)	DTG temp. T/K	Mass loss/% (experimental)	Average value of activation energy, $E/kJ mol^{-1}$
Compound I	I (endo) Elimination $thptH_4$	476	32.7	85
	II (endo) elimination $CF_3COCCOCF_3$	550	13.8	78
	III (exo) decomp. $Hg_2(CF_3COCHCOCF_3)_2$	578	53.5	140
Compound II	I (endo) elimination $CF_3COCCOCF_3$	556	20.9	121
	II (exo) decomp. $Hg_2(CF_3COCHCOCF_3)_2$	579	79.1	152
Compound III	I (endo) elimination $CH_3COCCOCF_3$	482	34.3	133
	II (exo) decomp. $Hg_2(CH_3COCHCOCF_3)_2$	519	65.7	138


Fig. 4 TG curves at different heating rates of compound **I**

Fig. 5 Arrhenius plot of compound **I**

The results from Fig. 6 confirm the prior fact, that in the compound **I** the first step of decomposition is the elimination process of $hfptH_4$. This process occurs in degrees of conversion up to 33% and $hfptH_4$ is weak-bonded in the compound which is visible from the low temperature of decomposition, as well as the low value of activation energy. The value of activation energy for the process of elimination of $hfptH_4$ for the first 30% which corresponds to the mass loss of two molecules of $hfptH_4$ is characterized by the average value of activation energy of $85 kJ mol^{-1}$.

After the elimination of $hfptH_4$, the residual compound is identical with **II** which can be seen from the same shape of plot in the degree of conversion vs. activation energy, Fig. 7. The first degree of the decomposition of **I** residue and started compound **II** is


Fig. 6 Calculated values of activation energy in dependence on conversion for **I**, **II** and **III** compounds

characterized by elimination process of $CF_3COCCOCF_3$. After that process, in both cases the decomposition of $Hg_2(CF_3COCHCOCF_3)_2$ occurred. The first part of the process is characterized by the linear increase of the activation energy depending on the degree of conversion and the final part in which the values of the activation energy reach their peak of $155 kJ mol^{-1}$. The difference in the slope of curve at Fig. 7 e.g. in the values of activation energies between compounds **I** and **II** is the consequence of the presence of two molecules of $hfptH_4$ in structure of compound **I** in the first step of decomposition. Related to the same shape of curve (activation energies vs. conversion) one can conclude that the process of degradation in both cases is taken place over the same mechanism.

As we noted before, $hfacH$ contains the strongest electron-withdrawing substituents of any β -diketone. However, the $tfacH$ has two different substituents (CH_3 and CF_3) in β positions and its asymmetric

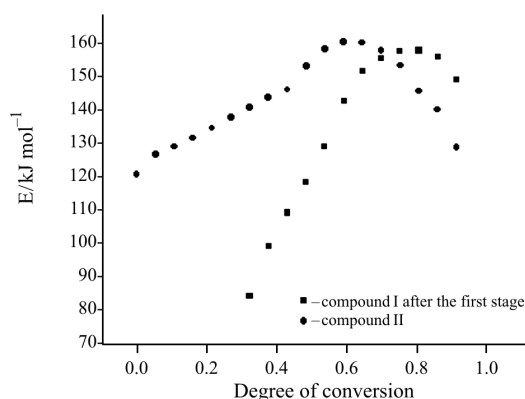


Fig. 7 Calculated values of activation energy in dependence on conversion for compound **II** and compound **I** after the first stage of decomposition

structure lays between the symmetric structures of hfacH and its parent molecule acetylacetonone. Furthermore, CF_3 functional group shows two different effects, electron-withdrawing and steric ones which extensively change the nature of the ring in tfacH [19].

This is supported by the degradation of the third compound

$\text{Hg}_2(\text{CH}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-(CH}_3\text{COCCOCF}_3)$. In this case the symmetry of the ring is disturbed by the missing of some fluorine atoms in the ring. The result is the decrease of the thermal stability, so the first step in the decomposition process is characterized by the elimination of tfacH, and separated part on plot degree of conversion vs. activation energy value of activation energy of 133 kJ mol^{-1} . The temperature of DTG maximum of that process is at lower temperature of the elimination of hfac in compound **I**, but the activation energy is apparently higher because of overlapping of decomposition stages, which is shown on Fig. 3. Further decomposition of residual species that is $\text{Hg}_2(\text{CH}_3\text{COCHCOCF}_3)_2$ occurs at lower temperature (in relation to the compounds **I** and **II**) at 529.4 K and lower average activation energy of 138 kJ mol^{-1} is needed.

Conclusions

In this paper, the thermal properties and thermal decomposition of $\text{Hg}_2(\text{CF}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-(CF}_3\text{COCCOCF}_3)$, $2(\text{CF}_3\text{C(OH)}_2\text{CH}_2\text{C(OH)}_2\text{CF}_3)$ (**I**), $\text{Hg}_2(\text{CF}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-(CF}_3\text{COCCOCF}_3)$ (**II**), $\text{Hg}_2(\text{CH}_3\text{COCHCOCF}_3)_2\text{-}\mu_2\text{-(CH}_3\text{COCCOCF}_3)$ (**III**) have been studied by thermogravimetry (TG). The TG analysis has shown that the thermal stability of compounds is in accordance with its structure assumed on IR results. The compounds **I** and **II** which contain six

fluorine atoms in acetylacetonone as ligand, were shown higher thermal stability than compound **II** which have only three fluorine atoms. Activation energies have been determined from the thermogravimetric data using heating rates $2, 5, 10, 15, 20 \text{ K min}^{-1}$ involving integral Flynn–Wall method. The values of activation energies obtained in this way enable us to follow the process such as three- and double step reaction. The activation energy vs. conversion are in agreement with the stability scale found for the admit compounds.

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