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The reactivity of metal β-diketonates in the thermal decomposition reaction

E I Tsyganova, L M Dyagileva

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Abstract. Characteristic features of the thermal decomposition of Group I–IV metal β-diketonates are surveyed and analysed. A systematic account is given of data concerning the influence of the nature of the metal and of the substituent in the β-diketone on the volatility of the metal β-diketonates and the kinetics and mechanism of their thermal decomposition. The bibliography includes 95 references.

I. Introduction

Metal β-diketonates are a class of compounds which have been quite adequately investigated.[1–5] The syntheses and properties of the β-diketonates of virtually all the metals in the Periodic System and the structures of the complexes[6–8] have been described in the literature and the nature of the bond in the chelate ring has been examined.[9,10]

Metal β-diketonates constitute a convenient model for the study of theoretical problems in the chemistry of coordination compounds and possess a series of properties of practical value which are responsible for their wide-ranging application as catalysts in oxidation, addition, and polymerisation processes,[11,12] for the separation of mixtures of lanthanides,[13,14] and for the preparation of metallic and oxide coatings.[15–26] Interest in the β-diketonates has again grown in recent years because, by virtue of their volatility and resistance to oxidation, they proved convenient starting compounds for the introduction of metals into high-temperature superconducting films by deposition from the gas phase.[27–36]

The volatility and thermal stability of the β-diketonates are fundamental factors in their use in the technology of the preparation of films. However, there are no data in the literature on the analysis of the thermal stability of these compounds.

The aim of the present review is to give a systematic account of the literature data and the authors own studies on the volatility and kinetics of the thermal decomposition of Group I–VIII metal β-diketonates, to discover the common features of the influence of the nature of the metal and the ligand on the volatility and on the kinetic and activation parameters of the thermal decomposition and on its mechanism.

E I Tsyganova, L M Dyagileva The Kinetics Laboratory, Institute of Chemistry at the Lobachevskii Nizhnii Novgorod State University, prosp. Gagarina 23, korp. 5, 603600 Nizhnii Novgorod, Russian Federation.
Fax (7-831) 235 64 80 Tel. (7-831) 265 74 12 (E I Tsyganova)

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II. The influence of the nature of the metal and the ligand on the volatility of metal β-diketonates

Vapour pressure is one of the most important physicochemical characteristics of pure compounds. Metal β-diketonates exhibit an enhanced volatility at temperatures in the range 373–573 K. Various methods are used nowadays to measure the vapour pressures of metal β-diketonates: the isoteniscope, membrane, and spectrophotometric methods, the flow method, and the Knudsen effusion method. The advantages and disadvantages of each of the above methods have been analysed in monographs.[37–39]

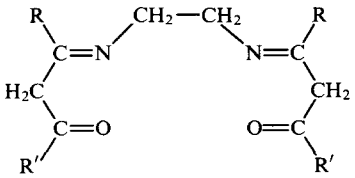
There have been fairly numerous studies on the vapour pressures of metal β-diketonates.[40–70] However, their results are contradictory. The establishment of the general characteristics of the influence of the nature of the metal and the ligand on the volatility of metal β-diketonates is therefore of undoubted interest.

There are quantitative data on the vapour pressures of metal β-diketonates mainly for Group II–IV and VIII metals, metals of the 3*d* series, and also the lanthanides and actinides.[41–65]

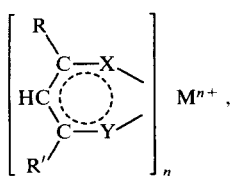
The results of vapour pressure measurements on metal β-diketonates obtained by the isoteniscope,[40–42,51–55] spectrophotometric,[56,57] membrane,[58,59] effusion,[60] and flow[61] methods have been analysed in a review by Igumenov et al.[43] Appreciable discrepancies between the experimental vapour pressures obtained by different methods have been noted.[41,52,57,61] It has been concluded that, in the study of fairly volatile and thermally stable β-diketonates, the static method with a membrane null-manometer is the most reliable.[43]

Table 1 presents the conventional designations of the metal β-diketonates investigated and Table 2 lists the thermodynamic parameters of their evaporation process obtained by the static method. All the compounds investigated exist in the gas phase as monomers and the thermodynamic parameters obtained refer to heterogeneous processes of the type A(solid, liq.) $\rightleftarrows$ A(gas). The authors of the above review[43] believe that the enthalpies of sublimation of the β-diketonates in the range 83.6 to 104.5 kJ mol^{-1} [58,59] are more reliable than the values in the range 12.5–58.5 kJ mol^{-1} established by Berg and his coworkers.[40–42]

Table 1. Conventional designations of β-diketones.

Name based on IUPAC nomenclature	Traditional name	Abbreviation	R	R′
R–CO–CH_2–CO–R′				
Pentane-2,4-dione	Acetylacetone	Hacac	Me	Me
1,1,1-Trifluoropentane-2,4-dione	Trifluoroacetylacetone	Htfacac	Me	CF_3
5,5-Dimethylhexane-2,4-dione	Pivaloylacetone	Hpacac	Me	Bu^t
2,2,6,6-Tetramethylheptane-3,5-dione	Dipivaloylmethane	Hdpm	Bu^t	Bu^t
1,1,1,5,5,5-Hexafluoropentane-2,4-dione	Hexafluoroacetylacetone	Hhfacac	CF_3	CF_3
6,6,7,7,8,8,8-Heptafluoro-2,2-dimethyloctane-3,5-dione	–	Hfod	C_3F_7	Bu^t
1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dione	Pivaloyltrifluoroacetone	Hptfacac	CF_3	Bu^t
1-Benzoylbutane-1,3-dione	Benzoylacetylacetone	Hbenacac	Me	PhCO
1-Benzoyl-4,4,4-trifluorobutane-1,3-dione	Benzoyltrifluoroacetylacetone	Hbentfacac	CF_3	PhCO
4,4,4-Trifluoro-1-thienylbutane-1,3-dione	Thenoyltrifluoroacetone	Htentfacac	CF_3	
4,4,4-Trifluoro-1-furylbutane-1,3-dione	Furoyltrifluoroacetone	Hfurtfacac	CF_3	
5-Oxaheptane-2,4-dione	Ethyl acetoacetate	Hetoxacac	CH_3	OEt
1,5-Diphenylpentane-2,4-dione	Dibenzoylmethane	Hdibenm	$PhCH_2$	$PhCH_2$
5,5,6,6,7,7,7-Heptafluoroheptane-2,4-dione	–	Hhfh	Me	C_3F_7
7-Ethyl-1,1,1,2,2,3,3-heptafluoro-nonane-4,6-dione	Isopentylheptafluoroacetyl-acetone	Hhfen	Et_2CH	C_3F_7
1,1,1,2,2,3,3,7,7,7-Decafluoroheptane-2,4-dione	Decafluoroacetylacetone	Hdfh	CF_3	C_3F_7
Heptane-3,5-dione	Dipropionylmethane	Hdprm	Et	Et
Nonane-4,6-dione	Di-n-butyrylmethane	Hdbtm	Pr	Pr
2,6-Dimethylheptane-3,5-dione	Diisobutyrylmethane	Hdibtm	Pr^i	Pr^i
3.8-Dimethylnonane-4,6-dione	Diisovalerylmethane	Hdivm	Bu^i	Bu^i
Tridecane-6,8-dione	Dicaproylmethane	Hdkm	$CH_3(CH_2)_4$	$CH_3(CH_2)_4$
R–C(NH)–CH_2–CO–R′				
4-Iminopentan-2-one	Acetylacetone imine	HAcim	Me	Me
1,1,1-Trifluoro-4-iminopentan-2-one	Trifluoroacetylacetone imine	Htfacim	Me	CF_3
1,1,1-Trifluoro-4-imino-5,5-dimethylhexan-2-one	Pivaloyltrifluoroacetone imine	Hptfim	Bu^t	CF_3
				
5,8-Diaza-4,9-dimethyldodeca-4,8-diene-2,11-dione	Ethylenediaminebisacetylacetone	H_2etdmacac	Me	Me
5,8-Diaza-1,1,1-trifluoro-4,9-dimethyl-dodeca-4,8-diene-2,11-dione	Ethylenediaminebistrifluoro-acetylacetone	H_2etdmtfacac	Me	CF_3

The volatility of chelates of the type



n = oxidation state of the metal,

may be influenced by the end groups R and R′, the nature of the metal and of the donor atoms X and Y, the stoichiometry of the complexes, and the crystal lattice structure.[43]

It has been noted[67] that the replacement of a hydrogen atom by alkyl groups diminishes the volatility of the complexes.

Among the Group I metal complexes, the volatility of copper(II) β-diketonates with fixed donor atoms (X = Y = O; X = O, Y = N) but different groups R and R′ has been investigated (Table 2).[2,48,68,69]

The following series based on the variation of the volatility of copper(II) complexes was obtained:

$$Cu(hfacac)_2 > Cu(fod)_2 > Cu(ptfacac)_2 > Cu(tfacac)_2 > > Cu(pacac)_2 > Cu(dpm)_2 > Cu(acac)_2 .$$

It was shown that the introduction of the CF_3 and C_3F_7 groups into the ligand increases the volatility of the copper complexes. The replacement of both groups R and R′ in $Cu(acac)_2$ by *tert*-butyl groups increases the volatility slightly, but the thermal stability of the complex rises sharply.[48] The presence of aromatic, heterocyclic, and ether groups lowers the volatility of the complexes drastically.[2] Comparison of the

Table 2. The coefficients in the equation for the temperature variation of the vapour pressure, $\lg P = B - A/T$ (at $P \times 1.33$ GPa), and the thermodynamic parameters of the vaporisation of metal β-diketonates.

Compound	A	B	ΔH_T° / kJ mol^{-1}	ΔS_T° / J mol^{-1} K^{-1}	T/K	Ref.
Al(acac)$_2$	4055.3 ± 41.5	6.89 ± 0.08	69.2 ± 0.3	131.6 ± 0.7	471 – 536	43
Al(tfacac)$_3$	3636.2 ± 56.7	6.83 ± 0.13	69.6 ± 0.5	130.6 ± 1.2	392 – 484	43
Al(ptfacac)$_3$	3621 ± 56.3	6.55 ± 0.13	69.3 ± 0.5	100.2 ± 1.2	378 – 488	43
Al(dpm)$_3$	3598.3 ± 35.9	5.37 ± 0.06	65.0 ± 1.0	102.7 ± 0.2	537 – 607	43
Sc(tfacac)$_3$	4294.6 ± 90.1	7.86 ± 0.21	82.1 ± 0.8	152.3 ± 1.6	397 – 457	43
Ga(tfacac)$_3$	3949.1 ± 61.8	7.23 ± 0.14	75.5 ± 0.5	138.3 ± 1.2	401 – 476	43
In(tfacac)$_3$	4044.8 ± 72.0	7.30 ± 0.16	77.4 ± 0.6	139.3 ± 1.4	398 – 478	43
Cr(tfacac)$_3$	4004.2 ± 68.5	7.24 ± 0.15	76.6 ± 0.6	138.5 ± 1.2	424 – 486	43
Cr(acac)$_3$	4280.4 ± 63.6	6.86 ± 0.12	81.8 ± 0.4	131.2 ± 1.1	491 – 563	43
Fe(tfacac)$_3$	4545.6 ± 135.8	8.47 ± 0.33	86.9 ± 1.2	162.0 ± 2.8	392 – 428	43
Ir(tfacac)$_3$	3972.0 ± 88.1	6.91 ± 0.20	76.0 ± 0.8	132.2 ± 1.6	402 – 476	43
Ni(dpm)$_2$ [a]	3854.5 ± 110.9	6.20 ± 0.21	73.7 ± 0.8	118.5 ± 1.6	515 – 536	43
V(tfacac)$_3$	3722.2 ± 85.1	6.61 ± 2.01	71.2 ± 7.8	126.4 ± 4.2	402 – 467	43
Cu(acac)$_2$	5579.6 ± 89.0	9.82 ± 1.9	106.7 ± 16.7	187.9 ± 3.6	424 – 454	48
Cu(tfacac)$_2$	6047.4 ± 80.8	11.78 ± 0.18	115.7 ± 1.6	225.3 ± 0.9	392 – 475	48
Cu(hfacac)$_2$	3216.0 ± 49.2	6.62 ± 0.12	61.5 ± 0.4	126.7 ± 1.2	377 – 423	43
Cu(pacac)$_2$	6513.5 ± 165.0	12.12 ± 0.37	124.56 ± 3.2	231.74 ± 6.9	426 – 465	48
Cu(dpm)$_2$	5843.2 ± 89.1	10.45 ± 0.21	111.73 ± 1.7	200.0 ± 3.6	434 – 468	48
Cu(dpm)$_2$ [b]	4069.5 ± 37.6	6.68 ± 0.08	77.83 ± 0.7	127.7 ± 1.46	468 – 519	48
Cu(ptfacac)$_2$ [b]	3703.9 ± 53.2	6.63 ± 0.12	70.9 ± 1.0	126.8 ± 2.26	385 – 505	48
Cu(acim)$_2$	5356.3 ± 172.1	9.64 ± 0.39	102.4 ± 3.3	78.5 ± 7.4	418 – 454	48
Cu(tfacim)$_2$	5519.7 ± 158.5	10.38 ± 0.49	105.6 ± 3.1	198.6 ± 8.8	426 – 460	48
Cu(ptfim)$_2$	6265.2 ± 598.1	10.11 ± 1.39	119.8 ± 11.5	231.3 ± 26.6	421 – 435	48
Cu(etdmacac)$_2$	4921.1 ± 145.6	7.41 ± 0.29	94.1 ± 2.8	141.7 ± 5.5	478 – 520	48
Ca(acac)$_2$	2877 ± 387	7.92 ± 0.8	–	–	410 – 430	44
Ca(tfacac)$_2$	1180 ± 120	4.12 ± 0.3	–	–	380 – 420	44
Ca(dpm)$_2$	4060 ± 450	11.5 ± 2.2	–	–	400 – 427	44
Ca(ptfacac)$_2$	8140 ± 500	21.9 ± 2.7	–	–	373 – 400	44
Sr(tfacac)$_2$	3250 ± 360	9.12 ± 0.7	–	–	410 – 450	44
Sr(ptfacac)$_2$	8600 ± 500	22.42 ± 2.9	–	–	400 – 420	44
Ba(dpm)$_2$	4750 ± 500	12.82 ± 2.6	–	–	397 – 421	45
Ba(ptfacac)$_2$	3100 ± 300	8.82 ± 0.6	–	–	406 – 450	45
Ba(tfacac)$_2$	1977 ± 496	6.82 ± 1.2	–	–	380 – 404	45
Ba(hfacac)$_2$	4740 ± 550	13.6 ± 1.3	–	–	378 – 401	45
Y(dpm)$_3$	4145 ± 260	11.82 ± 0.6	–	–	430 – 500	46
Y(ptfacac)$_3$	4060 ± 400	10.32 ± 0.8	–	–	426 – 463	46
Y(tfacac)$_3$	9400 ± 500	24.02 ± 5.9	–	–	412 – 434	46
Y(hfacac)$_3$	22100 ± 900	56.32 ± 0.8	–	–	403 – 416	46
Pr(tpfacac)$_3$	422.19 ± 21.42	3.32 ± 0.4	–	–	388 – 505	47
Pt(hfacac)$_2$ [a]	6670	12.88	55.2 ± 3.3	107 ± 7.9	419 – 439	49
Pt(dpm)$_2$ [a]	9820	16.16	81.5 ± 2.9	134.2 ± 6.7	447 – 467	49
Ir(tfacac)$_3$ [a]	9462	16.29	78.6 ± 2.51	136.7 ± 5.4	458 – 488	49
Ir(hfacac)$_3$ [a]	6793	13.79	56.4 ± 0.4	114.1 ± 0.8	401 – 443	49
Rh(hfacac)$_3$ [a]	7442	15.35	61.9 ± 0.4	127.7 ± 0.8	388 – 421	49
Ir(ptfacac)$_3$ [a]	8259	13.88	68.6 ± 0.4	111.6 ± 0.8	413 – 518	49
Ir(dpm)$_3$ [a]	8927	13.94	73.99 ± 0.8	115.8 ± 0.8	418 – 522	49
Sc(dpm)$_3$	3988 ± 54	9.24 ± 0.11	76.1 ± 0.8	121.8 ± 2.1	458 – 558	50
Y(dpm)$_3$	3977 ± 65	9.13 ± 0.13	76.1 ± 1.2	119.7 ± 2.5	463 – 574	50
La(dpm)$_3$	5630 ± 237	11.55 ± 0.44	107.9 ± 4.6	116.1 ± 8.4	530 – 567	50
Pr(dpm)$_3$	5449 ± 135	11.56 ± 0.26	104.3 ± 2.6	166.2 ± 5.0	496 – 550	50
Nd(dpm)$_3$	4850 ± 130	10.51 ± 0.26	92.9 ± 2.5	146.1 ± 5.0	492 – 546	50
Eu(dpm)$_3$	4253 ± 52	9.47 ± 0.10	81.4 ± 1.0	126.2 ± 2.0	467 – 625	50
Gd(dpm)$_3$	4117 ± 77	9.26 ± 0.14	78.8 ± 1.5	122.2 ± 2.7	480 – 600	50
Yb(dpm)$_3$	3981 ± 26	9.13 ± 0.05	76.2 ± 0.5	119.7 ± 10	477 – 588	50
Lu(dpm)$_3$	3938 ± 49	9.03 ± 1.0	75.4 ± 0.9	117.6 ± 1.7	457 – 591	50
Sc(acac)$_3$	5199.9	11.61	–	–	383 – 403	56
Zr(acac)$_4$	6050 ± 2000	13.2 ± 2.5	–	–	423 – 443	66
Hf(acac)$_4$	7240 ± 820	16.1 ± 1.9	–	–	423 – 443	66
Th(dpm)$_4$ [a]	18304 ± 371	36.92 ± 0.94	–	–	391 – 409	63
U(dpm)$_4$ [a]	17932 ± 184	35.83 ± 0.32	–	–	392 – 409	63
La(fod)$_3$ [a]	17479 ± 941	32.33 ± 0.87	–	–	387 – 403	64
Gd(fod)$_3$ [a]	18613 ± 101	40.25 ± 0.27	–	–	362 – 385	64
Yb(fod)$_3$ [a]	18608 ± 424	44.5 ± 1.2	–	–	339 – 355	64

continued over

Table 2 (continued)

Compound	A	B	ΔH_T° / kJ mol^{-1}	ΔS_T° / J mol^{-1} K^{-1}	T/K	Ref.
Th(fod)$_4$ [a]	17238 ± 173	39.88 ± 0.48	–	–	343–367	63
U(fod)$_4$ [a]	16654 ± 382	38.74 ± 1.07	–	–	344–367	63
Np(fod)$_4$ [a]	17779 ± 354	41.42 ± 0.98	–	–	350–368	63
Pu(fod)$_4$ [a]	18455 ± 947	43.60 ± 0.27	–	–	349–363	63

[a] Refers to the equation $\ln P = B - A/T$. [b] The substance is in the liquid phase.

volatilities of Cu(tfacac)$_2$ and Cu(fod)$_2$ shows that an increase in the length of the fluorinated chain hardly affects the volatility of the complexes.[48]

In the case of the N and O donor atoms, the dependence of the volatility on the nature of R and R′ remains the same as before.

$$Cu(acim)_2 < Cu(tfacim)_2 < Cu(ptfim)_2$$

It is essential to note the conventional nature of the series presented, since, depending on the temperature range in which the comparison is carried out, the relative volatilities of adjacent complexes may change. Only comparison of experimental $P-T$ curves can yield a concrete answer to the question of the greater or lower volatility of a complex in a particular temperature range.

Among Group II metal β-diketonates, the volatility of calcium,[44] strontium,[44] and barium[45] β-diketonates has been investigated. It was established that the volatility of the calcium compounds at temperatures below 400 K varies as follows:[44]

$$Ca(ptfacac)_2 > Ca(tfacac)_2 > Ca(dpm)_2 > Ca(acac)_2 .$$

In the temperature range 430–520 K, the series assumes a different form:

$$Ca(dpm)_2 > Ca(ptfacac)_2 > Ca(acac)_2 > Ca(tfacac)_2 .$$

Thus the introduction of the *tert*-butyl group into the calcium compounds increases the volatility of the complexes to a greater extent than the introduction of the trifluoromethyl group.

For the strontium compounds[44] in the temperature range from 430 to 500 K, the change in the volatility of Sr(tfacac)$_2$ is greater than for Sr(ptfacac)$_2$. At temperatures below 430 K and above 500 K, the opposite relation holds.

In terms of their volatilities, the β-diketonates can be arranged in the following series:[45]

$$Ba(tfacac)_2 \geqslant Ba(hfacac)_2 > Ba(ptfacac)_2 > Ba(dpm)_2 .$$

As in the case of copper β-diketonates, the volatility of the barium compounds increases following the introduction of the trifluoromethyl group into the ligand molecule. The introduction of the *tert*-butyl group lowers the volatility of these compounds. The lowest volatility is that of Ba(dpm)$_2$, which contains two *tert*-butyl groups. Here it was noted that the volatilities of Ba(dpm)$_2$ synthesised at different times differ significantly. A decrease in the volatility of Ba(dpm)$_2$ during its storage has been observed.[45]

It has been shown[70] that, according to mass-spectrometric data, Ba(dpm)$_2$ exists as a trimer in the gas phase and that its thermolysis is preceded by its depolymerisation. During the storage of Ba(dpm)$_2$ or Ba(dpm)$_2 \cdot 2H_2O$, the complex decomposes slowly with formation of Hdpm or the diketone $Bu^t-CO-CH=CH-CO-Bu^t$. It is therefore recommended that Ba(dpm)$_2$ be stored in vacuo.

We shall consider how the nature of the metal influences the volatility of the isotypical calcium, strontium, and barium β-diketonates.

The volatility of the complexes M(tfacac)$_2$ (M = Ca, Sr, Ba) increases with increase in the atomic number of the metal: Ca < Sr < Ba. For the complexes M(ptfacac)$_2$, the above series is reversed: Ca > Sr ≈ Ba. The same trend has been observed for M(dpm)$_2$: Ca > Ba.

Thus in the series of Group II metal β-diketonates we see no common trends in the variation of the volatility with the atomic number of the metal for different ligands.

Among the Group III metal diketonates, the variation of the volatility of the aluminium,[43] gallium,[43] indium,[43] scandium,[43,50] yttrium,[46] and the lanthanide and actinide [50,56,60–64,66] β-diketonates has been investigated.

For aluminium β-diketonates, the series based on increasing volatility has the following form:[43]

$$Al(tfacac)_3 > Al(ptfacac)_3 > Al(acac)_3 > Al(dpm)_3 .$$

The influence of the end groups has been clearly traced for the aluminium compounds. The introduction of the CF_3 group into the ligand of the chelate increases sharply the volatility of the complex. The joint presence of the *tert*-butyl and trifluoromethyl groups reduces the volatility of the complex compared with Al(tfacac)$_3$. Thus, in the case of the aluminium complexes, as for the copper and barium complexes, the trifluoromethyl group increases while the *tert*-butyl group diminishes the vapour pressure of the chelate.

A successive decrease in volatility with increase in the atomic number of the metal has been observed for the compounds M(tfacac)$_3$ (M = Al, Ga, In).[43]

In terms of their volatilities, scandium β-diketonates can be arranged in the following sequence: [43,50,56]

$$Sc(dpm)_3 > Sc(tfacac)_3 > Sc(acac)_3 .$$

The chelates with *tert*-butyl substituents proved to be more volatile than those with the trifluoromethyl substituents (although one should bear in mind that data obtained by different workers were compared). The following dependence of the volatility of the β-diketonates on the nature of the ligand has been established for yttrium β-diketonates:[46]

$$Y(hfacac)_3 > Y(tfacac)_3 > Y(ptfacac)_3 > Y(dpm)_3 > Y(acac)_3 .$$

The volatility of yttrium β-diketonates increases in proportion to the number of fluorine atoms introduced into the ligand molecule: in the series of fluorine-substituted acetylacetonates, the hexafluoroacetylacetonates have the highest vapour pressure. The greater volatility of the complexes with fluorine-containing ligands compared with their analogues without fluorine has been attributed to the mutual repulsion of the strongly electronegative terminal fluorine atoms and the corresponding decrease in the extent of van der Waals interactions.

The following series based on the variation of volatility has been observed for M(dpm)$_3$ (M = Sc, Y, La):[50]

$$Sc(dpm)_3 > Y(dpm)_3 > La(dpm)_3 .$$

Evidently, the volatility of the chelate diminishes with increase in the atomic number of the metal, as in the aluminium subgroup.[43]

The variation of the volatility of lanthanide β-diketonates Ln(dpm)$_3$ (Ln = La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) has been investigated.[50,62] A monotonic increase in the volatility of Ln(dpm)$_3$ with increase in molecular mass and with some decrease in the size of the molecule has been observed.

Konstantinov et al.[50] attribute this to the different degrees of association of the compounds in the condensed phase. It is suggested that, on passing to lighter elements, the concentration of the involatile dimeric molecules in the melt increases and the vapour pressure of the monomeric molecules over the melt diminishes. With increase in the temperature of the melt and hence with increase in the degree of dissociation of the dimeric molecules in the melt, the volatilities of different $Ln(dpm)_3$ are similar and they become indistinguishable as regards their ability to evaporate.

It has been shown for the actinides[62] that the compounds $M(fod)_3$ are more volatile than $M(dpm)_3$, the nature of the metal having a greater influence than that of the radicals.

The influence of the nature of the metal on the volatility of Group IV metal acetylacetonates is insignificant.[66]

The influence of the nature of the ligand substituent on the volatility of Group V metal β-diketonates has been investigated for bismuth.[71] It was shown that, depending on the type of substituent, the volatility of the complexes diminishes in the sequence

$$Bi(pacac)_3 > Bi(acac)_3 > Bi(tfacac)_3.$$

We observe a rare instance of a decrease in volatility following the introduction of the trifluoromethyl group into the ligand.

Factual data on the volatility of Group VIII metal (Pt, Pd, Ir, Rh) β-diketonates have been treated systematically by Igumenov et al.[49] The usual sequence based on the variation of volatility was observed for rhodium and iridium:

$$Rh(hfacac)_3 \geqslant Rh(tfacac)_3 > Rh(acac)_3;$$

$$Ir(hfacac)_3 \geqslant Ir(tfacac)_3 > Ir(acac)_3.$$

A greater volatility of the iridium complexes compared with the rhodium complexes was observed.[49] The following sequence based on the variation of volatility was established for platinum(II) chelates:

$$Pt(hfacac)_2 > Pt(ptfacac)_2 > Pt(tfacac)_2 > Pt(acac)_2 > > Pt(bentfacac)_2 > Pt(benacac)_2.$$

Igumenov et al.[49] note that all the octahedral platinum(IV) chelates, even dimeric ones, have appreciably higher vapour pressures than the isoligand pseudosquare platinum(II) chelates. It was shown that *trans*-$Pt(tfacac)_2$ occupies a special place among platinum(II) β-diketonates. Its volatility is lower than that of *cis*-$Pt(tfacac)_2$ and even that of $Pt(dpm)_2$. This is one of the few experimental confirmations of a decrease in volatility after the introduction of the CF_3 group into the ligand.

The introduction of the trifluoromethyl group into the ligand in nickel(II) complexes led to a significant increase in the vapour pressure.[72]

The study of the volatility of the trifluoroacetylacetonates of the metals in the first transition series (Sc, V, Cr, Fe, Co) led to the conclusion that the volatility decreases with increase in the atomic number of the element. It was noted in this connection that the influence of the nature of the metal on the volatility of the complexes for fixed groups R and R′ is insignificant.[43,68]

Igumenov et al.[49] observed a decrease in the thermodynamic parameters characterising the sublimination and evaporation of the β-diketonates after the introduction of the CF_3 group into the ligand. The decrease in ΔH_T°, which should entail a sharp increase in the vapour pressure, is compensated by the corresponding decrease in ΔS_T°. Analysis of the data for compounds belonging to one group in the Periodic System shows a decrease in the absolute values of the thermodynamic parameters with increase in the atomic number of the metal.

Analysis of the data presented above for metal β-diketonates shows that the decisive factor in the volatility of the chelates is the nature of the ligand. In terms of their influence on the volatility, the factors considered can be arranged as follows:[43]

(1) the influence of the nature of the terminal R and R′ groups of the ligand;

(2) the influence of the nature of the metal within the groups of the Periodic System;

(3) the influence of the nature of the metal within the periods of the Periodic System.

The fact that the volatility of copper, calcium, strontium, barium, yttrium, aluminium, gallium, indium, nickel, palladium, iridium, and platinum β-diketonates increases following the introduction of trifluoromethyl groups into the β-diketone and diminishes after the introduction of *tert*-butyl groups into the latter may be regarded as established. A decrease in the volatility after the introduction of CF_3 groups has been observed only for calcium (at 430–520 K), scandium, and bismuth β-diketonates and the *trans*-isomer of $Pt(tfacac)_2$.

General trends in the variation of the volatility of the β-diketonates as a function of the atomic number of the metal have not been noted. A decrease in volatility with increase in the atomic number of the metal has been observed in the calcium subgroup for the complexes $M(ptfacac)_2$ and $M(dpm)_2$ (M = Ca, Sr, Ba), in the aluminium subgroup for the complexes $M(tfacac)_3$ (M = Al, Ga, In), in the scandium subgroup for the complexes $M(dpm)_3$ (M = Sc, V, La), and in the group of metals of the first transition series (Sc, V, Cr, Fe, Co) for the $M(tfacac)_n$ complexes. On the other hand, an increase in volatility with increase in the atomic number of the metal has been observed for the compounds $M(tfacac)_2$ (M = Ca, Sr, Ba) and $M(dpm)_3$ (M = lanthanides).

It is at present impossible to establish an unambiguous correlation between the thermodynamic data and the structural parameters of metal β-diketonates because these compounds have been little investigated.[43]

III. Kinetics of the thermal decomposition of metal β-diketonates

In the present review an attempt is made to treat systematically the available literature data concerning the influence of the nature of the metal and the substituent on the kinetics and mechanism of the gas-phase pyrolysis of substituted metal β-diketonates. The thermal decomposition of the β-diketonates can occur both in the gas and solid phases. In the case of the gas-phase thermal decomposition of metal β-diketonates, the rate constant for the thermal decomposition serves as a measure of reactivity. In the solid-phase decomposition investigated by differential thermal analysis (DTA), the comparison of the reactivities was based on the temperatures of the onset of decomposition, while in the case of the solid-phase decomposition, investigated by the kinetic method, it was based on the initial rates of thermal decomposition.

1. Thermal decomposition of Group I metal β-diketonates

Among Group I metal β-diketonates, the kinetics of the thermal decomposition of copper(II) β-diketonates have been described in greatest detail.[73–78] The kinetics of the thermal decomposition of copper(II) complexes have been studied by static,[73] flow,[74] and mass-spectrometric[75] methods. The experimental conditions and the activation parameters for the thermal decomposition are presented in Table 3.

The gas-phase pyrolysis of $Cu(acac)_2$ under static conditions in vacuo is homogeneous-heterogeneous in character and is described satisfactorily by a first-order kinetic equation.[73] The acceleration of the thermal decomposition in the presence of oxygen has been noted.

Mass-spectrometric analysis led to the detection of the following components in the products of the total thermal decomposition at 573 K (in mol %): acetone (22.3), ethene (carbon monoxide) (38.0), ethyl methyl ketone (0.3), CO_2 (36.2), and H_2O (3.2). This product composition indicates appreciable degradation of acetylacetone, which is formed in the initial stages of the thermal decomposition. The splitting off of the ligand is observed at temperatures close to that of the onset of

Table 3. Kinetic parameters of the gas-phase pyrolysis of copper(II) β-diketonates obtained by a flow method [74] (A — pro-exponential factor).

Compound	Temperature range/K	lg$A$	E/kJ mol^{-1}
Cu(acac)$_2$ [a]	536–613	7.48 ± 0.98	115.4 ± 10.8
Cu(acac)$_2$	553–723	7.16 ± 0.65	58.7 ± 6.2
Cu(tfacac)$_2$	473–673	7.15 ± 0.48	46.9 ± 4.5
Cu(hfen)$_2$	473–723	7.07 ± 0.35	45.9 ± 5.4
Cu(hfh)$_2$	473–653	6.55 ± 0.52	39.3 ± 4.16
Cu(hfacac)$_2$	453–523	6.32 ± 0.32	33.5 ± 3.8
Cu(dfh)$_2$	453–593	6.28 ± 0.45	31.8 ± 8.2
Cu(dpm)$_2$ [b]	423–823	13.176	155.5 ± 7.1

[a] Data obtained by a static method.[73] [b] Data obtained by the mass-spectrometric method.[75]

decomposition.[77] The ligand Hdpm is also formed in the initial stages of the pyrolysis of Cu(dpm)$_2$.

It has been established[79] that acetylacetone has a higher thermal stability than that of the chelate complexes based on it. The M–O bond energy in acetylacetonates is 160–280 kJ mol^{-1}. The M–O bond is the least stable in the chelate molecule.[79]

The kinetics of the thermal decomposition of fluorine-substituted copper β-diketonates in an open system have been investigated in a stream of helium at temperatures in the range 453–723 K in a reactor the walls of which were lined with metallic copper having a constant catalytic activity (Table 3).[74]

Analysis of the dependence of the maximum rate of growth of the metallic copper film under dynamic deposition conditions enabled Mazurenko et al.[74] to conclude that the rate-limiting stage of the thermal decomposition of fluorine-substituted copper(II) β-diketonates is the decomposition of the adsorption complex. A linear dependence of the energy characteristics of the thermal dissociation process on the electronic structure of the coordination unit of the β-diketonate complexes has been observed. Thus, following the enhancement of the electron-accepting properties of the α-substituent, a decrease in the activation energy and an increase in the rate constants for the thermal decomposition of copper(II) β-diketonates have been observed in the sequence

$$\text{Cu(acac)}_2 < \text{Cu(tfacac)}_2 < \text{Cu(hfen)}_2 \approx \text{Cu(hfh)}_2 < \text{Cu(hfacac)}_2 < \text{Cu(dfh)}_2 .$$

Cu(acac)$_2$ has the highest kinetic stability in the thermal decomposition reaction. An increase in the number of fluorine atoms in the β-diketone leads to a successive increase in the thermal decomposition rate constant. Thus at 553 K the rate constant for the thermal decomposition of Cu(acac)$_2$ is accordingly smaller than those for the thermal decomposition of the fluorine-substituted analogues.

The greater thermal stability of Cu(acac)$_2$ compared with the substituted β-diketonates has been attributed[78] to the fact that the contribution of ring conjugation in copper(II) β-diketonates is greater than in the chelates of other metals by virtue of the π-bonding ($p\pi - d\pi$) nature of the Cu–O bond. The alkyl substituents in these chelates exhibit a hyperconjugation effect, which disrupts the resonance in ring-conjugated systems.

It was not possible to reach a conclusion about the comparative stabilities of Cu(acac)$_2$ and Cu(dpm)$_2$, since the thermal decomposition rate constants were obtained under different experimental conditions[73,75] and may refer to different rate-limiting stages.

A kinetic analysis of the thermal decomposition of copper(II) β-diketonates in vacuo and under an inert atmosphere, based on the results of thermogravimetric analysis, has been published.[76] In terms of the apparent activation energies, the compounds can be arranged in the following sequences [the values of E (kJ mol^{-1}) are given in brackets]:

(a) under an inert atmosphere:

$$\text{Cu(tentfacac)}_2\ (110.8) > \text{Cu(acim)}_2\ (106.6) \approx \approx \text{Cu(tfacac)}_2\ (102.4) > \text{Cu(acac)}_2\ (99.1);$$

(b) in vacuo:

$$\text{Cu(tentfacac)}_2\ (105.3) > \text{Cu(tfacac)}_2\ (80.7) > > \text{Cu(acac)}_2\ (77.3) > \text{Cu(acim)}_2\ (66.04).$$

However, no conclusions concerning the comparative thermal stabilities of the copper(II) β-diketonates can be reached on the basis of these series, since the pre-exponential factor in the rate constant equation is unknown.

The thermal stability of Na(acac) has been investigated by the DTA method[78] relative to the thermal stabilities of the acetylacetonates of divalent and trivalent metals: Cu(II), Ni(II), Co(II), Cr(III), Fe(III), Co(III), and Mn(III). It was shown that all the compounds M(acac)$_n$ investigated decompose in the temperature range from 423 to 673 K. In terms of the thermal stabilities of their acetylacetonates, the metals can be arranged in the following sequence:

$$\text{Na(I)} > \text{Cr(III)} > \text{Al(III)} > \text{Ni(II)} > \text{Cu(II)} > \text{Fe(III)} > > \text{Co(II)} > \text{Co(III)} > \text{Mn(III)}.$$

The principal gaseous products of the decomposition of M(acac)$_n$ [M = Co(II), Co(III), Al(III), Fe(III)] are acetone and carbon dioxide. In the case of Na(I) and Cr(III), methane appears in the thermal decomposition products on raising the temperature. The principal product of the thermal decomposition of copper(II) and manganese(III) acetylacetonates is acetylacetone over the entire temperature range.

The thermal decomposition of three types of chelate complexes of dimethylgold(III) having the general formula Me$_2$Au(R–CX–CH–CO–R′), where X = O, NH, or S and R and R′ = Me, Bu^t, or CF$_3$ in various combinations, has been investigated by the DTA method[79] in the solid and gaseous states. Thermolysis of all types of chelates proceeds in the same way regardless of the nature of the donor atoms and the type of substituents R and R′ in the ligand.

The complexes containing the *tert*-butyl group exhibit the highest thermal stability. The introduction of the CF$_3$ group into the β-diketonate complexes leads to an appreciable decrease in their thermal stability, while, conversely, the introduction of CF$_3$ groups into the β-iminoketonates increases the thermal stability of the complex.

The decisive factor governing the variation of the thermal stability of the complexes in the condensed state is not the type of substituents R and R′ but the nature of the donor atoms in the ligand. The introduction of sulfur atoms into the chelate ring leads to a sharp decrease in the thermal stability of the dimethylgold(III) complexes.

It has been established that, in the series of dimethylgold(III) chelates investigated, the thermal stability increases as a function of the chelate unit in the following sequence:

$$\text{S–S} < \text{O–S} < \text{O–O} < \text{O–NH}.$$

The thermal stability of the β-diketonate complexes in the gas-phase decomposition is analogous to their stability in the solid-phase decomposition.

When the CF$_3$ group is introduced into the chelate ligand, the series of the thermal stabilities of the gaseous β-iminoketonates is reversed.

The principal volatile products of the thermal decomposition of the compounds investigated are the free β-diketones, β-iminoketones, HL, CH$_4$, C$_2$H$_6$, and MeL (L = ligand). The presence of this set of products indicates the occurrence of competing rearrangements of the thermally excited species with opening of the chelate ring.

In the interaction of the β-diketonates with deuterium, the ketones R–CO–CDMe–CO–R′ and monosubstituted deuteriated β-diketones were detected in the reaction products. Deuteriated metal-containing products were not found. Appreciable temperature-dependent deuteriation of the molecules of the complexes has been observed for the β-iminoketonates. Mainly monosubstituted deuteriated metal-containing products are formed, whereas in the case of the free β-iminoketones, disubstituted molecules were detected, which confirms the above hypothesis of the initial opening of the chelate ring in the thermally excited molecule with subsequent decomposition via different paths.

2. Thermal decomposition of Group II metal β-diketonates

The following thermal stability series has been obtained from the results of the study of the relative reactivities of divalent Group II metal acetylacetonates:[80]

$$Be \geqslant Ni > Cu > Cd > Mn > Co.$$

The size of the alkyl substituent in beryllium β-diketonates has little effect of the stability of the complexes. Among Group II metal compounds fluorine-substituted calcium and strontium β-diketonates have been investigated in greatest detail.[44] The thermal decomposition of these compounds takes place in the gas phase and is described by a first-order kinetic equation (Table 4). From 1.5 to 6.0 moles of gaseous products are evolved per mole of the decomposed chelate. The complexes $Ca(dpm)_2$ and $Ca(acac)_2$ undergo the greatest and smallest degradation respectively. The main product of the thermal decomposition of calcium acetylacetonate is acetone, the content of which diminishes with increasing degree of conversion of the reactant. The first decomposition stage is the opening of the chelate ring with subsequent dissociation of the C–C bonds.[44] In terms of their kinetic stabilities, the calcium compounds can be arranged in the following sequence:

$$Ca(dpm)_2 > Ca(acac)_2 > Ca(tfacac)_2 > Ca(ptfacac)_2.$$

Table 4. Kinetic and activation parameters for the gas-phase pyrolysis of Group II–V metal β-diketonates (the initial pressures of the reactants were 50–200 GPa).

Compound	Temperature/K	lg*A*	*E*/ kJ mol^{-1}	Ref.
$Ca(acac)_2$	613–693	3.19 ± 0.83	74.9 ± 5.8	44
$Ca(tfacac)_2$	553–633	5.26 ± 0.33	92.0 ± 3.6	44
$Ca(dpm)_2$	673–798	5.71 ± 0.34	117.5 ± 4.9	44
$Ca(ptfacac)_2$	533–613	5.77 ± 0.82	97.6 ± 9.1	44
$Sr(tfacac)_2$	533–573	12.06 ± 0.72	159.0 ± 7.6	44
$Sr(ptfacac)_2$	483–523	7.64 ± 1.31	99.6 ± 12.5	44
$Ba(acac)_2$ [a]	536–633	6.50 ± 0.48	81.1 ± 5.1	73
$Ba(ptfacac)_2$	525–625	2.23 ± 0.34	53.1 ± 3.7	45
$Ba(hfacac)_2$	539–630	1.73 ± 0.63	52.0 ± 2.1	45
$Ba(tfacac)_2$	475–623	0.88 ± 0.19	35.6 ± 3.2	45
$Ba(dpm)_2$ [b]	623–773	0.42 ± 0.15	38.9 ± 2.0	45
$Y(acac)_3$ [a]	513–593	4.77 ± 0.43	50.6 ± 3.8	73
$Y(dpm)_3$	523–633	4.31 ± 0.14	76.5 ± 1.6	46
$Y(ptfacac)_3$	493–533	13.88 ± 0.9	166.6 ± 8.9	46
$Y(tfacac)_3$	453–523	1.93 ± 0.38	44.5 ± 3.5	46
$Y(hfacac)_3$	403–478	4.08 ± 0.77	53.3 ± 6.4	46
$Pr(ptfacac)_3$	553–613	2.90 ± 0.72	63.4 ± 7.8	47
$Ti(acac)_3$	573–633	5.32 ± 0.85	90.7 ± 9.6	82, 83
$V(acac)_3$	683–743	5.02 ± 0.56	102.4 ± 7.5	82, 83
$VO(acac)_2$	638–723	8.32 ± 0.44	143.0 ± 5.8	82, 83

[a] Pyrolysis in the solid phase. [b] Calculated from the initial rates of pyrolysis.

The thermal stability of the compound $Ca(dpm)_2$ is highest. The introduction of trifluoromethyl groups diminishes significantly the thermal stability of the calcium chelates.

Comparison of the kinetic parameters of the thermal decomposition of the strontium compounds shows that the complex $Sr(tfacac)_2$ is much more stable than $Sr(ptfacac)_2$. A considerable amount of trifluoromethane is present in the products of the decomposition of fluorinated strontium chelates.

Comparison of calcium and strontium β-diketonates containing isotypical ligands shows that the calcium compounds have a higher thermal stability than the corresponding strontium compounds. The difference between the thermal stabilities of the β-diketonates $M(tfacac)_2$ is smaller than in the case of $M(ptfacac)_2$. The thermal decomposition of the strontium compounds is retarded in the presence of oxygen, whereas the decomposition of the calcium chelates is accelerated under these conditions.[44] The rate constant for the thermal decomposition process diminishes with increase in the heterogeneous factor S/V (S is the surface area of the reactor and V its volume). This indicates a complex homogeneous-heterogeneous character of the thermal decomposition of the chelates, the main products of which are carbon oxides (for both low and high degrees of conversion) (Table 5).

The decomposition of barium β-diketonates takes place both in the solid and gas phases (Table 4).[45,73] The pyrolysis of barium acetylacetonate proceeds topochemically in the solid phase and is accompanied by the formation of both solid and gaseous products.[73] The composition of the solid phase has the empirical formula $BaC_{3.6}H_{6.06}O_{1.91}$. More extensive degradation of barium acetylacetonate to the carbide BaC_2 takes place in the presence of oxygen, the initial rate of thermal decomposition remaining unchanged. The following substances were detected among the products of the total pyrolysis of barium acetylacetonate at 573 K (mol %): acetone (86.6), ethanol (0.8), ethene (carbon monoxide) (9.3), ethyl methyl ketone (0.2), carbon dioxide (1.0), water (2.1).

The thermal decomposition of the fluorine-substituted barium β-diketonates takes place in the gas phase and is described satisfactorily by the kinetic equation for a first-order reaction.[45] The kinetic stability of barium β-diketonates in the thermal decomposition reaction varies in the following series:

$$Ba(dpm)_2 > Ba(hfacac)_2 > Ba(ptfacac)_2 > Ba(tfacac)_2.$$

The influence of oxygen on the rate of the thermal decomposition of fluorine-substituted barium β-diketonates is specific and is determined by the nature of the ligand.[45] In the thermal decomposition of $Ba(ptfacac)_2$ and $Ba(dpm)_2$, a decrease in the rate constant to a minimum value in the presence of 30% – 50% of added oxygen is observed. In the case of $Ba(hfacac)_2$, the addition of oxygen hardly affects the rate, whereas an appreciable increase in the rate constant is observed for $Ba(tfacac)_2$. As in the case of the analogous calcium and strontium compounds, a decrease in the decomposition rate constant with an increase in the heterogeneous factor is likewise observed for the barium chelates.[45]

The main products of the thermal decomposition of all the barium compounds investigated, in both the initial and final decomposition stages, were CO and CO_2, the content of which decreases on passing from the $Ba(hfacac)_2$ to the $Ba(dpm)_2$ complexes in the following series of ligands:

$$Hhfacac > Hptfacac > Htfacac > Hdpm;$$

$$Hhfacac \approx Htfacac > Hptfacac > Hdpm.$$

The amount of the main ligand in the total pyrolysis products does not exceed 0.2% – 1.4% for all the compounds investigated, which indicates its far-reaching degradation (Table 6). The trends in the variation of the contents of other products are determined by the nature of the initial ligand and by the degree of decomposition.

Comparison of the thermal stabilities of the Group II metal β-diketonates $M(tfacac)_2$ (M = Ca, Sr, Ba) shows that the kinetic

Table 5. Compositions (in mol %) of the volatile products of the thermal decomposition of calcium and strontium β-diketonates.[44]

Compound	Temperature/K	Degree of decomposition	CO	CO_2	Methyl pivaloyl ketone	iso-C_4H_8 (iso-C_4H_{10})	C_3H_8 (C_3H_6)	CH_4 (CF_4)	CF_3H (CF_2H_2)	L [a] (trifluoroacetone)	C_3H_7F (acetone)	H_2 (N_2)	C_2H_4 (C_2H_6)
$Ca(acac)_2$	673	0.3	16.0	2.6	–	–	–	12.2	–	0.08	(54.2)	2.2	11.9 (0.8)
$Ca(acac)_2$	673	1.0	23.5	2.7	–	–	–	21.0	–	0.2	(37.3)	3.3	11.1 (0.9)
$Ca(tfacac)_2$	573	0.3	54.6	23.8	–	–	–	5.1 (0.9)	3.5 (0.3)	0.01 (9.5)	1.8	–	(0.5)
$Ca(tfacac)_2$	573	1.0	54.6	22.6	–	–	–	5.1 (2.1)	4.7 (0.3)	0.05 (8.8)	1.3	–	(0.4)
$Ca(dpm)_2$	738	0.2	36.5	0.9	3.4	11.3	(12.8)	30.3	–	2.9 [b]	–	1.2	(0.7)
$Ca(dpm)_2$	738	1.0	32.3	4.3	12.6	16.2	(16.0)	13.7	–	2.4 [b]	–	1.6	(0.9)
$Ca(ptfacac)_2$	573	0.2	30.7	18.0	5.5	3.3 (1.0)	0.9 (1.4)	0.2 (4.3)	0.1 (0.2)	0.2	0.02	–	(0.4)
$Ca(ptfacac)_2$	573	0.6	18.8	7.3	3.8	1.6 (0.4)	2.3 (0.7)	0.6 (0.2)	0.2	0.2	0.1	0.08 (31.7)	(0.5)
$Sr(tfacac)_2$	573	0.3	49.6	29.1	–	–	–	5.6 (0.7)	11.5 (0.2)	0.05 (2.4)	(0.5)	–	(0.4)
$Sr(tfacac)_2$	573	1.0	38.4	32.9	–	–	–	5.2 (2.3)	13.7 (0.3)	0.02 (4.8)	(0.8)	–	(1.6)
$Sr(ptfacac)_2$	523	0.1	23.6	48.6	0.05	0.8	0.9 (0.2)	5.4	19.2 (0.4)	0.5	–	–	(0.4)
$Sr(ptfacac)_2$	523	1.0	35.2	34.4	0.3	0.9 (0.1)	0.4 (0.2)	2.4	25.6 (0.1)	0.2	–	0.02	(0.2)

[a] L = initial ligand. [b] Dimethylpropionaldehyde.

Table 6. Compositions (in mol %) of the volatile products of the thermal decomposition of metal β-diketonates (degree of decomposition 0.3).[45-47]

Compound	Temperature/K	CO	CO_2	H_2	CH_4 (CF_4)	CF_3H (CF_2H_2)	C_2H_6 (C_2F_6)	C_2H_2F (C_2F_4)	C_3H_6 (C_3H_8)	iso-C_4H_8 (iso-C_4H_{10})	Methyl pivaloyl ketone	L[a]
$Ba(ptfacac)_2$	623	35.7	33.6	0.2	4.3	4.5 (0.2)	0.5	–	2.5 (7.5)	4.2 (0.2)	6.4	0.2
$Ba(hfacac)_2$	630	46.2	29.1	–	(2.0)	15.6 (0.2)	(0.2)	0.2 (1.3)	–	–	3.8[b]	1.4
$Ba(dpm)_2$	623	33.2	1.5	4.3	6.2	–	0.9	–	23.8	13.3	5.8	0.4
$Ba(tfacac)_2$	623	38.9	22.8	–	4.7 (10.3)	3.0	0.5	0.8	–	–	–	0.1
$Y(dpm)_3$	623	20.7	7.8	0.04	0.4	–	3.1	–	10.0	3.7	13.4	0.1
$Y(ptfacac)_3$	623	30.3	13.7	0.1	3.0 (11.3)	0.9 (0.4)	10.3	(0.8)	2.6 (1.1)	4.2 (1.6)	10.3	0.4
$Y(tfacac)_3$	623	42.9	18.8	–	2.4 (7.7)	0.01 (0.7)	4.1	–	–	–	–	0.2
$Y(tfacac)_3$	630	39.3	25.3	–	(5.2)	7.0 (1.5)	(0.2)	0.6	–	–	–	0.2
$Pr(ptfacac)_3$	573	40.5	20.0	0.2	0.15	12.2	0.2	–	–	14.0	4.6 8.1[b]	–

[a] Initial ligand. [b] Trifluoroacetone.

stability of these compounds in the thermal decomposition reaction falls with increase in the atomic number of the metal:[44,45]

$$Ca(tfacac)_2 > Sr(tfacac)_2 > Ba(tfacac)_2 .$$

For the complexes $M(ptfacac)_2$ (M = Ca, Sr, Ba), the kinetic stability series assumes the following form:

$$Ca(ptfacac)_2 > Ba(ptfacac)_2 > Sr(ptfacac)_2 .$$

A study has been devoted to the radiation-induced thermal decomposition of zinc and cadmium acetylacetonates.[81] Zinc acetylacetonate is thermally less stable than cadmium acetylacetonate. The decomposition curves are S-shaped and, after the sigmoid section, there are long linear sections on the curves. The activation energies corresponding to the sigmoid and linear sections of the decomposition curves have been found.

3. Thermal decomposition of Group III metal β-diketonates

The thermal stability of aluminium β-diketonates, investigated by the DTA method, decreases in the following series:[43]

$$Al(dpm)_3 > Al(acac)_3 > Al(ptfacac)_3 > Al(tfacac)_3 .$$

As for copper,[74] calcium,[44] strontium,[44] and barium[45] β-diketonates, the introduction of the trifluoromethyl group into the ligand decreases and the introduction of the *tert*-butyl group increases the thermal stability of the aluminium complexes. In the Al, Ga, and In group, a successive decrease in the thermal stability of the trifluoroacetylacetone complexes with increase in the atomic number of the element is observed.[43]

The study of the thermal decomposition of aluminium acetylacetonate in the gas phase, which we carried out by the manometric method, showed that, at temperatures in the range 657–723 K, the degree of decomposition of the reactant is independent of the initial pressure in the range from 130 to 200 GPa. The kinetic decomposition curves at low temperatures are autocatalytic in character, which is induced by the aluminium oxide formed. With increase in the decomposition temperature, the autocatalytic character of the curves vanishes as a consequence of the high rates of decomposition. The first-order rate constant calculated for 723 K is 4.1×10^{-1} s^{-1}. The activation energy for the overall process, calculated by the method involving the transformation of the kinetic curve, is 68.1 kJ mol^{-1}. The primary product of the gas-phase decomposition is acetyl-acetone, which decomposes to acetone and carbon dioxide. The following substances have been found (mol %) among the products of the total pyrolysis of aluminium acetylacetonate at 673 K: acetylacetone (0.3), diacetyl (0.17), carbon dioxide (33.81), butane (9.54), methane (1.49), dimethylfuran (0.35), acetone (44.67), carbon monoxide (6.90), ketene (0.84), hydrogen (1.54), and unidentified products (0.7). The addition of oxygen accelerates the decomposition.

The trifluoroacetylacetonate chelates of other trivalent metals can be arranged in the following sequence in terms of their thermal stability:[68]

$$Cr(tfacac)_2 > Sc(tfacac)_3 > Fe(tfacac)_3 > Mn(tfacac)_3 .$$

The thermal decomposition of yttrium acetylacetonate takes place in the solid phase similarly to that of the barium analogue.[73] The gaseous products of the total pyrolysis of yttrium acetylacetonate at 573 K have the following composition (mol %): acetone (80.0), ethanol (0.4), ethene (carbon monoxide) (8.7), ethyl methyl ketone (0.2), carbon dioxide (1.0), water (0.4). On the other hand, the decomposition of the fluorine-substituted yttrium β-diketonates takes place in the gas phase in accordance with the kinetic law for a first-order reaction (Table 4).[46] From 2 to 8 moles of volatile products are evolved per mole of the compound decomposed depending on the temperature and the nature of the ligand. The ligand in the complex $Y(tfacac)_3$ undergoes degradation to the greatest extent, whilst those in the complexes $Y(dpm)_3$ and $Y(tfacac)_3$ are least degraded. The kinetic stability of yttrium β-diketonates diminishes in the sequence

$$Y(dpm)_3 > Y(ptfacac)_3 > Y(tfacac)_3 > Y(hfacac)_3 .$$

This sequence agrees well with the inductive influence of the *tert*-butyl and trifluoromethyl groups on the reaction centre. The electron-donating *tert*-butyl groups strengthen the Y–O bond, which leads to a greater thermal stability of the compounds $Y(dpm)_3$ and $Y(ptfacac)_3$ compared with the fluorine-substituted analogues $Y(tfacac)_3$ and $Y(hfacac)_3$, in which the strongly electron-accepting CF_3 groups weaken the Y–O bond. Thus the introduction of fluorine atoms into the ligands of the yttrium chelates not only increases the volatility but also diminishes the thermal stability of the complexes.

Evidence indicating a homogeneous-heterogeneous thermal decomposition of yttrium complexes as well as the accelerating effect of oxygen on the rate of thermal decomposition has been observed. The thermal decomposition of yttrium complexes is accompanied by far-reaching degradation of the ligands with formation of a wide range of products, including fluorine-containing hydrocarbons (Table 6).

Among the lanthanide derivatives, the kinetics of the thermal decomposition have been investigated only for the complex $Pr(ptfacac)_3$ (Table 4).[47] The thermal decomposition of the praseodymium complex in vacuo takes place in the gas phase and is described satisfactorily by the kinetic equation for a first-order reaction. About 4 moles of gaseous products are evolved per mole of the compound decomposed, the main products being CO and CO_2, which indicates a far-reaching degradation of the ligand (Table 6).

4. Thermal decomposition of Group IV – VII metal β-diketonates

The kinetic and activation parameters of the gas-phase thermal decomposition of titanium, vanadium, and vanadyl acetylacetonates in vacuo have been investigated.[82,83] The acetylacetonate derivatives of trivalent and tetravalent vanadium have comparable reactivities (Table 4). On the other hand, the replacement of the central metal atom has a much greater influence on the thermal stability of the acetylacetonates than the oxidation state of the metal. The thermal stabilities of the compounds investigated diminish in the sequence

$$V(acac)_3 \geqslant VO(acac)_2 > Ti(acac)_3 .$$

The complex homogeneous-heterogeneous character of the decomposition reactions of these compounds has been demonstrated. As in the case of the barium,[45] calcium,[44] and strontium[44] chelates, a decrease in the rate constant for the thermal decomposition of vanadium acetylacetonate is observed with increase in the surface area, whereas the nature of the surface does not influence the rate of the process. The principal volatile products of the thermal decomposition of vanadium acetylacetonate at 703 K and for low degrees of decomposition were (in moles per mole of the reactant decomposed): acetone (2.0), carbon dioxide (2.5), carbon monoxide (1.2), xylene (0.14), hydrogen (0.11), butene (0.29), and an unidentified product (with *m/e* 86) (0.02). Similar products have been detected also in the decomposition of vanadyl acetylacetonate. The set of kinetic and analytical data indicates the preferential operation of an intramolecular pathway leading to the decomposition of these compounds. However, the influence of the addition of substances which might serve as initiators of a radical process (acetone, oxygen) indicates indirectly a small contribution of the radical decomposition path. Thus the addition of acetone and oxygen increases the rate constants for the decomposition of vanadium and vanadyl acetylacetonates. The same trends have been observed in the pyrolysis of the copper,[73–75] yttrium,[46] barium,[45] calcium,[44] strontium,[44] and aluminium[43] chelates. The formation of the acetylacetonyl radical has also been postulated in the pyrolysis of the metal chelates.[84]

The thermal decomposition of zirconium acetylacetonate has been investigated by the DTA method under an inert atmosphere at temperatures from 293 to 773 K.[21] The process takes place in two stages. In the first stage (453 K), the displacement of two chelate ligands as a result of coordination polymerisation and the formation of an intermediate polymeric product are observed; in the second stage (623 K), zirconium dioxide in the cubic modification is formed. In contrast to the acetylacetonate derivative, the decomposition of the complex $Zr(ptfacac)_4$ takes place in one stage. It involves the dissociation of the bonds within the chelate ligand with formation of volatile low-molecular-mass products. This decomposition path is associated with the absence of α-hydrogen atoms from the side chains, which would lead to the possibility of the radical recombination of the carbon chains. On further heating, zirconium dioxide passes from the cubic to the pure monoclinic form.

The thermal decomposition of the bismuth chelates $Bi(tfacac)_3$, $Bi(hfacac)_3$, and $Bi(ptfacac)_3$ in the vapour and solid phase has been investigated in helium and oxygen streams.[71] The most characteristic gas-phase products of the thermolysis of the bismuth chelate vapours were the β-diketones and their fragments. The complex $Bi(ptfacac)_3$ decomposing at a temperature above 573 K, showed the highest thermal stability. This complex shows a smaller tendency to form oligomers owing to the steric hindrance generated by the bulky substituents in the ligands within the octahedral bismuth complex. The increase in the steric factor as a result of the replacement of the Bu^t groups by $MeOCMe_2$ rules out almost completely the possibility of dimerisation of the molecules.

Comparison of the thermal stabilities of chromium(III) and manganese(III) acetylacetonates and their alkyl and fluorine-substituted derivatives, carried out by the DTA method in terms of the initial decomposition temperatures, shows that the chromium chelates are more stable than the manganese chelates.[80] The pyrolytic decomposition of the β-diketonates of manganese(III) in an unstable oxidation state is accompanied by the transition of the central metal ion from the trivalent to the divalent state and the liberation of the ligand. It has been suggested that this process proceeds via a radical mechanism.[80]

5. Thermal decomposition of Group VIII metal β-diketonates

The thermal stability of iron(III), cobalt(II), cobalt(III), and nickel(II) β-diketonates in the solid phase has been investigated by the DTA method.[80] The thermal stability of divalent metal acetylacetonates increases on passing from cobalt to nickel: $Co(acac)_2 < Ni(acac)_2$. The thermal stability of the chelate nickel acetylacetonate complexes with bulky alkyl substituents increases in the sequence

$$Ni(acac)_2 < Ni(dprm)_2 < Ni(dbtm)_2 < Ni(divm)_2 < Ni(dpm)_2 < Ni(dkm)_2 .$$

This agrees with the increase in the number of carbon atoms in the alkyl substituents. A similar sequence has been observed also for cobalt(II) chelates. The thermal stability of these chelates depends on the electron-donating effect of the alkyl group, which increases the basicity of the ligand oxygen atom and this increases the strength of the M–O bond. At room temperature, the alkyl derivatives of cobalt(II) and nickel(II) have a polymeric octahedral structure. An increase in temperature favours the formation of chelates with a square planar structure in the liquid phase. This tendency intensifies with increase in the bulk of the alkyl substituents owing to steric hindrance. Near the temperature of the onset of decomposition, the axial M–O bond in cobalt(II) and nickel(II) β-diketonates is weakened, whilst the equatorial bond is strengthened. If one considers the decomposition of metal β-diketonates with the dissociation of the equatorial M–O bond, then the β-diketonates with less bulky alkyl substituents, which favour the formation of a polymeric hexacoordinate structure, should be less stable.

The influence of the structure of the compound on the thermal properties of the nickel complexes $Ni(acac)_2$, $Ni(dpm)_2$, $Ni(acim)_2$, and $Ni(tfacim)_2$ has been traced.[72] The introduction of the trifluoromethyl group into the ligand instead of the methyl group increases the thermal stability of the nickel acetylacetonate complexes and decreases the stability of the imino-derivatives. The thermal decomposition of the β-diketonate derivatives of nickel proceeds via a mechanism involving an intramolecular rearrangement with evolution of the free β-diketones into the gas phase. A second decomposition path with formation of a ligand radical operates for the ketoiminate complexes, the contribution of this path increasing with temperature. In the presence of hydrogen, the main products of the decomposition of all the nickel(II) complexes investigated are the free ligands.

Iron(III) acetylacetonates and alkylacetylacetonates are more stable than the analogous cobalt(III) compounds. The thermal stability of cobalt(III) β-diketonates increases in the sequence

$$Co(acac)_3 < Co(dprm)_3 < Co(dbtm)_3 < Co(dibtm)_3 < Co(dkm)_3 < Co(divm)_3 < Co(dpm)_3 .$$

A similar trend has also been observed for iron(III) β-diketonates, which is consistent with the increasing bulk of the alkyl substituent. The pyrolytic decomposition of cobalt(III) and iron(III) (an unstable oxidation state of the metal) β-diketonates is accompanied by the transition of the central metal ion from the trivalent to the divalent state and the liberation of the ligand. It has been suggested that the decomposition of these compounds proceeds via a radical path.

The characteristic features of the thermal decomposition of palladium, iridium, rhodium, and platinum β-diketonates have

been examined.[49,80,85] The dependence of the thermal stability of the β-diketonates of these metals on the type of substituents in the ligand is weak.[49] One can only confirm fairly unambiguously the ability, frequently noted above, of the *tert*-butyl group to increase somewhat the thermal stability of the complex. It has been noted for palladium(II) β-diketonates that the unsubstituted acetylacetonates have a higher thermal stability than the acetylacetonates with bulky alkyl groups.[80] The palladium complexes are characterised by a larger contribution of the ring conjugation than other metal chelates by virtue of the π-bonding ($p\pi - d\pi$) nature of the M – O bond. The alkyl substituents in these ligands exhibit hyperconjugation, which disrupts the resonance in the ring-conjugated systems and this increases the contribution of π-bonding in the M – O bond. Problems concerning the influence of substituents in the *cis*- and *trans*-positions in rhodium complexes with asymmetric substitution in a planar chelate ring have been examined on the basis of IR and NMR spectroscopic data.[86,87] The inductive effect of the alkyl substituents on the free energy of the gas-phase oxidation of ruthenium β-diketonates has been studied: $Ru(acac)_3$, $Ru(dprm)_3$, $Ru(dbtm)_3$, $Ru(dibtm)_3$, and $Ru(divm)_3$.[88] It was shown that it varies from -200.6 kJ mol^{-1} for the complexes with methyl substituents to -150.5 kJ mol^{-1} for the complexes with *tert*-butyl substituents. The one-electron oxidation energy varies from -79.4 to -66.9 kJ mol^{-1} and is not correlated with the size of the alkyl substituent.[88] The replacement of one of the donor oxygen atoms by nitrogen in the palladium, iridium, rhodium, and platinum complexes leads to an increase in the gas-phase thermal stability of the complexes. The products of the thermal decomposition of these compounds contain considerable amounts of the noncoordinated ligand molecules.[85]

IV. Conclusion

The above analysis of the literature data concerning the influence of the nature of the metal and the substituents in the β-diketone on the volatility and thermal stability of metal β-diketonates shows that the volatility of the complexes depends to a large extent on the nature of the substituent in the β-diketone, while their thermal stability is determined both by the nature of the metal and that of the substituent in the ligand.

Unambiguous rules governing the variation of volatility and thermal stability as a function of the atomic number of the metal have not been established. The kinetic stability of the metal β-diketonate complexes $M(tfacac)_n$ [M = Ca, Sr or Ba ($n = 2$) and Al, Ga, or In ($n = 3$)] decreases successively in the thermal decomposition reaction with increase in the atomic number of the metal: Ca > Sr > Ba, Al > Ga > In.

The parallel variation of the volatility and thermal stability of the complexes $M(tfacac)_3$ (M = Al, Ga, In) has been observed. The volatility of these compounds diminishes with increase in the atomic number of the element, which is associated with the characteristic features of the electronic structures of these compounds.[89] For $M(tfacac)_2$ (M = Ca, Sr, Ba), the opposite variation of this kind is observed: the volatility of the complexes increases with increase in the atomic number of the metal. The variation of the thermal stability with increasing atomic number of the metal presented above does not hold for the complexes $M(tfacac)_3$ (M = Sr, Cr, Mn, Fe). Their thermal stability and volatility vary in the following series of metals respectively:

Cr > Sc > Fe > Mn;

Sc > V > Cr > Fe > Co.

A clear-cut dependence of the thermal stability on the atomic number also does not occur for the acetylacetonate complexes of monovalent, divalent, and trivalent metals. The thermal stability of the complexes is influenced not only by the energy of the M – O bond, determined by the nature of the metal, but also by the steric structure of the complexes, the possibility of the formation of oligomers, and the phase in which the thermal decomposition takes place. The rate of the gas-phase pyrolysis is determined by the type of reaction — homogeneous, heterogeneous, and homogeneous – heterogeneous — and also by the type of the rate-limiting stage.

In the study of the kinetics of the thermal decomposition of fluorine-substituted calcium, strontium, and barium β-diketonates, the decrease in the rate constant for the thermal decomposition of the chelate with increase in the surface area of the reactor can be clearly traced, whilst in other cases it is rarely manifested. This may be associated with the retardation of the rate-limiting stage of the thermal decomposition — the conversion of the bidentate ligand into a monodentate one with subsequent splitting off of the free ligand.

A general rule is the increase, frequently emphasised in the literature, in volatility and the decrease in the thermal stability of the metal β-diketonates after the introduction of the trifluoromethyl group into the ligand. On the other hand, the introduction of the *tert*-butyl group decreases the volatility of the complex and increases its thermal stability.

The influence of chain length of the alkyl substituents in the β-diketone on the thermal stability of the chelates is determined by the structure of the complexes. The thermal stability of the cobalt(II), cobalt(III), iron(III), and nickel(II) complexes, which have polymeric octahedral structure at room temperature, increases with increase in the length of the alkyl group. This is associated with the electron-donating effect of the alkyl group, which strengthens the M – O bond. Among the palladium(II) and copper(II) complexes, which have a square planar structure, the acetylacetonate derivatives are more stable than the derivatives with alkyl substituents. This has been attributed to the hyperconjugation effect of the alkyl substituents, which disrupts the resonance in the ring-conjugated system of the chelate. A common feature of the thermal decomposition of the metal β-diketonates investigated is its acceleration in oxygen and also the complex and homogeneous – heterogeneous character of the process.[90]

The principal aspects of the gas-phase thermal decomposition of metal β-diketonates have been examined.[91–95]

The characteristic features of the mechanism of the thermal decomposition of the chelates are determined by the presence of two reaction centres — the M – O bond and the γ-CH proton. It has been suggested that the first stage of the thermal decomposition of the β-diketonates is the opening of the ring and the conversion of the bidentate ligand into a monodentate one. This is followed by decomposition via different paths:

(a) intramolecular decomposition with formation of the free ligand and low molecular mass products:

$$ML_n \longrightarrow M_{solid} + mHL + \text{molecular products},$$

$n > m$;

(b) decomposition with homolytic dissociation of the metal – ligand bonds and the formation of the ligand radical L$^{\cdot}$:

$$ML_2 \longrightarrow ML^{\cdot} + L^{\cdot};$$

$$ML_2 \longrightarrow M_{solid} + 2L^{\cdot} \text{ (for bis-β-diketonates)};$$

(c) decomposition with far-reaching degradation of the organic component of the complex, which results in the formation of both low molecular mass and radical products:

$$ML_n \longrightarrow (MC_xO_y)_{solid} + \text{molecular and radical products},$$

$x, y \geqslant 0$;

(d) decomposition with dissociation of the C – O bonds and the formation of gaseous products having the general formula $R^1C(O)CH_kCR^2$ (where $k = 0, 2$):

$$ML_n \longrightarrow L_{(n-1)}M(OH)_m + mR^1C(O)CH_2R^2,$$

$k = 0$; $n > m$;

(e) decomposition with formation of a cyclic diketone as a result of the intramolecular interaction of the opened chelate rings of two ligands:

$$ML_n \longrightarrow L_{(n-2)}M(OH)_2 + (C_2H_5O)_2,$$

L = Hacac, $n = 3, 4$.

Depending on the type of terminal substituents in the ligand and on the nature of the central metal atom, a particular decomposition path operates. The thermal decomposition can proceed via one of the paths enumerated or simultaneously via several.

Path (a) is the main one in the thermal decomposition of the complexes $Cu(dpm)_2$, $Ru(acac)_2$, and $Zr(tfacac)_4$. Thermolysis of the vapours of palladium β-diketonates takes place simultaneously via paths (a) and (b). With increase in temperature, path (b) becomes dominant. Path (c) operates in the thermolysis of the vapours of the complexes $Ru(tfacac)_3$ and $Y(dpm)_3$. Both the free ligand and its radical are absent from the products of the thermal decomposition of the $Ru(tfacac)_3$ vapour, the main bulk of the latter comprising the CO, CO_2, H_2O, and HF molecules and the $CF_3^{\cdot}$ radical. Complexes for which the thermal stability is higher than that of the ligand decompose via path (c).[95] The threshold decomposition temperature of these complexes is 763 ± 283 K.

The thermolysis of $Ba(dpm)_2$ takes place simultaneously via paths (a), (c), and (d) and includes in addition the depolymerisation reaction of the molecules and the oligomeric composition of the gas phase does not then correspond to the composition of the condensed phase. Thus the complex exists in the form $Ba_4(dpm)_3$ in the condensed phase, whilst in the gas phase it is present as a mixture of trimers, dimers, and monomers.

The thermal decomposition of the complexes $Al(acac)_3$, $Sc(acac)_3$, and $Hf(acac)_3$ proceeds simultaneously via paths (a), (c), and (d) near the threshold temperature, whereas the thermal decomposition of $Mg(acac)_2$ takes place via paths (a) and (c).[95]

A scheme for the thermal decomposition of the $Al(acac)_3$ and $Sc(acac)_3$ vapours is presented below (the postulated species are indicated in square brackets).

$$ML_3 \xrightarrow{\Delta T_1} HL + MeC(O)Me + CH_2CO + \text{solid phase} \quad (a)$$

$$ML_3 \xrightarrow{\Delta T_2} MeC{\equiv}CC(O)Me + [L_2M(OH)] \quad (c)$$

$$ML_3 \xrightarrow{\Delta T_3} MeC{=}CHC(O)CH_2Me{=}CHC(O)CH_2 + [LM(OH)_2] \quad (e)$$

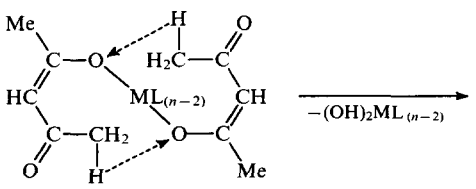
$$\downarrow$$

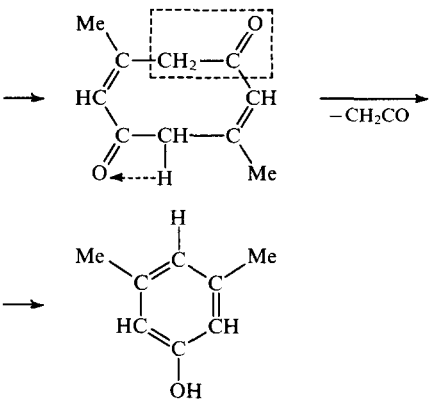
$$MeC_6H_3OH + CH_2CO$$

M = Sc, Al; L = $C_5H_7O_2$.

Each of the thermal decomposition paths operates in a particular temperature range ΔT.

The path leading to the formation of the $(C_5H_6O)_2$ species as a result of the cyclic dimerisation of two ligands coordinated as monodentate species on dissociation of the carbon–oxygen (enolic) bonds with migration of a hydrogen atom from the methyl group to the enolic oxygen atom of a neighbouring ligand has been demonstrated. The cyclic diketone formed eliminates ketene CH_2CO and is converted into the more stable 3,5-dimethylphenol.





On the basis of this scheme, one can postulate a path leading to the formation of metal oxides in the condensed phase.

$$2ML(OH)_2 \longrightarrow M_2O_{3(\text{solid})} + 2C_2H_6O_{(\text{gas})} + 3H_2O_{(\text{gas})},$$

M = Al, Sc;

$$ML_2(OH)_2 \longrightarrow MO_{2(\text{solid})} + 2C_5H_6O_{(\text{gas})} + 2H_2O_{(\text{gas})},$$

M = Hf, L = $C_5H_7O_2$.

The existence of path (c) for aluminium and scandium acetylacetonates constitutes experimental confirmation that the thermal decomposition is preceded by a stage involving the thermal excitation of the molecules, in which the coordination of the ligands changes from bidentate to monodentate (in terms of the isolated molecules approximation).[95]

Paths (d) and (e) are characteristic of thermal decomposition processes leading to the formation of oxides in the condensed phase as a result of intramolecular reactions.

In virtually all cases, the presence of oxygen diminishes the threshold decomposition temperature of the β-diketonates and increases the rate of reaction.[90, 95] Under these conditions, there is an appreciable increase in the fraction of simple molecular thermolysis products such as CO_2, CO, and H_2O. The influence of oxygen on the thermal decomposition process can be exerted in two ways.[95] If the reaction proceeds via path (a) with formation of the free ligand, then oxygen participates quantitatively in the reaction at the stage involving the oxidation of the free ligand. As a rule, this occurs at a higher temperature than the temperature of the onset of decomposition of the complex. On the other hand, if the thermal decomposition takes place via path (b) or (d), virtually all the gaseous products are oxidised immediately after the threshold temperature has been exceeded. Paths (c) and (e) do not then operate in the presence of oxygen. A similar situation is observed also on path (c).

The influence of hydrogen on the thermal decomposition of the metal β-diketonate vapours depends on the nature of the metal and the ligand.[95] In the case of the $Ru(acac)_3$, $Zr(tfacac)_4$, $Sc(acac)_3$, and $Al(acac)_3$ vapours, the threshold temperature increases by 283–353 K and the rate of thermal decomposition falls, whereas the threshold temperature decreases for $Ru(tfacac)_3$. Such different effects of hydrogen on the kinetics of the thermal decomposition process can be accounted for by the specific interaction of the hydrogen adsorbed on the surface with the molecules of the complex. Hydrogen does not influence appreciably the composition of the gaseous products and the path followed in the thermal decomposition of metal β-diketonates.

Thus the kinetics, the thermal decomposition path, and the composition of the condensed phase are determined by the nature of the metal and the ligand in the complex and by the decomposition temperature.

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