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Correlation between thermal and mass spectral techniques for the characterization of allenylidene and carbene complexes

Gehad G. Mohamed[a,*], Normen Szesni[b], Helmut Fischer[b]

[a] *Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt*
[b] *Fachbereich Chemie, Universität Konstanz, Fach M727, D-78457 Konstanz, Germany*

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Abstract

The fragmentation pathways of allenylidene and carbene complexes have been studied using FAB mass spectrometry in comparison with thermal analyses (TGA, DrTG and DTA). Both the decomposition modes are investigated and the possible fragmentation pathways are suggested. The use of mass and thermal analyses (TGA and DTA) in the analyses of allenylidene and carbene complexes allowed the characterization of the fragmentation pathways in MS. The major pathway includes successive loss of carbon monoxide followed by fragmentation of the organic part of the allenylidene or carbene molecules. This is also confirmed by thermogravimetric analysis (TGA) where the first step involves the loss of carbon monoxide followed by the organic ligand. The nature of each step; exothermic or endothermic, is also studied using DTA technique. The kinetic parameters of the thermal decomposition are also studied using the Coates-Redfern method.

Keywords: Allenylidene and carbene complexes; Thermal analyses; Mass spectrometry

1. Introduction

A large number of carbene complexes have been prepared and their properties and reactivity had been studied in detail [1]. Carbene complexes have found broad application in synthesis and catalysis and have evolved into one of the most powerful tools in organic and organometallic chemistry [2]. Unsaturated carbene complexes like allenylidene complexes, $[L_nM{=}C{=}C{=}C(R^1)R^2]$, have increasingly attracted interest in recent years [3]. Experimental and theoretical studies confirm their great potential for C–C and C–X bond formation [4]. In addition, allenylidene complexes exhibit interesting physico-chemical properties that make them potentially useful as one-dimensional wires [5] and for opto-electronic devices [6]. Most studies on the reactivity of alleneylidene complexes carried out until now were performed with non-heteroatom substituted complexes derived from 1,1-disubstituted propargylic alcohol bearing either alkyl or aryl groups at the terminal carbon atom [3a]. These complexes were readily available for a broad range of transition metals [7]. A new route to *N*-stabilized allenylidene complexes of Cr and W using propynoic acid amides, C-ethinylimines or ethinylpyridine as precursors has been introduced by Fischer et al. [3e,8].

A number of studies confirm the great potential of vinylidene and allenylidene complexes for C–C and C–X bond formation [9]. In contrast to diaryl- and dialkylallenylidene complexes, the number of heteroatom substituted allenylidene complexes was rather scarce although two of the very first allenylidene complexes to be synthesized carried a dimethylamino substituent at the terminal carbon atom [10]. These complexes; $(CO)_5M{=}C{=}C{=}C(NR'_2)(R'')$, were obtained by Fischer et al. from alkenyl(ethoxy) carbene complexes by Lewis acid induced alcohol elimination ($M = Cr$, W; $R' = Me$; $R'' = Ph$) [10]. Later on this method had been extended to the synthesis of some other amino stabilized allenylidene complexes [11]. Alkynyl carbene complexes had also turned out to be useful precursors for the preparation of monoamino allenylidene complexes [12]. The bonding situation in carbene and allenylidene complexes strongly depends on the substitution pattern. The same applies to the reactivity of these compounds.

The aim of this study is therefore to use the thermal analyses techniques (TGA, DrTG and DTA) to further characterize some allenylidene and carbene complexes and to study their thermal behaviour. A correlation between the thermal and the mass fragmentation pattern as well as schemes for the thermal

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* Corresponding author.
E-mail address: ggenidy@hotmail.com (G.G. Mohamed).

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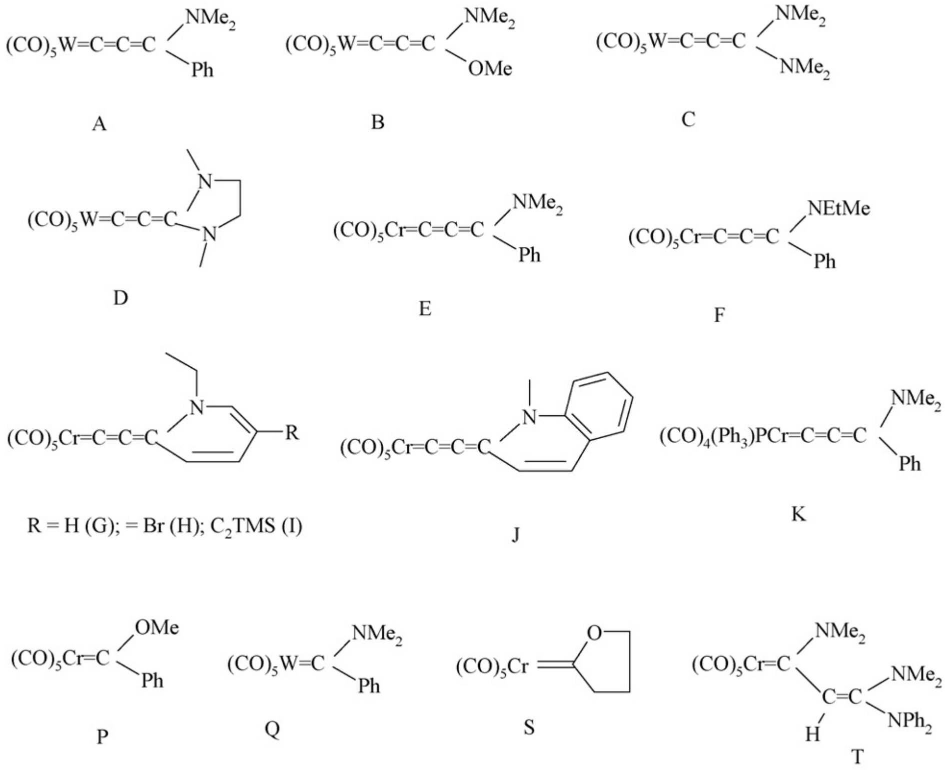

Fig. 1. Structure of complexes A–K, P, Q, S and T.

fragmentation will be proposed. Also the kinetic parameters for the steps of decomposition will be calculated using the Coats-Redfern method [13].

2. Experimental

2.1. General

All operations were performed in an inert gas atmosphere using standard Schlenk techniques. Solvents were dried by distillation from $CaH_2(CH_2Cl_2)$, $LiAlH_4$ (pentane, Et_2O) and sodium (THF). The silica gel used for chromatography (Baker, silica gel for flash chromatography) was argon saturated. The reported yields refer to analytically pure substances and are not optimized. Instrumentation: The thermogravimetric analysis (TGA and DrTG) and differential thermal analysis (DTA) were carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of 10 °C min^{-1} using Shimadzu TGA-50H and DTA-50H thermal analyzers, respectively. MS: Finnigan MAT 312. Elemental analysis: Heraeus CHN-O-Rapid. All transition metal complexes were prepared as reported in the literature [1,8]. The structures of the prepared complexes under study are given in Fig. 1.

3. Results and discussion

The transition metal allenylidene complexes were prepared by introduction of a preformed C3 fragment into the coordination sphere of the metal as reported earlier [8]. Thus, amino substituted allenylidene complexes A, B and E–J were prepared by the reaction of the appropriate deprotonated alkynes with the solvent complexes $\{(CO)_5M[THF]; M = Cr \text{ and } W\}$and subsequent alkylation with suitable alkylating agent [8a,b]. Compound C was synthesized via the reaction of deprotonated 1,1,1-tris(dimethylamino)propyne with $(CO)_5W[THF]$ and subsequent silica induced elimination of dimethylamide [8c]. The reaction of the allenylidene complex $(CO)_5W{=}C{=}C{=}C(OMe)_2$ with *N*,*N*′-dimethylamino ethylene diamine delivers complex D [8d]. The tetracarbonyl allenylidene complex was obtained by the photochemical reaction of complex A with triphenylphosphine [8e]. The carbene complexes P–T were prepared by the established methods published in the literature [1,8f,g]. The complexes were characterized by spectroscopic (IR, ^1H and ^{13}C NMR and mass spectra) and elemental analyses. These data are in good agreement with those in the literature.

3.1. Thermal analyses (TGA, DrTG and DTA)

The thermal decomposition of the allenylidene and carbene complexes is used to obtain information about their properties as well as about the nature of the intermediates and final products. The samples were measured in the temperature range from ambient temperature up to 1200 °C. The calculated and estimated weight losses are given in Table 1 together with the DTA data. Figs. 2–4 show the TGA, DrTG and DTA curves of complexes A, C, E, G, J, P and S.

The TGA curves of allenylidene complexes A–D, refer to three to five stages of mass losses at the temperature range 90–1200 °C. These stages involved mass losses of 23.98% (found 24.50%), 32.18% (found 33.00%), 24.99% (found

Table 1
Thermal analyses (TGA, DrTG and DTA) data of allenylidene and carbene complexes

Complex	TG range (°C)	DrTG$_{max}$ (°C)	*n**	Estimated (Calculated) (%)		Assignment	Metallic residue	DTA (°C)
				Mass loss	Total mass loss			
(A)	90–150	140	1	24.50 (23.98)		Loss of 4CO	WO	140(+), 210(+), 450(−), 570(+), 627(−), 754(+), 774(−), 882(+), 920(−), 1000(−).
	150–1200	220, 330, 881	4	33.79 (33.18)	58.29 (57.16)	Loss of $C_{11}H_9N$		
(B)	100–220	156, 181	2	33.00 (32.18)		Loss of 5CO	WO	158(+), 187(−), 200(+), 410(−), 520(+), 600(−), 700(−), 880(−), 899(+), 910(−), 960(+).
	220–1000	230, 898	3	22.13 (21.84)	55.13 (54.02)	Loss of C_6H_9N		
(C)	90–210	196	1	25.73 (24.99)		Loss of 4CO	WO	147(+), 180(−), 200(+), 320(−), 420(+), 510(−), 840(+), 900(−), 1100(+).
	210–1200	400, 900	2	31.00 (30.35)	56.73 (55.34)	Loss of $C_8H_{12}N_2$		
(D)	80–300	226	1	25.89 (25.11)		Loss of 4CO	WO	100(+), 229(+), 495(+), 530(−), 873(+), 900(−), 1090(+)
	300–1200	350, 871, 1050	3	30.88 (30.04)	56.77 (55.15)	Loss of $C_8H_{10}N_2$		
(E)	90–150	132	1	16.38 (16.03)		Loss of 2CO	CrO_3	125(+), 134(−), 227(+), 350(−), 430(+), 560(−), 970(+), 1050(−)
	150–1200	201, 241, 350	5	54.36 (54.79)	70.74 (71.00)	Loss of $C_{14}H_{11}N$		
(F)	80–200	107, 150, 167	3	30.47 (30.83)		Loss of 4CO	CrO	94(+), 115(−), 150(+), 167(+), 350(+), 460(+), 550(−), 940(−), 1070(−)
	200–1200	208, 430	4	49.11 (50.10)	79.58 (80.93)	Loss of $C_{13}H_{13}N$		
(G)	80–200	160, 180	2	26.61 (25.99)		Loss of 3CO	CrO_2	70(+), 130(+), 170(−), 205(+), 390(−), 470(+), 580(−), 670(+), 730(−), 925(+), 960(−), 1030(−).
	200–1200	300, 600, 850	4	45.20 (44.86)	71.81 (70.85)	Loss of $C_{10}H_{11}N$		
(H)	100–220	152	1	32.14 (32.83)		Loss of 3CO and C_4	CrO_2	153(−), 200(+), 450(−), 510(+), 580(−), 610(+).
	220–1200	500	3	43.60 (43.27)	75.74 (76.10)	Loss of C_6H_8BrN		
(I)	120–200	165	1	15.74 (15.26)		Loss of CO and C_3.	CrO_2+ SiO_2	114(+), 171(−), 230(−), 390(−), 600(−), 930(+), 1100(−).
	200–1200	260, 930	3	50.27 (50.31)	66.01 (65.57)	Loss of $C_{15}H_{17}N$		
(J)	100–220	170	1	31.24 (31.18)		Loss of 4CO	CrO	130(+), 150(−), 170(+), 171(−), 200(−), 320(+), 480(−), 530(+), 580(−), 760(−), 930(+), 1030(−)
	220–1200	360, 700, 910	4	49.49 (49.82)	80.73 (81.00)	Loss of $C_{13}H_9N$		
(K)	50–180	151	1	9.28 (9.58)		Loss of 2CO	CrO_2	110(+), 163(+), 192(−), 290(+), 341(+), 952(+)
	180–300	293	1	31.25 (31.02)		Loss of $C_{13}H_{11}N$		
	300–1200	339, 953	3	45.41 (44.38)	85.94 (84.98)	Loss of PPh_3		
(P)	50–210	194	1	50.15 (49.65)		Loss of 5CO and CH_3	CrO	49(+), 197(−), 220(+), 320(−), 570(+) 650(+), 960(+), 1050(−)
	210–1000	260, 580	2	28.91 (28.51)	79.06 (78.16)	Loss of C_7H_5		
(Q)	50–620	266	2		57.12 (56.20)	Loss of 4CO and $C_{10}H_{11}N$	WO	103(+), 250(−), 268(+), 360(−), 460(−) 550(+), 607(−)
(S)	80–250	159, 172	2		74.31 (74.01)	Loss of 5CO and C_4H_6	CrO	157(−), 165(+), 170(−), 185(+).
(T)	30–150	105	1	5.90 (5.77)		Loss of CO	CrO_2	110(−), 150(+), 205(−), 390(−), 520(−) 580(+), 630(−), 950(+), 1100(−)
	150–250	190	1	27.19 (26.78)		Loss of 2CO and $C_4H_{12}N$		
	250–1100	350, 850	2	46.70 (47.59)	79.79 (80.14)	Loss of $C_{16}H_{11}N_2$		

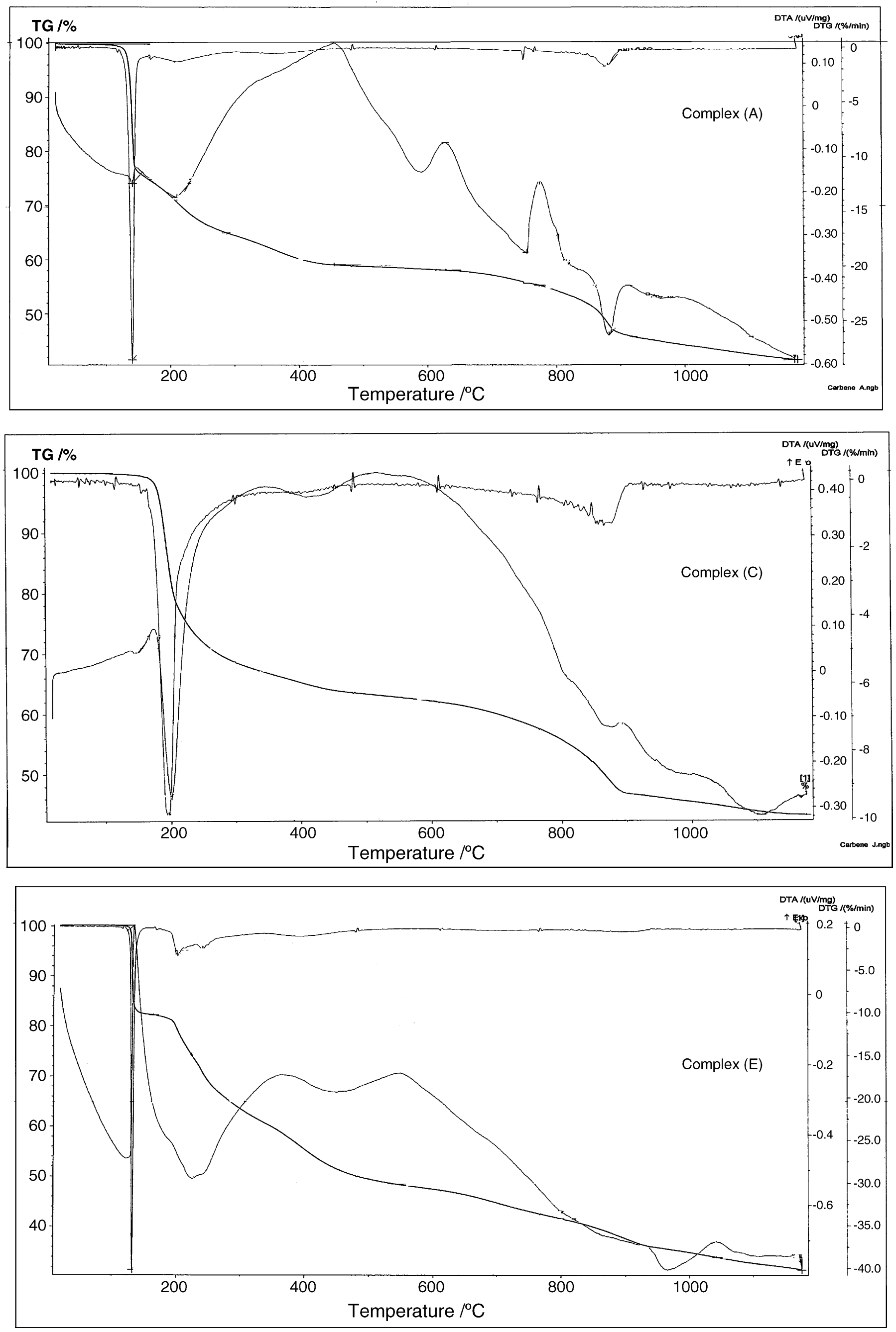

Fig. 2. TGA, DrTG and DTA curves of complexes A, C and E.

25.73%) and 25.11% (found 25.89%) for the first (complexes A, C, D) and first and second steps (complex B) of decomposition for complexes A, B, C and D, respectively. These mass losses may be due to the successive losses of CO at the given temperature ranges (Table 1), respectively. The DTA curves show one endothermic peak at 140 °C for complex A; two endothermic peaks at 158 and 200, and 147 and 200 °C and one exothermic peak at 187 and 180 °C for complex B and C, respectively. The activation energy of this decomposition step due to the loss of CO ligands is 43.90, 40.63–68.22, 51.95 and 43.15 kJ mol^{-1} for complexes A, B, C and D, respectively. The remaining steps of decomposition (4, 3, 2 and 3 steps for complexes A, B, C and D, respectively) within the temperature range 150–1200, 220–1000, 210–1200 and 300–1200 °C correspond to the loss of organic part of the ligand leaving WO as a residue with a mass loss of 33.79% (calcd. 33.18%), 22.13% (calcd. 21.84%), 31.00% (calcd. 30.35%), and 30.88% (calcd. 30.04%), for complexes A, B, C and D, respectively. The energies of activation were 72.17–195.7, 102.2–185.7, 90.05–114.3 and 65.92–162.4 kJ mol^{-1} for the remaining steps for complexes A, B, C and D, respectively. According to the DTA data listed in Table 1, the loss of the organic part as gases shows endothermic and exothermic peaks within the temperature range of decomposition. The overall weight loss amounts to 58.29% (calcd.

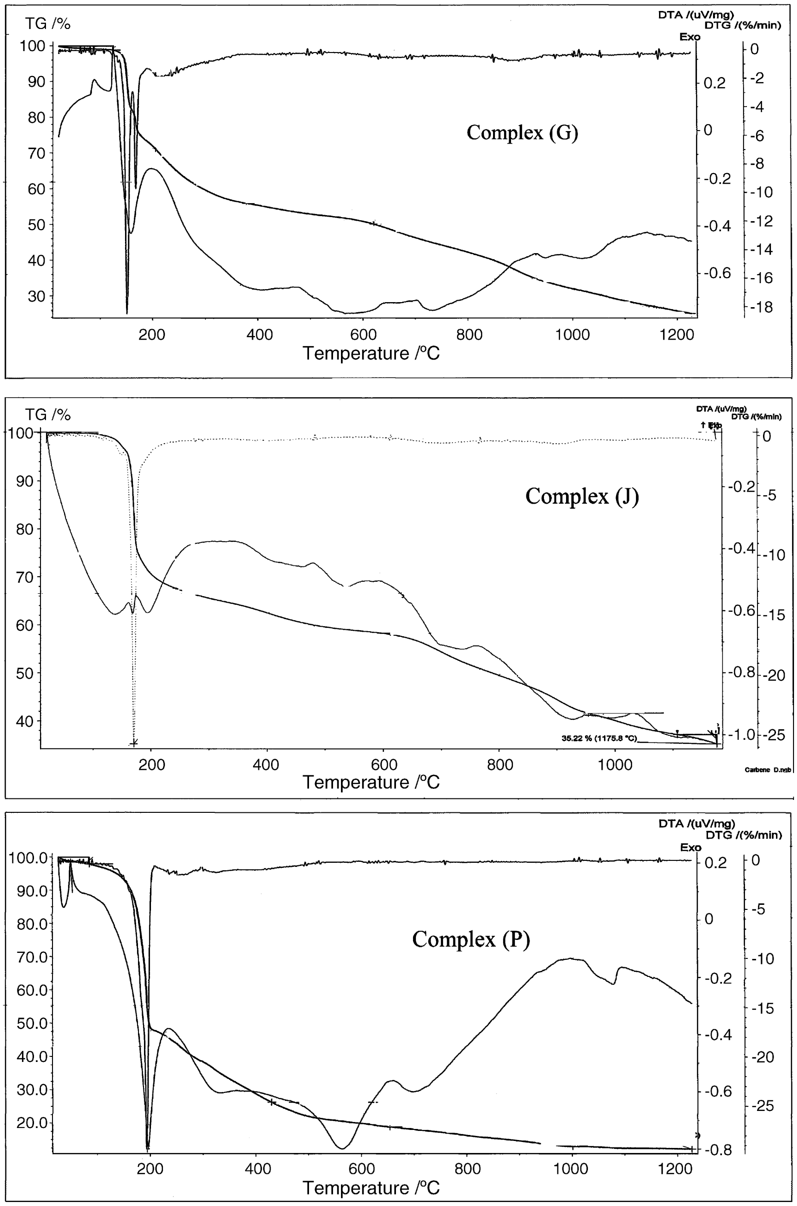

Fig. 3. TGA, DrTG and DTA curves of complexes G, J and P.

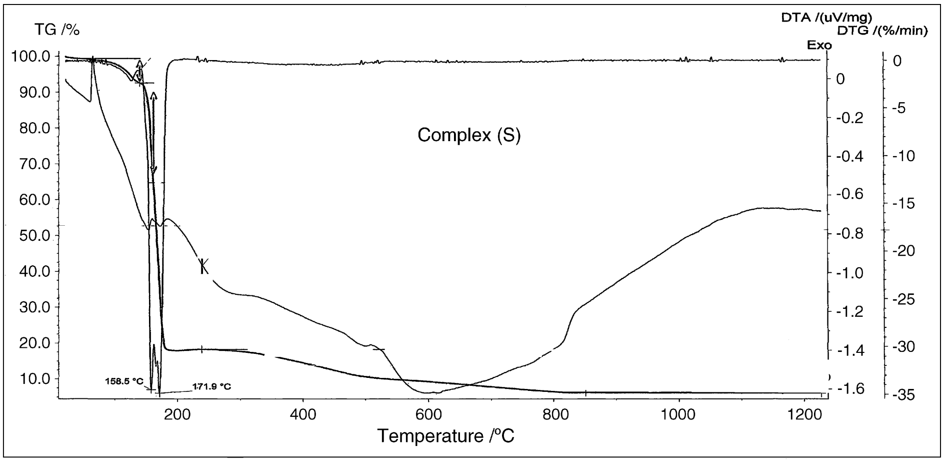

Fig. 4. TGA, DrTG and DTA curve of complex S.

Table 2
Thermodynamic data of the thermal decomposition of allenylidene and carbene complexes

Complex	Decomposition temperature (°C)	E^*(kJ mol^{-1})	A (s^{-1})	ΔS^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
(A)	90–150	43.90	1.35×10^6	−33.45	70.55	45.93
	150–275	72.17	4.03×10^9	−62.92	96.86	86.62
	275–430	115.2	1.67×10^8	−99.54	117.4	99.63
	430–910	146.2	5.04×10^{11}	−108.7	146.2	142.2
	910–1200	195.7	6.23×10^7	−155.4	176.1	172.2
(B)	100–150	40.63	2.07×10^{10}	−46.55	78.15	84.77
	150–220	68.22	3.17×10^7	−75.67	99.66	64.53
	220–630	102.2	5.09×10^7	−107.4	132.4	122.4
	630–910	126.4	4.12×10^9	−142.3	173.2	154.2
	910–1000	185.7	7.94×10^{11}	−173.8	202.2	165.3
(C)	90–210	51.95	2.73×10^{10}	−39.85	50.83	48.06
	210–600	90.05	1.32×10^9	−68.95	99.99	97.44
	600–1200	114.3	4.69×10^{11}	−97.85	153.4	145.2
(D)	80–300	43.15	3.55×10^8	−63.28	87.96	78.99
	300–520	65.92	4.97×10^7	−102.3	106.1	99.67
	520–800	107.3	6.49×10^9	−142.1	166.2	143.9
	800–1200	162.4	5.28×10^{11}	−173.2	195.1	177.2
(E)	90–150	33.96	2.13×10^9	−39.80	55.93	78.26
	150–270	67.15	3.09×10^{10}	−89.45	99.86	107.3
	270–570	99.85	2.80×10^7	−118.7	136.1	155.1
	570–780	135.2	7.24×10^{11}	−137.4	169.6	195.2
	780–1000	165.3	4.52×10^9	−165.9	199.5	223.3
	1000–1200	201.5	6.54×10^8	−211.3	232.2	254.7
(F)	80–130	40.89	2.95×10^9	−56.44	78.06	74.62
	130–170	70.68	4.19×10^7	−85.19	109.9	106.5
	170–200	112.9	5.65×10^{10}	−106.7	130.5	155.6
	200–300	156.3	4.25×10^{11}	−136.4	168.2	199.4
	300–530	189.7	6.09×10^8	−167.2	200.1	234.2
	530–940	211.3	7.65×10^9	−196.8	235.4	267.4
	940–1200	194.2	3.95×10^{10}	−225.6	267.2	290.1
(G)	80–140	50.33	1.87×10^9	−29.78	50.13	68.16
	140–200	70.45	4.47×10^{10}	−69.95	105.6	117.3
	200–370	97.87	5.23×10^7	−80.66	156.8	165.3
	370–600	125.3	6.44×10^{12}	−117.3	200.7	215.2
	600–920	165.7	3.25×10^{10}	−147.2	229.3	240.1
	920–1200	198.7	5.39×10^8	−167.9	249.8	259.6
(H)	100–220	34.69	3.95×10^{10}	−50.44	68.16	74.62
	220–310	65.23	4.69×10^9	−80.19	109.8	126.2
	310–600	92.67	5.15×10^7	−116.7	130.5	145.6
	600–1200	112.3	3.66×10^8	−132.5	145.8	176.6
(I)	120–200	53.24	2.37×10^9	−32.65	55.65	65.13
	200–370	72.97	1.84×10^{10}	−62.42	86.63	96.22
	370–720	105.4	2.76×10^{11}	−92.54	107.7	119.3
	720–1200	149.2	5.80×10^{13}	−138.2	166.3	172.5
(J)	100–220	24.78	3.47×10^{10}	−26.55	38.45	44.77
	220–580	48.94	3.17×10^9	−55.67	70.06	84.53
	580–800	82.73	4.99×10^8	−87.22	112.7	126.4
	800–950	109.6	5.82×10^{10}	−132.6	153.7	174.2
	950–1200	135.6	6.04×10^{12}	−163.7	198.2	265.3
(K)	50–180	39.50	1.08×10^{10}	−29.85	42.73	58.66
	180–300	67.15	4.22×10^9	−58.95	75.53	97.55
	300–410	89.89	4.29×10^8	−87.85	103.6	125.4
	410–820	125.4	3.56×10^{10}	−117.7	153.2	162.3
	820–1200	178.7	6.28×10^{12}	−134.3	203.6	212.1
	50–210	33.45	3.05×10^6	−73.78	67.96	58.69
(P)	210–660	75.02	5.27×10^{11}	−98.77	86.15	90.67
	660–1000	117.7	4.49×10^9	−132.3	76.87	103.4

Table 2 (*Continued*)

Complex	Decomposition temperature (°C)	E^*(kJ mol^{-1})	A (s^{-1})	ΔS^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
(Q)	50–280	43.56	2.13×10^{9}	−39.78	55.93	68.56
	280–620	87.95	4.39×10^{11}	−69.95	105.6	117.3
(S)	80–160	27.69	3.25×10^{10}	−46.84	58.26	64.62
	160–250	85.93	5.29×10^{9}	−75.99	99.78	101.2
(T)	30–150	33.96	3.13×10^{10}	−29.98	45.93	58.06
	150–250	67.95	2.69×10^{11}	−61.95	90.96	107.5
	250–450	104.2	4.56×10^{9}	−90.66	126.1	145.4
	450–1100	145.2	6.64×10^{10}	−117.1	133.7	185.7

57.16%), 55.13% (calcd. 54.02%), 56.73% (calcd. 55.34%) and 56.77% (calcd. 55.15%), for complexes A, B, C and D, respectively.

The TGA curves of the Cr-allenylidene complexes E–K, show four to seven stages of decomposition within the temperature range of 50–1200 °C (Table 1). The first stage at 50–220 °C corresponds to the loss of CO ligands with an estimated weight loss of 16.38% (calcd. 16.03%), 30.47% (calcd. 30.83%), 26.61% (calcd. 25.99%), 32.14% (calcd. 32.83%), 15.74% (calcd. 15.26%), 31.24% (calcd. 31.18%) and 9.28% (calcd. 9.58%) for complexes E, F, G, H, I, J and K, respectively. The activation energy is 33.96, 40.89–112.9, 50.33–70.45, 34.69, 53.24, 24.78 and 39.5 kJ mol^{-1} for complexes E, F, G, H, I, J and K, respectively. The DTA curves show an endothermic and exothermic peaks within the temperature of decomposition as given in Table 1. While the subsequent (2nd to 7th) stages involve the loss of the organic ligand as CO_2, NO_2, NO or H_2O gases. The energies of activation are 67.15–201.5, 156.3–211.3, 97.87–198.7, 65.23–112.3, 72.97–149.2, 48.94–135.6 and 67.15–178.7 kJ mol^{-1} for the second to seventh steps of decomposition of the complexes E, F, G, H, I, J and K, respectively. These processes of decomposition are accompanied by many endothermic and exothermic peaks within the temperature range mentioned in Table 1. The overall weight loss amounts to 70.74% (calcd. 71.00%), 79.58% (calcd. 80.93%), 71.81% (calcd. 70.85%), 75.74% (calcd. 76.10%), 66.01% (calcd. 65.57%), 80.73% (calcd. 81.00%) and 85.94% (calcd. 84.98%) for the complexes E, F, G, H, I, J and K, respectively.

On the other hand, the Cr-carbene complexes (P, S and T) and W-carbene complex (Q) exhibit two to four decomposition steps. The complexes Q and S decomposed in two successive steps within the temperature range 50–620 and 80–250 °C with a mass loss of 57.12% (calcd. 56.20%) and 74.31% (calcd. 74.01%), respectively, as the result of the loss of CO and the organic ligands leaving a metal oxide residue. As shown in Table 1, the mass losses for the decomposition steps of complexes P and T amount to 79.06% (calcd. 78.16%) and 79.79% (calcd. 80.14%), respectively. They correspond to the removal of CO and organic ligands leaving CrO or CrO_2 as a residue with energies of activation that amount to 33.45–117.7 and 33.96–145.2 kJ mol^{-1} for the complexes P and T, respectively.

It is clear from the TGA data listed in Table 1 that the complexes lose CO molecules in the first step. This result agrees well with that of the mass spectra where the loss of CO molecules also may occurs in successive steps. Therefore, both techniques provide an excellent correlation between their fragmentation patterns.

3.2. Kinetic studies

The activation parameters of the decomposition processes of allenylidene and carbene complexes, namely, activation energy (E^*), enthalpy (ΔH^*), entropy (ΔS^*) and Gibbs free activation energy change of the decomposition (ΔG^*) were evaluated graphically by employing the Coats-Redfern relation [13]:

$$\log\left[\frac{\log\{W_\mathrm{f}/(W_\mathrm{f}-W)\}}{T^2}\right] = \log\left[\frac{AR}{\theta E^*}\left(1-\frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303\,RT} \qquad (1)$$

where W_f is the mass loss at the completion of the reaction, W is the mass loss up to temperature T; R is the gas constant, E^* is the activation energy in kJ mol^{-1}, θ is the heating rate and $(1-(2\mathrm{RT}/E^*)) \cong 1$. A plot of the left-hand side of Eq. (1) against $1/T$ gives a slope from which E^* was calculated and A (Arrhenius factor) was determined from the intercept. The entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and the free energy change of activation (ΔG^*) were calculated using the following equations:

$$\Delta S^* = 2.303\left[\log\left(\frac{Ah}{kT}\right)\right]R \qquad (2)$$

$$\Delta H^* = E^* - RT \qquad (3)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (4)$$

The data are summarized in Table 2. The activation energies of decomposition were found to be in the range 25.97–254.3 kJ mol^{-1}. The high values of the activation energies reflect the thermal stability of the complexes. The negative values of S^* indicate that the reactions are slow in nature, hence assisted by the wide range of decomposition temperature [14].

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References

[1] (a) E.O. Fischer, A. Maasböl, Angew. Chem. 76 (1964) 645;
(b) E.O. Fischer, A. Maasböl, Angew. Chem., Int. Ed. Engl. 3 (1964) 580.

[2] (a) K.H. Dötz, Angew. Chem. 96 (1984) 573;
(b) W.D. Wulff, in: B.M. Trost, I. Fleming, L.A. Paquette (Eds.), Comprehensive Organic Synthesis, vol. 5, Pergamon Press, Oxford, 1991;
(c) L.S. Hegedus, Tetrahedron 53 (1997) 4105;
(d) K.H. Dötz, J. Pfeiffer, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, vol. 1, Wiley-VCH, Weinheim, 1998;
(e) F. Zaragoza-Dorwald, Metal Carbenes in Organic Synthesis, Wiley-VCH, Weinheim, 1999;
(f) A. de Meijere, H. Schirmer, M. Duetsch, Angew. Chem., Int. Ed. Engl. 112 (2000) 4124;
(g) A. de Meijere, H. Schirmer, M. Duetsch, Angew. Chem., Int. Ed. Engl. 39 (2000) 22.

[3] (a) V. Cadierno, M.P. Gamasa, J. Gimeno, Eur. J. Inorg. Chem. (2001) 571;
(b) R.F. Winter, S. Zalis, Coord. Chem. Rev. 248 (2004) 1565;
(c) S. Rigaut, D. Touchard, P.H. Dixneuf, Coord. Chem. Rev. 248 (2004) 1585;
(d) V. Cadierno, M.P. Gamasa, J. Gimeno, Coord. Chem. Rev. 248 (2004) 1627;
(e) H. Fischer, N. Szesni, Coord. Chem. Rev. 248 (2004) 1659;
(f) V. Cadierno, S. Conejero, M.P. Gamasa, J. Gimeno, Organometallics 20 (2001) 3175;
(g) S. Conejero, J. Diez, M.P. Gamasa, J. Gimeno, S. Garcia-Granda, Angew. Chem. 114 (2002) 3589;
(h) S. Conejero, J. Diez, M.P. Gamasa, J. Gimeno, S. Garcia-Granda, Angew. Chem., Int. Ed. 41 (2002) 3439;
(i) V. Cadierno, S. Conejero, J. Diez, M.P. Gamasa, J. Gimeno, S.G. Granda, Chem. Commun. (2003) 840;
(j) J. Diez, M.P. Gamasa, J. Gimeno, E. Lastra, A. Villar, Organometallics 24 (2005) 1410;
(k) N. Mantovani, L. Marvelli, R. Rossi, V. Bertolasi, C. Bianchini, I. de Los Rios, M. Peruzzini, Organometallics 21 (2002) 2382;
(l) M.R. Buil, M.A. Esteruelas, A.M. Lopez, E. Onate, Organometallics 22 (2003) 5274;
(m) E. Bustello, M.J. Tenorio, K. Mereiter, M.C. Puerta, P. Valerga, Organometallics 21 (2002) 1903;
(n) M.J. Tenorio, M.D. Palacios, M.C. Puerta, P. Valerga, J. Organomet. Chem. 689 (2004) 2776;
(o) S. Rigaut, J. Massue, D. Touchard, J.L. Fillaut, S. Golhen, P.H. Dixneuf, Angew. Chem. 114 (2002) 2776;
(p) S. Rigaut, J. Massue, D. Touchard, J.L. Fillaut, S. Golhen, P.H. Dixneuf, Angew. Chem. 114 (2002) 4695;
(q) B.C. Gaspar, M. Laubender, H. Werner, J. Organomet. Chem. 684 (2003) 144;
(r) H. Werner, R. Wiedemann, M. Laubender, B. Windmüller, P. Steiner, O. Gevert, J. Wolf, J. Am. Chem. Soc. 124 (2002) 6966.

[4] (a) M. Bassetti, F. Centola, D. Semeril, C. Bruneau, P.H. Dixneuf, Organometallics 22 (2003) 4459;
(b) I. Ozdemir, E. Cetinkaya, B. Cetinkaya, M. Cicek, D. Semeril, C. Bruneau, P.H. Dixneuf, Eur. J. Inorg. Chem. (2004) 418;
(c) R. Castarlenas, D. Semeril, A.F. Noels, A. Demonceau, P.H. Dixneuf, J. Organomet. Chem. 663 (2002) 235;
(d) Y. Nishibayashi, Y. Inada, M. Hidai, S. Uemura, J. Am. Chem. Soc. 124 (2002) 7900;
(e) Y. Nishibayashi, H. Imajima, G. Onodera, Y. Ishii, M. Hidai, S. Uemura, Organometallics 23 (2004) 26;
(f) R. Akiyama, S. Kobayashi, Angew. Chem. 114 (2002) 2714;
(g) T. Suzuki, M. Tokunaga, Y. Wakatsuki, Tetrahedron Lett. 43 (2002) 7531.

[5] (a) U.H.F. Bunz, Angew. Chem., Int. Ed. Engl. 35 (1996) 969;
(b) F. Paul, C. Lapinte, Coord. Chem. Rev. 178–180 (1998) 431.

[6] (a) S. Barlow, D. O'Hare, Chem. Rev. 97 (1997) 637;
(b) S.R. Marder, Inorganic Materials, Wiley, Chichester, 1996.

[7] J.P. Selegue, Organometallics 1 (1982) 217.

[8] (a) H. Fischer, N. Szesni, G. Roth, N. Burzlaff, B. Weibert, J. Organomet. Chem. 683 (2003) 301;
(b) N. Szesni, M. Drexler, J. Maurer, R.F. Winter, F. de Montigny, C. Lapinte, S. Steffens, J. Heck, B. Weibert, H. Fischer, Organometallics 25 (2006) 5774;
(c) G. Roth, H. Fischer, Organometallics 15 (1996) 1130;
(d) N. Szesni, B. Weibert, H. Fischer, Inorg. Chim. Acta 359 (2006) 617;
(e) N. Szesni, B. Weibert, H. Fischer, Inorg. Chim. Acta 357 (2004) 1789;
(f) E.O. Fischer, M. Leupold, Chem. Ber. 105 (1972) 599;
(g) K.H. Dötz, W. Sturm, H.G. Alt, Organometallics 6 (1987) 1424.

See for instance

[9] (a) H. Fischer, D. Reindl, M. Gockel, C. Troll, Organometallics 17 (1998) 1393;
(b) V. Cadierno, S. Conejero, M.P. Gamasa, J. Gimeno, Organometallics 21 (2002) 3716;
(c) V. Cadierno, M.P. Gamasa, J. Gimeno, E.P. Carreno, S.G. Granda, J. Organomet. Chem. 670 (2003) 75;
(d) M. Baya, M.L. Buil, M.A. Esteruelas, A.M. Lopez, E. Onate, J.R. Rodriguez, Organometallics 21 (2002) 1841;
(e) B.M. Trost, Acc. Chem. Res. 35 (2002) 695.

[10] (a) E.O. Fischer, H.J. Kalder, A. Frank, F.H. Kohler, G. Huttner, Angew. Chem. 88 (1976) 683;
E.O. Fischer, H.J. Kalder, A. Frank, F.H. Kohler, G. Huttner, Angew. Chem. Int. Ed. Engl. 15 (1976) 623;
(b) H. Berke, Angew. Chem. 88 (1976) 684;
H. Berke, Angew. Chem. Int. Ed. Engl. 15 (1976) 624.

[11] R. Aumann, B. Jasper, R. Frohlich, Organometallics 15 (1996) 3173.

[12] (a) M. Duetsch, F. Stein, E. Pohl, R.H. Irmer, A. de Meijere, Organometallics 12 (1993) 2556;
(b) H. Werner, T. Rappert, R. Wiedemann, J. Wolf, N. Mahr, Organometallics 13 (1994) 2721;
(c) R. Aumann, Chem. Ber. 127 (1994) 725.

[13] A.W. Coats, J.P. Redfern, Nature 20 (1964).

[14] M.M. Omar, G.G Mohamed, A.M.M. Hindy,. J. Therm. Anal. Cal. 86 (2006) 315.