

THERMONANALYTICAL INVESTIGATIONS OF MONOCHLOROBIS (2,4-PENTANEDIONATO) VANADIUM(IV) ARYLOXIDES

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Abstract

The thermal decomposition of the complexes $[VCl(acac)_2(OAr)]$ (where $acac=2,4$ -pentanedionato anion; $OAr=OC_6H_4O-M-4$, $OC_6H_4OBu^t-4$) has been studied using non-isothermal techniques (DTA and TG). The TGA indicate that the substitution of chlorine in $VCl_2(acac)_2$ with aryloxide ligands results in an increase in the initial temperature of decomposition (*IDT*) of the new complexes. The role of the substituent at the aryloxide ring on the thermal stability of the complexes is depicted and hence described. The ultimate decomposition product in all the complexes has been identified as V_2O_5 . The kinetic and thermodynamic parameters namely, the energy of activation E , the frequency factor A , entropy of activation S and specific reaction rate constant k_r etc. have been rationalized in relation to the bonding aspect of the aryloxide ligands.

Keywords: aryloxides, Coats-Redfern method, DTA, non-oxovanadium(IV), TG

Introduction

Metal alkoxides [1] and aryloxides [2] constitute such a fascinating class of compounds that the literature abounds with the reports pertaining to their synthetic chemistry while the studies on the thermal behaviour of these compounds are rather limited [3, 4]. Of these, the phenolate chemistry of vanadium, in particular, is known to display interesting reactivity behaviour such as the capability of dinitrogen fixation [5–7]. Compared to the extensive work done on oxovanadium(IV) compounds [8–12], only a few non-oxovanadium(IV) species are described [13–19] and to our knowledge virtually no thermal studies have been made on bare vanadium(IV) compounds. As a part of our studies to detail the chemistry of vanadium [20–22], the present communication reports the thermal behaviour and kinetic parameters of complexes $[VCl(acac)_2(OAr)]$ by Coats and Redfern method.

Experimental

$\text{VO}(\text{acac})_2$ [23] and $\text{VCl}_2(\text{acac})_2$ [18], the starting materials were prepared by literature methods. Complexes of compositions $[\text{VCl}(\text{acac})_2(\text{OAr})]$ were prepared as previously reported [22]. Thermal analyses of the complexes were carried out on SHIMADZU DT-40 simultaneous TG-DTA thermal analyzer. The thermocouple used was Pt/Pt–Rh with a temperature range of 20–1200°C. Thermal investigations were carried out by heating the sample (5–7 mg) in Pt crucible in a static air atmosphere and a heating rate of 20°C min⁻¹ was employed. Vanadium and chlorine in the intermediate were estimated as V_2O_5 gravimetrically and by Volhard's method respectively. The IR spectra were recorded as KBr pellets on a Beckman IR-4250 spectrophotometer.

Results and discussion

A comparison of the thermal decomposition of $\text{VO}(\text{acac})_2$ (I), $\text{VCl}_2(\text{acac})_2$ (II) and complexes $[\text{VCl}(\text{acac})_2(\text{OAr})]$ (III–VI), derived from the substituted phenols in air has revealed an interesting set of results (Table 1). The TG of $\text{VO}(\text{acac})_2$ has indicated it to be fairly stable upto 200.6°C beyond which it decomposes in a single step. The total mass loss of 67.2% in the temperature range 200.6–314.0°C corresponds to yield V_2O_5 as the ultimate product. The DTA curve has shown an endothermic peak at 256.9°C accompanied by an exothermic peak at 267.8°C which may be attributed to the sublimation followed by decomposition of (I) in the form of volatile products such as CO_2 , CH_4 etc. leaving behind V_2O_5 .

The TG of $\text{VCl}_2(\text{acac})_2$ has displayed diminished stability as is evident from its early decomposition ~23°C which takes place in two steps. An initial mass loss of 38.5% in the temperature range 23–264.7°C corresponds to the possible formation of $\text{VOCl}(\text{acac})$ as an intermediate. The subsequent mass loss of 33.5% in the temperature range 264.7–490°C has been proposed to be due to the oxidative decomposition of the intermediate to give V_2O_5 . Thermal decomposition of $\text{VCl}_2(\text{acac})_2$ is supplemented by the appearance of a single exothermic peak at 477.6°C in DTA curve.

A perusal of the TG/DTA curves of the complexes $\text{VCl}(\text{acac})_2(\text{OAr})$ (III–VI) have indicated them to be stable upto 176.1, 132.3, 132.1 and 122.8°C respectively, thus exhibiting a decreased order of stability. Interestingly, the substitution of chlorine in $\text{VCl}_2(\text{acac})_2$ with aryloxide ligand results in an increase in the initial temperature of decomposition (*IDT*) for the new complexes and the observed variation in *IDT* seems to be markedly dependent upon the nature of the substituent on the aryloxide ring. The role of both the electronic and steric effects can be considered to explain the observed trend. Of the different substituents in the phenols used, the –OM group having the highest electron releasing tendency is expected to demonstrate a strong oxygen pπ to metal dπ donation and has been confirmed by the higher *IDT* of $\text{VCl}(\text{acac})_2(\text{OC}_6\text{H}_4\text{OM}-4)$ as compared to its other aryloxide counterparts.

Another interesting feature of monochlorobis(2,4-pentanedionato)vanadium(IV) aryloxides is that they exhibit a two-step decomposition pattern. The first stage decompo-

sition amounting to mass losses of 52.95, 56.39, 54.65 and 53.11% for III, IV, V and VI complexes respectively in the temperature ranges 176.1–264.1, 132.3–263.3, 132.1–265 and 122.8–266.9°C has been attributed to the formation of VOCl(acac) as the possible intermediate in each case being formed around 265°C as is evident from the prominent inflexion in the TG curves of all the complexes including the parent compound VCl₂(acac)₂ at this temperature. Further evidence for the proposition of VOCl(acac) as the probable intermediate has been gathered by arresting the heating of the complexes at 265°C and thereby analyzing the resultant material by chemical analysis and IR spectra. The elemental analyses (vanadium and chlorine) was found to be entirely consistent with its formulation as VOCl(acac). The appearance of entirely new bands at ~980 cm⁻¹ (not present in parent complexes) assigned to $\nu_{(V=O)}$ in the IR spectra has reinforced the formulation of intermediate as VOCl(acac). The sharp band observed ~390 cm⁻¹ has been attributed to $\nu_{(V-Cl)}$ mode.

The second stage of decomposition has been observed as an oxidative decomposition of the intermediate VOCl(acac) to yield V₂O₅ as the final product of decomposition in contrast to the reported formation of V₂O₃ and VO₂ in the thermal decomposition of vanadium(IV) oxalate [24] and vanadium(IV) formate [25] respectively. The formation of V₂O₅ as the final product in the present complexes is substantiated by an endotherm in DTA at ~660°C attributed to the melting of V₂O₅. Moreover, the entire thermal decomposition of the complexes (III–VI) is an exothermic process with peak maxima at the temperatures given in the Table 1. Thus on the basis of the observed two-step thermal decomposition of the aryloxide complexes of bare V (IV) coupled with the analytical and IR spectral analyses of the intermediate and the ultimate residue, the following scheme of decomposition may be proposed



Kinetic parameters

Of the several methods, developed to allow kinetic analysis of the thermogravimetric data, methods due to Coats and Redfern [26, 27] and Achar [28] have been known to give satisfactory analysis provided that the experimental conditions are such as to minimize temperature gradient within the reactants. In view of the complexity of the thermal decomposition of vanadium complexes, an attempt has been made to select an appropriate method for determining various kinetic parameters of thermal decomposition of the complexes. The method of Coats and Redfern being less tedious than other methods and which also avoids the determination of tangents has been found to be suitable in the present investigations.

Using TG data, both the stages of decomposition were subjected to non-isothermal kinetic analysis. The activation parameters were computed using Coats-Redfern equation [26].

The parameters like entropy S^* [29], free energy G^* [30], specific reaction rate constant k_r [31] and enthalpy of activation H were obtained from their standard relations and results are being presented in Table 1.

Table 1 Thermal decomposition data and kinetic parameters for vanadium(IV) complexes computed by Coats-Redfern equation

Complex	Decomposition data							
	Sample mass/mg	IDT/°C	Stage	TG temp. range/°C	Mass loss/%		DTA peak temp./°C	Nature
					expt.	theor.		
VO(acac) ₂ (I)	6	200.6	1st	200.6–314.0	67.2	65.6	256.9 267.8	endo exo
VCl ₂ (acac) ₂ (II)	5	23	1st	23.0–264.7	38.5	37.03	477.6	exo (br)
			2nd	264.7–490.0	33.5	34.53		
[VCl(acac) ₂ (OC ₆ H ₄ OMe-4)] (III)	6.2	176.1	1st	176.1–264.1	52.95	50.49	261.1	exo
			2nd	264.1–502.3	28.09	27.15	422.4	exo
[VCl(acac) ₂ (OC ₆ H ₄ Bu ^t -4)] (IV)	6.65	132.3	1st	132.3–263.3	56.39	53.51	237.9 249.5	exo db
			2nd	263.3–501.3	21.17	25.52	479.2	exo
[VCl(acac) ₂ (OC ₆ H ₄ Bu ^t -2,6-Me-4)] (V)	7	132.1	1st	132.1–265.0	54.65	59.94	249.7	exo
			2nd	266.9–468.3	26.87	26.18	430.3	exo
[VCl(acac) ₂ (OC ₆ H ₄ NO ₂ -4)] (VI)	6	122.8	1st	122.8–266.9	53.11	52.25	260.8	exo

Table 1 Continued

Complex	Stage	Kinetic parameters					
		$E^*/$ kcal mol ⁻¹	$A/$ s ⁻¹	$S^*/$ J K ⁻¹ mol ⁻¹	$G^*/$ kcal mol ⁻¹	$H^*/$ kcal mol ⁻¹	k_r
VO(acac) ₂ (I)	1st	27.766	2.39·10 ¹¹	-58.067	57.738	27.343	0.683
VCl ₂ (acac) ₂ (II)	1st	3.395	12.83	-57.48	25.639	3.336	0.152
	2nd	9.63306	92.9	-58.89	47.18	1.988	0.162
[VCl(acac) ₂ (OC ₆ H ₄ OMe-4)] (III)	1st	23.824	2.12·10 ⁹	-57.97	52.491	23.795	0.0576
	2nd	5.612	7.548	-58.474	42.86	5.56	0.0895
[VCl(acac) ₂ (OC ₆ H ₄ Bu ^t -4)] (IV)	1st	17.727	2.856·10 ⁷	-57.874	44.957	17.653	0.156
	2nd	8.88	6.62·10 ²	-58.65	49.725	8.144	1.057
[VCl(acac) ₂ (OC ₆ H ₂ Bu ^t -2,6-Me-4)] (V)	1st	16.494	8.25·10 ⁶	-57.869	43.663	16.417	0.163
	2nd	11.012	4.78·10 ²	-58.492	48.662	10.957	0.084
[VCl(acac) ₂ (OC ₆ H ₄ NO ₂ -4)] (VI)	1st	25.213	3·10 ⁷	-58.55	63.973	25.123	0.136

A perusal of the thermal decomposition kinetic parameters has indicated some specific patterns for the complexes under study. It has thus been tempting to compare the activation energies of $\text{VO}(\text{acac})_2$ with that of $\text{VCl}_2(\text{acac})_2$ and amongst the new $\text{VCl}(\text{acac})_2(\text{OAr})$ complexes. The trend in activation energies for the first stage of decomposition has revealed a compatibility with the order of thermal stability suggesting that higher the value of E^* , the more stable is the complex. This consideration has been fully corroborated and reflected in their initial temperature of decomposition. The second stage of decomposition, has however exhibited a reversal order of activation energies for which no definite explanation can be given at present.

Generally the value of A increases with decrease in E^* . However no such observations have been made in the present investigations. The contribution of some more inherent physical and chemical factors viz. thermodynamic, kinetic, stereospecific etc. may be attributed to cause a change or deviation in this trend [32]. The entropy of activation S for all the complexes has been found to be negative. The negative values obtained for S generally indicate that activated complexes have more ordered structures [33] than the reactants and that the reactions are slower than normal [34, 35]. The magnitudes of E^* and H^* differ only by 0.029–0.358 and 0.052–0.736 kcal mol⁻¹ for the respective steps, suffice to say that E^* and H^* are equivalent. The values of other kinetic parameters are within the range usually observed for a first order reaction. Thus it can be concluded that the best linear fit for the complexes under study has been obtained for $n=1$ in the first stage of decomposition in Coats and Redfern method.

The present work has thus allowed us to draw useful comparisons as to how the thermal stability and kinetic parameters of the complexes $[\text{VCl}(\text{acac})_2(\text{OAr})]$ compared to $\text{VO}(\text{acac})_2$ and $\text{VCl}_2(\text{acac})_2$ undergo variation with the change in the nature of the substituents in the aryloxide ligand in vanadium(IV) complexes.

References

- 1 D. C. Bradley, R. C. Mehrotra and D. P. Gaur, 'Metal Alkoxides', Academic Press, London (1978); D. C. Bradley, *Prog. Inorg. Chem.*, 2 (1960) 305; *Adv. Inorg. Chem. Radiochem.*, 15 (1972) 259.
- 2 K. C. Malhotra and R. L. Martin, *J. Organomet. Chem.*, 239 (1982) 159.
- 3 J. Lukasiak, L. A. May, I. Ya. Strauss and R. Piekos, *Rocznik, Chem. Am. Soc. Chim. (Polonorum)*, 44 (1975) 1675.
- 4 G. Pfeifer and T. Flora, *Magyar Kém. Folyóirat*, 70 (1964) 375.
- 5 A. Flamini, D. J. Cole-Hamilton and G. Wilkinson, *J. Chem. Soc. Dalton Trans.* 454 (1978).
- 6 A. E. Shilov, In *Energy Resources Through Photochemistry and Catalysis*, M. Gratzel, Ed. Academic, New York 1983, p. 535.
- 7 E. F. Van Tamelen, *Acc. Chem. Res.*, 3 (1970) 361.
- 8 J. Selbin, *Coord. Chem. Rev.*, 1 (1966) 293; *Chem. Rev.*, 65 (1965) 153.
- 9 D. Nichollas, *Coord. Chem. Rev.*, 1 (1966) 379.
- 10 D. A. Rice, *Coord. Chem. Rev.*, 37 (1981) 61; 45 (1982) 67.
- 11 W. A. Nugnet and B. L. Haymore, *Coord. Chem. Rev.*, 31 (1982) 123.
- 12 E. M. Page, *Coord. Chem. Rev.*, 57 (1984) 237.

- 13 P. Comba, L. M. Engelhardt, J. M. Harrowfield, G. A. Lawrence, L. L. Martin, A. M. Sargeson and A. H. White, *J. Chem. Soc., Chem. Commun.*, (1985) 174.
- 14 R. Seangprasertkij and T. L. Riechel, *Inorg. Chem.*, 25 (1986) 3121.
- 15 D. E. Matsubayashi, K. Akiba and T. Tanaka, *Inorg. Chem.*, 27 (1988) 4744.
- 16 J. H. Welch, R. D. Bereman and P. Singh, *Inorg. Chem.*, 27 (1988) 2862.
- 17 C. J. Hawkins and T. A. Kabanos, *Inorg. Chem.*, 28 (1989) 1084.
- 18 T. W. Hambley, C. J. Hawkins and T. A. Kabanos, *Inorg. Chem.*, 26 (1987) 3740.
- 19 A. A. Diamantis, J. B. Raynor and P. H. Rieger, *J. Chem. Soc., Dalton Trans.*(1980) 1731.
- 20 K. C. Malhotra, B. Bala, N. Sharma and S. C. Chaudhry, *Synth. React. Inorg. Met. Org. Chem.*, 23 (1993) 1561.
- 21 K. C. Malhotra, B. Bala, N. Sharma and S. C. Chaudhry, *Trans. Met. Chem.*, 20 (1995) 388.
- 22 N. Sharma, A. K. Sood, S. S. Bhatt, S. B. Kalia and S. C. Chaudhry, *Trans. Met. Chem.*, 23 (1998) 557.
- 23 M. Bhattacharjee, *J. Chem. Res.*, 5 (1992) 415.
- 24 K. C. Satapathy, R. Parmar and B. Sahoo, *Ind. J. Chem.*, 1 (1963) 402.
- 25 K. C. Satapathy, R. Parmar and B. Sahoo, *Ind. J. Chem.*, 1 (1963) 271.
- 26 A. W. Coats and J. P. Redfern, *Nature*, 20 (1964) 68.
- 27 A. W. Coats and J. P. Redfern, *J. Polymer Sci. Polymer Letters*, 3 (1965) 917.
- 28 B. N. Achar, G. W. Brindley and J. H. Sharp, *Proc. Int. Clay Conf., Jerusalem*, 1 (1966) 67.
- 29 J. Zsakó, Cs. Várhelyi and E. Kékedy, *J. Inorg. Nucl. Chem.*, 28 (1966) 2637.
- 30 P. V. Khadikar, S. M. Ali and B. Heda, *Thermochim. Acta*, 82 (1984) 253.
- 31 S. Glasstone, 'Textbook of Physical Chemistry', 2nd Edn., Macmillan, India 1974.
- 32 S. W. Benson, *Thermochemical Kinetics*, 2nd edn. New York, Wiley 1976.
- 33 A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, Wiley, New York 1961.
- 34 S. S. Sawney and A. K. Bansal, *Thermochim Acta*, 66 (1983) 347.
- 35 P. Chourasia, K. K. Suryesh and A. P. Mishra, *Proc. Ind. Acad. Sci., (Chem. Sci.)*, 105 (1993) 173.