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THERMAL STUDIES ON BIS(η^5-CYCLOPENTADIENYL/INDENYL) OXINATO HAFNIUM(IV) CHELATES

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ABSTRACT

Ionic chelates of the type $[(\eta^5\text{-R})_2\text{HfL}]^+ \text{HgCl}_3^-$ (R = cyclopentadienyl (C_5H_5), indenyl (C_9H_7); HL = oxine) have been synthesised. Spectral studies (IR, UV, PMR and CMR) indicate that the oxinato group is chelating. From thermogravimetric curves, the order, activation energy and apparent activation entropy of the thermal decomposition reaction have been elucidated. The thermal reaction in each case follows an F_1 type mechanism. From differential thermal analysis the activation energy and the heat of transition for thermal effects have been calculated. The heat of reaction has been calculated from differential scanning calorimetry.

INTRODUCTION

Doyle and Tobias [1] pointed out that coordination of four oxygen atoms by strong covalent bonds to the $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}^{2+}$(IV) moiety (M = Ti, V) would lead to weakening of the metal–ring bonds. In order to investigate whether or not the coordination of two nitrogen and two oxygen atoms to the $(\eta^5\text{-R})_2\text{Hf}^{2+}$(IV) moiety (R = C_5H_5, C_9H_7) would produce a weakening of metal–ring bonds, we studied the interaction of $(\eta^5\text{-R})_2\text{HfCl}_2$ with oxine in aqueous medium. We failed to isolate derivatives in which two oxinato groups coordinate to the $(\eta^5\text{-R})_2\text{Hf}^{2+}$(IV) moiety. However, ionic complexes of the type $[(\eta^5\text{-R})_2\text{HfL}]^+\text{Cl}^-$ (HL = oxine) in which only one bidentate oxinato group is coordinated to hafnium (IV) ion were readily obtained. Such complexes possess a low solvation energy as is evident from the ease of their preparation. This suggested that these complexes may be isolated as salts of trichloromercury(II) anions. Hence, complexes of the type $[(\eta^5\text{-R})_2\text{HfL}]^+\text{HgCl}_3^-$ were synthesised.

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The chelating behaviour of the oxinato group in these complexes is confirmed from spectral studies. Thus, in the IR spectra, whereas the C $\dot{=}$ N bond in free oxine absorbs at 1450 cm^{-1}, in the case of metal complexes the absorption is shifted to ~ 1330 cm^{-1} [2]. The UV spectra of oxine show a very intense band at 200 nm (log ϵ 3.5) due to $\pi-\pi^*$ absorptions of the chromophoric C$\dot{=}$N group. In the case of metal complexes, this band is shifted to ca. 230 nm, although the intensity remains virtually the same. The PMR spectra reveal that the C(2) proton of the oxinate group, in the case of metal complexes, shows a signal at δ 9.10 ppm (q, J 4, 1.8 Hz). This is downfield as compared to the value of δ 8.73 ppm for free oxine. In the CMR spectra the signal for the C(2) carbon appears at 147.9540 ppm in the case of free oxine. The signal is shifted to ca. 149.5 ppm in the case of the complexes. The shifts in various spectral parameters as recorded for metal complexes vis-à-vis free oxine are attributed to the involvement of the C$\dot{=}$N group in the complexation process.

Screening of the literature reveals that reports of thermal studies on ionic organometallic chelates are scanty. In this communication we report the results of TG, DTA and DSC interpretations for such complexes.

EXPERIMENTAL

The following instruments were used: Perkin-Elmer 621 grating spectrometer for IR spectra; Perkin-Elmer UV-VIS spectrophotometer, model 554 for UV spectra; Perkin-Elmer R-32 spectrometer for PMR spectra; JEOL FX-200 spectrometer (Japan) for CMR spectra; G-70 thermoanalyser, Setaram (Lyon, France) for TG studies in air at a heating rate of 8°C min^{-1}; Mettler TA-20 device for DTA studies in air at a heating rate of 8°C min^{-1} and chart speed 30 cm h^{-1}; Perkin-Elmer DSC-IB for DSC studies in air atmosphere at a heating rate of 8°C min^{-1}.

An aqueous solution of $[(\eta^5\text{-R})_2HfL]^+Cl^-$ was obtained by stirring an aqueous solution of $(\eta^5\text{-R})_2HfCl_2$ with slight excess of solid oxine in about 100 ml double distilled water. After about 3 h, the contents were filtered and the aqueous solution was shaken with ~ 25 ml benzene. The aqueous phase was collected and added to an aqueous solution of $HgCl_2$. The contents were warmed to 50°C and the resulting green precipitates of $[(\eta^5\text{-R})_2HfL]^+HgCl_3^-$ were filtered, washed with water followed by petroleum ether, and then reprecipitated from acetone solution by the addition of petroleum ether.

RESULTS

$[(\eta^5\text{-}C_5H_5)_2HfL]^+HgCl_3^-$

From the TG curve it is observed that the mass change begins at 463 K. The weight loss in the temperature range 463–573 K corresponds to the formation of a mixture of HfO_2 and HgO. At 713 K HgO slowly volatilizes and at about 1223 K the volatilization is complete, leaving HfO_2 as the lone product of thermal decomposition. The net observed weight loss for these changes is 77.77%, while the calculated weight loss is 75.26%.

In the DTA curve the thermal effect begins at 433 K and an exothermic peak with T_{max} 463 K is observed. This peak corresponds to the decomposition of the complex, resulting in mixture of HgO and HfO_2. The corresponding peak in the DSC curve is observed at 463 K.

$[(\eta^5\text{-}C_9H_7)_2HfL]^+HgCl_3^-$

The TG curve indicates that the decomposition begins at 453 K. The weight loss in the temperature range 453–553 K corresponds to the formation of a mixture of HfO_2 and HgO. The latter starts volatilizing at 743 K and the volatilization is complete at 1223 K. At this temperature HfO_2 remains the only product of thermal decomposition. The overall observed weight loss for these changes is 83.33% which closely corresponds with the calculated value of 82.66%.

In the DTA profile the thermal effect begins at 433 K and an exothermic peak with T_{max} 457 K is observed. This peak corresponds to the decomposition of the complex into a mixture of HgO_2 and HgO. This peak is also observed in the DSC curve at 457 K.

DISCUSSION

The results of TG, DTA and DSC evaluations are presented in Table 1. From the TG curves, the order (n) and activation energy (E_a) of the thermal decomposition reaction have been elucidated by the method of Coats and Redfern [3]. The linearization curves are shown in Fig. 1.

TABLE 1
Thermal data

Complex	TG			DTA			DSC	
	n	E_a (kcal mol^{-1})	S^* (e.u.)	T_{max} (K)	E_a kcal mol^{-1})	ΔH_t (cal g^{-1})	$T_p(T_m)$ (K)	ΔH_r (kcal mol^{-1})
$[(\eta^5\text{-}C_5H_5)_2HfL]^+\text{-}HgCl_3^-$	1	9.76	6.31	463	54.91	35.96	463 (460)	3.83
$[(\eta^5\text{-}C_9H_7)_2HfL]^+\text{-}HgCl_3^-$	1	5.33	1.56	457	36.60	34.40	457 (460)	5.88

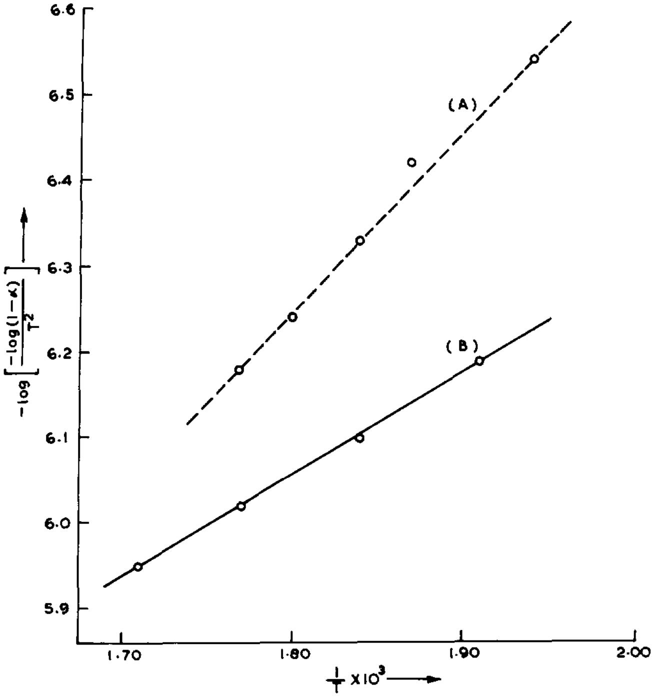

Fig. 1. Kinetic parameters from TG: (A) $[(\eta^5\text{-}C_5H_5)_2HfL]^+ HgCl_3^-$; (B) $[(\eta^5\text{-}C_9H_7)_2HfL]^+$-$HgCl_3^-$.

The order of reaction in each case in one. A comparison of the activation energy data reveals that the decomposition of the $[(\eta^5\text{-}C_9H_7)_2HfL]^+HgCl_3^-$ complex, as against the $[(\eta^5\text{-}C_5H_5)_2HfL]^+HgCl_3^-$ analogue, involves a lower value of E_a. This may be attributed to steric reasons. The C_9H_7–Hf bond is broken easily vis-à-vis the C_5H_5–Hf bond because of the steric repulsion arising due to the bulkier indenyl group, thus making the cleavage relatively more spontaneous.

The apparent activation entropy ($S^{\neq}$) has been calculated by the method of Zsakó [4]. A comparison of $S^{\neq}$ values for the two complexes indicates that the thermal decomposition of the $[(\eta^5\text{-}C_5H_5)_2HfL]^+HgCl_3^-$ complex involves a greater degree of randomness as compared to the corresponding indenyl derivative.

The mechanism of thermal degradation has been elucidated by the method of Šatava [5]. In this method, the function $f(\alpha)$, which depends upon the mechanism, is given by $\int f^{-1}(\alpha)\ d\alpha = g(\alpha)$, where α is the fraction decomposed at temperature T_α. For the correct mechanism $\log g(\alpha)$ must be a linear function of $1/T$. In the present cases it has been observed that only the curve corresponding to the F_1 mechanism is a straight line. For the F_1 mechanism, the rate equation is $-\ln(1-\alpha) = Kt$ (where K is the rate constant and t is time) and the rate-controlling process is random nucleation. The curves for mechanism elucidation are presented in Fig. 2.

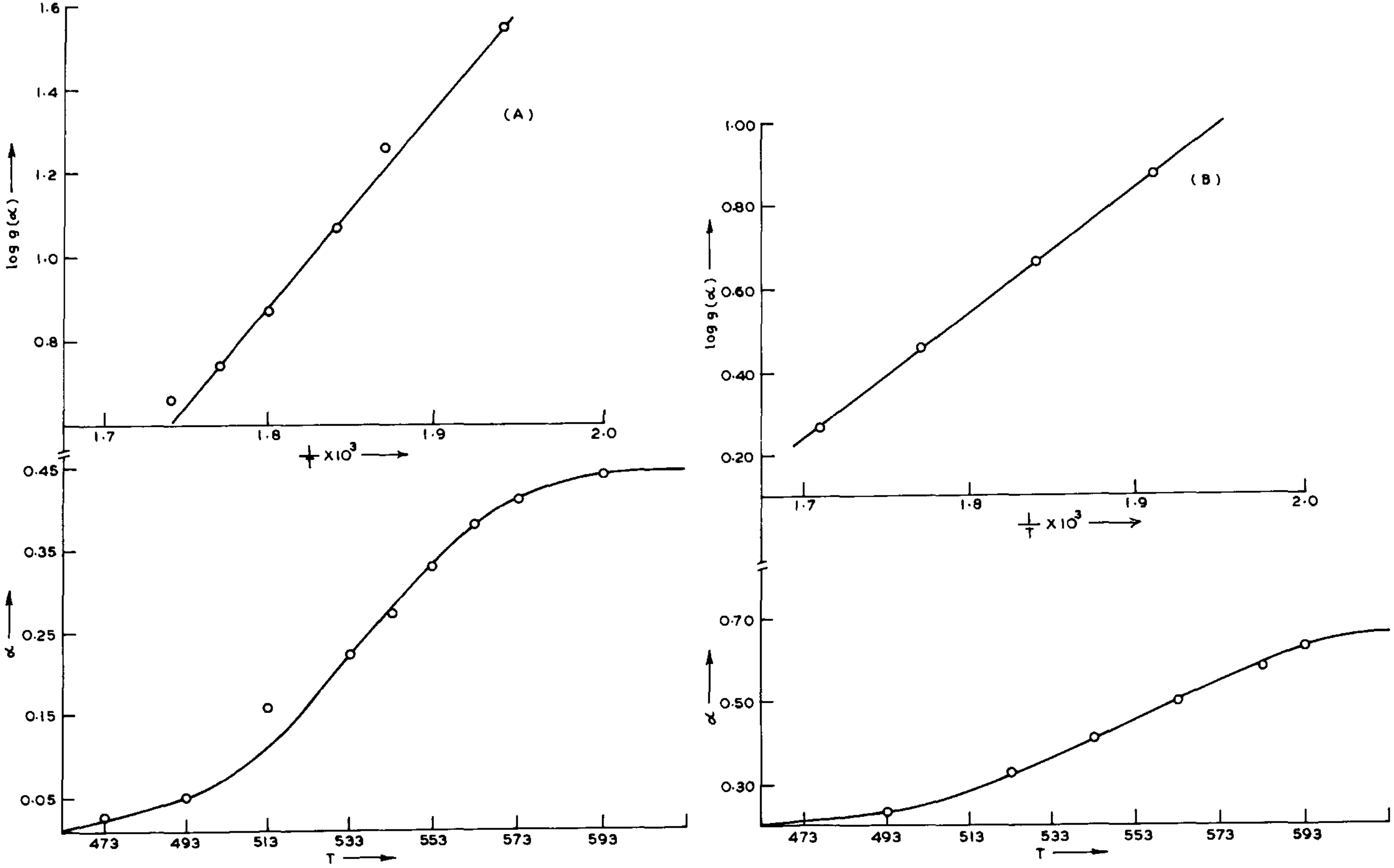

Fig. 2. Mechanism elucidation by TG: (A) $[(\eta^5\text{-}C_5H_5)_2HfL]^+ HgCl_3^-$; (B) $[(\eta^5\text{-}C_9H_7)_2HfL]^+ HgCl_3^-$.

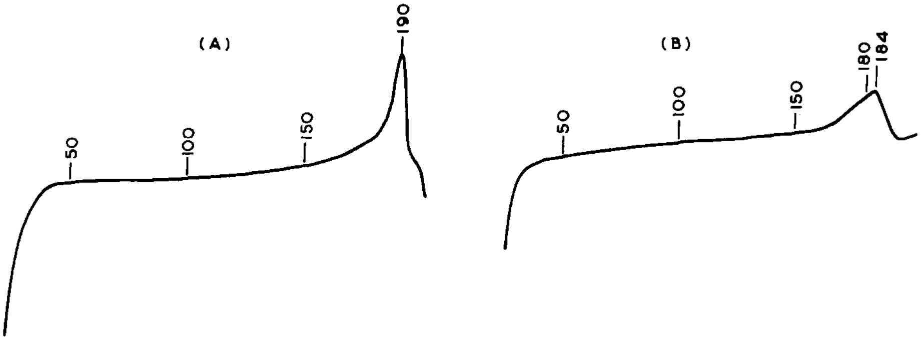

Fig. 3. DTA curves: (A) $[(\eta^5\text{-}C_5H_5)_2HfL]^+ HgCl_3^-$; (B) $[(\eta^5\text{-}C_9H_7)_2HfL]^+ HgCl_3^-$.

The TG data are supplemented by differential thermal analysis (DTA) studies. The DTA curves are shown in Fig. 3. The thermal effects on DTA curves are exothermic in nature. The activation energy (E_a) for the thermal effect, in each case, has been determined [6]. The linearization curves are shown in Fig. 4. The sequence of E_a values is the same as in the case of TG. For the calculation of heat of transition (ΔH_t) [7], the temperature-dependent calibration coefficient was obtained from the Currell equation [8].

From the differential scanning calorimetry (DSC) curves, the heat of reaction (ΔH_r) has been calculated by the method of Beech et al. [9]. As expected, the peak temperature, T_p, deviates slightly from T_m, the mean of the initial, T_i, and final, T_f, temperatures.

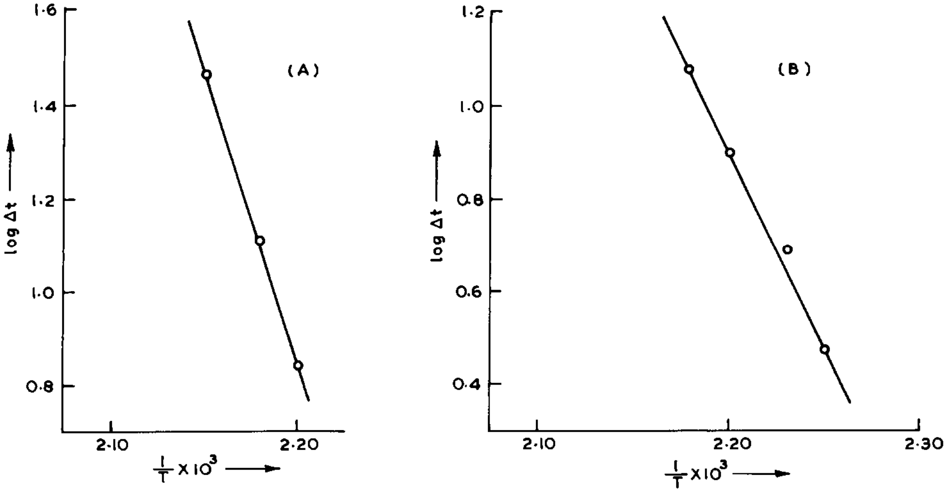

Fig. 4. Kinetic parameters from DTA: (A) $[(\eta^5\text{-}C_5H_5)_2HfL]^+ HgCl_3^-$; (B) $[(\eta^5\text{-}C_9H_7)_2\text{-}HfL]^+ HgCl_3^-$.

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