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Comparison of the activation energies for the thermal decomposition of copper and nickel compounds obtained by various thermogravimetric methods

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Abstract

The thermal decomposition of representative transition metal compounds has been examined using both standard and high resolution thermogravimetry. Using two approaches for plotting variable heating rate data, it has been demonstrated that comparable values for activation energies may be obtained by either method. Thus high resolution thermogravimetry is reliable method for the determination of decomposition activation energies. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermogravimetry; Activation energy; Thermal decomposition

1. Introduction

Thermogravimetry (TG) has found great utility in the analysis of polymeric materials, particularly in the elucidation of degradation pathways available for the thermal decomposition of these materials [1]. Less prominent, perhaps, but nonetheless, important has been the influence of the thermogravimetric analysis of inorganic and organometallic compounds [2–5]. In this case information about both decomposition mode and elemental composition may be obtained [2]. In either case kinetic information which reflects the rate of degradation (and thermal stability) may be obtained. Still the most reliable method for determining kinetic perimeters is carefully-controlled isothermal decomposition in which weight loss at a constant temperature is monitored as a function of time [1]. However, this procedure requires multiple determinations at several temperatures to permit the construction of a reliable Arrhenius plot and the extraction of an activation energy. For this reason, several dynamic methods have been developed for the estimation of the activation energy for decomposition processes to which the material of interest may be subject [6]. The most popular of these is the Flynn–Wall constant heating rate method which requires three or more determinations at different linear heating rates [7]. For first order processes, a plot of the natural logarithm of the heating rate ($\ln \beta$) vs the reciprocal of the absolute temperature ($1/T$) affords a slope which may be used to calculate the activation energy (E_a) [6]. In the constant reaction rate approach the heating rate is adjusted as required to maintain a selected rate of weight loss [8,9]. Assuming a reaction order of one, the activation energy may be determined directly by plotting $\ln(1/1-\alpha)$ vs $1/T$ where α represents the

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fraction of decomposition and T the absolute temperature [6]. With the advent of high resolution thermogravimetry a dynamic heating rate approach has become available [10–12]. In this approach both the heating rate and rate of weight loss continuously vary during decomposition. As the rate of weight loss increases, the heating rate decreases. Thus the heating rate is high when no weight loss is occurring but low when weight loss is high, i.e., when a thermal event is occurring. Consequently, the advantages of both high heating rate (rapid throughput) and very low heating rate (good resolution) may be at hand in the same experiment. The heating rate at maximum decomposition is a function of the initial heating rate and an instrumental resolution parameter. Using this approach and assuming a reaction order of one, the activation E_a for decomposition may be obtained from a plot of $\ln(H_r/T^2)$ vs $1/T$, where H_r is the heating rate at maximum weight loss and T is the absolute temperature at maximum weight loss [5].

Examination of the thermal decomposition for four representative transition metal compounds using both standard and high resolution TG and these variable rate methods was undertaken to explore the reliability of the methods and the applicability of the high resolution approach for the determination of kinetic parameters.

2. Experimental

2.1. Materials

Diethyl dithiophosphate, 1,10-phenanthrolein, and 2,2′-bipyridine were obtained from the Aldrich Chemical Company. Nickel chloride hexaydrate, copper (II) chloride dihydrate, and common solvents were obtained from Fisher Scientific Company.

2.2. Characterization

Infrared spectra were recorded using approximately 1% solid solutions in anhydrous potassium bromide (as discs) and a Perkin-Elmer model 1600 FT-IR spectrophotometer. Mass spectra were obtained at an ionizing potential of 70 eV using a Hewlett-Packard 5995 gas chromatograph/mass spectrometer equipped with a direct insertion probe.

2.3. Synthesis

2.3.1. bis(Diethyl dithiophosphato)nickel(II)

A solution of 2.01 g (0.00845 mole) of nickel chloride hexahydrate in 30 ml of methanol was treated with a solution of 3.11 g (0.016 mole) of sodium diethyl dithiophosphate in 30 ml of methanol. The product, a violet solid, which formed immediately was collected by filtration at reduced pressure, washed with three 20 ml of portions of methanol, and allowed to dry at room temperature and atmospheric pressure: mass spectrum, M^+(*m/e*) 428; ir (cm^{-1}, KBr) 2880 (C-H), 650 (asymmetric P-S stretch), 539 (symmetric P-S stretch).

2.3.2. bis(Diethyl dithiophosphato)copper(II)

bis(Diethyl dithiophosphato)copper(II) was obtained as a blue solid in manner directly analogous to that used for the preparation of the corresponding nickel compound: mass spectrum, M^+(*m/e*) 433; ir (cm^{-1}; KBr) 2980 (C-H), 630 (asymmetric P-S stretch), 520 (symmetric P-S stretch).

2.3.3. Dichloro(1,10-phenanthrolein)copper(II)

A solution of 2.50 g (0.014 mole) of 1,10-phenanthrolein in 30 ml of ethanol was added dropwise to a stirred solution of 2.50 g (0.015 mole) of copper(II) chloride dihydrate in 25 ml of water. The blue solid which formed was collected by filtration at reduced pressure, washed with three 20 ml portions of ethanol, and dried at 40°C and 20 torr for 48 h: mass spectrum, M^+(*m/e*) 313; ir (cm^{-1}, KBr) 1560 ($\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N}$).

2.3.4. Dichloro(2,2′-bipyridine)copper(II)

Dichloro(2,2′-bipyridine)copper(II) was obtained as a blue solid in a manner directly analogous to that used for the preparation the 1,10-phenanthrolein compound: mass spectrum, M^+(*m/e*) 289; ir (cm^{-1}) 1508 ($\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{N}$).

2.4. Thermogravimetry

The thermal degradation of bis(diethyl dithiophosphato)nickel(II), bis(diethyl dithiophosphato)copper(II), dichloro(1,10-phenanthrolein)copper(II), and dichloro(2,2′-bipyridine)copper(II) was examined under a variety of conditions using a TA Instruments model 2950 TGA unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. Decay plots, weight loss vs temperature, were generated by feeding the analyzer output (TA Instruments software was used for all data manipulation) to a model 7440 Hewlett-Packard plotter. The TGA cell was swept with nitrogen at 50 ml/min during degradation runs and the sample, approximately 10 mg, was contained in a platinum sample pan. Kinetic plots were generated using statView 512$^+$ software and an Apple Macintosh IIci computer.

3. Results and discussion

The thermal decomposition of four representative transition metal compounds, bis(diethyl dithiophosphato)nickel (II) [$Ni(dtp)_2$], bis(diethyl dithiophosphato)copper (II) [$Cu(dtp)_2$], dichloro(1,10-phenanthrolein)copper (II) [$Cu(phen)_2Cl_2$], and dichloro(2,2′-bipyridine)copper (II) [$Cu(bpy)_2Cl_2$] has been examined by thermogravimetry. The thermogram for the decomposition of bis(diethyl dithiophosphato)nickel (II) is displayed in Fig. 1.

In this case complete loss of both ligands occurs in a single step. The decomposition begins at 141°C and is accompanied by a loss of 81% of the initial sample weight corresponding to the mass of both ligands. The degradation is complete at 242°C and a residue of 19% of the initial sample weight, corresponding to the mass of metal present in the compound, remains. The analagous copper compound displays a similar decomposition pattern. In contrast, the decomposition of dichloro(2,2′-bipyridine)copper(II) and dichloro-(1,10-phenanthrolein)copper(II) begins at approximately 100°C higher temperature and occurs in two steps with the initial loss corresponding to the organic ligand followed by loss of the chloride ligands. In all cases the residue remaining after decomposition corresponded to the metal component of the compound.

The activation energy for the initial decomposition step for each compound was determined by two methods using both standard and high resolution techniques. The results are displayed in Table 1.

While the activation energies for the decomposition of the dithiophosphate compounds are considerably smaller than those for the decomposition of the phe-

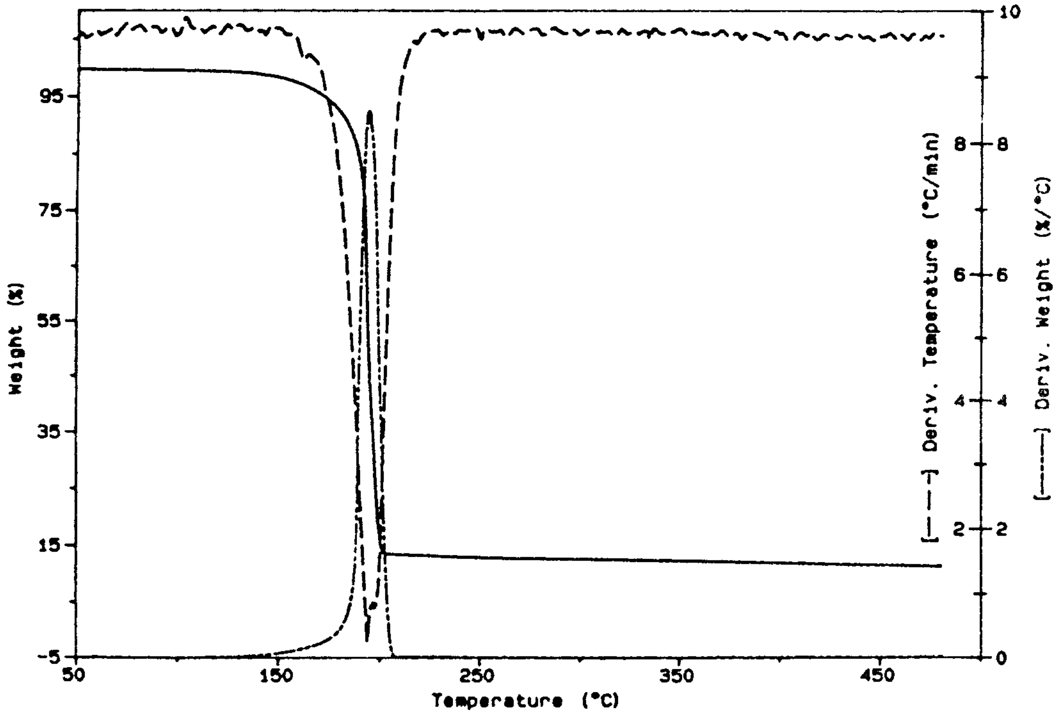

Fig. 1. Thermogram for the decomposition of bis(diethyl dithiophosphato)nickel (II).

Table 1
Activation energies (kcal/Mole) for the thermal decomposition of selected transition metal compounds

Compounds	Methods			
	ln β vs 1/*T*		$\ln(H_r/T^2)$ vs 1/*T*	
	Standard[a]	Hi-Res[b]	Standard[a]	Hi-Res[b]
$Ni(dtp)_2$	16.33	12.92	14.45	14.63
$Cu(dtp)_2$	18.21	17.71	17.45	16.27
$Cu(bpy)Cl_2$	40.25	42.68	38.01	40.48
$Cu(phen)Cl_2$	42.44	43.05	40.00	40.48

[a] Determined at heating rates of 5°, 10° and 20°C/min without the high resolution feature of TA Instruments.

[b] Determined with an initial heating rate of 20°C/min with Hi-Res control at resolution parameters of 3, 4 and 6. For $Cu(bpy)Cl_2$ this corresponded to heating rates of 3.10, 1.11 and 0.75°C/min with temperatures of maximum degradation rate at 311.5°, 295.3° and 289.2°C, respectively.

nanthrolein and bipyridine compounds, it is clear that the variation in values obtained using the various methods is rather small, 2–3 kcal/mole. In general, the values obtained using a plot of ln β vs 1/*T* are larger by about 2 kcal/mole than the corresponding values obtained from a plot of $\ln(H_r/T^2)$ vs 1/*T*. More importantly the variation between values obtained using standard vs high resolution techniques is smaller, usually 1–2 kcal/mole. It is clear that satisfactory values for activation energies for the decomposition of metal compounds may be obtained using the high resolution feature of the TA instrument. As has been noted previously for the degradation of polymeric systems using Hi-Res TG [12], somewhat better results were obtained by maintaining a constant initial heating rate and varying the resolution parameter to obtain a variable heating rate at the temperature of maximum decomposition rate rather than by selecting a particular resolution value and varying the heating rate.

4. Conclusion

Using two approaches for plotting variable heating rate data, it has been demonstrated that Hi-Res TG may be used to obtain satisfactory values for activation energies for the decomposition of transition metal compounds. The values obtained using this technique are quite comparable to those obtained using standard variable heating rate methods. Thus the Hi-Res technique may be used with confidence for the determination of decomposition activation energies.

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