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Note

The thermogravimetry and differential thermal analysis curves of some di-2-pyridyl ketone nickel(II) complexes

D. L. PERRY, C. VAZ AND W. W. WENDLANDT
Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)
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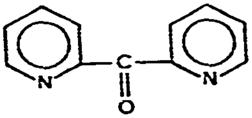
The ligand, di-2-pyridyl ketone (I) (dpk), has recently been shown to form complexes with various nickel(II) salts[1] having the general formula, $NiX_2 \cdot 2dpk \cdot xH_2O$, where X is $1/2SO_4^{2-}$, $C_2H_3O_2^-$, Br^-, and I^-, and x varies from 0 to 8. These compounds were reported to be fairly stable thermally; the melting points (with decomposition) were as follows: $Ni(C_2H_3O_2)_2 \cdot 2dpk \cdot xH_2O$, $153\,°C < NiSO_4 \cdot 2dpk \cdot xH_2O$, $198\,°C < NiI_2 \cdot 2dpk$, $245\,°C < NiBr_2 \cdot 2dpk$, 345°C. As can be seen, the bromide complex is extremely stable for a compound of this type. It was of interest to investigate the thermal properties of these compounds by use of thermogravimetry (TG) and differential thermal analysis (DTA) techniques.



(I)

Experimental

Thermal analysis apparatus. A DuPont Model 950 thermobalance was used in conjunction with the Model 900 DTA console. The DuPont DSC cell module was used for the DTA (DSC) studies. Sample size ranged in mass from 4 to 7 mg, and the samples were pyrolyzed in a dynamic nitrogen atmosphere at a heating-rate of 10°C/min.

Nickel complexes. The compounds used were the same as previously described[1].

Results and discussion

The TG and DTA (DSC) curves of the nickel(II) di-2-pyridyl ketone complexes are given in Figs. 1 and 2, respectively.

Chelating agent. The DTA curve for di-2-pyridyl ketone indicates a narrow fusion endothermic peak at a $\Delta T_{min.}$ of 60°C which is followed by a broad vaporization (or sublimation) peak in the temperature range from 125 to 230°C. According to the TG curve, vaporization (or sublimation) occurs starting at a procedural initial temperature, T_i, of 115 °C, to a final temperature, T_f, of 275 °C. At the latter temperature, a mass-loss of 96.6% was observed.

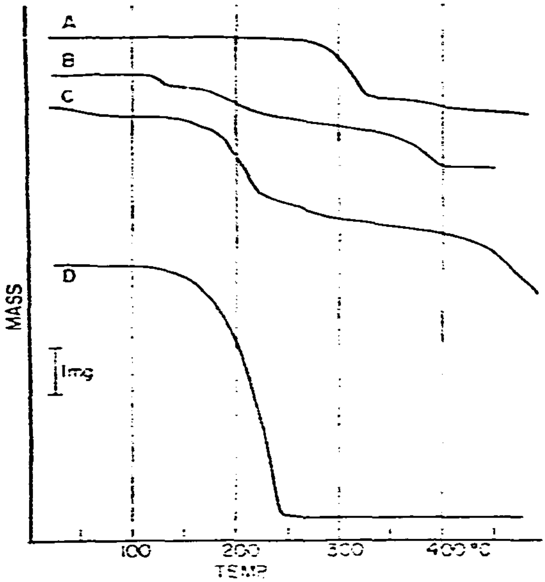


Fig. 1. TG curves of nickel(II) complexes. (A) $NiI_2 \cdot 2dpk$; (B) $Ni(C_2H_3O_2)_2 \cdot 2dpk \cdot xH_2O$; (C) $NiSO_4 \cdot 2dpk \cdot xH_2O$; (D) pure dpk.

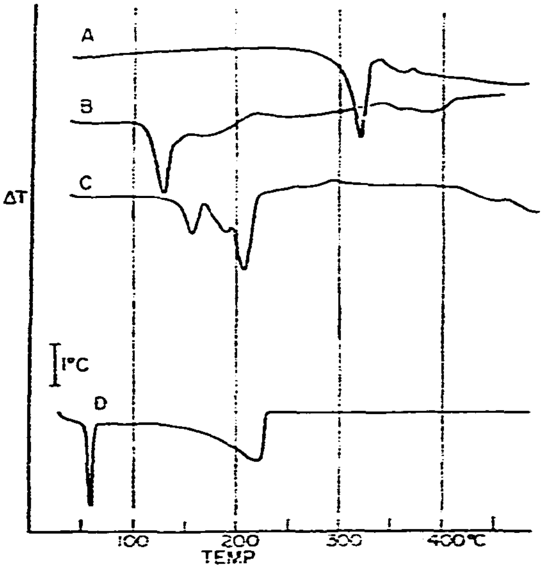


Fig. 2. DTA (DSC) curves of nickel(II) complexes. (A) $NiI_2 \cdot 2dpk$; (B) $Ni(C_2H_3O_2)_2 \cdot 2dpk \cdot xH_2O$; (C) $NiSO_4 \cdot 2dpk \cdot xH_2O$; (D) pure dpk.

Nickel(II) complexes. Since the nickel(II) sulfate and acetate complexes are hydrated, the first mass-losses are due to water evolution. In the case of $NiSO_4 \cdot 2dpk \cdot xH_2O$, initial mass-loss to the 2-hydrate takes place between ambient room temperature and 100°C; this is followed by the loss of two additional moles of water per mole of complex, giving the anhydrous $NiSO_4 \cdot 2dpk$ complex at about 175°C. The disruption of the latter complex then takes place with no horizontal mass-levels observed in the curve up to 500°C. It is evident that dissociation of the $NiSO_4$ takes place during the latter stages of the total decomposition reaction.

Similarly, for the $Ni(C_2H_3O_2)_2 \cdot 2dpk \cdot xH_2O$ complex, the mass-loss up to 135°C corresponds approximately to 1 mole of water per mole of complex. Additional hydrate water is evolved up to about 200°C, which corresponds to about another 1.5 moles of water per mole of complex. This is then followed by the total disruption of the complex and the nickel(II) acetate. The residue at 425°C does not correspond to any stoichiometric composition.

The TG curve for $NiI_2 \cdot 2dpk$ indicates a mass-loss at a T_i of 250°C to a T_f of about 335°C. This mass-loss corresponds approximately to the evolution of 1 mole of dpk per mole of complex (31.1% found; 27.05% calculated). However, total disruption of the complex must occur, because the mass-loss found is greater than that calculated.

The DTA (DSC) curves indicate endothermic peaks due to the dehydration or dissociation reactions. In the case of $NiI_2 \cdot 2dpk$, the dissociation peak occurs at a $\Delta T_{min.}$ of 315°C. The curve for $NiSO_4 \cdot 2dpk \cdot xH_2O$ has peaks with $\Delta T_{min.}$ values of 155 and 205°C, respectively, and a shoulder peak at 190°C. Only a well-defined dehydration peak ($\Delta T_{min.} = 130$°C) appears in the curve for $Ni(C_2H_3O_2)_2 \cdot 2dpk \cdot xH_2O$; the dissociation peaks are all rather broad and spread out over a fairly large temperature range.

As far as the initial thermal dissociation of the anhydrous complexes is concerned, the order of decreasing stability appears to be: acetate < sulfate < iodide. From this investigation, it was not possible to determine the composition of the evolved gaseous products.

REFERENCES

1 J. D. Ortego and D. L. Perry, *J. Inorg. Nucl. Chem.*, 35 (1973) 3031.