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KINETICS OF THERMAL DECOMPOSITION OF THE TETRACYANO COMPLEXES OF SOME TRANSITION METALS CONTAINING THE $[R_3S]^+$ CATION

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ABSTRACT

The kinetics of thermal decomposition of the tetracyano complexes of transition metals containing the $[Me_3S]^+$ cation were investigated by the isothermal thermogravimetric method. It is found in all cases that the decompositions accomplished under analogous experimental conditions are governed by the reaction order $n = 2/3$. The kinetic quantities obtained for individual compounds are correlated and on the basis of this correlation some common conclusions are drawn.

INTRODUCTION

Tetracyano complexes containing the $[Me_3S]^+$ cation represent an interesting class of compound. At present we have information about the conditions of their preparation and identification. Moreover, numerous pieces of knowledge of their thermal properties are available in respect of the stoichiometry of their thermal decomposition [1,2].

In the first stage of thermal decomposition of these compounds Me_2S is liberated in a one-step process. This liberation is accompanied by an endothermic effect irrespective of whether the decomposition takes place in an inert or an air atmosphere. The character of this first stage of decomposition enables us to evaluate the course of liberation kinetically and thus to obtain information about the mechanism of this process. As a large series of the clathrates of tetracyano complexes of the Hoffman and related type had been kinetically evaluated by the isothermal thermogravimetric technique [3,4], an equivalent procedure was applied to the compounds investigated here. In this way, a comparison of our results with the results obtained for the series of clathrates was made possible.

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EXPERIMENTAL

The following compounds were studied: Me_3SI, $[Me_3S]_2[Pd(CN)_4]$, $[Me_3S]_2[Zn(CN)_4]$, $[Me_3S]_2[Cd(CN)_4]$, $[Me_3S]_2[Hg(CN)_4]$ and $[Me_3S]_2[Ni(CN)_4]$. The preparation and identification of these compounds has been decribed in the literature [1,2]. The elemental analysis and IR spectra showed that the substances were suitable for further measurements.

The isothermal thermogravimetric technique was used for studying the kinetics of liberation of Me_2S from the compounds investigated. The isothermal decompositions took place in large-area platinum crucibles in an air atmosphere. The crucibles were put in a furnace of original construction which allowed heating up to 200 ° C. The change in mass was recorded with a Derivatograph MOM OD 102. The temperature was regulated to within $\pm 1°$ C. The granularity of the investigated samples was under 0.06 mm. The released Me_2S was captured in CH_2Cl_2 and immediately determined. The weighed amounts for experiments in Figs. 1 and 6 were 100 mg and for Figs. 2–5 were 50 mg.

RESULTS AND DISCUSSION

The kinetics of Me_2S liberation from the investigated compounds were studied by measuring the mass decrease at certain temperatures for times up to 100 min.

The course of Me_2S liberation is represented in Figs 1–6. The degree of conversion was invariably calculated from the measured isothermal curves

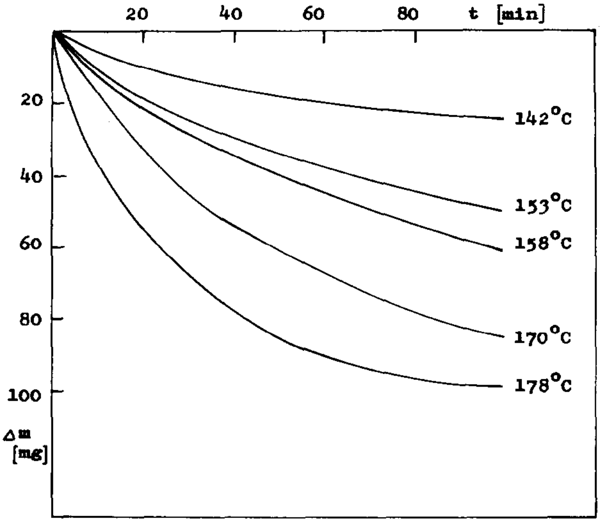

Fig. 1. Graphical representation of the isothermal decomposition of Me_3SI.

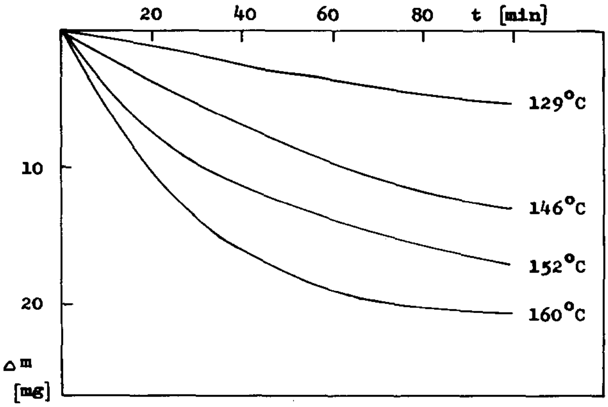

Fig. 2. Graphical representation of the isothermal decomposition of $[Me_3S]_2[Pd(CN)_4]$.

and the results were correlated with the general differential equation $d\alpha/dt = k(1-\alpha)^n$

The best agreement appeared at $n = 2/3$ for all compounds investigated. Therefore the kinetic equation describing the decomposition assumes the form $d\alpha/dt = k(1-\alpha)^{2/3}$. On integrating, we obtain $1-(1-\alpha)^{1/3} = k't$.

On the basis of this kinetic equation, the dependence of $1-(1-\alpha)^{1/3}$ on time was plotted for all investigated compounds. From these plots it was found that the relationship is linear in all cases. These results were processed by the method of least squares and used for calculating the rate constants. The list of these constants is given in Table 1.

The relationships between rate constants and temperature satisfy the logarithmic form of the Arrhenius equation, on the basis of which the relationship between log k and $1/T$ are plotted in Figs. 7 and 8. Common

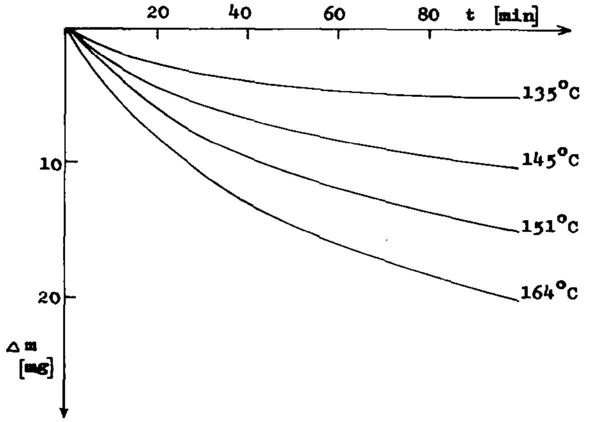

Fig. 3. Graphical representation of the isothermal decomposition of $[Me_3S]_2[Cd(CN)_4]$.

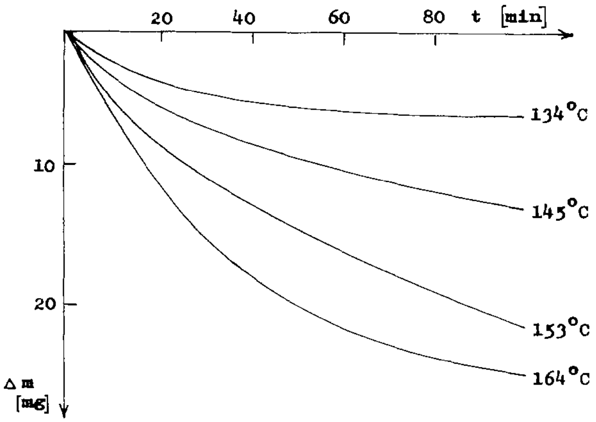

Fig. 4. Graphical representation of the isothermal decomposition of $[Me_3S]_2[Ni(CN)_4]$.

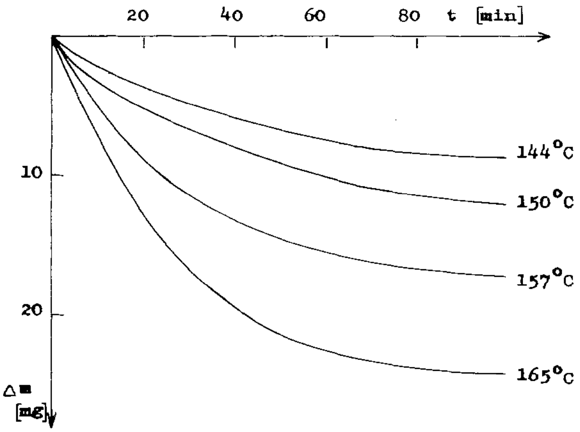

Fig. 5. Graphical representation of the isothermal decomposition of $[Me_3S]_2[Zn(CN)_4]$.

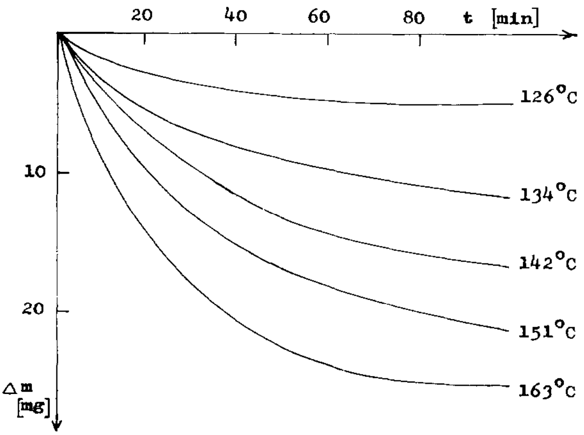

Fig. 6. Graphical representation of the isothermal decomposition of $[Me_3S]_2[Hg(CN)_4]$.

TABLE 1

Values of rate constants at given temperatures

Compound	T (K)	$1/T\times10^{-3}$	k (min)	log k
Me_3SI	415	2.409	1.31×10^{-5}	−4.8239
	426	2.347	3.31×10^{-5}	−4.4771
	431	2.320	4.00×10^{-5}	−4.3979
	443	2.257	7.60×10^{-5}	−4.1153
	451	2.217	11.10×10^{-5}	−3.9520
$[Me_3S]_2[Pd(CN)_4]$	402	2.487	1.83×10^{-5}	−4.7367
	419	2.386	4.33×10^{-5}	−4.3631
	425	2.352	6.80×10^{-5}	−4.1653
	433	2.309	10.50×10^{-5}	−3.9788
$[Me_3S]_2[Cd(CN)_4]$	408	2.450	1.33×10^{-5}	−4.8755
	418	2.392	2.25×10^{-5}	−4.5341
	424	2.358	3.75×10^{-5}	−4.4258
	437	2.288	8.28×10^{-5}	−4.0818
$[Me_3S]_2[Ni(CN)_4]$	407	2.457	1.74×10^{-5}	−4.7502
	418	2.392	3.11×10^{-5}	−4.5073
	426	2.347	6.60×10^{-5}	−4.1803
	437	2.288	12.17×10^{-5}	−3.9145
$[Me_3S]_2[Zn(CN)_4]$	417	2.398	1.47×10^{-5}	−4.8301
	443	2.364	2.28×10^{-5}	−4.6417
	430	2.325	4.33×10^{-5}	−4.3626
	438	2.283	5.51×10^{-5}	−4.0215
$[Me_3S]_2[Hg(CN)_4]$	399	2.506	1.26×10^{-5}	−4.8986
	407	2.457	3.13×10^{-5}	−4.5042
	415	2.409	5.16×10^{-5}	−4.2873
	424	2.358	7.48×10^{-5}	−4.1261
	436	2.283	12.55×10^{-5}	−3.9014

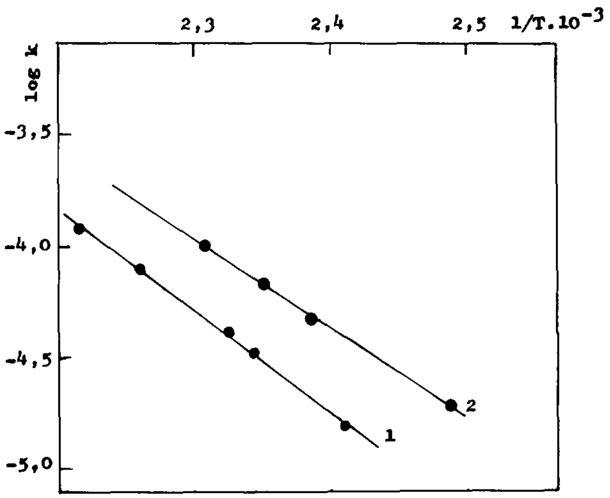

Fig. 7. Variation of rate constant with reciprocal value of temperature for (1) Me_3SI; (2) $[Me_3S]_2[Pd(CN)_4]$.

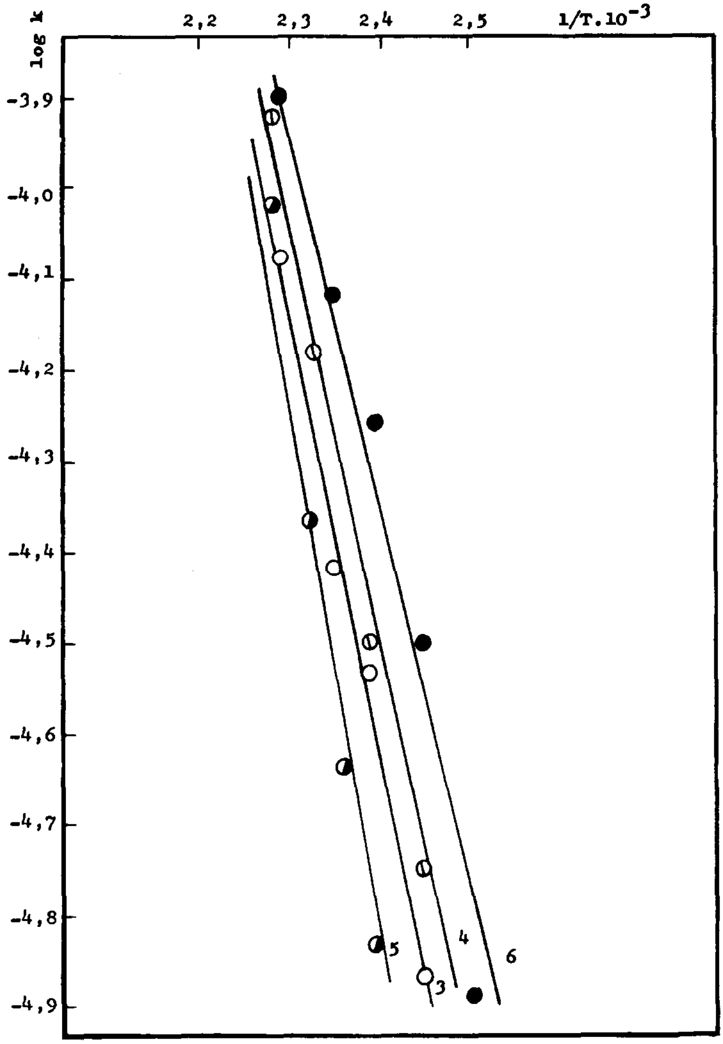

Fig. 8. Variation of rate constant with reciprocal value of (3) $[Me_3S]_2[Cd(CN)_4]$; (4) $[Me_3S]_2[Ni(CN)_4]$; (5) $[Me_3S]_2[Zn(CN)_4]$; (6) $[Me_3S]_2[Hg(CN)_4]$.

logarithms were used for calculating and plotting the graphs. The individual values of activation energies for the decompositions investigated are quoted in Table 2.

From the values given in Table 2 it can be seen that the reaction order of thermal liberation of Me_2S under given conditions assumes the value of 2/3. The results of analogous studies of tetracyano complexes of the Hoffman type have given the same value for the reaction order [5,6]. It is therefore clear that the reaction order of thermal decomposition of the clathrate inclusion component or the liberation of Me_2S from the compounds in-

TABLE 2

Values of activation energies and reaction order

Compound	n	E_A (kJ mol^{-1})
Me_3SI	2/3	83
$[Me_3S]_2[Pd(CN)_4]$	2/3	82
$[Me_3S]_2[Cd(CN)_4]$	2/3	86
$[Me_3S]_2[Ni(CN)_4]$	2/3	83
$[Me_3S]_2[Zn(CN)_4]$	2/3	85
$[Me_3S]_2[Hg(CN)_4]$	2/3	83

vestigated here have not only some common features but also some significant dissimilarities, due to the character of individual compounds.

If the decomposition occurs on the surface of the crystals then the reaction will be "two thirds order". The surface area is proportional to $(\text{distance})^2$ whereas the decrease in volume is proportional to $(\text{distance})^3$. For example, for spherical crystals of surface area = S and volume = V

$$-\frac{dv}{dt} = kS$$

$$-\frac{dv}{dt} = k4\pi r^2 = k(36\pi)^{1/3}V^{2/3}$$

This would probably be the reason for the decomposition behaviour of clathrates, but may be too simple for these $[Me_3S]^+$ complexes.

As for the $[Me_3S]^+$ complexes, the C–S bond is evidently destroyed in the first stage of decomposition and further decomposition reactions continue to proceed. This is also confirmed by the fact that the measured values of activation energy are approximately equal to 80 kJ mol^{-1} whereas the energy of the C–S bond is essentially higher.

This conclusion indicates that there are also substantial differences in thermal decomposition of different clathrates in spite of some common features.

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