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VAPOUR PRESSURE AND THERMOANALYTICAL STUDY OF DIETHYLDITHIOCARBAMATES OF PLATINUM METALS

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Abstract

A thermoanalytical study of the diethyldithiocarbamates of the platinum metals Pt(II), Pd(II), Rh(III), Ir(III) and Ru(III) was carried out by means of DTA techniques in an inert atmosphere and in vacuum. Decomposition temperatures were determined and the mass loss curves were obtained for these compounds in helium and in vacuum. The X-ray diffraction patterns of the solid products of $M(dtk)_n$ thermolysis were studied. The temperature dependences of the saturated vapour pressures of the listed chelates were measured by flow and Knudsen methods, and the vaporization parameters were determined.

Keywords: diethyldithiocarbamates of platinum metals, DTA, vapour pressure

Introduction

Studies of metal dithiocarbamates are of special interest because this class of compounds exhibits striking structural features; another reason is the diversified applications of these compounds as accelerators in vulcanization, as high-pressure lubricants in industry, and also as fungicides and pesticides [1]. A large number of papers and reviews dedicated to the synthesis, physicochemical and X-ray diffraction studies of diethyldithiocarbamate complexes of metals [1–6] involve thermogravimetry, differential thermal analysis, differential scanning calorimetry, gas chromatography and mass spectrometry. Data have been reported on the temperature dependences of the saturated vapour pressure for the diethyldithiocarbamates of Co(II), Cd(II), Pb(II), Cu(II), Zn(II) and Ni(II) [6–8]. However, data on thermoanalytical studies and on the determination of evaporation parameters for the diethyldithiocarbamates of the platinum metals are practically absent from the literature, with one exception [9], where thermal studies of the complexes in an atmosphere of nitrogen were carried out.

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The goal of the present investigation was to study the thermal stabilities of the diethyldithiocarbamate complexes of certain platinum metals and to determine the parameters of the chelate vaporization processes.

Experimental

Synthesis

The diethyldithiocarbamates of Pt(II), Pd(II), Ir(III), Rh(III) and Ru(III) ($M(dtk)_n$) were synthesized according to the standard procedure described in [5]. The following salts were used as the initial compounds: K_2PtCl_4, K_2PdCl_4, $IrCl_3$, K_3RhCl_3 and $RuCl_3$. Sodium diethyldithiocarbamate ($(C_2H_5)_2NCS_2Na{\cdot}3H_2O$) was used as ligand source. A weighed quantity of the platinum metal salt was dissolved in a minimum amount of distilled water heated to 40°C, and an equivalent amount of an aqueous solution of the sodium salt of the ligand was then added. The required chelate complex gradually precipitated from the solution. The precipitated crystals were placed onto a filter, thoroughly rinsed with water and dried. The compounds obtained in this way were purified by recrystallization (from a chloroform-hexane mixture) and by column chromatography on silica gel, a mixture of benzene and heptane being used as eluent. The complexes were additionally purified by means of zone sublimation in a vacuum gradient furnace at $P=10^{-2}$ torr and $T=250°C$ (except for $Ru(dtk)_3$). The yield of the complexes after purification was 60 –80%. The compounds proved to be readily soluble in chloroform, but somewhat less so in benzene. Crystalline $Pt(dtk)_2$ is bright-yellow, $Pd(dtk)_2$, $Ir(dtk)_3$ and $Rh(dtk)_3$ are orange, and $Ru(dtk)_3$ is dark-brown.

The compounds were characterized by melting temperatures (Table 1) and mass spectrometric data.

Thermoanalytical investigation

Studies of the thermal behaviour of the diethyldithiocarbamates of these platinum metals were carried out with a Q-1000 Derivatograph (MOM), in helium, in open ceramic crucibles. The masses of the weighed samples were 40–50 mg. The rate of gas admittance into the working chamber of the derivatograph was maintained identical in all experiments, at 20±2 l min^{-1}. Melting and decomposition temperature measurements were carried out with an accuracy of ±10°C. The rate of heating was 5°C min^{-1}.

Thermal investigation of the complexes in vacuum (0.001 torr) was carried out with a Thermal Analyzer Basic Component TA 7000 (ULVAC Sinku-Riko) at a heating rate of 5°C min^{-1} (platinum crucibles), on weighed samples of 10 mg.

Mass spectrometric studies of gas-phase $Ru(dtk)_3$ were carried out with a MX-1310 mass spectrometer in the amu region up to 2000 *m/z*, the energy of the ionizing electrons being 50 eV and the resolution 0.0001 amu.

X-ray diffraction patterns of the products of metal diethyldithiocarbamate thermolysis were studied with a DRON-3MC diffractometer, using CuK_{α} irradiation. The obtained phases were identified by using the ICPDS database [1, 2].

Vapour pressure

The density of the saturated vapour above solid and liquid $Pd(dtk)_2$, and solid $Rh(dtk)_3$, $Ir(dtk)_3$ and $Pt(dtk)_2$ was determined according to the flow transpiration method. A detailed description of the experimental technique is given in [10]. A measured volume of preliminarily dried inert carrier gas (helium) was passed through the voluminous source with the initial compounds kept at a constant temperature. Temperature was measured with an accuracy of ±0.5°C, and the gas flow rate with an accuracy of ±2%. Preliminary calibration with reference compounds showed that the experimental error did not exceed ±5%. The amount of substance transferred into a definite volume of the carrier gas was determined under quasi-equilibrium conditions from the mass loss in the source and from the mass increase in the deposition zone. Comparison of these two values permitted conclusions concerning the thermal stabilities of the compounds under investigation. The helium flow rate was varied within the range 0.5–5 l h^{-1}. Within the limits of the experimental error, the results of vapour density measurements were independent of the flow rate and experiment duration. This shows that sublimation, evaporation and condensation processes take place in these experiments under quasi-equilibrium conditions. This means that the carrier gas is saturated with the vapour of the chelate under investigation, and the influence of vapour diffusion is small. The data obtained allowed calculation of the pressure of saturated vapour, assuming that the studied compounds were transferred to the gas phase only in monomolecular form. In the event of partial decomposition of the compound during evaporation, vapour pressure was calculated from the data on the mass of the substance deposited in the cold zone.

The experiments involving studies of the temperature dependence of $Ru(dtk)_3$ vapour pressure were carried out in a cylindrical Knudsen chamber made of molybdenum (the dimensions of the inner volume were d=7 mm, h=8 mm). The effusion hole was 0.3 mm in diameter, and the length of the channel was 0.2 mm. Weighed samples of 3–10 g of the initial compound were evaporated at different temperatures within one run of the experiment up to complete disappearance of the chelate vapour. The temperature of the Knudsen chamber was set stepwise in arbitrary steps, and at every established temperature the total mass spectrum was recorded for 40–60 min. The coefficients B_i in the equation $P=B_iJ_i+T$ (which links the values of the measured intensities of the ion current corresponding to the molecular forms with the partial pressure of the vapour in the Knudsen chamber) were calculated from the amount of the evaporated substance, using a known equation [11].

The experimental data obtained with the flow and Knudsen methods were processed according to a special procedure [12]. The results are shown in the form of the equation $\ln P(\text{bar})=B-A/T$. The standard thermodynamic parameters ΔH_T^0 and ΔS_T^0 describing the vaporization of the studied complexes were calculated from the temperature dependences of the saturated vapour pressure.

Results and discussion

The mass loss curves obtained by heating the samples in the flow of helium are shown in Fig. 1, while those obtained in vacuum are shown in Fig. 2. The data relating to the thermoanalytical studies of the diethyldithiocarbamates of the platinum metals in helium and in vacuum are shown in Table 1. The X-ray diffraction patterns of the solid products of thermolysis formed on heating the chelates in a helium flow up to 500°C show that only metal phases are present.

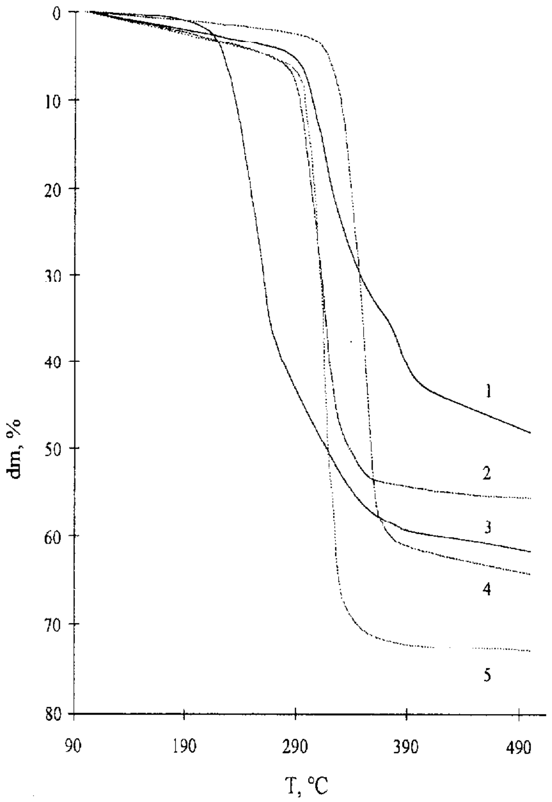

Fig. 1 Curves of mass loss in helium atmosphere for the complexes $Ir(dtk)_3$ (1), $Pt(dtk)_2$ (2), $Ru(dtk)_3$ (3), $Rh(dtk)_3$ (4) and $Pd(dtk)_2$ (5)

In our opinion, the initial temperatures of the complex decompositions listed in [9], which were obtained from the data of DTA in nitrogen, are too low (~200°C for $Ir(dtk)_3$, $Rh(dtk)_3$ and $Ru(dtk)_3$), since the chelates melt without decomposition at higher temperatures (Table 1). This may be connected with the purities of the obtained compounds, as the authors of [9] did not carry out any additional purification of the compounds after the synthesis. The formation of metal sulfides at temperatures higher than 350°C, reported by the same authors [9], is also doubtful, since this fact has not been confirmed by any additional studies. The data we obtained from the X-ray diffraction patterns did not reveal phases of metal sulfides in the products of thermolysis of the platinum metal diethyldithiocarbamates.

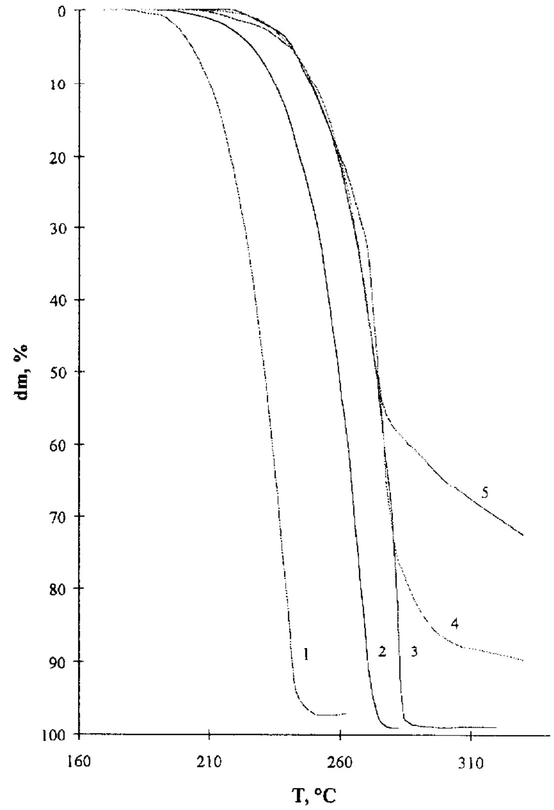

Fig. 2 Curves of mass loss in vacuum for the complexes $Pd(dtk)_2$ (1), $Pt(dtk)_2$ (2), $Rh(dtk)_3$ (3), $Ir(dtk)_3$ (4) and $Ru(dtk)_2$ (5)

The 100% mass loss of the samples of chelates heated at 340°C (Fig. 2) is evidence of the high sublimation ability of the studied compounds, except for $Ru(dtk)_3$.

Table 1 Thermal properties of platinum metal diethyldithiocarbamates

Compounds	$T_{\mathrm{melt.}}$/°C (Keffler table)	$T_{\mathrm{melt.}}$/°C (DTA/He)	$T_{\mathrm{decomp.}}$/°C (DTA/He)	$T_{(\Delta G,\ 50\%)}$/°C (vacuum)	% sub. (vacuum)
$Pt(dtk)_2$	>265	275	300	260	~100
$Pd(dtk)_2$	244	240	335	328	~100
$Ir(dtk)_3$	265	265	320	270	90
$Rh(dtk)_3$	260	260	350	270	~100
$Ru(dtk)_3$	235	235	250	275	70

The following qualitative sequence of increasing volatility of the platinum metal diethyldithiocarbamates in vacuum was obtained from thermoanalytical studies:

$$Ru(dtk)_3 \sim Ir(dtk)_3 \sim Rh(dtk)_3 < Pt(dtk)_2 < Pd(dtk)_2$$

The temperature dependences of the saturated vapour pressure of the synthesized compounds are shown in Fig. 3. The data for Pt(II), Pd(II), Ir(III) and Rh(III) were obtained by the flow method. It should be noted that $Rh(dtk)_3$, $Pd(dtk)_2$ and $Ir(dtk)_3$ sublime practically without decomposition. The vaporization of $Pd(dtk)_2$ and the sublimation of $Pt(dtk)_2$ are accompanied by partial thermal decomposition. For $Ru(dtk)_3$, the temperature dependence of the saturated vapour pressure was measured by the Knudsen method, with mass spectrometric registration of the composition of the gas phase, since the partial decomposition of the compound at a measured partial pressure and the catalytic properties of the metal did not allow use of the flow method. An additional mass spectrometric study showed that the complex sublimes in high vacuum at temperatures above 440 K. The mass spectra suggest the following results: the maximum ion mass registered in the used range of mass units corresponds to $[Ru(dtk)_3]^+$ (100%), $[Ru(dtk)_3-64]^+$ (47%), $[SRu(dtk)_2]^+$ (20%), $[Ru(dtk)_2]^+$ (57%), $[Ru(dtk)_2-32]^+$ (26%), $[Ru(dtk)_2-64]^+$ (9%), $[Ru(dtk)+64)^+$ (17%), $[Ru(dtk)+32)^+$ (13%) and $[Ru(dtk)-2)^+$ (14%). Mass spectrometric analysis of the products formed from $Ru(dtk)_3$ during heating showed the presence of the metal-containing forms $Ru(dtk)_3$ and $Ru(dtk)_2$ in the gas phase. It was found that the effusing flow of $Ru(dtk)_3$ at a constant temperature within the range 440–490 K was independent of time, while that of $Ru(dtk)_2$ at the same temperature decreased with time. Further, in this temperature range we observed an increase in concentration of metal-free products corresponding to ligand fragments. The concentrations of these products reached their maximum at a temperature near 470 K and decreased strongly with further increase of temperature and time. At temperatures above 500 K, both flows were observed to decrease rapidly with time down to complete

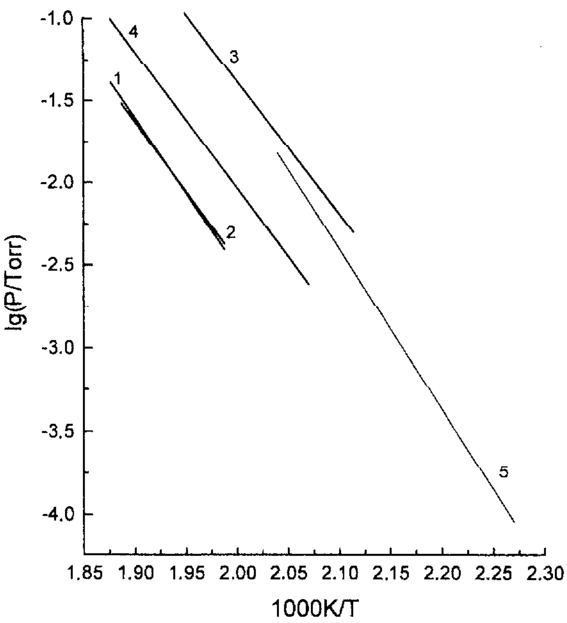

Fig. 3 Dependences of the logarithm of saturated vapour pressure on reciprocal temperature for the complexes $Ir(dtk)_3$ (1), $Rh(dtk)_3$ (2), $Pd(dtk)_2$ (3), $Pt(dtk)_2$ (4) and $Ru(dtk)_3$ (5)

disappearance of the corresponding molecular forms from the gas phase. The residual substance was non-volatile, at least up to 650 K. The listed facts allow the assumption that the heating of $Ru(dtk)_3$ causes oligomerization in the condensed phase. On the assumption that oligomerization had no impact on the partial pressure of $Ru(dtk)_3$ saturated vapour within the temperature range 440–490 K, we measured the temperature dependence of $Ru(dtk)_3$ vapour pressure. The vaporization parameters obtained for all the compounds under investigation are presented in Table 2.

It can be concluded from these data that the complexes with octahedral structure are less volatile than those with square planar structure, which is likely to be due to the increase in molecular mass of the compounds $M(dtk)_3$. The following sequence of increasing chelate volatility was obtained (for P=0.01 torr):

$$\begin{array}{ccccccccc} Ir(dtk)_3 & \sim & Rh(dtk)_3 & < & Pt(dtk)_2 & < & Ru(dtk)_3 & < & Pd(dtk)_2 \\ (514\ K) & & (514\ K) & & (500\ K) & & (485\ K) & & (481\ K) \end{array}$$

For comparison, Fig. 4 shows the temperature dependences of the saturated vapour pressure for the synthesized compounds: $Pd(dtk)_2$ (ΔH°_T (kJ mol^{-1})=153.1; ΔS°_T (J K mol^{-1})=224.4), $Ir(dtk)_3$ (ΔH°_T (kJ mol^{-1})=175.1; ΔS°_T (J K mol^{-1})=245.8), and literature data for $Cu(dtk)_2$ (ΔH°_T (kJ mol^{-1})=149.1; ΔS°_T (J K mol^{-1})=291.2) and $Co(dtk)_2$ (ΔH°_T (kJ mol^{-1})=177.5; ΔS°_T (J K mol^{-1})=315.0 [6]. It should be

Table 2 Thermodynamic parameters of vaporization processes of dietyldithiocarbamates of platinum group metals

Compound	Process	Number of points	T_{range}/ °C	$\mathrm{Ln}P\pm\sigma=B-A/T$			ΔH°_{T}/ kJ mol^{-1}	ΔS°_{T}/ J (mol K)$^{-1}$
				B	A	σ^2		
Rh(dtk)$_3$	sub	11	230–260	28.35	20365	$128616/T^2-492/T+0.47$	169.3±3.0	235.7±5.7
Ir(dtk)$_3$	sub	9	230–260	29.57	21063	$236029/T^2-910/T+0.88$	175.1±4.0	245.8±7.8
Ru(dtk)$_3$	sub	7	170–220	34.55	22284	$497870/T^2-2132/T+2.3$	185.3±5.7	287.3±12.6
Pt(dtk)$_2$	sub	15	210–260	26.53	18894	$57772/T^2-226/T+0.22$	157.1±2.0	220.6±3.9
Pd(dtk)$_2$	sub	14	220–240	26.99	18419	$49536/T^2-199/T+0.20$	153.1±1.9	224.4±3.7
Pd(dtk)$_2$	vap	5	250–285	16.33	12940	$22369/T^2-83/T+0.08$	107.6±1.2	135.8±2.3

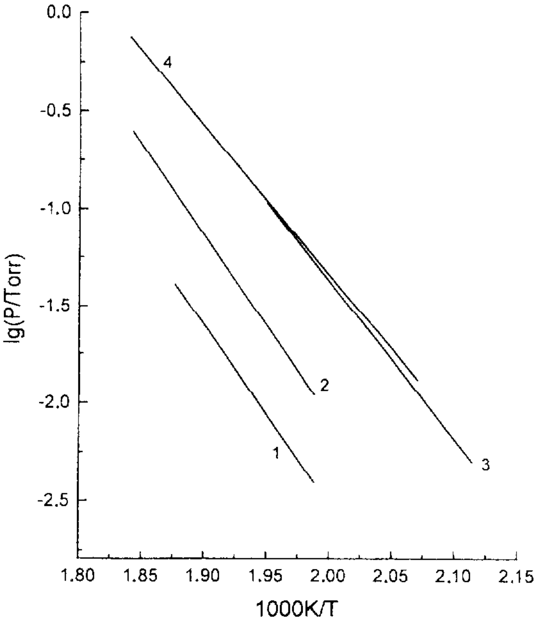

Fig. 4 Dependences of the logarithm of saturated vapour pressure on reciprocal temperature for the complexes Ir(dtk)$_3$ (1), Co(dtk)$_3$ (2) [6], Pd(dtk)$_2$ (3) and Cu(dtk)$_2$ (4) [6]

noted that the sublimation enthalpy values for the diethyldithiocarbamates of the metals in identical oxidation states are close to each other. However, the difference in volatility of the complexes of the trivalent metals is higher than that for the bivalent metals.

Thus, data on the thermal stabilities of platinum metal diethyldithiocarbamates have been obtained in the present work, and the vaporization parameters of the compounds have been determined. It can be concluded that the thermal properties of these platinum metal diethyldithiocarbamates allow the use of these compounds to obtain metal coatings by vapour deposition.

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References

1 S. K. Sengupta and A. S. Kumar, Thermochim. Acta, 72 (1984) 349.
2 S. V. Larionov, Zh. Neorg. Khim., 38 (1993) 1616.
3 S. V. Larionov and L. A. Kosareva, Thermal Analysis, Proc. IVth ICTA Budapest, 1 (1974) 877.
4 A. S. Kumar, Thermochim. Acta, 104 (1986) 339.
5 L. H. Pignolet, Inorg. Chem., 13 (1974) 2051.

6 A. Tavlaridis and R. Neeb, Fresenius Z. Anal. Chem., 293 (1978) 211.
7 K. J. Cavell, J. O. Hill and R. J. Magee, Thermochim. Acta, 33 (1979) 383.
8 K. J. Cavell, J. O. Hill and R. J. Magee, Thermochim. Acta, 34 (1979) 155.
9 S. Kumar and N. K. Kaushik, Indian, J. Chem., 20A (1981) 512.
10 S. V. Sysoev, A. N. Golubenko, L. D. Nikulina and T. N. Martynova, Thermochim. Acta, 225 (1993) 137.
11 L. N. Sidorov, M. V. Korovob and L. V. Zhuravlyeva, Mass spectrometric thermodynamical studies. Moscow, MSU, 1985, p. 92–93.
12 V. A. Titov and G. A. Kokovin, Mathematics in chemical thermodynamics, Nauka, Novosibirsk, 1980, p. 98–105 (in Russian).