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VAPOR PRESSURE MEASUREMENTS IN CARRIER GAS CONTAINING LIGAND VAPOR USING THE TRANSPIRATION TECHNIQUE

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ABSTRACT

The vapor pressures of 1,1,1-trifluoro-2,4-pentanedionates were measured in 0.1–10 mm Hg using the transpiration technique with helium or helium containing the ligand vapor as carrier gas. The injection chamber of a gas chromatograph equipped with a ligand vapor generator was used. The vapor pressure of bis(1,1,1-trifluoro-2,4-pentanedionato)nickel(II) was measured for the first time, stabilized in ligand vapor atmosphere. The vapor pressures of standard samples (naphthalene and benzoic acid) agreed well with previously reported values.

INTRODUCTION

There are several methods for measuring the vapor pressure of substances, e.g., direct static method by an isoteniscope, indirect static method by a Bourdon gauge, and the Knudsen effusion method. However, these methods need a high vacuum, require a long time to reach equilibrium, and are subject to traces of volatile impurities. In contrast, the transpiration method, which is a dynamic method first used by Regnault [1], had long been erroneous because of unsaturation of the sample vapor in the carrier gas and the miscalculation of the vapor pressure based on the extrapolation of a flow rate to zero [2]. Recently, this method has been used increasingly with modification [3,4]. There are several advantages for this method, i.e., it is not influenced by a small amount of volatile impurities, and it is possible to measure the equilibrium vapor pressure within a short time by diminishing the dead volume of a sample chamber over the substances and it is also possible to make measurements in any atmosphere by changing the carrier gas.

In this paper, the applicability of the transpiration method to the measurement of the vapor pressure of chelates was investigated, and a satisfactory result was obtained for bis(1,1,1-trifluoro-2,4-pentanedionato)nickel(II), Ni(tfa)$_2$, for the first time, stabilized in a carrier gas containing the ligand vapor.

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EXPERIMENTAL

Reagents and preparation of chelates

Benzoic acid was a standard sample for calorimetry (Nenryo-Kyokai, Japan) dried in a silica gel desiccator for > 48 h. Anthraquinone was recrystallized twice from toluene. Naphtalene was used without further purification. The chelates were prepared according to the previously reported procedures [5].

Apparatus and procedures

A Shimadzu model GC-6A gas chromatograph equipped with a ligand vapor generator was used (Fig. 1). The ligand concentration in the carrier gas was about 1.0% v/v. A Pyrex sample tube (88 × 3.5 mm ID, 0.5 mm wall thickness) was used.

A precisely weighed sample tube containing the measuring substance (15–25 mg) was inserted into the injection chamber (5 mm bore) which was preheated at a chosen temperature, and the entrance of the injection port was tightly closed with a silicone rubber stopper (Fig. 2). The carrier gas (helium or helium containing the vapor of 1,1,1-trifluoro-2,4-pentanedione) was passed through the tube at a constant flow rate. The tube was kept at the chosen temperature for a definite time, removed from the injection chamber, cooled in a desiccator, and reweighed. The temperature of the injection chamber was raised in a stepwise manner, and the procedure was repeated as above. For $Ni(tfa)_2$, the sample was preheated at 120°C for 10 min to dehydrate [5] coordinated water, both ends of the tube were sealed with caps, and it was cooled in a desiccator.

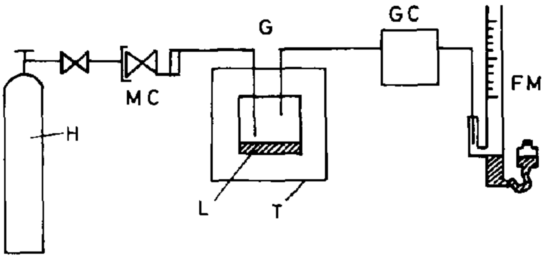

Fig. 1. Schematic diagram of the apparatus. H, helium cylinder; MC, mass-flow controller; G, ligand vapor generator; L, ligand (1,1,1-trifluoro-2,4-pentanedione), T, thermostat; GC, gas chromatograph. FM, flow meter.

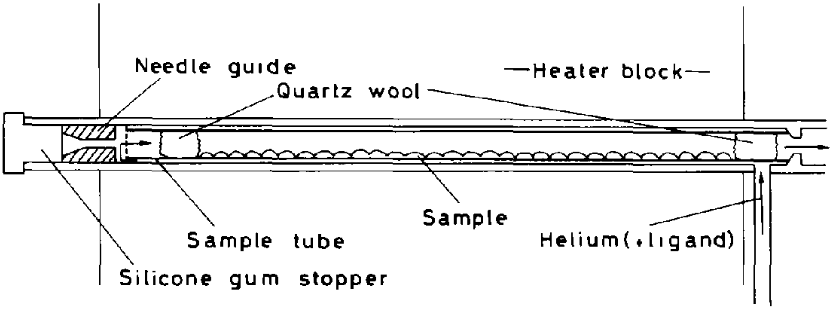

Fig. 2. Sample chamber.

RESULTS AND DISCUSSION

Calculation of vapor pressure

It is possible to calculate the vapor pressure of a substance from weight loss (amount vaporized), the flow rate, and the heating time. The following equation was used

$$P = 62.36\frac{wT}{Mvt}$$

where P = vapor pressure of the substance (mm Hg); w = weight loss (mg); T = room temperature (K); M = molecular weight of the substance in the vapor phase; v = flow rate of the carrier gas at room temperature (ml min^{-1}); t = heating time (min). In this paper it was assumed that all the substances were monomers in the vapor phase.

Vapor pressure of standard samples

The accuracy of the method was confirmed by the measurements of organic substances. Naphthalene and benzoic acid were chosen for this purpose because they are thermally stable and easily obtainable pure substances.

First, the time from the insertion of a sample tube to the equilibrium was investigated. Figure 3 shows that the plots of the weight loss of a sample against heating time form a straight line passing through the origin. Therefore, the time to reach equilibrium is negligibly short compared with the heating time. This fact applies to both naphthalene and benzoic acid when the heating time is more than 1 min. As an example of a chelate, bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II), $Cu(tfa)_2$, was investigated and the same result was observed as in Fig. 3. From this fact, the heating time for the measurement of vapor pressure was settled at > 1 min so that the weight loss is in the range 5–15 mg.

The effect of flow rate was investigated to see the degree of saturation of the sample vapor in a carrier gas. The results are shown in Fig. 4. The calculated vapor pressure was constant at 15–60 ml min^{-1} for naphthalene and at 10–60 ml min^{-1} for benzoic acid. Likewise, tris(1,1,1-trifluoro-2,4-pentanedionato)aluminum(III), Al(tfa)$_3$, and Cu(tfa)$_2$ as an example of a chelate, indicated a constant value at 20–40 ml min^{-1} for Al(tfa)$_3$, at 20–45 ml min^{-1} at 130°C and at 5–40 ml min^{-1} at 160°C for Cu(tfa)$_2$. For the precision of the vapor pressure in this range, the average and standard deviation of five measurements of Cu(tfa)$_2$ at 130°C was 0.394 and 0.004 mm Hg and those of 15 measurements at 160°C was 3.96 and 0.1 mm Hg, respectively. It is concluded that the saturated vapor pressure is measured at 20–40 ml min^{-1} by this apparatus independent of the vapor pressure or the type of substance.

Figure 5 shows the Clausius–Clapeyron plots of naphthalene and benzoic acid. The broken line is the value of the reference. The results agreed well with those of the reference within the experimental error. The calculated sublimation and evaporation enthalpies also coincided with the reference values (Table 1). Measurements at higher temperatures were examined by using anthraquinone. In the temperature range measured, the vapor pressure was reported only by Bardi et al. [6]. The sublimation enthalpy extrapolated to 230°C according to their equation, 25.0 kcal, is close to the present result, 25.3 kcal.

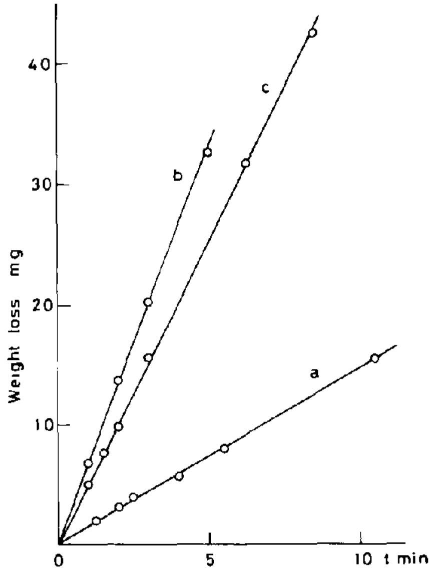

Fig. 3. Relationship between the heating time and the weight loss of standard samples and Cu(tfa)$_2$: Flow rate, 30 ml min^{-1}; (a) naphthalene at 80°C; (b) benzoic acid at 160°C; (c) Cu(tfa)$_2$ at 170°C.

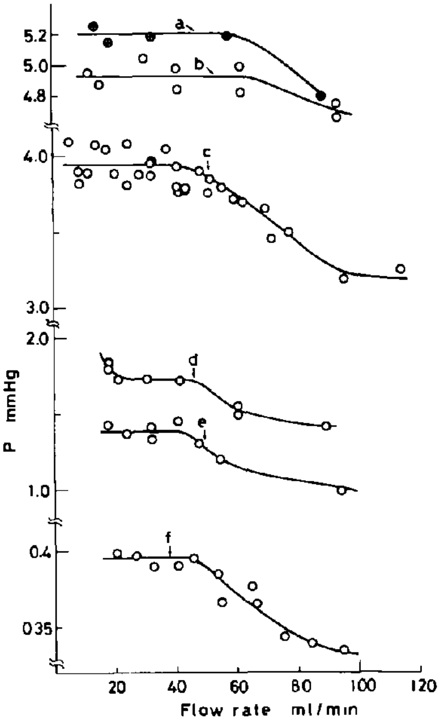

Fig. 4. Relationship between the flow rate and calculated vapor pressure of standard samples and chelates: (a) naphthalene at 75°C; (b) benzoic acid at 120°C; (c) $Cu(tfa)_2$ at 160°C; (d) $Al(tfa)_3$ at 120°C; (e) $Ni(tfa)_2$ at 180°C; (f) $Cu(tfa)_2$ at 130°C.

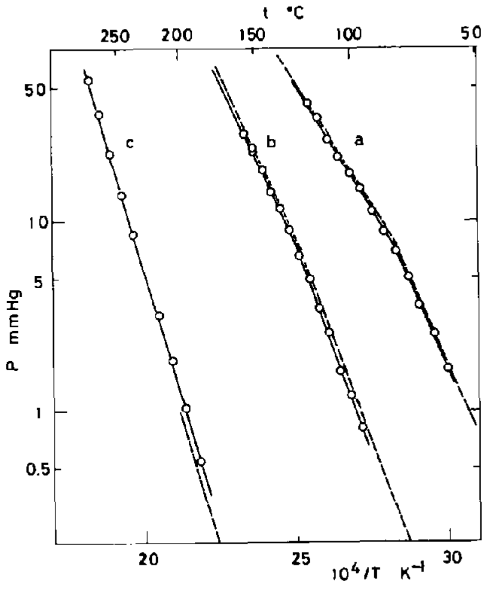

Fig. 5. Clausius–Clapeyron plots of standard samples and anthraquinone; (a) naphthalene; (b) benzoic acid; (c) anthraquinone. Dotted lines show the reference values: (a) ref. 15; (b) ref. 18; (c) ref. 6.

Vapor pressure of 1,1,1-trifluoro-2,4-pentanedionates

Al(tfa)$_3$ and tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III), Cr(tfa)$_3$, are relatively thermally stable and well studied. As shown in Fig. 6, the results agree with the reference values except for one report. The result reported by Berg and Truemper [7] is erroneous, as is pointed out by Wolf et al. [8] and Igumenov et al. [9,10], since an isoteniscope is not favored for measurements of the vapor pressure of chelates because of the decomposition on contact with mercury. The data on tris(1,1,1-trifluoro-2,4-pentanedionato)iron(III), Fe(tfa)$_3$, and Cu(tfa)$_2$ are scarce. The data of the present investigation were almost identical to the results measured with a spoon gauge reported by Igumenov and co-workers [10,11].

As mentioned above, it is concluded that this method is suitable for the measurement of various substances which have a vapor pressure of 0.1–10 mm Hg at 50–280°C.

In contrast to anhydrous chelates, hydrated chelates such as Ni(tfa)$_2$ [12], bis(1,1,1-trifluoro-2,4-pentanedionato)cobalt(II), Co(tfa)$_2$ [13], bis(1,1,1-trifluoro-2,4-pentanedionato)manganese(II), Mn(tfa)$_2$ [14] do not elute from gas chromatographic columns in helium or other inert carrier gas, but can be quantivatively eluted by using helium containing the ligand vapor as carrier

TABLE 1

Sublimation and evaporation enthalpies of naphthalene and benzoic acid

Author	Method	Temp. range	Sublimation enthalpy (kcal mol^{-1})	Evaporation enthalpy (kcal mol^{-1})
Naphthalene				
Fowler et al. [15]	quartz helix gauge	40–180°C	16.7[a]	12.0[a]
Sinke [16]	transpiration	200–500 K	16.9[a]	–
Ambrose et al. [17]	diaphragm gauge	263–343 K	16.7[a]	–
This work	transpiration	60–120°C	16.7	12.3
Benzoic acid				
Klosky et al. [18]	isoteniscope	50–247°C	20.2[a]	17.3[a]
Davies and Jones [19]	transpiration	70–114°C	21.9[a]	–
Malaspina et al. [20]	Knudsen effusion	338–383 K	20.6	–
This Work	transpiration	95 155°C	20.8	16.2

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[a] Calculated from reported vapor pressures by the Clausius–Clapeyron equation.

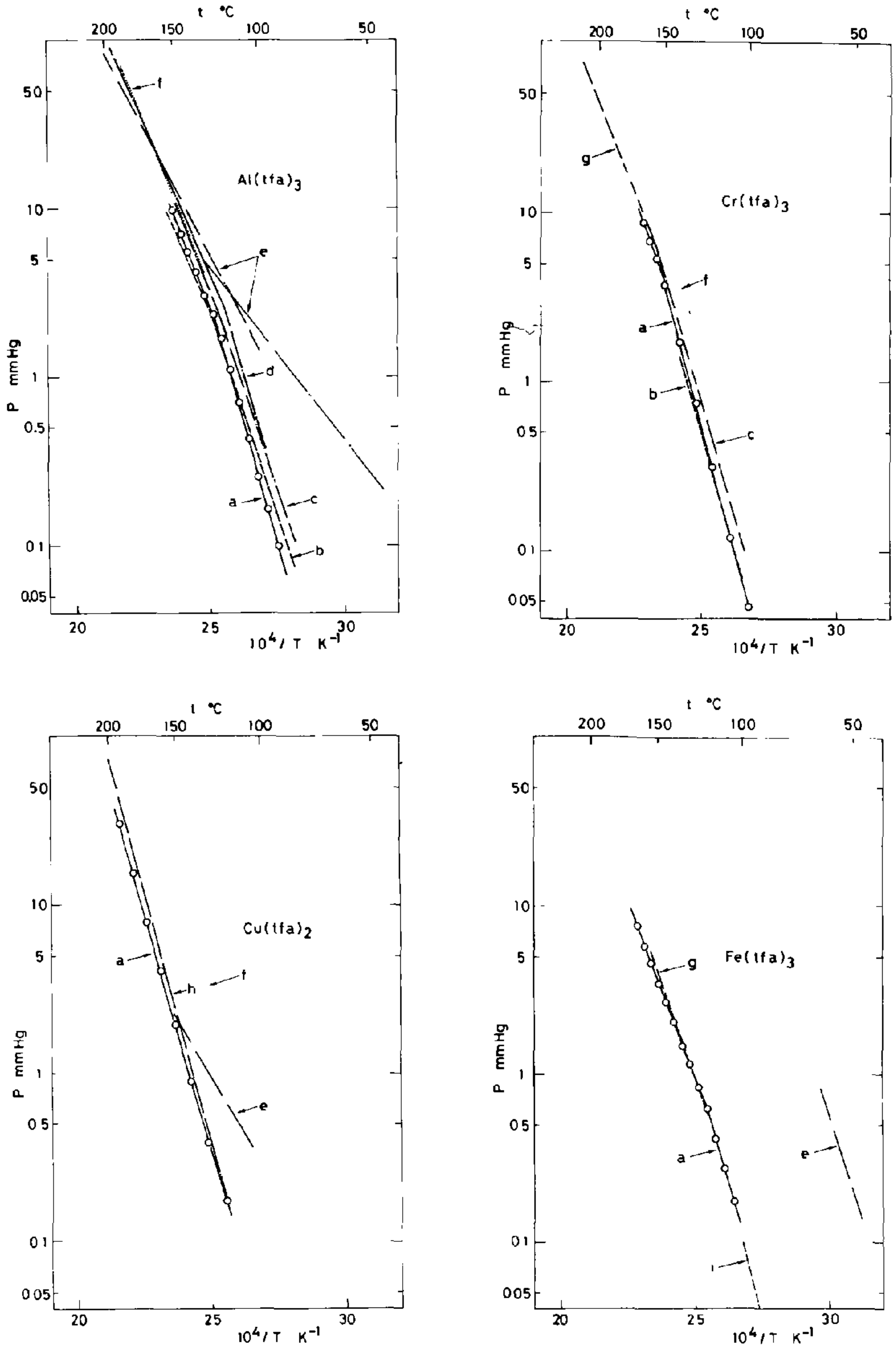

Fig. 6. Clausius–Clapeyron plots of the chelates of 1,1,1-trifluoro-2,4-pentanedione. (a) This work, (b) ref. 21; (c) ref. 8; (d) ref. 9; (e) ref. 7; (f) ref. 22; (g) ref. 11; (h) ref. 10; (i) ref. 23.

gas. This is because the thermal dissociation of the ligands was depressed by ligand vapor additives. This technique was applied to the measurement of vapor pressure of $Ni(tfa)_2$.

In Fig. 4, the relation between flow rate and calculated vapor pressure is shown. A constant vapor pressure was indicated at 20–40 ml min^{-1} in the

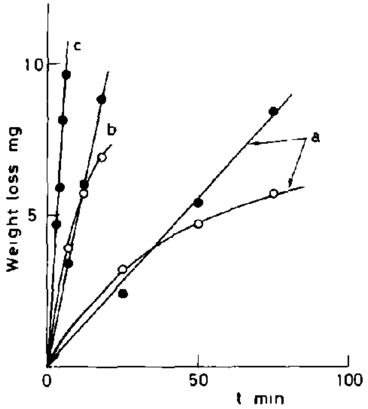

Fig. 7. Relationship between the heating time and the weight loss of $Ni(tfa)_2$. (○) In helium; (●) in helium containing the ligand vapor. (a) 150°C; (b) 170°C; (c) 190°C.

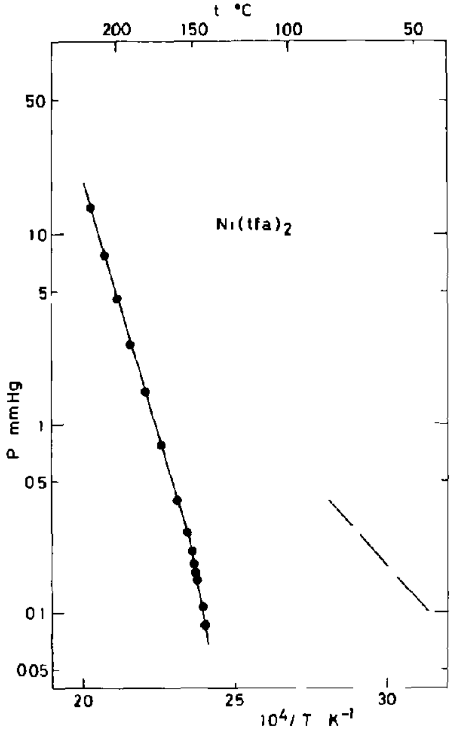

Fig. 8. Clausius–Clapeyron plots of $Ni(tfa)_2$ in helium containing ligand vapor (solid line). Dashed line shows the value reported in ref. 7.

carrier gas containing the ligand vapor.

Figure 7 shows the relation between heating time and sample weight loss. In the carrier gas containing ligand vapor, the weight loss is proportional to the heating time at 150, 170 and 190°C. In helium carrier gas, the weight loss is not linear with the heating time, and is greater within a short time than that of the carrier gas containing the ligand vapor because thermal dissociation occurred together with sublimation. As the heating time increased, the line became curved and the weight loss decreased because of thermal decomposition. In contrast, the presence of ligand vapor had no effect on the weight loss of $Al(tfa)_3$, $Cu(tfa)_2$ and $Fe(tfa)_3$.

The measurement results are shown in Fig. 8. A clear break-point at 153°C indicates the melting point of $Ni(tfa)_2$ in ligand vapor atmosphere. Since $Ni(tfa)_2$ does not melt in air or in helium up to its decomposition temperature, this is one of the remarkable features in ligand vapor atmosphere. The details will be reported separately. Compared with the authors' result, that reported by Berg and Truemper [7] shows a too high vapor pressure, probably due to the dissociation of coordinated water. Their measurements by the static method are subject to traces of more volatile impurities which were not completely removed.

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