Vacuum Sublimation Behavior of Metal Complexes of Thio-β-diketones. Purification of Manganese(II), Iron(III), Cobalt(III), Nickel(II), Copper(II), Zinc(II), Palladium(II), Silver(I), and Cadmium(II) with 1,1,1-Trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one

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(Received June 13, 1983)

Synopsis. A vacuum sublimation apparatus with a continuous temperature gradient (25—260 °C) along the tube (0—50 cm) at 2×10^{-2} Torr (1 Torr≈133.322 Pa) was used. STTA (1,1,1-trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one) and its metal chelates of Mn^{II}, Fe^{III}, Co^{III}, Ni^{II}, Cu^{II}, Zn^{II}, and Pd^{II} sublimed quantitatively without thermal decomposition, while the chelates of Ag^{I} and Cd^{II} were accompanied by thermal decomposition.

The vacuum sublimation method is useful for the purification and separation of metal chelates.[1,2] Of the 14 chelating reagents other than β-thioxo ketones, diethyldithiocarbamates and oxine were found to offer the greatest promise for this purpose.[1] The present research aims to find suitable β-thioxo ketones for the purification of metals as their chelates by vacuum sublimator with continuous temperature gradient under low pressure. Some aspects of vacuum sublimation behavior of the chelate compounds will also be discussed.

Experimental

Materials. Various monothio analogs of β-diketones were synthesized by the reaction of hydrogen sulfide with β-diketones in an anhydrous ethanol in the presence of hydrogen chloride for 30—60 min, as described previously.[3,6] Nickel(II) chelate compounds with disulfur analogs of β-diketones were also prepared by the modification of the reaction of a corresponding β-diketone dissolved in an anhydrous ethanol with hydrogen sulfide in the presence of nickel(II) chloride and hydrogen chloride as a catalyst for 1—5 h.[7] Nickel(II) dithioacetylacetone was also prepared by the two electron reduction of 3,5-dimethyl-1,2-dithiolium cation with sodium tetrahydroborate in the presence of nickel(II) ion.[8] The chelating reagents and their nickel(II) chelates tested were as follows: SAA (4-mercapto-3-penten-2-one), SSAA (4-mercapto-3-penten-2-thione), SDBM (3-mercapto-1,3-diphenyl-2-propen-1-one), SBFA (1,1,1-trifluoro-4-mercapto-4-phenyl-3-buten-2-one), SSBFA (1,1,1-trifluoro-4-mercapto-4-phenyl-3-butene-2-thione), STTA (1,1,1-trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one), SSTTA (1,1,1-trifluoro-4-(2-thienyl)-4-mercapto-3-butene-2-thione), and their parent β-diketones of AA (2,4-pentanedione), BA (1-phenyl-1,3-butanedione), DBM (1,3-diphenyl-1,3-propanedione), BFA (benzoyltrifluoroacetone), TTA (2-thenoyltrifluoroacetone). All other metal chelates were prepared by solvent extraction mentioned previously.[2] These materials were purified by recrystallization from carbon tetrachloride or by sublimation *in vacuo* before usage. The content of sulfur in the products was ascertained by using the Sn^{II}-strong phosphoric acid method;[9] the results were in good agreement with the theoretical values.

Sublimation Procedure. A vacuum sublimation apparatus providing a continuous temperature gradient (25—260 °C) along the tube (0—50 cm) at 2×10^{-2} Torr was used, as previously described.[1] The patterns of the rise in temperature along the sublimation tube are shown in Fig. 1. These patterns were obtained by supplying the following electric power through the mantle heaters; 50, 20, 10, and 4.2 V at 1.38 A. Metal chelates were placed inside the apparatus for 2 h after establishment of the thermal equilibrium. The temperature gradient along the sublimator is shown in Fig. 2; this was obtained after the thermal equilibrium. The temperature gradient in the region of 25 (room temperature) to 260 °C is about 4 °C/cm with the deviation of ±4 °C. The sublimate zone along the sublimation tube was decided from the color of the chelate and its position of deposition.

Results and Discussion

Effect of ligands on the sublimation-recrystallization temperatures for various nickel(II) chelates of β-thioxo ketones and their parent β-diketones are shown in Fig. 3. The temperature range of the deposited zones, the recovery, and the colors of the various nickel(II) chelates after sublimation are summarized in Table 1. The

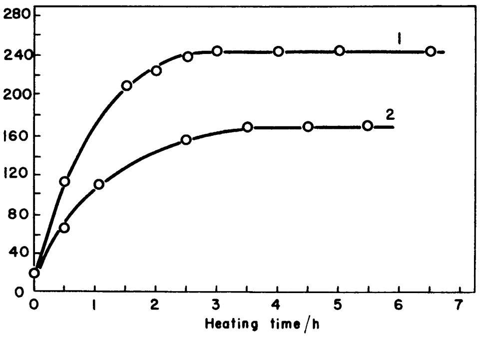

Fig. 1. Rate of rise in temperature along vacuum sublimator. Distance of the places from the high temperature end of the sublimator: (1) 15 cm, (2) 30 cm.

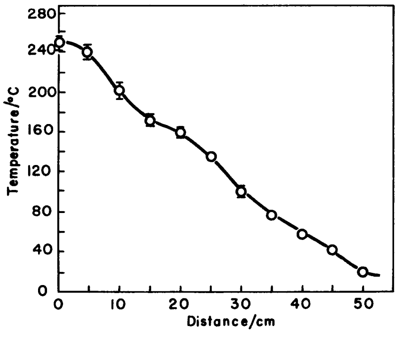

Fig. 2. Continuous temperature gradient along vacuum sublimator.

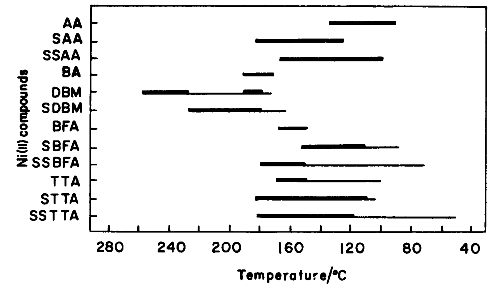

Fig. 3. Effect of ligands on the sublimation-recrystallization temperatures for nickel(II) chelates with various β-thioxo ketones and their parent β-diketones.

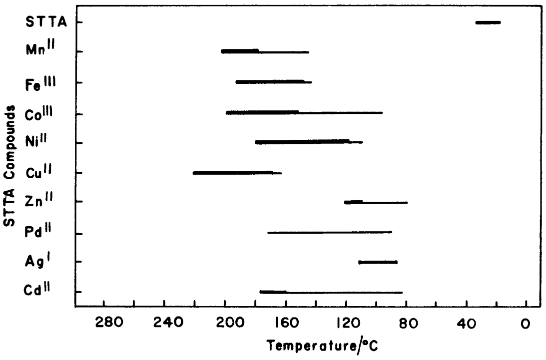

Fig. 4. Sublimation-recrystallization temperature for various metal STTA chelates.

TABLE 1. SUBLIMATION-RECRYSTALLIZATION ZONE TEMPERATURES, AMOUNTS REMAINING, AND COLORS OF VARIOUS NICKEL(II) CHELATES AFTER SUBLIMATION AT 2×10^{-2} Torr

Nickel chelates	Recrystallization zone temperature/°C	Color	Chelate taken (mg)	Metal chelate remaining[a]
AA	134— 91	yellow green	14.1	none
SAA	124—183	light gray	3.2	much
SSAA	168— 98	dark gray	12.2	much
BA	191—172	yellow green	5.6	none
DBM	258—171	yellow green	11.1	none
SDBM	228—164	dark brown	3.9	none
BFA	168—148	yellow green	6.4	none
SBFA	153— 88	brown	2.5	a little
SSBFA	178— 70	brown	4.8	much
TTA	170—100	yellow green	26.9	none
STTA	181—108	deep red	18.5	none
SSTTA	181— 50	brown	4.5	a little

a) None, 0—10%; a little, 10—30%; much, >30%.

TABLE 2. SUBLIMATION-RECRYSTALLIZATION ZONE TEMPERATURES, AMOUNTS REMAINING, AND COLORS OF VARIOUS METAL STTA CHELATES AFTER SUBLIMATION AT 2×10^{-2} Torr

STTA chelates	Recrystallization zone temperature/°C	Color	Chelate taken (mg)	Metal compound remaining[a]
STTA	< 45	red	11.3	none
Mn^{II}	204—145	brown	1.8	a little
Fe^{III}	194—144	deep orange	18.7	none
Co^{III} [b]	200— 96	dark orange	53.5	none
Ni^{II}	181—108	deep red	18.5	none
Cu^{II}	221—163	olive brown	1.6	none
Zn^{II}	121— 79	yellow orange	6.5	none
Pd^{II}	173— 90	deep orange	1.7	a little
Ag^{I}	112— 86	orange	4.5	much
Cd^{II}	178— 82	orange	4.4	much

a) None, 0—10%; a little, 10—30%; much, >30%. b) Ascertain the tervalent cobalt by spectrophotometry and solvent extraction method.[3,13,14]

sublimation-recrystallization temperature of nickel(II) chelates generally increased in the following order: AA<BFA, TTA<BA<DBM; SSAA, SBFA, SSBFA, STTA, SSTTA, SAA<SDBM. All of the chelates sublimed within 30 min to 2 h, and deposited inside the wall of the glass tube in the temperature range of 50 to 260 °C. The preliminary examination on the sublimation behavior of nickel(II) chelates of various β-thioxo ketones revealed that the STTA chelates were more volatile and stable on heating, so that a series of metal chelates of STTA was examined in detail. The results are schematically shown in Fig. 4, in which a thicker line indicates the deposited zone of uniformity with a large amount of metal chelate. The data are listed in Table 2. The STTA and its metal chelates of Mn^{II}, Fe^{III}, Co^{III}, Ni^{II}, Cu^{II}, Pd^{II}, and Zn^{II} sublimed quantitatively without thermal decomposition, while the chelates of Ag^{I} and Cd^{II} were accompanied by thermal decomposition. Berg and Reed reported that the STTA chelates of Cd^{II}, Co^{II}, Cu^{II}, Ni^{II}, Pb^{II}, Pd^{II}, and Zn^{II} partially sublimed with remarkable thermal decomposition at 1.3 Torr in a stream of air.[11] The thermal decomposition may be due to an air oxidation of STTA chelates under higher pressure. In the present investigation, it was found that the STTA chelates (1.6—53.5 mg) sublimed quantitatively without thermal decomposition at 2×10^{-2} Torr. The sublimation-recrystallization temperature of individual chelates increased in the following order: Ag^{I}<Zn^{II}<Pd^{II}<Cd^{II}<Ni^{II}<Fe^{III}<Co^{III}<Mn^{II}<Cu^{II}. In general, when a large amount of metal chelate (20—200 mg) sublimed, the deposited zone appeared at a temperature higher by about 50 °C than the ordinary position. Therefore the sublimation is useful for purification of each metal chelate, since highly pure crystals, especially large-sized pure crystals, can be obtained.

The authors wish to thank Professor Emeritus Toshiyasu Kiba of Kanazawa University for his helpful advice.

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