Volatile Characteristics of Some Cobalt(III) And Iron(II) β-Diketone Chelates

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RECENTLY Berg and Truemper (*1*) reported on the volatile characteristics of a series of β-diketone chelates involving beryllium(II), aluminum(III), manganese(II), iron(III), cobalt(II), nickel(II), and copper(II) and the ligands: acetylacetone (AA), acetyltrifluoroacetone (ATA), benzoylacetone (BA), benzoyltrifluoroacetone (BTA), 2-furoyltrifluoroacetone (FTA), and 2-thenoyltrifluoroacetone (TTA). The molar heats of sublimation (vaporization) of these compounds were calculated from vapor pressure–temperature data and used as a criterion of volatility of the metal chelates: the larger the molar heat of sublimation, the less volatile the compound. An evaluation of the data indicated symmetry and polarity were determinative with regard to the magnitude of the molar heat of sublimation, but the results were not conclusive because of the inability to assign definitely true structural forms to all of the chelates. Nevertheless, it was observed that tetrahedral and octahedral arrangements of the nonfluorinated ligands about the central metal atom resulted in lower molar heats of sublimation than planar arrangements. Just the opposite effect was observed with the fluorinated ligands. The substitution of a trifluoromethyl, aromatic, or heterocyclic group for a methyl group of the ligand increased the molar heat of sublimation of the chelate.

The present study was undertaken to elucidate further the effect of the central metal atom on chelate volatility by comparing chelates of the same metal in different oxidation states.

EXPERIMENTAL

The source of ligands and the experimental technique used in this study are adequately described in the earlier work (*1*).

The following general method was used for the preparation of the cobalt chelates. An aqueous solution of tetramine carbonatocobalt(III) was added slowly in excess to an alcoholic solution of the diketone and the reaction mixture was allowed to stand overnight. The cobalt(III) chelates were then collected by filtration, washed, and dried, overnight in a vacuum oven at 50° C. The crude chelates were recrystallized twice from benzene and dried at 50° C.

Tris(acetylacetono)cobalt(III). Dark green crystals, m.p. 195–96° C., reported (*3*) 196° C. [Analysis, calcd. for $Co(C_5H_7O_2)_3$: Co 16.69. Found: Co 16.54.]

Tris(acetyltrifluoroacetone)cobalt(III). A green solution formed during reaction time, but all attempts to isolate the chelate were unsuccessful.

Tris(benzoylacetono)cobalt(III). Light green crystals, m.p. 117–18° C. [Analysis, calcd. for $Co(C_{10}H_9O_2)_3$: Co 10.86. Found Co 10.73.]

Tris(benzoyltrifluoroacetone) cobalt(III). Light green crystals, m.p. 156–7° C. [Analysis, calcd. for $Co(C_{10}H_6O_2F_3)_3$: Co 8.37. Found: Co 8.46.]

Tris(2-thenolytrifluoroacetone) cobalt(III). Light green crystals, m.p. 157–58° C. [Analysis, calcd. for $Co(C_8H_4O_2F_3S)_3$: Co 8.16. Found: Co 8.23.]

Tris(2-furoyltrifluoroacetone) cobalt(III). Light green crystals, m.p. 181–82° C. [Analysis, calcd. for $Co(C_8H_4O_3F_3)_3$: Co 8.74. Found: Co 8.74.]

The general scheme of preparation of the iron(II) chelates was to add an excess of a 10% aqueous solution of ferrous ammonium sulfate to an alcoholic solution of the diketone buffered with sodium acetate. The reaction mixture was filtered immediately in an inert atmosphere and the crude product treated as follows.

Tris(2-thenoyltrifluoroacetono)iron(II). The purple crystals were recrystallized twice from benzene and dried at 50° C., m.p. 86–7° C.

The cation associated with the precipitate could not be positively identified, but the percentage of iron would vary from 7.52 for $Na[Fe(C_8H_4O_2F_3S)_3]$ to 7.57 for $NH_4[Fe(C_8H_4O_2F_3S)_3]$ to 7.75 for $H[Fe(C_8H_4O_2F_3S)_3]$. Found: Fe 7.65. A plot of the logarithm of the vapor pressure *vs.* $1/T$ for this substance was a straight line from room temperature to the melting point.

Tris(2-furoyltrifluoroacetono)iron(II). The purple crystals were sublimed at 133–38° C., at a pressure of approximately 5 mm. Hg, m.p. 189° C. The cation associated with the chelate was not identified.

DISCUSSION

Plots of the vapor pressure *vs.* the reciprocal of the absolute temperature are given in Figures 1 and 2 for the chelates studied. The molar heats of sublimation calculated from these data are compared with the values for the corresponding cobalt(II) and iron(III) chelates in Table I.

The octahedral cobalt(III) compounds are more volatile than the planar (?) cobalt(II) compounds for the nonfluorinated ligands and less volatile for the fluorinated ligands. The trends observed in the earlier work indicated that this was to be expected. Thus, for the cobalt chelates at least, it seems that the spatial arrangement of the ligands about the central metal atom is the primary factor determining chelate volatility.

Much less can be determined from a comparison of the iron(II) and iron(III) chelates, since it was possible to isolate only two of the iron(II) chelates, tris(2-thenoyltrifluoroacetono)iron(II) and tris(2-furoyltrifluoroacetone)-iron(II), and their characterization was not absolute. Even so, it was felt that these compounds should be included here because a survey of the literature failed to turn up any successful preparation of these iron(II) chelates in the solid state.

The iron(II) chelates are more volatile than the corresponding iron(III) chelates, but since both have an octahedral arrangement of ligands about the central metal atom, the difference in volatility must be attributed to something other than the spatial arrangement of the ligand. The presence of a cation in the iron(II) chelate so compli-

Table I. Molar Heats of Sublimation of Some Cobalt(III) and Iron(II) β-Diketone Chelates

Metal	Ligand AA	BA	BTA	FTA	TTA
	Kilocalories				
Co(III)	3.11	9.31	12.2	8.50	10.9
Co(II)[a]	15.0	22.9	...	...	4.24
Fe(III)[a]	4.67	2.68	8.56	14.3	11.1
Fe(II)	...	...	...	6.70	5.68

[a] From (*1*).

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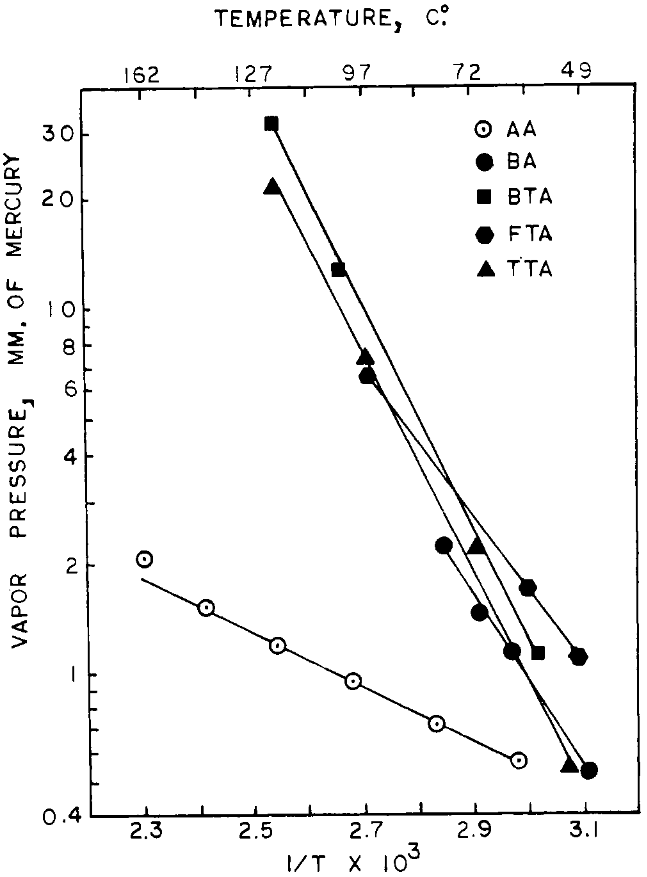

Figure 1. Vapor pressure *vs.* 1/*T* for some β-diketone chelate compounds of cobalt(III)

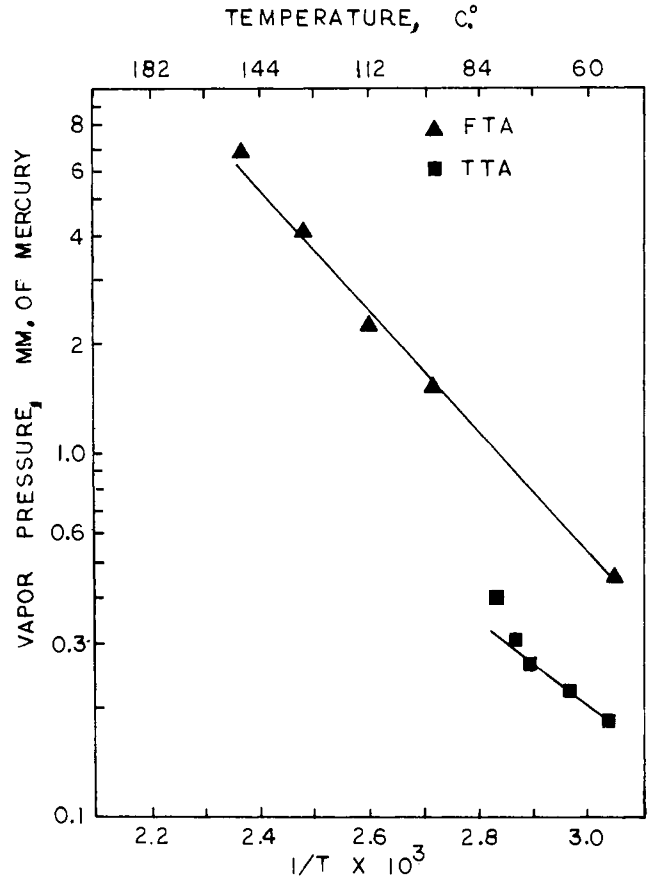

Figure 2. Vapor pressure *vs.* 1/*T* for some β-diketone chelate compounds of iron(II)

cates the matter that no logical explanation for the observed differences can be presented.

Attempts to isolate the iron(II) chelates of acetylacetone, benzoylacetone, and benzoyltrifluoroacetone were not successful, but there was ample evidence for their existence in solution. Reaction mixtures turned purple immediately upon mixing reagents, but the purple products reverted to the red iron(III) form on exposure to the atmosphere. It is well known that this type reaction can take place in solutions or solids very easily and that the more electrophilic the substituent group, the more stable is the iron(II) chelate (*2*). This is the probable explanation for the greater stability of the iron(II) FTA and TTA chelates, since the furoyl, thenoyl, and trifluoromethyl groups act as electrophilic groups.

LITERATURE CITED

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Sorption of *n*-Butylammonium and *n*-Dodecylammonium Acetate by Sodium Montomorillonite and Sodium Vermiculite

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A CHEMICAL or physical-chemical reaction takes place between certain organic materials and soils, clays, and resins. This reaction was attributed (*8*) to an ion exchange mechanism, wherein the organic salt ions formed complexes with the solid materials by displacing the inorganic ions originally present in the solid. Originally, it was assumed and some experimental evidence indicated (*4*) that the major portion of the exchangeable cations were located on the surface.

Later evidence (*5*) indicated that the reaction involved more than surface cation replacement by the organic salt ion because the *C*-axis spacing of montmorillonite was increased, indicating an interlayer cation reaction. This observation was substantiated by later work (*1, 4, 6, 9*) which showed that the sorption of large aliphatic ammonium ions exceeded that of the "normal" ion exchange capacity of the solid structure.

The solid materials on which these studies have been made and reported on are: bentonite (montmorillonite), vermiculite, and synthetic ion exchange resins.

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