CHEMISTRY

A. I. GRIGOR'EV, Corresponding Member of the Academy of Sciences of the USSR A. V. NOVOSELOVA

1958

SovietRxiv

Abstract

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CHEMISTRY

A. I. GRIGOR' EV, Corresponding Member of the Academy of Sciences of the USSR A. V. NOVOSELOVA
and K. N. SEMENENKO

COMPOUNDS OF BERYLLIUM OXYACETATE WITH SULFUROUS ANHYDRIDE

For beryllium oxyacetate, addition products have been described chiefly with substances containing amine nitrogen ([1]-[3]). These compounds are sufficiently stable and are formed, probably, at the expense of the free electron pair of nitrogen. However, for $Be_4O(CH_3COO)_6$ one may also expect compounds with a weaker bond, of the type of the so-called "inclusion compounds" ([4]). The possibility of the formation of such compounds by beryllium oxyacetate was indicated by Powell in a report at the international conference on complex compounds in 1956 ([5]).

A compound of this type is probably the compound of beryllium oxyacetate with sulfurous anhydride, the preparation of which we briefly reported earlier ([2]). In the present article the results are presented of a more detailed study of the interaction of beryllium oxyacetate with sulfurous anhydride. The compound $Be_4O(CH_3COO)_6$ with SO_2 separates on evaporating a solution of beryllium oxyacetate in liquid sulfurous anhydride in the form of well-formed octahedra. At room temperature this compound is extremely unstable and rapidly decomposes into beryllium oxyacetate and sulfurous anhydride; therefore preparative isolation and exact determination of its composition by ordinary methods of chemical analysis are difficult.

To study the interaction of beryllium oxyacetate with sulfurous anhydride, we employed the method of constructing composition–vapor pressure diagrams in the system $Be_4O(CH_3COO)_6$–SO_2 at constant temperature. For this purpose a Hüttig tensieudiometer ([6]) was used, which permits simultaneous measurement of the phase composition and the pressure in the system. The procedure was as follows. To a weighed portion of about 800 mg of beryllium oxyacetate in a reaction vessel of 10 ml capacity, placed in a thermostat, a certain amount of sulfurous anhydride was added until the beryllium oxyacetate had completely dissolved; then the sulfurous anhydride was transferred in separate portions into a preliminarily evacuated space connected with the reaction vessel, the volume of which was known. The vapor pressure in the system was measured with a mercury manometer. Thus, knowing the volume and the pressure, it was possible each time to take into account the amount of sulfurous anhydride removed and to determine the composition of the mixture. Equilibrium in the

Fig. 1. Isothermal vapor-pressure curves for SO_2 in the system
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system was reached after 10-20 hours (in different experiments). In Fig. 1 are given the isothermal composition-pressure curves obtained for −9.5, −15, −20, and −30°.

From the general form of the isotherms it follows that, on evaporating a saturated solution of $Be_4O(CH_3COO)_6$ in liquid sulfurous anhydride, a compound of composition $Be_4O(CH_3COO)_6 \cdot 2SO_2$ separates. Thus, it was established that the compound of composition $3Be_4O(CH_3COO)_6 \cdot 4SO_2$, described by us in work (^{2}), is a product of partial decomposition of the compound of beryllium oxyacetate with two molecules of sulfurous gas. Besides the compound

of composition 2 : 1, the existence in the system of a 1 : 1 compound, $Be_4O(CH_3COO)_6 \cdot SO_2$, formed upon decomposition of the 2 : 1 compound, was found. No other compounds were found within the temperature range from −10 to −30°. With increasing temperature the stability of the compounds decreases; this is indicated by the ever-increasing slope of the plateaus on the isothermal curves. At −10° the decomposition of the compounds still proceeds in two stages, but already by way of formation of phases of variable composition.

Fig. 1. Isothermal vapor-pressure curves for SO_2 in the system $Be_4O(CH_3COO)_6$—SO_2

The values of the SO_2 pressures corresponding to the compositions of the 2 : 1 and 1 : 1 compounds were used to find the functions $\lg P = f\left(\frac{1}{T}\right)$. The graphical dependence of the dissociation pressure of the compounds on temperature is shown in Fig. 2. The dependence of the SO_2 pressure on temperature in the system

$$Be_4O(CH_3COO)_6 \cdot SO_2 \mathrm{leftarrows} Be_4O(CH_3COO)_6 + SO_2$$

can be expressed by the equation:

$$\lg P = -\frac{2507.68}{T} + 12.10,$$

whence

$$\Delta H_1 = -Q_{p_1} = 11.47 \text{ kcal/g-mol}$$

in the temperature interval from 243 to 263°.

Fig. 2. Change in dissociation pressures of the compounds $Be_4O(CH_3COO)_6 \cdot SO_2$ (I) and $Be_4O(CH_3COO)_6 \cdot 2SO_2$ (II) as a function of temperature

Figure 2: Fig. 2. Change in dissociation pressures of the compounds $Be_4O(CH_3COO)_6 \cdot SO_2$ (I) and $Be_4O(CH_3COO)_6 \cdot 2SO_2$ (II) as a function of temperature

The dependence of the SO_2 pressure on temperature in the system

$$\mathrm{Be_4O(CH_3COO)_6 \cdot 2SO_2 leftarrows Be_4O(CH_3COO)_6 \cdot SO_2 + SO_2}$$

is described by the equation

$$\lg P = -\frac{1525.44}{T} + 8.54,$$

and

$$\Delta H_2 = -Q_{p_2} = 6.98 \text{ kcal/g-mol}$$

in the interval 243-263°. The total equation for the reaction of formation of $Be_4O(CH_3COO)_6 \cdot 2SO_2$, taking into account the thermal effect of the reaction, has the form:

$$\mathrm{Be_4O(CH_3COO)_6 + 2SO_2 = Be_4O(CH_3COO)_6 \cdot 2SO_2 + 18.45 \text{ kcal}.}$$

The average heat of formation is equal to 9.22 kcal per 1 g-mol of SO_2.

Thus, the values of the heats of formation are lower than usual for coordination compounds—approximately the same as for urea inclusion compounds (^{4}), 5-10 kcal/g-mol; hydroquinone (^{5}), 9–10 kcal/g-mol; cyclodextrin compounds (^{4}), 12 kcal/g-mol, etc. It should be noted here that the heat of vaporization of sulfur dioxide is 6.32 kcal/g-mol. In this connection it is also noteworthy that at $-10°$ (the boiling temperature of SO_2) the compounds have the character of solid solutions and can exist only at elevated pressure of the sulfurous gas. At temperatures above 10° the crystals of $Be_4O(CH_3COO)_6 \cdot 2SO_2$ melt in sealed capillaries.

Fig. 2. Change in the dissociation pressures of the compounds $Be_4O(CH_3COO)_6 \cdot SO_2$ (*I*) and $Be_4O(CH_3COO)_6 \cdot 2SO_2$ (*II*) as a function of temperature.

We carried out an X-ray study of the compound $Be_4O(CH_3COO)_8 \cdot 2SO_2$ by the rotation method in an RKOP camera using Cu radiation from a BSVL-type tube. The X-ray exposure was made at a temperature of 0-3°; the single crystal was sealed in a thin-walled capillary made of Pyrex glass.

The compound $Be_4O(CH_3COO)_6 \cdot 2SO_2$ crystallizes in a cubic diamond-like lattice with unit-cell parameter $a = 17.1$ Å. The density, determined at −12° by the method of differential weighing in an ethyl bromide-dichloroethane mixture, is 1.43; the X-ray density is 1.42. It is evident that the crystal structure of $Be_4O(CH_3COO)_6 \cdot 2SO_2$ is very close to the crystal structure of pure beryllium oxyacetate and may be regarded as a derivative of it—with some expansion of the lattice, from 15.7 Å for pure beryllium oxyacetate to 17.1 Å for the double compound.

Comparison of the data on the composition and properties of the compound makes it possible to outline the following picture of the structure of this substance.

According to Pauling and Sherman ([7]), the beryllium oxyacetate molecule possesses four "cups" —depressions situated on the faces of the Be_4O tetrahedron. Owing to the existence of such depressions in the crystal lattice of cubic beryllium oxyacetate, there are closed cavities, two cavities corresponding to each beryllium oxyacetate molecule. It may be assumed that, during crystallization from solution, molecules of sulfur dioxide become included in these cavities; at the same time the crystal lattice expands in comparison with the lattice of beryllium oxyacetate. When the cavities are completely filled, a compound of the type $Be_4O(CH_3COO)_6 \cdot 2SO_2$ is formed; when they are incompletely filled, a compound of the type $Be_4O(CH_3COO)_6 \cdot SO_2$ is formed. The sulfur dioxide molecules enclosed in the cavities are not acted upon by any forces other than the usual intermolecular van der Waals forces. This explains the comparatively small heat of formation of the compounds $Be_4O(CH_3COO)_6 \cdot 2SO_2$ and $Be_4O(CH_3COO)_6 \cdot SO_2$. The compounds of beryllium oxyacetate with sulfur dioxide may therefore be regarded as true clathrate compounds of the type of the hydroquinone clathrates with SO_2 or with CH_3OH ([4,5]).

Moscow State University
named after M. V. Lomonosov

Received
4 VI 1958

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