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NOTES

$H_2\{C_6H_4(COO)_2\cdot[(CH_3)_2SO]_2\}$

The manufacture of terephthalic acid (TPA), an important polymer intermediate, by various techniques produces a product containing impurities the nature and concentration of which is dependent on the method of preparation. Purification of TPA is difficult because this acid is rather insoluble in common solvents under normal conditions.

According to a patent,[1] purification of TPA can be achieved by recrystallization of this acid from dimethylsulfoxide. We wish to report that when TPA is recrystallized from DMSO, not TPA but its double salt with DMSO, $H_2\{C_5H_4(COO)_2\cdot[(CH_3)_2SO]_2\}$, (TPA·2DMSO) is obtained. TPA is soluble to the extent of 40 g./100 ml. DMSO at 130°C. and 19 g./100 ml. DMSO at 25°C. The solubilizing effect of DMSO is that of a Lewis base reacting with an acid to afford a soluble salt. DMSO is known to undergo salt formation with other acids.[2-4]

EXPERIMENTAL

When 0.5 mole of TPA (83 g.) was dissolved in 250 ml. DMSO at 130°C. and the solution subsequently cooled to room temperature, a precipitate crystallized in large transparent plates. It was filtered by suction while covered with dental dam; recovery of 89.54 g. of this material was effected. When it was treated with 500 ml. of acetone the plates disintegrated and a fine white precipitate, 46.14 g., was isolated and identified by infrared spectroscopy to be TPA. The plates contained, according to this experiment, 0.278 mole TPA and by difference 43.40 g. of 0.56 mole DMSO, which gives 1 TPA + 2.01 DMSO and suggests the stoichiometry TPA·2DMSO.

This material can be handled only with difficulty. It is decomposed by contact with common organic solvents such as acetone, alcohols, ether and halocarbons as well as by water. In each of these cases, TPA is obtained. It is fairly stable against petroleum ether, however. It decomposes on warming as well as on standing in air but can be kept for prolonged periods of time by refrigeration in sealed containers.

In view of the instability of this compound, it was difficult to obtain good values for its elemental composition $C_{12}H_{18}O_6S_2$ (C, 44.68%; H, 5.62%. Found: C, 45.01%, H, 5.80%). The molecular weight of the compound as determined by cryoscopy was in very good agreement with the theoretical value 322.39 (found 323). A further proof for the composition of this compound was obtained by thermogravimetry on a thermogravimetric balance (system Chevenard). When the compound was subjected to heating at the rate of 5°C./min. no measurable weight loss occurred below 50°C., at which temperature slow loss of weight became apparent. Rapid decomposition set in at 72°C. A break in the curve occurred at 176°C., at which temperature the sample had lost 49.5% of its weight (loss of 2 moles DMSO would correspond to 48.5%). No further decomposition of the sample occurred up to 247°C., at which temperature rapid loss of weight occurred up to 373°C. at which temperature the sample was completely evaporated. The second step in the thermogram (between 247 and 373°C.) corresponded to the sublimation of one mole of TPA.

References

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