Letters to the Editor

Unusual reaction of hexaethylphosphorous triamide with mercuric chloride leading to the formation of metallic mercury

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As a rule, trivalent phosphorus compounds form stable adducts with metal salts. For example, a stable complex[1] of mercuric chloride with triisopropylphosphine is known (^{31}P NMR ($CDCl_3$), δ_P: 78.49, $J_{^{199}Hg-^{31}P}$ = 6966 Hz*).

However, we found that a complex of mercuric chloride with hexaethylphosphorous triamide, which is readily formed in dry acetonitrile, gradually decomposes in air to give metallic mercury in quantitative yield. The reaction mixture contains diethylamine hydrochloride and a mixture of phosphorus compounds with chemical shifts characteristic of pyrophosphates. Apparently, this process involves atmospheric moisture:

$$(Et_2N)_3P + HgCl_2 + 4\ H_2O \longrightarrow$$

$$\longrightarrow Hg + 2\ Et_2NH \cdot HCl +$$

$$+ \text{(a mixture of phosphorus-containing compounds)}.$$

Hexaethylphosphorous triamide (1.1 g, 0.0049 mol) was added dropwise to a solution of mercuric chloride (1.1 g, 0.004 mol) in dry acetonitrile (2 mL). This is a slightly exothermic reaction. According to the ^{31}P NMR data, the reaction mixture contains a phosphorus compound with δ_P 110.75, $J_{^{199}Hg-^{31}P}$ = 11540 Hz. The reaction mixture was left in an open vessel at ~20 °C. After 10 days, ether (20 mL) was added to a thick gray-green mass with mercury drops, and the mixture was filtered. The filtrate was concentrated *in vacuo* to dryness. The total weight of the combined dry residue and precipitate containing metallic mercury was 2.33 g. The mercury was washed with CH_2Cl_2; the yield of metallic mercury was 0.79 g (98%). The ^{31}P NMR spectrum recorded in CH_2Cl_2 shows two sets of signals at δ_P −10 to −12 and −23 to −26 ppm, including a singlet at δ_P −11.61 (24%) and doublets and triplets with J_{P-P} = 21—22 Hz. Apparently, these are diethylammonium acid di- and triphosphates. Methylene dichloride was evaporated, and the powder (1.5 g) was crystallized from methylene dichloride—ether. The yield of colorless crystals was 0.4 g, m.p. 226—227 °C. The ^{1}H NMR spectrum is identical with that of diethylamine hydrochloride.

This transformation is probably the first example of the reduction of metal chlorides with amides of P^{III} acids in the presence of moisture.

References

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* $J_{^{199}Hg-^{31}P}$ in Ref. 1 is not correct.

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