Reaction of Alkali Metals with Phosphite Esters

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Summary Reaction of dialkyl phosphonates (or dialkyl hydrogen phosphites), at normal temperatures, with metallic sodium, yields appreciable amounts of phosphine.

The preparation of alkali-metal derivatives, usually those of sodium, from dialkyl phosphites has long been a common starting point for the synthesis of esters of phosphonic acid by the Michaelis–Becker reaction:

$$(\mathrm{RO})_2\mathrm{PHO} + \mathrm{Na}(\mathrm{K},\ etc.) \rightarrow (\mathrm{RO})_2\mathrm{PNaO} + 0{\cdot}5\ \mathrm{H}_2.$$

At rather elevated temperatures (*e.g.* in hot toluene or xylene with powdered molten sodium or potassium) the process appears to follow the above equation quite closely in stoicheiometry.[1]

However, when the reaction is run at or near room temperature the amount of the alkali metal called for by the equation is always excessive, indicating a deviation from the "expected" route. It was a common result, noted by many workers in this field, who indicated (in the days of more extensive experimental sections in publications) that "left over" metal had to be removed, prior to proceeding with the remainder of the Michaelis–Becker reaction. The reaction, when run at a relatively low temperature, produces a "phosphine" odour, and many workers in the field have felt that "phosphines" appear to be formed.

We now report a clarification of this reaction. When the calculated amount of dialkyl phosphite (say, diethyl) is added gradually to a hot suspension of finely divided sodium drops in such a medium as toluene or xylene, the reaction is completed rapidly and in accord with the above equation. Essentially no "phosphine" odour results.

However, when finely divided sodium (1 g.) was frozen in suspension in toluene (*ca.* 100 ml.) by means of liquid nitrogen, and diethyl phosphite (4·14 g., 0·03 mole) was added to this mixture in the usual vacuum-line apparatus, which was then evacuated while cold and allowed to warm up to 0°, a reaction took place slowly with evolution of gas and formation of the sodium derivatives as expected. The reaction ceased only after 24 hr. and evolved hydrogen to the extent of only 86% of the theoretically expected volume. When the volatile products were pumped off and the condensible materials in the vapours were trapped in a chilled trap, the condensate was found to contain only some toluene and a substance that proved to be phosphine, identified by g.l.c. and by its i.r. spectrum, with characteristic bands at 2330, 1080, and 960 cm.$^{-1}$. Phosphine, PH_3, was the only compound present that contained the P–H bond.

Evidently, a form of reduction or hydrogenolysis takes place on the surface of the alkali metal when the reaction takes place slowly at low temperature. This explains the "excess" of metal that is invariably left over in such a reaction when run in a low-boiling solvent such as ether or hexane, especially when rather large slices of the metal are used in place of a fine suspension.

Since it is clear that the very hazardous (healthwise) phosphine is generated in such reactions, a clear word of caution is needed to those using this reaction. The use of an effective hood vent system is essential during the operation.

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[1] G. M. Kosolapoff, *J. Amer. Chem. Soc.*, 1945, 67, 2259.