

actual reduction to the alkali metal alone; that is, the primary reduction process is assumed to be addition of the alkali metal to the unsaturated compound. It is considered that the function of the solvent is merely to replace the metal in the addition compound with hydrogen by a hydrolytic process and that direct reaction between the solvent and the free alkali metal (or its amalgam) is a side reaction.<sup>2</sup> It has been shown definitely that certain specific reduction processes actually follow the course prescribed by the second hypothesis.<sup>3</sup>

We have now discovered another specific reduction reaction which appears definitely to follow the course prescribed by the *first* hypothesis. This reaction is the reduction of toluene with sodium (or potassium) and water in liquid ammonia. Toluene is not attacked by solutions of these alkali metals in liquid ammonia in the absence of water for the blue color of the alkali metal solutions is not discharged by addition of a large excess of toluene even when the mixture is allowed to stand for several hours. Furthermore, the presence of the total amount of metal in the free state may be demonstrated by the addition of ethyl bromide, ammonium chloride or a catalyst (iron rust) which initiates reaction between the metal and the solvent ammonia. Under these conditions the theoretical amount of ethane or hydrogen is always evolved and the toluene may be recovered. On the other hand, when water is added to the mixture much less than the theoretical amount of hydrogen is evolved and there is obtained a highly unsaturated liquid product which boils over the range 110–115°, chars

(2) Willstätter, Seitz and Bumm, *Ber.*, **61**, 871 (1928).

(3) Wooster and Smith, *THIS JOURNAL*, **53**, 179 (1931).

with fuming sulfuric acid, reacts vigorously with liquid bromine and rapidly decolorizes a solution of bromine in carbon disulfide.

It is evident that although toluene does not react with liquid ammonia solutions of these alkali metals, it is immediately attacked (doubtless reduced) when water also is added. These facts are especially significant because under such conditions a very appreciable concentration of toluene is always present in the same phase with the ammonia and the alkali metal so the action of water cannot be ascribed to any purely surface phenomenon. It is also noteworthy that the effective combination is relatively specific, thus the hydrogen produced by reactions between the alkali metals and ammonia or ammonium chloride does not attack the toluene.

Finally, these observations have an important bearing on the technique of studying reactions in liquid ammonia, because two common practices are the use of toluene as a diluent to facilitate the reaction of organic substances sparingly soluble in ammonia, and the measurement of the hydrogen evolved on addition of water to determine the amount of excess free alkali metal remaining at the end of a reaction. It is now clear that a combination of these two practices will give misleading results, and that ammonium chloride (or an ammonolysis catalyst) should be used instead of water under such circumstances.

These studies are being continued in the hope of obtaining further significant information regarding the mechanism of such reduction processes.

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## COMMUNICATIONS TO THE EDITOR

### OCCURRENCE OF ACETOVANILLONE IN WASTE SULFITE LIQUOR FROM CONIFEROUS WOODS

Sir:

Investigation of the products of alkaline degradation of waste sulfite liquor from the pulping of coniferous woods (mixture of spruce and balsam) on a large laboratory scale has disclosed the presence therein of acetovanillone ( $\beta$ -methoxy-4-hydroxyacetophenone) identical in every way

with the synthetic product made from guaiacol acetate. *Anal.* OCH<sub>3</sub>, 18.65; calcd. 18.68; m. p. 114.5°. Synthetic acetovanillone: m. p. 115°; mixed m. p. 114–115°. Semicarbazone: m. p. 165.5–166°; mixed m. p. 164.5–165.5°.

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