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The Reactions of Aqueous Bromoalkyltriphhenylphosphonium Bromides with Zerovalent Metals

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Water-soluble bromoalkyl compounds provide a useful model for investigating aqueous reactions of alkyl bromides and metals. Bromoalkyltriphenylphosphonium bromides, $(C_nH_s)_nPR^*Br$, have proven particularly useful for this purpose.

Tetraorganophosphonium bromides repress aqueous dissolution of copper through the reaction

$$Cu_{(aq)}^{2+}$$
 + $Cu_{(s)}$ \rightarrow 2 $CuBr_{(s)}$

However, bromoalkyltriphenylphosphonium bromides enhance copper dissolution; the degree of enhancement depends on the particular compound used. Kinetic studies indicate that the rate of dissolution is initially linear, depending on the concentration of reagent and the surface area of metal [1].

Various comparative studies showed the following:

- (1) For the series $\{(C_6H_5)_3P(CH_2)_nBr'Br', dissolution increased as <math>\underline{n}$ increased.
- (2) For R = bromobutyl, the 3-bromo isomer was considerably more active than the 4-bromo isomer.
- (3) For [ECH₂CH₂Br]*Br (E = (C₆H₅)₃P, (CH₃)₃N) and brass, the P compound dissolved more Cu and less Zn than the N compound.
- (4) For (C₆H₅)₃PCX₂Br (X = H,F), the fluoro species was considerably more reactive.

Attachment of alkyl halide to the metal surface is a requirement for reaction to occur [1-3]. Our results suggest that the phenyl groups on phosphorus may enhance reaction with copper by forming pi-linkages. This has been suggested as the reason for the differing behavior of bromoalkenes towards brass [2].

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