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# Phosphorus, Sulfur, and Silicon and the Related Elements

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## Reaction of Trivalent Phosphorus Compounds with Viologens

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#### REACTION OF TRIVALENT PHOSPHORUS COMPOUNDS WITH VIOLOGENS

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When trivalent phosphorus compounds ( $Z_3P$ ) reacted with viologens, either a single-electron transfer (SET) or a polar reaction takes place, depending on the kind of substituents of viologens.

Keywords: Kinetic isotope effect; single-electron transfer; trivalent phosphorus compounds; viologen

Whereas  $Z_3P$  is a nucleophile,  $Z_3P$  undergoes single-electron transfer (SET) reaction with electron deficient compounds to generate the corresponding radical cations. We followed the reaction of  $Z_3P$  with various viologens in MeCN: MeOH = 1:1 under an argon atmosphere at  $45^{\circ}C$  on a UV-vis spectrophotometer. We looked to find if the kind of substituents of viologens determines whether  $Z_3P$  undergoes SET to viologen or attacks viologen nucleophilically. Moreover, we observed a considerably large kinetic isotope effect  $(k_H/k_D \approx 4.0)$  in

SET
$$Z_{3}P^{*+} + R^{1} - N + N + R^{2}$$

$$R^{1} \text{ or } R^{2} = Me$$
Nucleophilic Reaction
$$R^{1} - N + N + R^{2}$$

$$+ PZ_{3}$$

$$R^{1} \text{ and } R^{2} \neq Me$$

#### SCHEME 1

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the SET reactions. From these results, SET from  $Z_3P$  to viologen takes place via "tight" encounter complex.

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