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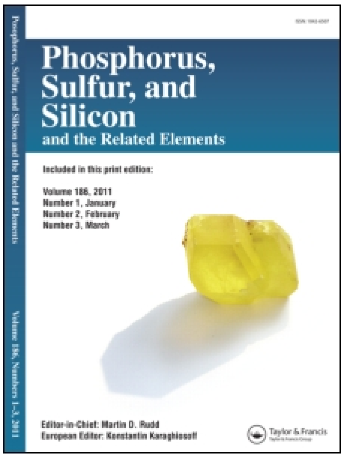

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Radical and Electrophilic Reactions of Anodic Oxidation Intermediates of Organophosphorus Compounds

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RADICAL AND ELECTROPHILIC REACTIONS OF ANODIC OXIDATION INTERMEDIATES OF ORGANOPHOSPHORUS COMPOUNDS

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Cationic radicals generated by anodic oxidation of organophosphorus(III) compounds are superelectrophilic radicals. This determines the pattern of their reactivity towards various substrates. The oxidation of $(RO)_2PO^-$ and $(RO)_2PS^-$ gives corresponding radicals. Interaction of the mentioned radical species with ArH and olefines includes a common stage of radical adduct formation. It has been stated that the oxidation of the adduct into corresponding carbonium ion plays an important role in the following adduct conversions. This is particularly confirmed by the difference in the composition of products obtained in conditions of homogeneous (via photolysis or with stable radical cations) and heterogeneous (on the anode surface) generation of phosphorylating species.

In the reactions with such mobile hydrogen containing compounds HY as H_2O, ROH, RSH and other, two possible competitive processes were found to take place. Hydrogen is eliminated from HY to give protonated form of the parent organophosphorus compound ($\geqslant\overset{+}{P}H$) and $Y^{\bullet}$ free radical, either $\geqslant P^{+\bullet}$ coupling with $\geqslant P$ is followed by second electron transfer to yield biophosphonium dication which then reacts with HY giving $\geqslant\overset{+}{P}H$ and $\geqslant\overset{+}{P}Y$.