

Intramolecular Assistance of Dissociative Electron Transfers

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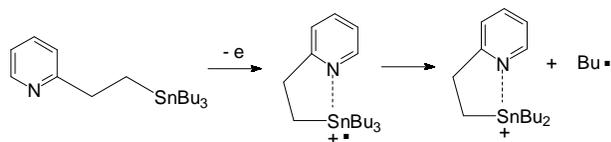
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The possibility of favoring chemical reactions by specific interactions involving the reaction center represents an important area of research, also because of synthetic implications. For example, an electron transfer (ET) reaction can be favored kinetically and/or thermodynamically if the developing ionic center is stabilized by specific coordination. If the coordinating moiety is present in the reacting molecule itself, an intramolecular assistance to the ET may in principle take place. In this communication we will show how to obtain relevant thermodynamic and kinetic information on the intramolecular assistance to redox processes by electrochemical means. In particular, we studied the oxidation of a series of tetraalkylstannanes. Upon electrooxidation, these compounds are known to undergo the breaking of one of the Sn–C σ -bonds.¹

Convolution analysis of the dissociative oxidation^{2,3} of tetrabutylstannane (SnBu₄) allowed us to estimate the standard potential, the standard rate constant of the heterogeneous ET (k_{het}°), and the intrinsic barrier. The ET is characterized by a rather small k_{het}° and a large reorganization energy that can be ascribed to a significant modification of inner molecular coordinates during the generation of the cation radical intermediate. According to *ab initio* molecular orbital calculations,¹ the main contribution to the barrier can be envisaged as the elongation of the Sn–C bond. These results were taken as typical for the oxidation of tetraalkylstannanes in the absence of any intramolecular assistance.

Previously, it was also reported that the introduction of carbonyl, alkoxy, or pyridyl groups decreases the oxidation potential of tetraalkylstannanes. Convolution analysis was applied extensively to this series of compounds to show how and to what extent intramolecular assistance could be modulated by changing the nature of the remote coordination end. For all compounds, the results are in agreement with a stepwise oxidation mechanism in which the Sn–C bond cleavage rapidly follows the formation of an intramolecularly-stabilized radical cation, as shown in the following scheme for the pyridyl derivative:



Analysis of the data showed that the thermodynamics of the oxidation is largely affected by the stabilization brought about by intramolecular assistance. The oxidation rate, as indicated by the value of the intrinsic barrier, is also affected by the presence of a

coordinating group, as expected on the basis of the increased nuclear reorganization.

References

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