ONE-ELECTRON REDOX REACTIONS BETWEEN RADICALS AND MOLECULES.
DOMINANCE OF INNER-SPHERE MECHANISMS

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ABSTRACT. In aqueous solution the electron transfer between (reducing) carbon-centered radicals or (oxidizing) heteroatom-centered inorganic radicals and organic molecules often proceeds by covalent bond formation between the radical and the molecule followed by heterolysis of the so-formed bond between the carbon and the heteroatom. It is the heterolysis step in which the actual electron transfer between the radical and the molecule takes place. This makes electron transfer a part of the area of (heterolytic) solvolysis reactions. Structure-activity relations for heterolysis of the radical-molecule adducts and thus the electron transfer between the adduct components can be rationalized in terms of the classical solvolysis concepts.

1. Introduction

Radicals \( R^\cdot \), whose oxidation state is by definition in-between the two (stable) even-numbered systems \( R^+ \) and \( R^- \), are prone to engage in one-electron transfer (ET) reactions because this type of behavior constitutes the simplest way for the molecules to lose their radical nature, cf. eq 1:

\[
(A^- \cdot +) \xrightleftharpoons{+A} R^+ \xrightarrow{+D} R^- (\pm D^\pm) \tag{1}
\]

In order for this transfer to occur, there has to be an electron donor (D) or acceptor (A). If \( R^\cdot \) and D or A are neutral species, electron transfer leads to the ionic products \( R^+ \), \( R^- \), \( A^- \cdot \), \( D^\pm \cdot \), and the transition state must therefore have some ionic character. The alternative to the outer-sphere ET mechanism of scheme (1) is a reaction in which the electron transfer occurs via an addition/elimination sequence:

\[
R^\cdot + A \xrightarrow{k_{ad}} R-A^\cdot \xrightarrow{k_{bs}} R^+ + A^- \cdot \tag{a}
\]

\[
R^\cdot + D \xrightarrow{k_{ad}} R-D^\cdot \xrightarrow{k_{bs}} R^- + D^\pm \cdot \tag{b}
\]
This scheme represents an inner-sphere path of overall electron transfer. The transition state for the addition step (rate constant $k_{ad}$) can be but does not necessarily have to be polar; however, the heterolysis (elimination) step (rate constant $k_{le}$) must have a polar transition state. Therefore, in a situation in which the heterolysis of the adduct RA* or RD* is rate determining, the dependence on structural or environmental conditions of the rates of redox product formation will be similar for the outer-sphere (eq 1) and the inner-sphere (eq 2) case. The two types of mechanism can therefore not easily be distinguished by studying, e.g., substituent effects on R, A, or D or solvent effects.

In the following, examples will be presented for reactions that proceed according to scheme 2, with the radicals serving as electron-donors (eq 2a) or electron-acceptors (eq 2b). In the former case the radicals involved are carbon-centered and substituted at C by heteroatoms which provide - via their lone pairs - the necessary electron density ("nucleophilic" radicals); in the latter case the radicals are heteroatom-centered, their oxidizing power being due to the higher electron affinity of the heteroatom as compared to carbon.

2. Carbon-centered radicals as electron donors (eq 2a).

2.1 NITROBENZENES AS OXIDANTS

Interest in the mechanism of reduction of nitro compounds is in part due to the (potential) importance of this class of chemicals as sensitizers in the radiotherapy of cancer. It has long been recognized that many organic radicals produced by ionizing radiation, photolysis, or by transition metal ion catalyzed decomposition of peroxides eventually lead to the one-electron reduction of the nitro compounds. The rates and yields of these reactions increase with increasing reducing power of the radicals and with increasing oxidizing power (reduction potential) of the nitro compound. This behavior is suggestive of an electron transfer mechanism, and the radiobiological effect of sensitizers has in fact been interpreted on this basis. On the other hand, oxygen, still the best radiosensitizer, typically does not react by electron transfer but by addition, and this in spite of the fact that electron transfer is often highly exergonic ($\Delta G > 1$ eV). The question thus arises whether the radiosensitizing action of nitro compounds is related to their ability to scavenge radicals by addition, a reaction type that is well documented for them, and whether addition and the equally well documented electron transfer are just different aspects of a more general reaction mechanism. As pointed out below, the latter is in fact the case. The unified mechanism, which allows for addition as well as electron transfer, involves an ion pair type transition state (scheme 4). Competition between ion combination (which leads to addition) and ion separation by solvation (which results in electron transfer) determines the product distribution, as will be seen from the following examples.

2.1.1. $\alpha$-Hydroxyalkyl Radicals.

The simplest of this type of radical, CH$_2$OH, reacts with nitrobenzenes in aqueous solution exclusively by addition, eq 3, to give the hemiacetal-type alkoxy nitroxyl radical.