Activation and Propagation of Electron-Transfer Chain Reactions†

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A model for chain reactions is presented based on the concept of occupation number dependence of correlation diagrammatic topology and HOMO-LUMO gap increase from reaction exothermicity. The model is useful toward the understanding of two essential events in these chain processes: First, the reaction barrier is lowered when an electron is either removed or added to a metastable system. Second, the electron transfer is driven by the shift of the orbital energy level of the radical electron. Some speculation on the catalytic mechanism in general is also presented in light of these special electron-transfer chain processes.

Introduction

There appears to be a growing interest in electron-transfer chain reactions, as indicated by several recent review articles1 in this area. An electron-transfer chain reaction is indeed fascinating. However, its driving force is not always obvious. The purpose of this paper is to provide a simple model to account for the energy barrier reduction in the ionic reaction on the one hand and the driving force for the electron-transfer process on the other hand. Our model is based on the general concepts of electron occupation number dependence of the correlation diagrammatic topology and the HOMO-LUMO gap increase from the reaction exothermicity. It appears that the model can accommodate both the cationic and the anionic reaction mechanisms in a unified manner. Some conceptual implication for the catalyst reaction mechanism in light of these ionic reactions will also be presented.

Electronic Energy Amplification

Consider first a common reaction type, the combustion which converts the reactant system A exothermically to the product system B. After supplying just enough heat for the system to surmount the energy barrier, the system may slide smoothly down toward the valley B and releases an even large amount of heat, available for driving further A → B conversions. Thus, in one sense, such A + Δ → B + Δ' conversions may be viewed as a process of heat amplification and, in another sense, the whole event is to be recognized as a chain reaction. Similarly, the photochemical reaction

A + hν → A* → B* → B + hν'

also exhibits a photon amplification. Our major interest is in electron-induced chain processes like

A + e → A* → B* → B + e

(1)

which are especially useful if the A → B transformation involves an insurmountable energy barrier. The activation energy reduction for the ionic species A* → B* will be discussed in the next section. The interest here is the phenomena of electron or hole energy amplification because of an increase of the HOMO-LUMO gap from A to B. The larger gap implies that B is both photochemically and thermochemically more inert. The reason for the latter is that, with a larger gap, B is both a weaker electron donor and weaker electron acceptor. The gap increase along the reaction coordinate is quite common in the case of Jahn-Teller distortion

where a molecule seeks its thermodynamical stability. An exothermic A → B chemical transformation can be viewed as one type of pseudo-Jahn-Teller distortion. One important consequence of the HOMO-LUMO gap increase is that, after the transforma-

LUMO

HOMO

A

B

A+

B+

B

A-


motion involving charge species, A+ → B+ becomes a stronger electron donor than A- and B- becomes a stronger electron acceptor than A+. Thus, the charge-transfer process between the product ion and the neighboring neutral reactant, B+ + A- → B + A+, is ensured and the chain process is able to propagate.

Activation Energy Reduction

For the activation reduction in the reaction of charged radicals in the second step in eq 1, we begin with a simple model for orbital transformations in neutral 2 + 2 and ionic 2 + 2 processes.

a2(A) → χ(B)

a(A+) → χ(B+)

a2(χ(A)) → aχ2(B+)

(2)

Here, a and χ refer to π1 and π2 and π1* + π2* delocalized orbitals constructed from localized olefin orbitals. For the forbidden process in neutral systems, the transformation is induced by a two-electron operator with transition matrix element (a21/())),. But in the charged cases, the two-electron matrix element switches to the one-electron one (aχfχ), with consequent reduction in forbiddenness. In other words, both anionic and cationic reactions are facile relative to the neutral one. Of course, the exothermicities for the A* → B* transformation are also reduced from that of A → B.

Another way of looking at the same problem is in terms of orbital energies. In the 2 + 2 reaction, the four-electron energy 2e + 2e* at the initial stage corresponds to the bonding and

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The chain process of the anionic 2 + 2 type is rare. One example is the dioxetanedione decomposition to yield CO₂ in the presence of an electron donor, usually a large hydrocarbon molecule.

\[
\begin{array}{c}
\text{A} \\
\text{B}
\end{array}
\xrightarrow{\text{2CO}_2} \begin{array}{c}
\text{A} \\
\text{B}
\end{array}
\]

In the presence of such electron donors, many peroxides are reported to have their lifetimes reduced by several orders of magnitude. The hydrocarbon which is the electron donor serves as the catalyst without any overall net change in itself. The species that is actually decomposed was proposed to be the corresponding peroxide radical anion intermediate. The overall scheme is a chain reaction with an electron being transferred from one peroxide to the other to trigger the decomposition sequentially as shown schematically.

\[
\begin{array}{c}
\text{A} \\
\text{B}
\end{array} \xrightarrow{\Delta} \text{B}^- \xrightarrow{\text{A}^+} \begin{array}{c}
\text{A} \\
\text{B}
\end{array}
\]

After the decomposition of the radical anion, the excess electron undergoes a final return to the hydrocarbon. The main interest of the so-called chemically initiated electron exchange luminescence (CIEEL) mechanism is the recombination of the hydrocarbon cation and the returning electron to generate light. The quantum yield is maximum when only one peroxide is consumed during the round trip of the electron. Again, the HOMO-LUMO gap increase in the A → B transformation is responsible for the chain propagation as shown in (7).

The two important features of chain processes discussed in this paper are activation reduction and electron transfer. We are interested in some explicit examples and their diagrammatic representations. We would like to demonstrate that many diagram types are only variations of a more basic diagram and they may be unified in a unified way. The first example is Dewar benzene (A) – benzene (B) isomerization. The general pattern of such a chain process can be represented schematically as

\[
A \xrightarrow{e^-} A^+ \xrightarrow{-e^-} B
\]

It results from the folding of the three arrows in the process

\[A \xrightarrow{e^-} A^+ \xrightarrow{-e^-} B\]

with \(e^-\) and \(-e^-\) canceled. The two arrows on the right indicate the electron-transfer \(B^+ + A \xrightarrow{e^-} B + A^-\) due to a stronger electronegativity of the product \(B^+\) relative to that of the reactant \(A\).

It also makes clear that an exit of one \(B\) will induce an entry of another \(A\). Another related example is chain dimerization of olefins to form cyclobutane involving the olefin cation. The HOMO-LUMO gap increase in the \(A \xrightarrow{-e^-} B\) transformation is responsible for the hole transfer as shown in (5).

Electron or Hole Transfer

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Electron-Transfer Chain Reactions

fragments E and F, some possible side reactions are

$$E - F - X'(R - X') \rightarrow E - F - X^+ \text{ or } E^+ + F - X.$$  

Each of the resulting fragments may be represented by a different opening on the basic chain scheme.

If we count the carbon center in RX or RY as a nine-electron species, it is interesting to note that the $S_{nn1}$ scheme for organic reactions can be extended to the realm of inorganic chemistry by

isobal analogies between 7, 8, and 9e species and 17, 18 and 19e species, respectively.

For instance, the ligand substitution reaction $X^- + [PtCl_6]^{2-} \rightarrow PtCl_iX^2 + Cl^-$ is known to follow this mechanism. The 17e and 19e species are referred to PtL$_3^{2+}$ and PtL$_4^{2+}$, respectively.

Implication for Catalytic Reactions

The driving force behind Schuster’s charge-exchange chemiluminescence can be easily understood in terms of kinetic instability of the anion and the energy amplification of the unpaired electron from A to B transformation. The reaction sequence can be written as $D + A \rightarrow D^e + A^- \rightarrow D^e + B^- \rightarrow D^e + B$ (or D + B). The electron donated from a large hydrocarbon D induces the kinetic instability of a peroxide anion A. After its transformation to B, the high-energy odd electron can either propagate to the neighboring A to induce more A → B transformation as mentioned previously or it may return to the D to generate light by electron-cation annihilation. Certainly, a more common type of the annihilation process is simply to form the ground-state D. The regeneration of D in such a B-catalyzed reaction can be understood in terms of (11). With the HOMO of D intervening

between (LUMO)$_A$ and (LUMO)$_B$, D may first donate an electron to A to trigger A → B anionic transformation and later retrieve the electron from B$^-$. One may generalize this scheme for a catalytic cycle between an acceptor X and A → B system with the (LUMO)$_X$ intervening between the HOMO’s of A and B. The corresponding reaction sequence is $X + A \rightarrow X^- + A^+ \rightarrow X^- + B^+ \rightarrow X + B$. Interestingly, the redox cycle for the catalysts D and X here have a close analogy to many catalytic schemes in inorganic chemistry. It is often stated that in the first phase of a catalytic cycle a metal undergoes oxidation, say, from M(II) to M(III). Subsequently, it is regenerated after a reduction process. In the scheme described above, the driving force for the catalyst regeneration is attributed to the exothermicity of the catalyzed reaction. Note that the oxidation number assigned for the metal is only an approximation. Form the nature of metal-ligand bonding, there is only a partial electron exchange between ligand and metal, unlike the process of a whole electron transfer as in Schuster’s system. However, the reactivity enhancement in the two situations can be understood similarly. One expects for example that certain ions like Ag$^+$ present in the reaction can remove part of the harmful antibonding HOMO electron density from the transition state. The reactivity improvement from a four-electron system to a pseudo-three-electron system like 2 + 2 thus results. It is well-known that a highly strained organic molecule may rearrange upon exposure to a transition-metal complex. Examples of this type are

On the other hand, when a catalyst donates some charge to the A → B system, a pseudo-anionic system results. Incidentally, the terms like acid catalyst and base catalyst are well-known. Our interest is the conceptual connection between energy barrier reduction in ionnic reaction and catalytic reaction systems in general. To carry it further, the back-bonding between a metal M and A gives rise to the “valence-state” configuration of A, crudely represented as $a_{y^1}^\alpha$ compared with $a_{y^2}^\alpha$ for the free A. Therefore, the metal not only reduces the charge density from the unfavorable orbital which ascends along the A → B reaction coordinate but also adds the charge density to the favorable orbital which descends along the reaction coordinate. In other words, back-bonding provides simultaneously the anion-like and the cation-like mechanisms for the energy barrier reduction. The topic of catalytic mechanism is complicated and has been discussed in many different contexts: Mando and Schachtzneider considered that it is a symmetry-allowed process for the metal–ligand joint system in spite of the symmetry forbiddenness for each subsystem; Yamaguchi and co-workers emphasized the concept of orbital stability and the removal of the diradical property; Van der Lugt considered the importance of the decrease in the HOMO-LUMO gap along with many others. The connection between the ionnic reaction and the catalytic reaction emphasized in this work is qualitative and speculative. However, the former does shine some new light on the latter system on the driving force for the regeneration of a catalyst. There appears to be a weaker M−B HOMO–LUMO type interaction relative to M−A, for B has a larger HOMO-LUMO gap, causing the interaction with the metal nonbonding orbitals to be less favorable after the A → B reaction.

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