Electron-Transfer Reactions of Organometallic and Coordination Compounds in the Absence of Solvent: Experimental Results and Theoretical Approaches

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by

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ELECTRON-TRANSFER REACTIONS OF ORGANOMETALLIC 
AND COORDINATION COMPOUNDS IN THE ABSENCE OF SOLVENT: 
EXPERIMENTAL RESULTS AND THEORETICAL APPROACHES 

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Abstract 

The kinetics of gas-phase electron transfer reactions for a variety 
of metal-containing reactants have been studied by using Fourier transform 
ion cyclotron resonance mass spectrometry. Classes of ion/molecule 
processes studied include both self-exchange (thermoneutral) and exoergic 
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overall rates of these reactions on the molecular properties of the 
reactants. In particular, the role of Franck-Condon factors in charge- 
transfer reactions is examined, and theoretically estimated factors are 
compared to experiment for a typical metallocene, ferrocene.
Introduction

Studies of electron-transfer (charge-transfer) phenomena have usually involved reactants of one of two general types: first, atoms and small molecules (containing a few atoms) in the gas phase [1-8] or, second, large polyatomic molecules in solution [9-11]. The literature contains many articles that consider theoretical models for one or the other type of reaction, but little cross referencing of ideas or language occurs between these treatments. Obviously such a distinction is arbitrary and results from the differences in the experimental approaches employed as well as the relative ease with which detailed quantum mechanical models can be applied. Thus, few researchers have carried out extensive investigations of the kinetics of gas-phase electron transfer involving large polyatomic reactants [12-19], and, until recently [12-15], very little had been done with metal-containing compounds. The level of theory that can be used to model these reactions will necessarily be far more approximate than that applicable to, say, H⁺ + Kr. However, such investigations do bridge the gap between the two reaction types mentioned above and can potentially provide insight into the role of solvent in determining the rates and thermodynamics of condensed-phase reactions.

We have recently studied [12-15] the kinetics and thermodynamics of electron-transfer reactions of organometallic and metal coordination compounds in the gas phase by using Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) [20, 21]. In considering the results from our work and that of others, it has been necessary to describe a general theoretical framework for these types of reactions in
order to understand the various experimental observations. We have found
that a model employing aspects of both solution ("Marcus") and gas-phase
theories can be used to rationalize the experimental results [12,13]. In
some cases, reactions with direct solution counterparts have been studied
in the gas phase; thus, the unusual opportunity arises to compare the
reactivities of metal-containing molecules in the presence and absence of
solvent. Relatively few comparative studies of this type exist (see, for
example, photochemical studies of chelate complexes by Kutal and coworkers
[22]), and until our work [14] no systematic studies of gas-phase electron
transfer involving metal centers had appeared.

In this report, we will first describe some of the experimental
results that have been obtained by using FTICR-MS. A theoretical model
will then be outlined and discussed in light of the results. In
particular, these studies lend some insight into cross reactions that
should occur in the kinetic "inverted" region [23], and potential
limitations of theories [9-11] commonly applied to condensed-phase
electron-transfer reactions will be described.

Experimental Results

The reactions studied in our work are of the general type

$$k_f$$

$$ML^n + X \xrightleftharpoons{\text{in}} k_r ML + X^\pm$$

(1)
where MLₙ represents an organometallic or coordination compound and X is either another metal-containing molecule or a non-metallic donor (or acceptor) compound. When X = MLₙ, the familiar case of the self-exchange reaction applies. Note that dissociative charge transfer is not usually encountered in our reactions, i.e., no bond breaking occurs as a result of the electron transfer event. Ions are prepared in the ICR trap by electron impact (cations) or low-energy electron attachment (anions). The pressure of neutrals is adjusted so the time dependence of the trap’s ion population can be followed by using standard FTMS techniques [20,21]. Isotopic enrichment of the ion population can be used to follow self-exchange processes. With appropriate corrections for ion loss and mass-spectral sensitivity the rate constant for the reactions of interest can be deduced. In a few cases, reaction 1 comes to equilibrium, and both kᵢ and kᵣ can be obtained.

Rate constants for a selected group of gas-phase charge-transfer reactions are given in Table I [12-15]. Also given in Table I are the efficiencies, which are the ratios of the observed rate constant to the estimated collision rate constant. In ion/molecule reactions the collision rates are determined primarily by ion-dipole and ion-induced dipole forces and can be estimated by a variety of models [24]. Although absolute error is rather large for these rate constants and efficiencies, the relative rates for analogous reactants (e.g., the metallocenes) are expected to be more reliable.

Solution-phase rate constants are available for two of the entries in Table I. The self-exchange reactions Cp₂Fe⁰⁺ and [Ru(hfac)₃]⁰⁻ were studied by using the NMR line-broadening method, and both have rate...
constants of ca. 5 x 10^6 M^-1s^-1 at 298 K in acetonitrile [25, 26]. Thus, referring to the values of k_f in Table I, removing the solvent increases the rates of these two electron-transfer processes by a factor of ~10^4. These results are a dramatic direct illustration of the extent to which charge trapping by the solvent contributes to the barriers to electron-transfer in solution. In principle, a number of the other reactions listed in Table I could be examined in solution for comparison to their gas-phase counterparts, but reliable values are not available.

Although many of the reactions in Table I approach collisional efficiency (eff = 1 for cross reactions and 0.5 for self-exchange), exceptions have been noted. The classic electron capture system, SF_6^0/-, has an immeasurably slow self-exchange rate by our method, as found by others [27]. Among the metallocenes, the slow reactions are generally associated with manganocene, Cp_2Mn, and its derivatives. Manganocene is anomalous among the metallocenes because of its high-spin d^5 Mn(II) ground state (all other known neutral metallocenes of transition metals are low-spin). The 6A_1g (assuming D_5d symmetry) manganocene has unusually long M-C bond lengths as a consequence of the filled antibonding metal d molecular orbitals. On the other hand, the ion Cp_2Mn^+ is expected to have the same electronic configuration as Cp_2Cr:(3E_2g) and the Cp-Cp distance should contract about 50 pm upon ionization of the neutral. In addition, the 6A/3E exchange is multiplicity forbidden, which may lead to nonadiabaticity in the reaction. Increasing exoergicity in cross reactions of manganocene is seen to increase the efficiency (Table I) until all suggestion of a kinetic barrier is eliminated (e.g., Cp_2Mn/Cp_2Fe^+).
Methyl substitution on the cyclopentadienyl ring of manganocene has a profound effect on the rates of charge self exchange (Table I). We have interpreted this effect as resulting from an increasing amount of the low-spin ($^2E_{2g}$) form of the neutral in equilibrium with the high-spin form. Thus, the $^2E_{2g}$ /$^3E_{2g}$ charge exchange is expected to be of near-collisional efficiency. Indeed, permethylation of the rings leads to essentially all low-spin doublet ground state and a near-collisional efficiency.

Volatile O-donor coordination complexes have been investigated recently [15], in particular those in the tris(β-diketonate) class (Figure 2). The highest vapor pressure is found for the hexafluoroacetylacetonate (hfac) complexes, and most of our studies have involved this ligand. The complexes formed are classical pseudo-octahedral tris chelate compounds of the type often studied in solution, and thus an opportunity exists to compare gas-phase experiments to a large catalog of condensed-phase results. In some cases of the self-exchange charge transfers, we have encountered experimental difficulties associated with facile ligand exchange reactions. The M(hfac)$_3$ self exchange entries in Table I are currently thought to be inert to ligand exchange on the charge-transfer time scale and apparently represent true electron-transfer rate constants. In addition, we have recently obtained values for the adiabatic electron affinities of many of the first transition series tris(hfac) complexes [15].

Theoretical Approaches
Following early theoretical studies by Bates and coworkers on atomic and small molecule charge-exchange reactions [28], many detailed quantum mechanical treatments of gas-phase electron transfer have appeared [see for example refs 29, 30]. These theories are primarily for ion beam reactions in which a small atomic or molecular ion with known velocity is collided with a thermal gas or beam. The models also accurately predict the kinetic energy dependence and absolute cross sections of these types of reactions. In the cases of molecular reactants, the theories emphasize the need for energy matching of reactant/product states and favorable Franck-Condon factors for interconversion of the neutrals and their ions.

In contrast to the above theories, models for solution electron transfer for polyatomic reactants must account for the role of solvent in trapping charge on one center; indeed, the earliest explanations of the activation barriers to solution electron transfer due to Marcus and Short center on the role of the solvent [9-11]. Later, the effects of intramolecular reorganization energies and nonadiabaticity were incorporated. In the gas-phase reactions we have investigated, solvation is obviously not a factor. Therefore, adequate models must address how the molecular properties of the reactants lead to the observed kinetics described in the previous section. Clearly, a model cannot incorporate the fine details concerning the electronic and vibrational properties of the reactants possible with small molecules such as Hg. An approximate model has been described in other publications in some detail [12, 33]. Here we will provide a brief outline and explore consequences of the results for theories for condensed-phase reactions.
A potential energy surface useful for describing these ion/molecule reactions is shown in Figure 2. The formation of the precursor complex \((A^+, B)\) occurs at the collision rate. Electron transfer within this complex produces the successor complex \((A, B^+)\). Decomposition of the precursor and successor complexes can be modeled via unimolecular rate theories such as RRKM and will not be considered further here; instead, the focus is on the interconversion of precursor and successor complexes.

The activation barrier for this process, \(\Delta E^*\) in Figure 2, results from the reorganization energies associated with changes in the molecular bond lengths upon conversion of the ion to its neutral and vice versa. Table II gives some estimates of these bond length changes and values of \(\Delta E^*\) calculated by using a purely classical model and assuming that only the M-C distances change in the metallocene reactions [13].

Elsewhere we have derived a simple quantum model for electron transfer within the loosely associated precursor complex [12]. The starting point is the Fermi golden rule, and the result for \(k_{et}\) with electron motion coupled to a single vibrational mode is given in eq 2 for a cation (+)/neutral(n) reaction.

\[
k_{et} = \frac{4\pi^2 H_{PS}^2}{h} \sum_{k} \sum_{l} \sum_{\rho} \sum_{q} F(E_{n,k}^P + E_{+,l}^P) |\langle n, k | +, q \rangle|^2 \delta(E_{n,k}^P + E_{+,l}^P - E_{n,\rho}^S - E_{+,q}^S + \Delta E_{PS})
\]

In eq 2, \(H_{PS}\) is the electronic coupling integral for the precursor (P) and successor (S) states, \(h\) is Planck's constant, the sums are over the vibrational states of the precursor (quantum numbers \(k, l\)) and successor
(p,q) complexes, the Franck-Condon overlap integrals \(<n,k|+,q>\) and \(<+,1|n,p>\) describe the overlaps of initial and final vibrational wave functions located on each of the reactants, and the \(\delta\) function ensures energy conservation. The energy distribution function \(F(E^P)\) requires some special comment as it is not the usual Boltzmann function. Unlike a precursor complex thermalized by collisions with solvent molecules, at low pressures the gas-phase precursor complex has an internal kinetic energy determined by both the reactants' initial thermal energy and the stability associated with the ion-molecule attractive forces (\(\Delta E_{im}\), Figure 2)). This latter energy can be significant (e.g., for the benzene dimer ion, \(\Delta E_{im} \approx -0.6\) eV). Since the frequency of collision of the precursor complex with third bodies is low, the additional kinetic energy released upon precursor formation must initially enter the available intramolecular degrees of freedom. Thus, the precursor is prepared with a vibrational state distribution different from the usual Boltzmann function. Methods for calculating \(F(E^P)\) are available [31].

The treatment of eq 2 has several significant limitations, a few of which will be mentioned here: (1) To apply the golden rule, the density of states in the product manifold is assumed to be large and the P-S electronic interaction is assumed to be weak. Given the large number of degrees of freedom and anharmonicity in the metal complex reactants and the small values of orbital overlap expected, these requirements are likely to be met. (2) Only a single vibrational mode is assumed, although in actuality more than one mode may be coupled to the electronic ionization or electron attachment process in the complexes (e.g., the three other \(A_{1g}\) modes of ferrocene may be active along with the \(A_{1g}\) Cp-M-
Cp stretch). (3) The presence of accessible excited electronic states in the successor complex must be included for many exoergic reactions. This inclusion is especially important for reactions involving transition metal complexes, which tend to have low-lying excited states associated with electron promotion and spin flips within the primarily metal d molecular orbitals. (4) Application of eq 2 to real cases requires inclusion of vibronic state broadening to overcome the limitations of the δ function. In solution treatments, the solvent continuum serves as a convenient energy sink to account for unmatched vibronic states in the molecular reactants [9-11]. (5) The calculation of the Franck-Condon factors is made in practice by using vibrational information for the separated reactants, ignoring anharmonicity and perturbations due to precursor complex formation.

Despite the limitations of eq 2, it does provide insight into the central role of Franck-Condon factors $\langle n, k |+, q \rangle$ and $\langle +, l |n, p \rangle$ in gas-phase electron transfer. When estimated for solution reactions, these factors are calculated from data concerning vibrational frequencies and bond distortions (the latter often from crystal structures). When considering gas-phase reactants, direct experimental Franck-Condon factors can often be estimated by photoionization spectroscopy. It is of interest to see how well the theoretical estimates match experiment, since the theoretical approach has been used almost exclusively for condensed-phase reactions.

As an example, we will consider the case of ferrocene, $\text{Cp}_2\text{Fe}$, and its ion, $\text{Cp}_2\text{Fe}^+$. Using only the $A_{1g}$ Cp-M-Cp stretch and the bond distance information of Table I, the theoretical photoelectron band for the lowest energy ionization of ferrocene can be derived, and the result is shown in
Figure 3 along with the experimental manifold [32, 33]. Clearly, the observed FC manifold is far broader than expected from the simple model and the bond distortions given in Table II. One explanation for the difference is that the gas-phase value of $\Delta r$ is different from the value used in Figure 3. An attempt to fit the PE spectrum with $\Delta r = 7$ pm is shown in Figure 4. The fit is better but not perfect. Other factors such as spin-orbit coupling, Jahn-Teller distortions in the ion, and excitation of other vibrational modes also contribute to some degree to the observed FC width. Assuming for the moment that the difference lies solely in the value of $\Delta r$ chosen, one can calculate a $\Delta E^*$ value of 0.06 eV for the ferrocene/ferrocnium self exchange with $\Delta r = 7$ pm (compare to 0.02 eV given in Table II). One can conclude that theoretical estimation of FC factors associated with molecular bond reorganizations may be misleading in both gas-phase and, potentially, condensed-phase treatments for the metallocenes and probably other reactants. Application of kinetic models will be most successful when the models for the reactants and products are as complete as possible and yield accurate Franck-Condon factors. Direct comparison to experimental factors provides a check of the theoretical estimates.

Marcus predicted many years ago the presence of a kinetically inverted region in electron-transfer reactions in which the rates actually decrease with increasing exoergicities [23]. From a quantum viewpoint, this inversion of rates occurs as a consequence of increasingly poor Franck-Condon factors beyond a certain value of the driving force. No convincing examples of the inverted region have been reported for bimolecular processes in solution, although other experiments involving
linked donor-acceptor molecules and geminate radical pairs do show a bell shaped dependence on exoergicity. Interestingly, it has been known for some time that rates of many bimolecular gas-phase charge-transfer reactions show a strong dependence on Franck-Condon factors, and the inverted region has clearly been observed in those cases [34, 35]. Many factors contribute to the failure to observe the inverted behavior in solution reactions [36]. The difficulties described above in the fitting of PE data to a simple model suggest that failure to calculate the inner-sphere molecular reorganization energies accurately can be a contributing factor. Unfortunately, except for cases of the type we have investigated, one cannot readily test the accuracy of the Franck-Condon calculations for solvated reactants since techniques such as photoelectron spectroscopy are not easily applied.

Understanding the rates of charge transfer processes of polyatomic species in the gas phase requires an appreciation of the many complexities introduced with a large number of degrees of freedom and multiple low-lying electronic states. The principle perturbations that lead to electron exchange are the ion-molecule electrostatic forces rather than the significant electronic interactions usually present for atomic and small molecule processes. Systems such as \( \text{Cp}_2\text{Mn}^{0/+} \) are ideal for more detailed theoretical studies to determine the relative importance of factors such as nonadiabaticity and bond reorganizational barriers in the charge exchange reactions of large transition metal reactants. An increased accuracy in modelling these complex reactions will ultimately allow a deeper understanding of the role of solvation in determining the kinetics of related reactions in solution.
Acknowledgement. The authors gratefully acknowledge the support of this work by the National Science Foundation, the Petroleum Research Fund (administered by the American Chemical Society), Research Corporation, and the Office of Naval Research.
TABLE I. SELECTED RATE CONSTANTS FOR GAS-PHASE ELECTRON TRANSFER REACTIONS.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>$k_f \text{ (cm}^3 \text{s}^{-1})$ $^a$</th>
<th>est. eff. ($k_f/k_{coll}$) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Self exchange reactions:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cp}_2\text{Fe} (0/+)$</td>
<td>$2.7 \times 10^{-10}$</td>
<td>0.27</td>
</tr>
<tr>
<td>$\text{Cr(CO)}_6 (0/+)$</td>
<td>$2 \times 10^{-10}$</td>
<td>0.15</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{Mn} (0/+)$</td>
<td>$1.3 \times 10^{-11}$</td>
<td>0.013</td>
</tr>
<tr>
<td>$(\text{MeCp})_2\text{Mn} (0/+)$</td>
<td>$4.2 \times 10^{-11}$</td>
<td>0.040</td>
</tr>
<tr>
<td>$(\text{Me}_5\text{Cp})_2\text{Mn} (0/+)$</td>
<td>$3.1 \times 10^{-10}$</td>
<td>0.28</td>
</tr>
<tr>
<td>$\text{SF}_6 (0/-)$</td>
<td>$&lt;5 \times 10^{-14}$</td>
<td>$&lt;0.0001$</td>
</tr>
<tr>
<td>$\text{Ru(hfac)}_3 (0/-)$</td>
<td>$3.0 \times 10^{-11}$</td>
<td>0.03</td>
</tr>
<tr>
<td>$\text{Cr(hfac)}_3 (0/-)$</td>
<td>$7 \times 10^{-11}$</td>
<td>0.07</td>
</tr>
<tr>
<td><strong>Cross Reactions:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cp}_2\text{Mn}/\text{Cp}_2\text{Fe}^+ (\Delta E = -0.6 \text{ eV})$</td>
<td>$5.0 \times 10^{-10}$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{Mn}/\text{Cp}_2\text{Ni}^+ (\Delta E = -0.05 \text{ eV})$</td>
<td>$3.1 \times 10^{-11}$</td>
<td>0.03</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{Ni}/\text{Cp}_2\text{Mn}^+ (\Delta E = -0.05 \text{ eV})$</td>
<td>$1.3 \times 10^{-11}$</td>
<td>0.013</td>
</tr>
</tbody>
</table>

$^a$ Error estimated as 30%. Temperature - 375 K.

$^b$ Estimated efficiency, defined as ratio of $k$ forward/$k$ collision, where the collision rate is estimated by the Langevin rate constant.
Table II. ESTIMATED INNER REORGANIZATIONAL BARRIERS FOR SELF-EXCHANGE REACTIONS.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Δr (M-L), pm</th>
<th>ΔE* (eV) a</th>
</tr>
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<tr>
<td>SF$_6$ (0/-)</td>
<td>14.5</td>
<td>0.96</td>
</tr>
<tr>
<td>Cp$_2$Mn (0/+)</td>
<td>25</td>
<td>0.38</td>
</tr>
<tr>
<td>Cp$_2$Fe (0+/+)</td>
<td>4</td>
<td>0.02</td>
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a

Details of calculations can be found in reference 13.
FIGURE CAPTIONS


2. Potential surface for gas-phase electron transfer reactions. The solid curve is for thermoneutral processes (A = B) while the dashed line applies for exothermic reactions. Further description of the surface can be found in reference 13 and in the text.

3. Experimental (solid line) and calculated photoelectron spectra for ferrocene. Experimental spectrum based on data in reference 32. Calculated room temperature spectrum based on an adiabatic IP of 6.80 eV and the harmonic oscillator approximation. Frequency of ion Cp-M-Cp mode, 300 cm\(^{-1}\). The difference in M-Cp distances for the ion and neutral is 4 pm for the calculation.

4. Same as Figure 3 except a M-Cp bond distance change of 7 pm is used.
Bibliography


[33] The vibrational fine structure found by Rabalais and coworkers (ref 32) for ferrocene has not been reproduced by other workers (D. Lichtenberger, private communication). The bandshape shown in Figures 3 and 4 is a smoothed version of the experimental spectrum presented in ref 32.
29, 249 (1979).


1,3-DIKETONATES

\[
\begin{align*}
M^{+3} & \quad \text{acac} \\
acetylacetone & \quad \text{benzoylaceton} \\
\text{trifluoroacet} & \quad \text{hexafluoroacet} \\
\end{align*}
\]

LIGAND

\[
\begin{align*}
R_1 & \quad \text{CH}_3 \\
R_2 & \quad \phi \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CF}_3 \\
\text{CF}_3 & \quad \text{CF}_3 \\
\end{align*}
\]
\[ A^{\pm} + B \rightarrow (A,B)^{\pm} \rightarrow A,B^{\pm} \]
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