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Is Hexaamminecobalt(III/II) Electron Self-exchange Spin-forbidden? Analogy to Photochemical Processes

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Abstract

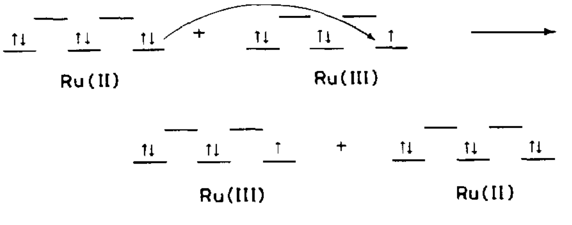
The hypothesis that the electron self-exchange reaction of hexaamminecobalt(III/II) is spin-allowed and adiabatic is presented and compared to previous treatments of the reaction which considered it spin-forbidden. The hypothesis is based on the concept that since the reactant and product have the same spin, it is unnecessary to invoke interaction with other spin states to 'allow' the reaction. To justify the hypothesis, an analogy is drawn between the cobalt self-exchange reaction and the photochemical processes of triplet–triplet annihilation and triplet–triplet exchange.

Introduction

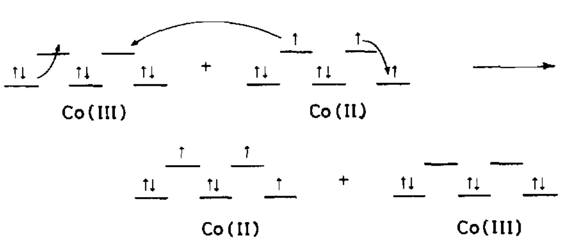
Despite the success of the Marcus theory [1] of electron transfer in explaining and predicting the rates of a variety of redox reactions, some very simple reactions are still the objects of considerable discussion, especially with regard to their adiabaticity [2–5]. Notable among these reactions is the electron self-exchange of hexaamminecobalt(III/II)

$$[Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+} \rightleftharpoons [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$$

The prevailing theoretical opinion about the hexaamminecobalt(III/II) reaction is that it is spin-forbidden [5–9]. The rationale, given originally by Orgel [10], is as follows. Most electron transfer reactions can be viewed as the transfer of a single electron between two metal atoms. For example, for a Ru(III/II) couple, the orbital picture can be viewed as below



However, in the cobalt case, transfer of a single electron must be accompanied by promotion and demotion of two electrons with change in spin



Since change in spin for a single metal complex is a forbidden process, it was concluded that the electron transfer process must also be spin-forbidden.

The prediction on other grounds that this should be a slow reaction dates back at least to 1952 [11], and experimental and theoretical aspects have been reviewed [12]. The explanation of this reaction's inertia centered initially on the inner-sphere reorganizational (Franck–Condon) barrier of the reaction. This was supported for some time by a report that the rate constant was less than 10^{-10} M^{-1} s^{-1} at 65 °C [13]. The inner-sphere reorganizational barrier was initially overestimated [11], then underestimated [17], based on early values of Δr^0 (the difference in metal–ligand bond lengths between Co(II) and Co(III) in the couple), but the value of Δr^0 is now fairly well established [6, 14, 15]. Additionally, the value of the rate constant has been redetermined [16]. Based on the recent results, the hexaamminecobalt(III/II) reaction appears to be nearly adiabatic [12, 14–16].

The purpose of this paper is to review briefly the theoretical treatments of the hexaamminecobalt exchange as a spin-forbidden reaction and to present an alternate hypothesis, that the electron self-exchange reaction is actually spin-allowed and adiabatic. This hypothesis represents a departure from most treatments of this reaction.

Treatment of Buhks et al.

The treatment of Buhks *et al.* [8] was the first to attempt to explain why the apparently spin-forbidden

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electron exchange reaction of hexaamminecobalt should have a non-zero rate constant. The authors take the view that for the pure spin states the reaction consists of a transfer of a single electron from Co(II), $s = 3/2$, converting it to a Co(III) state with $s = 1$ or 2, either being orthogonal to ground state Co(III), with $s = 0$. Thus they consider ground state electron transfer between Co(II) (^{4}T) and Co(III) (^{1}A) to be spin-forbidden. The reaction is allowed in this treatment only by the spin-orbit coupling which mixes the ^{2}E excited state of Co(II) with the ground state. The mixing of the $J = 3/2$ and 5/2 components of the ^{4}T state with the ^{2}E excited state leads to two additional Co(II) states at low energy above the ground state. Additionally the mixing of the ^{3}T excited state of Co(III) with the ^{1}A ground state gives the Co(III) ground state ^{3}T character. Based on spin–orbit coupling constants of 515 cm^{-1} for Co(II) and 600 cm^{-1} for Co(III), and vertical energies of 9000 cm^{-1} for the ^{2}E and 13 400 cm^{-1} for the ^{3}T states, mixing coefficients were calculated using first-order perturbation theory.

The authors considered that the interaction matrix element for the reaction of a Co(II) in a state k with Co(III) to yield a product Co(II) in state l was proportional to the one-electron matrix element for e_g electron transfer

$$\mathcal{H}_{kl} = \alpha_{kl}\langle e_g(a)|\mathcal{H}|e_g(b)\rangle$$

where α_{kl} is a simple function of the mixing coefficients for the ^{4}T character in the particular Co(II) state and the ^{3}T character in the Co(III) state. (For interaction of the pure ^{2}E state with the ^{1}A or ^{3}T, the matrix element would simply be the one-electron integral.) A Fermi Golden Rule approach was then employed whereby the rate constant is proportional to the square of $\mathcal{H}_{kl}$. The values were averaged over the thermal distribution of the three reactant Co(II) states. The results of these calculations were compared to the results for the $[Ru(NH_3)_6]^{3+/2+}$ couple. The effective spin barrier for the cobalt reaction was calculated to be a factor of 1 X 10^{-4} in rate constant.

Treatment of Newton and Sutin

Newton states that since the spin quantum numbers of the ground state reaction partners differ by 3/2 in hexaamminecobalt exchange rather than the more common 1/2, the value of $\mathcal{H}_{if}$, the interaction energy for the initial and final states, is greatly reduced [7]. Using an *ab initio* self-consistent field spin-restricted Hartree Fock method, he calculated the matrix element $\mathcal{H}_{if}$ for the spin-allowed reaction of ^{2}E-Co(II) with ^{1}A-Co(III) at close contact [7] to be 940 cm^{-1}. The authors [6, 7] then used the treatment of Buhks *et al.* [8] to calculate that the ^{4}T/^{1}A reaction would have $\mathcal{H}_{if}$ reduced by a factor of about 2 X 10^{-2} to about 20 cm^{-1}. This 98% reduction in $\mathcal{H}_{if}$, taken in the Landau–Zener formalism, leads to a spin-barrier transmission coefficient of approximately 4.0 X 10^{-3}.

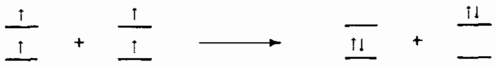
Treatment of Larsson, Ståhl and Zerner

The authors [9] expanded on the treatment of Buhks *et al.* [8]. They considered the ground spin–state reaction to be non-adiabatic with a transmission coefficient of about 1 X 10^{-4}, but considered the ^{2}E-Co(II)–^{1}A-Co(III) pathway, through thermal population of the ^{2}E state, as important. They calculated that this route was nearly adiabatic with a transmission coefficient of about 0.5. The authors further calculated the energy of the ^{2}E state at various metal–ligand distances and concluded that this pathway was of low enough energy to account for the experimentally observed rate constant.

An Alternate Hypothesis

The purpose of this paper is to propose an alternate way of viewing the hexaamminecobalt electron self-exchange reaction. The main thrust of the argument is this. The reactant state consists of a ^{4}T-Co(II) plus a ^{1}A-Co(III). The product state consists of ^{1}A-Co(III) plus ^{4}T-Co(II), equivalent to the reactant species simply exchanged in position. The overall spins of the product and reactant states are therefore identical, as they are in any electron self-exchange reaction. Thus $\Delta S = 0$, and the reaction is spin-allowed. No spin-flipping is necessary for the reaction to proceed.

It is useful here to draw an analogy between this reaction and the commonly observed photochemical reactions of triplet–triplet annihilation and triplet–triplet energy transfer, shown schematically below.



Triplet - triplet annihilation

Triplet- triplet energy transfer

In each of these processes, both the donor and acceptor molecules interconvert between triplet and singlet, making both processes apparently doubly spin-forbidden. However, both processes have not only been observed, but are extremely facile. Triplet–triplet annihilation is very important in the photochemical phenomenon of delayed fluorescence [18, 19]. Triplet–triplet transfer reactions commonly have bimolecular rate constants of 10^7 to 10^9 M^{-1} s^{-1}, depending on driving force [18, p. 124]. Moreover, the optical selection rules of the donor and acceptor complexes do not correlate with the overall efficiency of the process [19, p. 136].

The general consensus on these two photochemical processes is that they are in fact spin-allowed. A theory of triplet–triplet annihilation has been worked out by Merrifield and Johnson [20, 21] which assumes that of the nine spin-states of the reacting pair of triplets, the singlet component may react leading to the singlet product state. This theory accounts well for the observed effect of magnetic field on the rate of triplet–triplet annihilation [22]. Likewise, in triplet–triplet energy transfer, the overall spin of the reactants and products is the same, and the reaction is allowed.

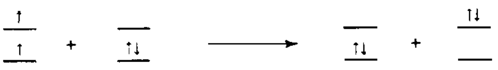
Thus, although these reactions involve triplet–singlet interconversions for the individual reactants, they are not spin-forbidden. The key, of course, is the contribution of electron exchange in these reactions, as first pointed out by Dexter [23]. In a crude sense, then, the energy transfer process may be viewed as follows

Triplet - triplet annihilation

Triplet - triplet energy transfer

Although no net electron transfer occurs, a 'virtual' electron exchange leads to net energy transfer.

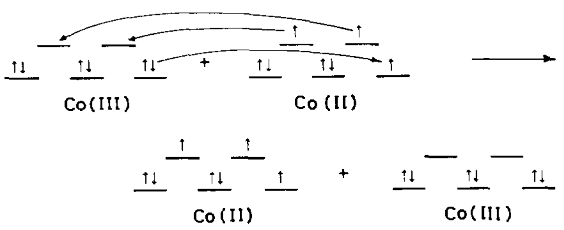
By way of contrast, these two spin-allowed processes may be compared with the process of triplet–singlet exchange



Triplet - singlet exchange

In triplet–singlet exchange, only one of the reactants undergoes triplet–singlet conversion, but there is a net difference in spin between the reactants and the products. This process is theoretically spin-forbidden. Although it is observed, triplet–singlet exchange is generally much less facile than triplet–triplet annihilation of triplet–triplet exchange, consistent with its being a non-adiabatic process [18, p. 123].

By analogy, in the hexaamminecobalt electron transfer there is no net difference in spin between reactants and products. The overall transfer of one electron can be viewed as the exchange of three electrons (or as the transfer of one and exchange of two electrons) as shown below.



It should be noted that the importance of electron exchange in the Co(III/II) electron transfer has been treated theoretically by Endicott and Ramasami [24]. Their conclusion is somewhat different than that presented here. They consider the interaction for the pure cobalt ground states to be forbidden, and the reaction to be allowed by mixing with the Co(III) charge-transfer state when it is accessible.

It is certainly reasonable to expect that the overlap of the product and reactant states, $\mathcal{H}_{if}$, will be smaller for the 'three-electron' exchange than it would be for the corresponding 'one-electron' reaction of ^{1}A-Co(III) with ^{2}E-Co(II). However, there is currently no reason to conclude that the overlap in the 'three-electron' case would be so small so as to make it non-adiabatic. The amount of coupling necessary for adiabaticity may even be overestimated by the Landau–Zener formalism. There is some evidence that long-range electron-transfer reactions, with little coupling between reactant and product states, may be adiabatic or at least have considerably larger transmission coefficients than would be expected [25, 26]. Thus it is possible that it is not necessary to invoke spin–orbit coupling to 'allow' this reaction. Even if the spin–orbit coupling constants for the cobalt complexes had values of zero, the electron transfer might be allowed.

Recent studies of the hexaamminecobalt electron self-exchange reaction suggest that it and related reactions proceed via the ^{4}T–^{1}A states [24, 27] and that it is essentially adiabatic [12, 14–16]. It is evident that this process is not strongly spin-forbidden. We suggest that the possibility be considered that the reaction is, in fact, spin-allowed and fully adiabatic.

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