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Review

# Spin catalysts: A quantum trigger for chemical reactions

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ABSTRACT

Spin catalysis allows restrictions of the spin conservation rule to be overcome, and, moreover, provides a tool for fine control of elementary reactions. Spin-conductive solid catalysts make processes over surfaces strongly correlated and also can trigger the direction of the reaction via external magnetic field application. Activation/deactivation of $O_2$ and non-polar small molecules, homolytic bond cleavage, and coupling of radicals are within the practical scope of spin catalysis.

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## 1. Introduction

Catalysis is usually considered in terms of the energy difference between initial and transition states to increase the rate of reaction required to either enable an alternative reaction pathway with a lower energy transition state to occur or increase the energy of the initial state of the reagents, e.g., by changing the solvent or adsorbing molecules on a specific surface. However, in certain classes of reactions, this might not be sufficient because the reagents and products possess different spin states, and the spin conservation rule formally prohibits such processes (e.g., formation of water from $H_2$ and $O_2$, oxidation of NO, and oxidative complexation of $Co^{3+}$). Even overcoming the energetic barrier, the system cannot resolve into stable products without change of the electronic spin multiplicity state. Such reactions can still occur, but they require specific non-thermodynamic conditions. Usually, they are referred to as processes where spin is not conserved.

The most straightforward way to change the electronic spin of a system is a spin-flip of an electron by interaction with the spin of the atom nucleus. This event is realized through spin-orbital coupling, and thus its probability strictly depends on the atomic number of the element. Starting from 3*d* metals, it might occur even more frequently because of higher coupling efficiency with *d* orbitals, so spin-crossing is a conventional way to explain why spin-forbidden reactions take place. However, the probability of spin flipping of light atoms is negligible (for hydrogen it is of the order of 10–15 $s^{-1}$). Thus, when considering metal-free chemistry, one should consider the second way of spin prohibition rule cancellation: spin catalysis, which is not related to interaction of the unpaired electron with particles within an atom.

Spin catalysis is defined as "phenomena in which chemical reactions are promoted by substances which assist in overcoming spin-prohibition or in which the activation barrier is lowered through spin uncoupling induced by a paramagnetic

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catalyst" [1]. More simply, to obtain the desired (and more thermodynamically favorable) spin state, one of the reacting particles can exchange its magnetic moment with the third body (spin catalyst), which presumably has pseudo-spin-degenerate ground or low-lying excited states. Thus, the overall spin state of the system is still conserved but the reaction can proceed (Fig. 1).

It should be emphasized that the spin catalyst term might indicate both molecular and solid states, with the latter often being much more convenient for industrial application.

## 2. Basics of spin catalysis

Historically, spin catalysis has been investigated in the paradigm of spin chemistry concurrently with chemically induced dynamic nuclear polarization and reactions in external magnetic fields, mainly for processes in solution, and investigated by electron paramagnetic resonance spectroscopy. The theory of such processes can be found in the works of Buchachenko, Minaev, and Schwarz [2–5]. Only brief excerpts are given here.

First, we will discuss a radical pair in the gas phase. It is obvious that the pair can recombine to form a covalent bond only in the singlet state (i.e., in the case when the spins of the radicals are opposite). The probability of such a collision is 25% because two radicals can equiprobably form one singlet and three triplet states, with the latter being anti-bonding. However, in the case of the presence of a third radical (spin catalyst), one of the triplet states ($^1T$) can turn into a reactive singlet ($^1S$) through spin-spin interaction with $R_3$, with the probability of this process exponentially decreasing with increasing distance between the interacting radicals. It should be noted that to make spin catalysis effective, the values of the spin-spin interactions in the $R_1$–$R_3$ and $R_2$–$R_3$ pairs should be different, which can be realized either by the different nature of the interacting radicals $R_1$ and $R_2$ (e.g., different spin-centering atoms) or different distances $d(R_1–R_3)$ and $d(R_2–R_3)$ (Fig. 1(b)).

The equilibrium of the $R_A$–$R_B$ radical pair in dilute media is shown in Scheme 1. For covalent bond homolytic cleavage, constant $k_1$ is much larger than $k_{-1}$, so the overall rate is mostly controlled by diffusion step 2. Singlet-triplet transformation is formally forbidden because of the spin conservation rule and depends on the probability of the spin flip, which is extremely

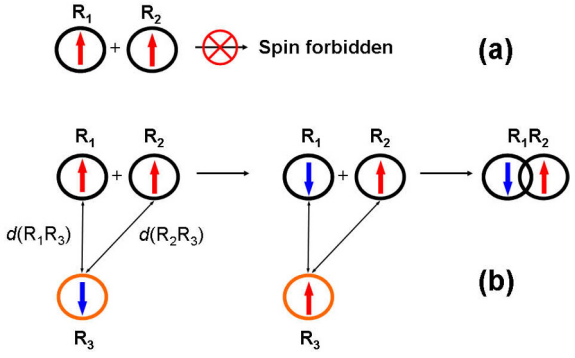
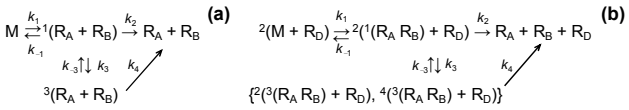



**Fig. 1.** (a) Spin-forbidden elementary reaction of a radical pair. (b) Radical $R_3$ catalyses recombination of radicals $R_1$ and $R_2$ via spin-spin interaction with $R_1$ (because of the shorter distance between $R_1$ and $R_3$).




**Scheme 1.** (a) Equilibrium of the $R_A$–$R_B$ radical pair. (b) Equilibrium of the radical pair in the presence of paramagnetic admixture $R_D$ (spin catalyst). Adapted from Selihov's lectures on spin chemistry [6].

improbable. Hence, this stage is the subject of spin catalysis, which opens the possibility of reaction 3, so that overall rate of the reaction comprises diffusion of both singlet ($k_2$) and triplet ($k_4$) radical pairs (Scheme 1(b)). The probability of interaction between the radical pair and the paramagnetic admixture can be estimated by the Smoluchowski equation. The reverse reaction can be described with a similar set of equations, so it is clear that the elementary reactions of the recombination of radicals and covalent bond homolytic cleavage are both spin catalysis phenomena, because they enable additional reaction pathways to form the singlet or triplet radical pair, respectively [7–9]. However, the opposite direction of the processes might require different catalysts.

## 3. Requirements for the spin catalyst

It should be emphasized that there is no opposition between conventional catalysis and spin catalysis, and the same material can serve as both a conventional catalyst and a spin catalyst, decreasing the barrier of the reaction and providing a radical center for spin-exchange (examples will be discussed below). Moreover, a lot of modern materials combine classical and spin-catalyst properties, although this has never been emphasized. Some processes in nature occurring at polynuclear magnetic metalo-centers also might combine the effects of conventional catalysis (by activation of substrates), spin-crossing (owing to interaction with *d* metals), and spin catalysis (owing to low-energy ferromagnetic-antiferromagnetic transitions in metal-oxide clusters) [10–14].

The main problem for practical implementation of spin catalysis in the gas phase is rather trivial: the probability of three-particle collision is low in dilute systems. In this regard, catalysis by solids has a number of advantages. First, the requirements for the solid to be a spin catalyst have to be defined:

(1) Active centers should have a small energy difference between at least two spin states (e.g., singlet and triplet). Presumably, this difference should be less than the energy of thermal motion at the temperature of the process.

(2) The solid should have high specific surface area (this coincides with the requirements for conventional heterogeneous catalysts).

(3) Optionally, the materials should be spin-conductive (i.e., spin centers should be conjugated and thus have a common electronic system). Although this requirement is not obligatory, it can give the catalyst valuable additional properties, as will be shown below.

We will now discuss the role that each of the above-mentioned criteria plays in the efficiency of the spin catalyst. Isolated free radicals in the absence of an external magnetic field

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