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An anatomy of the two-state reactivity concept: Personal reminiscences in memoriam of Detlef Schröder

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ABSTRACT

Two-state reactivity (TSR) has become a widely used concept in bioinorganic and metallo-enzymatic chemistry. This concept was conceived in response to puzzling data on the reactivity of $Fe{=}O^+$ with H_2 [1], and in the reactivity patterns of the enzyme Cytochrome P450. The TSR concept has been developed through a very intense interaction of the author with Helmut Schwarz and the late Detlef Schröder between the years 1993 and 1998. The paper is written as a tribute to Detlef Schröder who passed away untimely, and is still remembered by his many friends as a wonderful scientist with scintillating energy, goodness and enthusiasm.

1. Introduction

In August 1992, I moved from Ben-Gurion University to the Hebrew University. That was a move that eventually changed my scientific life in a major way! From that point on, many things came to pass, and within four years of the move to the Hebrew University; I became a computational chemist, I largely abandoned organic chemistry for transition metal chemistry, and last but not least, I became the Director of the Lise Meitner-Minerva Center for Computational Quantum Chemistry. One of the catalysts of some of these changes and of the reorientation in my scientific interests was Helmut Schwarz who became also a close friend. Helmut's right-arm at the time was Detlef Schröder who also became my close friend.

At that time, Helmut and Detlef were leading an exciting research on bond activation by transition metal cations and small cationic complexes. After our first meeting in 1993, soon enough I found myself totally immersed in this science, and was interacting almost daily with Detlef and Helmut as well as with the many wonderful students of the Berlin group. This intense interaction culminated in the concept of two-state reactivity (TSR), which provided a nice and predictive rationale for the puzzling results generated in the group by the PhD student the late Andreas Fiedler, and then sprouted to reactivity patterns in Cytochrome P450, and beyond.

When I was asked to participate in this volume as homage to Detlef Schröder, I thought that the story of the development of this concept would be a fitting way to pay tribute to a wonderful research group, and remember a friend and a scientist with whom I shared the excitement of *sudden* understanding. I therefore decided to use the notes from a diary I have been keeping for years, and tell the story with personal reminiscing on this intense period; sketching how the initial idea of TSR has grown into a scientific territory in directions hardly envisioned then in 1993 when we first met in the TU Berlin. This story is all about the social and human part of science. As such, my account will naturally focus on this common work and on the work done in my group at the same time and subsequently. I hope this focus will not be interpreted that I am ignoring the work done by others.

2. An anatomy of collaboration

2.1. June 14–23, 1993

It all began in June 14th, 1993, when Helmut picked me up at Tegel, and before anything else he took me to see a beauty: The bust of Nefertiti ("The Beauty Cometh"), Fig. 1. What an atypical gesture of a chemistry professor! This was more a gesture of a romantic motivated by inspiration.

On June 15th, I met Wolfram Koch and Max Holtahusen who told me about their extended CASSCF and CASPT2 studies. This was

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Fig. 1. The bust of Nefertiti.

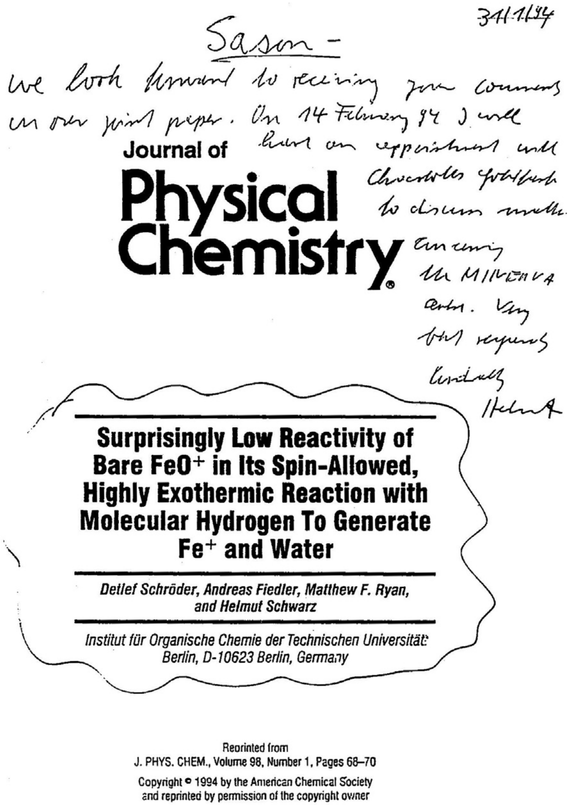
the first time I heard about the FeO^+ molecule. In the afternoon, there were two group seminars, one by Ian McGregor from Sydney, and the other by me. I talked about bonded electron transfer, and I saw Helmut and Detlef discussing something fervently. Something was already in the planning . . .

In the morning of June 16th, Helmut met me in his office, and suggested submitting together a Volkswagen grant on electron transfer. He then hinted that they have a mysterious result in bond activation by FeO^+ he would like my advice on, and so on . . . The pace of incoming ideas overwhelms me but I keep nodding positively to everything he suggests . . .

In the afternoon of June 16th, I gave my second seminar to the group; this time it was on the valence bond (VB) modeling of chemical reactivity. At the end of my talk Jan Hrusák, the Czech postdoc, asked me a question: Why is the association reaction, $2N \rightarrow N_2$, slow, if it has no barrier of the type I described to occur due to VB avoided crossing? My explanation was that this might well be due to spin forbiddenness (now I know that it is actually more complicated than that). As it turned out, the word "spin" will become very important in our little scientific universe. My answer to Jan's question triggered immediately a question from Detlef, "*so what about the reaction of FeO^+ with H_2*"? The question was asked with gusto, which I would soon learn is a second nature for Detlef. I was caught off guard. I forgot what was the precise reaction that Helmut was telling me about yesterday. So, Helmut patiently explained that the reaction was the following:

$$FeO^+(^6\Sigma^+) + H_2 \rightarrow Fe^+(^6D) + H_2O \qquad (1)$$

As can be seen from the terms in parentheses, the reaction is spin allowed and nevertheless it is highly inefficient. Perhaps the best way to appreciate the question posed to me is to read the title of the paper that the Berlin group eventually published in the *Journal of Physical Chemistry* [1], and is shown below in Fig. 2 with Helmut's hand written notes (see if you can decipher the note, or else, send me an email . . .). At that time, I had little experience with transition metal chemistry and it was the first time, in my career till then, that I have no answer. Very frustrating!



31.1.94

Sason -

We look forward to receiving your comments on our joint paper. On 14 February 94 I will have an appointment with [illegible] [illegible] to discuss matters concerning the MINERVA center. Very best regards

Cordially

Helmut

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Surprisingly Low Reactivity of Bare FeO^+ in Its Spin-Allowed, Highly Exothermic Reaction with Molecular Hydrogen To Generate Fe^+ and Water

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Fig. 2. The cover page of Ref. [1]. Note the title. Helmut's handwritten note refers, inter alia, to the first paper we shall be publishing eventually [2].

Let me reconstruct the reasons for the surprise expressed by the title in Fig. 2 about the efficiency of this reaction [1]. Firstly, the reaction is highly exothermic, $\Delta H = -37$ kcal/mol, and as a gas phase reaction should have proceeded with 100% efficiency, unless it had for some odd reason an energy barrier (ca. 3 kcal/mol). Secondly, during the reaction there are in principle good orbital interactions between the two reactants, which should have led to a low barrier. And third, the reaction starts and ends with a sextet spin, and is hence spin-allowed. And despite all these rosy prospects, the measure reaction efficiency was only 0.6% (of the collision rate at the conditions of the experiment) [1]. With NiO^+ and CoO^+, the reactions are even more exothermic. Yet, the measured reaction efficiencies were even smaller than 0.1%. These data, and the fact that FeO^+ does not assume perfect pairing and it prefers a sextet ground state, were puzzling. This was a challenge!

In the morning of June 17th I toured Berlin and visited the Brücke Museum, with these questions humming in my head . . . Helmut is an inspirational motivator. In the evening he invites me to a nice Italian restaurant and then to listen to "Don Giovani". When I return to my hotel room, the mixture of Mozart, Expressionism, and Italian food has its influence on my brain: I begin to understand the electronic structure of FeO^+. It is an analog of O_2.

On Monday, June 22nd, I flew back to Israel. Life is crazy! Sara, my spouse, and I have to sell our house in Beer Sheva and sign a contract to buy a new apartment in Jerusalem, and then travel to conferences in France, in the US, etc. All memories on FeO^+ evaporate, until the next visit to Berlin in November . . .

2.2. November 11–23, 1993

On November 11th, I flew again to Berlin to deliver a mini-course on application of VB theory to chemical reactivity. During the flight I scribbled fervently on a piece of paper, and using the O_2-analogy and VB mixing ideas, I could predict that the transition state (TS) for the reaction of $FeO^+ + H_2$ (Eq. (1)) should be a concerted four-centered species. In the morning of November 12th just before the first VB lecture, Helmut and I met and had a discussion on the Volkswagen grant application, and the FeO^+ issues. I told him about the