Proton coupled electron transfer tunneling reactions in WO$_3$ and MoO$_3$ nanostructured films

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Abstract. WO$_3$ and MoO$_3$ are famous hydrogenphilics, hydrogen loving materials, capable of performing various functions concerning atomic hydrogen. They are active catalysts in photochemical reactions connected with detachment of hydrogen atoms, being, at the same time, capable of accommodating great quantities of the detached hydrogen atoms, and transporting them to other functional materials via employment of various heterostructures. It was shown that tunneling proton-coupled electron transfer is the mechanism of the photochemical hydrogen abstraction reaction on the surface of highly disordered nanostructured WO$_3$ and MoO$_3$ thin films. Specially selected hydrogen donor molecules were adsorbed on the oxide surface bonding via donor-acceptor and hydrogen bonds which yield a decrease in the energy barrier for the hydrogen transfer from the adsorbed hydrogen donor molecule to the oxide surface. The very rough and heterogeneous film surface yields space fluctuations of the energy barrier parameters whereas intermolecular vibrations yield time fluctuations; the fluctuative barrier preparation being responsible for the tunneling photo-stimulated proton-coupled electron transfer.

1. The main features of hydrogen transfer between the hydrogen donor molecules and the oxide surface

WO$_3$ and MoO$_3$ films attract attention due to a variety of interesting properties; among those, electrochromism and photochromism being worth to mention [1-7]. The main aim of this work is to describe the hydrogen transfer triggered by incident light between specially selected adsorbed molecules (hydrogen donors) and the oxide surface:

$$\text{MO}_3(\text{RH}_n)_{\text{ads}}^{+} + h\nu \rightarrow \text{H}_x\text{MO}_3(\text{RH}_{n-x})_{\text{ads}}$$

where MO$_3$ is a transition-metal oxide (hydrogen acceptor), (RH$_n$)$_{\text{ads}}$ is an adsorbed molecule (hydrogen donor) and H$_x$MO$_3$ is a hydrogen metal bronze.

The scheme of the bonding for the adsorbed molecule is presented in figure 1; dimethylformamide (DMFA), (CH$_3$)$_2$NCHO being the hydrogen donor, although it is not exceptional, and similar results can be achieved with other oxygen-containing organic molecules, e.g. ethanol or methanol.

A surface cation always has in its coordination sphere one or two terminal oxygen atoms O$_t$ with one σ- and one π-bond (figure 1). The nuclearphilic attack is carried out by the DMFA oxygen atom O$_c$ in the vicinity of the O$_t$ since the Coulomb repulsion between the O$_t$ and the O$_c$ is smaller as compared with that between the bridging oxygen atoms O$_{br}$ and the O$_c$ since the O$_t$ has only one strong bond. This bond is formed by overlapping of vacant d orbitals of the surface cation and p orbitals of the oxygen atoms with lone electron pairs.

The bonding atomic metal and oxygen orbitals form the valence band (σ- and π-states), whereas the anti-bonding orbitals form the conduction band (σ*- and π*-states). σ-bonds are formed by overlapping of transition-metal hybridized d, s, and p–orbitals and p–orbitals of an oxygen atom, and π-bonds are formed by overlapping of d–cation orbitals and p–oxygen orbitals of the O$_i$ oxygen atom [8, 9]. The top of the valence band is formed by oxygen lone-pair orbitals, whereas the bottom of conduction band is formed by vacant metal d- orbitals (non-bonding n-states) (figure 2). The DA bonds between the
molecule and oxide surface yield the bonding and anti-bonding surface states close to the top of the valence band (\(\pi\)-states) and the bottom of the conduction band (\(\pi^*\)-states) (figure 2).

Proton systems are bonded via hydrogen (H) bonds arising between hydrogen atoms of the molecule and the \(O_t\) atoms. For being an effective hydrogen donor these molecules must contain first an oxygen atom and, second, H-C=O\(_c\) or O\(_{br}\)-CH\(_n\)- groups, where \(n=2,3\) [7]. It is well known that O–H⋯O-bonding is easily achieved, whereas C–H⋯O-bonding is much less effective owing to the small C–H bond polarity, although, after long-last ed discussions, the possibility of the C–H⋯O-bonding is recognized. The DA-bonding can in turn facilitate the C–H⋯O-bonding, since the electron density outflow from the oxygen atom of the adsorbed molecule stimulates in turn the electron density outflow to electronegative \(O_c\) within the H–C=O\(_c\)-group, inducing an additional polarization of the C–H bond, which enhances the inclination for the H-bonding (figure 1). Although the H-bond is weak, it plays a very important role determining the direction of the C-H vibration and preparing the system for the hydrogen transfer.

When the surface is illuminated by photons with energy, exceeding the oxide forbidden band gap width, electron-hole pairs are created. If a photogenerated hole reaches the surface, it flows up to the top of the valence band appearing at the \(O_t\), and can be scavenged by an electron of the lone pair of the \(O_t\) of the donor molecule, what yields in turn the translocation of the hydrogen bonded proton to the surface oxygen; thus, hydrogen atoms being transferred from the molecule to the surface. The exchange of the hole for the proton makes it impossible recombination of the photogenerated electron; it is localized at a cation forming lower-valency cation.

The reaction may be considered as the hydrogen transfer from the initial \(U_i\) to the final \(U_f\) potential energy terms along the proton coordinate \(r\) with the fixed distance \(r_0=r_0^e-r_0^i\) and the solvation parameter \(q^*\) corresponding to the initial solvation of the system after appearance of the photogenerated hole in the vicinity of the reaction site (figure 3); \(a\) and \(b\) denoting the turning points. A hydrogen atom can be transferred from the molecule to the oxide surface either in a classical way by overcoming the energy barrier or via tunneling under the barrier. \(\Delta E^*\) is the difference between the ground and excited electronic states at the proton coordinate \(r^*\); the splitting arising due to the possibility of tunneling for the electrons.

There is a manifold of localized proton states on the initial side, and a corresponding manifold of states on the final side [10]. Different solvent configurations produce different initial and final energy levels. The scale of the energetic solvent fluctuations is consonant with the proton level separation. For this reason proton can easily find an appropriate excited state on the final state \(E_f\) whither it can
be transferred. The proton transfer may occur between the excited states \( E_i^* \) in the initial side and the excited states \( E_f^* \) in the final side (figure 3). The energy released due to the electron-hole recombination can excite the C-H vibration modes or other vibration modes of the oxide and of the adsorbed molecule yielding the changes in the solvent configuration of the proton. The proton is first transferred to the excited state \( E_i^* \) and then either tunnels to the final states “cutting” the top of the energy barrier \( \Delta E \) (figure 3) or overcomes the barrier in the classical way. Then the relaxation of the solvent configuration follows and the proton occurs in the final ground state \( E_{of} \) (figure 3).

The possibility of the proton tunneling between two potential energy terms separated by the energy barrier causes the splitting of the initial levels for the value \( E_p \), which means that the resonance condition should be fulfilled with an accuracy \( \sim E_p \). The transitional configuration \( q^* \) ensuring the equalizing of the proton energy levels is characterized by the finite lifetime \( \tau_s \) during which the proton must tunnel from the initial side to the final side; the reaction of the proton transfer should be adiabatic. The same holds true also for the adiabatic electron transfer, since the electron should follow in time the motion of the medium dipoles as well as the proton motion.

![Figure 3. Potential energy terms for the hydrogen transfer.](image)

The probability for the proton transfer from the ground state \( E_{oi} \) is low. The C–H····O interaction is weak to form a low-barrier hydrogen bond; the C–H····O bond length being \( \sim 2-2.5 \) Å [11].

The electron and the proton are transferred to the same cite, to the \( O_n \), and the reaction runs without charge transfer.

To find some intriguing possibility of the tunneling component in the hydrogen transfer, it is necessary to prepare the energy barrier for tunneling. The very first step in the preparation of the energy barrier is the selection of the hydrogen donor molecule with an oxygen atom since, in the latter case, the electron energy levels of the oxide and the molecules lie in the same energy range (see figure 2); thus the possibility for electron tunneling being created. The other important step is to create highly disordered heterogeneous oxide surface which ensures space fluctuations of the energy barrier for the hydrogen transfer.

### 2. Preparation of highly disordered heterogeneous oxide surface

To achieve mostly disordered surface the WO\(_3\) and MoO\(_3\) films were evaporated directly in DMFA vapor at a \( 6-8 \times 10^{-4} \) mbar pressure.

Two-dimensional AFM images for the MoO\(_3\) films are shown in figure 4. The films were found to be nanocomposites, whereas the absence of long-range order was confirmed by X-ray analyses. For this reason, the films are characterized as ‘quasi-amorphous’. The films possess a high porosity with an average pore size of \( \sim 100 \) nm diameter and \( \sim 200 \) nm depth, where the adsorbed molecules can freely move, rotate and bond to the film surface (figure 4); the surface being essentially heterogeneous, which predetermines different reactivity for different surface reaction centers. \( \sim 25 \) nm
diameter clusters have coalesced to form irregular-shaped ∼100-200 nm diameter grains (figure 4a). Similar images were observed in WO\textsubscript{3} films; all films being macroporous with a rough and highly disordered surface. Some of the mesopores can be observed. Analysis of micro-quantities of the organic molecules adsorbed on the film surface were carried gave the number of the adsorbed DMFA molecules per transition-metal atom at 0.6–1 for the MoO\textsubscript{3} and WO\textsubscript{3} films evaporated in DMFA vapor. This value can be enhanced up to 0.9–1.5 for the MoO\textsubscript{3} and the WO\textsubscript{3} films by additional adsorption of DMFA molecules at a 10\textsuperscript{-1} mbar pressure, which was carried out immediately after the film deposition.

### 3. Experimental results

A reaction rate of the hydrogen transfer was investigated by measuring the optical density spectra before and after illumination for all types of the films at various temperatures; the dependences of the photo-induced optical density at the band maxima \(D_{\text{max}}\) and derivatives \(dD_{\text{max}}/dt\) were plotted versus illumination time \(t\). The example of \(dD_{\text{max}}/dt\) versus \(t\) is shown in figure 5 which illustrate the kinetic isotopic effect at 20K in the WO\textsubscript{3} films; According to Smakula’s equation, the concentration of inserted hydrogen atoms \(N\) (cm\textsuperscript{-3}) is estimated as [12]:

\[
N \cdot f = 0.87 \times 10^{17} \frac{n}{(n^2 + 2)^2} \alpha_{\text{max}} W
\]

where \(f\) is the oscillator strength, \(n\) is the refractive index, \(\alpha_{\text{max}}\) is the absorption coefficient in the band maximum, in cm\textsuperscript{-1}, \(W\) is the half-bandwidth in eV. At the initial stages of the photoinjection of hydrogen (in the vicinity of the illumination time \(t=0\)), the optical density changes are mainly caused by an increase in the absorption coefficient, whereas an income due to reflectivity changes may be neglected [7, 12]. Then the photoinduced optical density \(D_{\text{max}}\) may be determined by the formula:

\[
D_{\text{max}} = \alpha_{\text{max}} d / 2.3
\]

where: \(\alpha_{\text{max}}\) is the absorption coefficient in the band maximum, in cm\textsuperscript{-1}, and \(d\) is the film thickness, in cm. If the bandwidth does not change during illumination, what holds true for the initial stage of the process, then, the concentration of injected hydrogen atoms is linearly proportional to \(D_{\text{max}}\), whereas \(dD_{\text{max}}/dt\) is linearly proportional to the reaction rate of the hydrogen transfer. For the investigated films, \(dD_{\text{max}}/dt\) has a maximum at \(t=0\) and decreases dramatically with illumination time \(t\) due to a decrease of the lifetime for the photogenerated holes with the concentration of injected hydrogen atoms.
hydrogen [4, 5, 7]. The hydrogen diffusion coefficient strongly depends upon temperature; very different surface distributions of injected hydrogen atoms occurring at different temperatures. Thus, comparison of the reaction rates at various temperatures makes sense only at t=0, when the concentration of hydrogen in the films is zero and the conditions for hydrogen transfer are identical.

With the oscillator strength \( f = 0.18 \) for the MoO\(_3\) films and of \( f = 0.3 \) for the WO\(_3\) films [13], \( n = 2 \) for the MoO\(_3\) and WO\(_3\) films [7], and \( W \approx 1 \) eV [2, 3], the reaction rate for the photoinjection of hydrogen atoms \( dN_t/dt \) (atoms*cm\(^{-2}\)*min\(^{-1}\)) at \( t = 0 \) was calculated with the help of exp. (2) and (3):

\[
(dN_t / dt)_{max} = 0.87 \times 10^{17} \frac{n}{f(n^2 + 2)^2} 2.3(dD_{max} / dt)W
\]

Arrhenius plots, \( \text{lg}(dN_t/dt)_{max} \) versus \( 1/k_bT \) at \( t=0 \), where \( k_b \) is the Boltzmann constant are presented in figure 6a. Plots of the derivatives \( d[\ln(dD/dt)_{max}]/dt \) versus \( 1/k_bT \) at \( t=0 \) yield the activation energy \( E_a \) for the hydrogen transfer (figure 6b), whose physical sense will be discussed later.

4. Discussion

Figure 6 unambiguously shows that plots of \( \text{lg}(dD/dt)_{max} \) versus \( 1/kT \) exhibit a non-zero reaction rate limit for all samples, providing direct evidence for the quantum character of the reaction [14]. The reaction rate for the hydrogen transfer process has two temperature regions: activation at high temperatures and a practically temperature independence at low temperatures (figure 6a). Figure 6b shows that the activation energy \( E_a \) for the hydrogen transfer tens to zero with a decrease in temperature for all samples. Only these highly disordered MoO\(_3\) and WO\(_3\) films of the “cauliflower” morphology exhibit the non-zero reaction rate limit (figure 6a). Other types of the oxide films (amorphous and polycrystalline) prepared at elevated substrate temperatures have been also investigated. Having sometimes very high photochromic sensitivity at room temperature, they very quickly lose it with a decrease in temperature; the reaction rate dropping down to a value beyond the sensitivity of our measurements even higher than liquid nitrogen temperatures. For those samples, the plots \( \text{lg}(dD/dt)_{max} \) versus \( 1/kT \) exhibit nearly linear dependence of Arrhenius type. The line 1 in figure 6a illustrates typical temperature dependence for the reaction rate of the hydrogen transfer in these samples. One can see the great difference in the behavior of the films simply evaporated in DMFA (MoO\(_3\)-1) and the films evaporated in DMFA and undergone additional treatment after evaporation at a 10\(^{-1}\) mbar DMFA pressure (MoO\(_3\)-2): the additional adsorption under an enhanced pressure of DMFA vapor yields an essential enhancement of the reaction rate at room temperature, whereas much less of that is achieved in the low-temperature reaction rate limit (compare relevant curves in figure 6a). Thus, under additional pressure, DMFA molecules are adsorbed at reaction cites having a higher energy barrier; the hydrogen transfer being not achieved at low temperatures at these cites. At the same time, the activation energy at room temperature \( E_a \) is enhanced in the MoO\(_3\) films compared with the MoO\(_3\) films evaporated in DMFA without additional treatment from 0.04 eV to 0.11 eV (figure 6b).

The other bright result is a very small kinetic isotope effect inferred only at 20K obtained with the use of different modification of DMFA (figure 5). Both the non-zero low-temperature reaction rate limit and the kinetic isotope effect at 20K show the tunneling character for the hydrogen transfer, whereas the small value for the kinetic isotopic effect shows in turn the small value of the energy barrier for the hydrogen transfer. The rate \( k \) constant for the tunneling reaction may be expressed as:

\[
k = v w,
\]

where \( v \) is the preexponential factor and \( w \) is the probability to tunnel under the barrier per one collision. For a rectangular shape barrier \( w \) may be determined from the simplified Gamov’s formula:

\[
w = \exp(-2 \sqrt{2mE \cdot d / h})
\]
where, $\hbar = h/2 = 1.055 \times 10^{-34}$ J sec, $m$ is the mass of a tunneling particles, $\Delta E$ is the difference between the barrier height and the total energy of a tunneling particle, $d$ is the barrier width. Rough estimations of the approximate barrier parameters in this approach yielded the value $\sqrt{\Delta E \cdot d}$ which determines the barrier transparency reduces by a factor of $\sim 57$ as compared with the characteristic values for

![Figure 5](image1.png)

Figure 5. The kinetic isotope effect in 0.9 $\mu$m thick WO$_3$ films at 20K; two modifications of DMFA (normal and with an isotope exchange for deuterium, exceeding 99% in all hydrogen groups) being used.

![Figure 6](image2.png)

Figure 6. Reaction rate $k$ (a) and activation energy $E_a$ (b) vs. $1/kT$ at $t=0$ for the MoO$_3$ and the WO$_3$ films. Film thickness for MoO$_3$-1 films: $d=0.4 \mu$m; for MoO$_3$-2 films: $d=1.2 \mu$m; for WO$_3$-1 films: $d=0.6 \mu$m.

chemical reactions, $E \sim 1$ eV and $d \sim 1$ Å [14] If the barrier width $d$ is $\sim 1$ Å, than the barrier height $\Delta E$ is reduced by a factor of $(57)^2=3250$, i.e. down to 0.0003 eV. If $d$ is $\sim 0.1$ Å, $\Delta E$ is 0.03 eV.

The criterion was derived for the critical tunneling temperature $T_t$ (the upper bound for exponential prevailing of tunneling transitions over Arrhenius ones) which is connected with the estimated parameters of the energy barrier [14]:

$$T_t = \frac{h}{k_v \cdot d} \sqrt{\frac{\Delta E}{2m}} \cdot r \quad (8)$$

where $r$ is the parameter characterizing the barrier shape; with the electron mass $m_e = 9.11 \times 10^{-31}$ kg, the characteristic values $d=1$ Å and $\Delta E=1$ eV, and $r=2/\pi$ (for a parabolic-shape barrier), one obtains $T_t \approx 13600$ K [14], which means that electron tunneling transitions prevail over activated ones over the great temperature range, if the resonance condition is fulfilled. With the same values of $d$ and $\Delta E$ for a proton, one obtains $T_t \approx 320K$ [14]. Thus, tunneling for both particles may be preferential over a very wide temperature range, if the resonance conditions are fulfilled, which is facilitated by medium dynamics stimulated by the energy dissipated in the result of collapse of the electronic excitations triggered by photons.
The non-zero low temperature reaction rate limit and the small kinetic isotopic effect show that, at least at the range from 20 up to 90 K (figure 6), the hydrogen transfer is achieved via tunneling of both quantum particles: electrons and protons. There is no doubt about preference for electron tunneling transitions over activated transitions over the whole temperature range since, for electrons, $T_t$ is much higher than room temperature, even for high values of the energy barrier. What concerns the proton tunneling, it is not obvious to determine a priori the temperature range where it prevails over activated transitions. The energy $E_p$ in the activation part of the dependence $\ln k = f(1/k_B T)$ (figure 6b) may be the energy needed either to provide an activated proton transition coupled to an electron tunneling transition, or to prepare the system for tunneling of both particles. The small kinetic isotope effect at 20K shows that the energy barrier is very small in the range between 20 and 90K, where the tunneling of both particles is observed. The energy barriers differ at different reaction cites, which yields a distribution for the barrier parameters. Medium dynamics affects the barrier, yielding, sometimes, its total elimination; this process being named in as “fluctuative” preparation of the barrier for chemical reactions [14]. Barrier height and width determine the reaction probability, and the former depends upon the latter. When the inter-reagent interactions are strong, the donor–acceptor distance fluctuations are enhanced causing a fluctuation of the barrier height, thereby reducing the effective barrier, sometimes even to zero. To verify whether this model is valid in our case, plots $\ln(D_{\text{max}}/dt)$ versus temperature $T$ were made for all samples. Figure 7 shows that all plots exhibit a fairly good linear dependence.

In our case, the fundamental reasons exist for this reaction mechanism. First, the fluctuative preparation of the barrier is achieved by the topological surface disorder (space fluctuations of the barrier parameters) since the oxide surface is essentially heterogeneous having the variety of reaction cites with different barrier parameters; for a definite number of the centers, the topological surface disorder providing the highest degree of interaction between the adsorbate and adsorbent, which yields the most effective reduction of the barrier. The time fluctuative preparation of the barrier is achieved by phonon stimulation. At very low temperatures phonon modes excited due to the recombination of the electron photo-excitations provide the time fluctuation of the barrier; in the first turn, the C-H stretching vibration being excited. These fluctuations together with the space fluctuations provide hydrogen transfer at the most low-barrier reaction centers. For the centers with the higher value of $\sqrt{\Delta E} \cdot d$, the “unfreezing” of other vibration modes adds the contribution to this process at higher temperatures providing the hydrogen transfer. For the reaction cites with the lowest energy barrier, the configuration appropriate for the electron and proton tunneling is achieved even at very low temperatures, whereas for the others it is achieved only at high temperatures. For all films the non-zero low-temperature limit is achieved within the same temperature range ~90K (figure 6), which may be is
attributed to „unfreezing” of the same intermolecular vibration modes [14]. Thus, the activation energy $E_a$ (figure 6b) is the energy needed to achieve the desired atomic configuration for providing the proton-coupled electron transfer, whereas the electron and proton tunneling transitions prevail over activated transitions over the whole temperature range.

Conclusions
The new oxide structure was created having very disordered heterogeneous surface with macropores, which provides the highest possible fluctuations of the parameters of the energy barrier for the hydrogen transfer. In this system, the non-zero low temperature reaction rate limit was inferred. The small kinetic isotope effect and linear dependence of the reaction rate upon temperature showed that the reaction proceeds via tunneling of both quantum particles: the electron and the proton; the reaction being essentially activationless. The reaction mechanism is the fluctuative preparation of the energy barrier: the barrier being eliminated due to unfreezing of the intermolecular vibration modes at higher temperatures.

The tunneling PCET on the transition metal oxide surface can be very useful to mimic hydrogen abstraction reactions occurring in biological systems.

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