



The mechanism of hydrogen abstraction by high valence transition metal oxo compounds

Gang Fu^a, Ruming Yuan^a, Huilin Wan^{a,*}, Xin Xu^{b,**}

^a Department of Chemistry, State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry & Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China

^b Department of Chemistry, MOE Laboratory for Computational Physical Science, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China

ARTICLE INFO

Article history:

Received 17 August 2016
Revised 27 August 2016
Accepted 9 October 2016
Available online 23 November 2016

Keywords:

C–H bond activation
Polanyi relationship
Oxygen radical
Valence bond state correlation diagram
DFT calculation

ABSTRACT

We present here a systematic theoretical study to explore the underlying mechanisms of the H abstraction reaction from methane. Various abstracting agents have been modeled, using oxygen radicals and a set of high valence metal oxo compounds. Our calculations demonstrate that although H abstraction from CH₃–H by metal oxoes can be satisfactorily fitted into the Polanyi correlation on the basis of oxygen radicals, the mechanisms behind are significantly different. The frontier orbital analyses show that there are three electrons and three active orbitals (3e,3o) involved in H abstraction by oxygen radicals; whereas an additional orbital of π^*_{M-O} is involved in H abstraction by M=O, resulting in a (4e,4o) interaction. In terms of valence bond state correlation diagram, we find that H abstraction by a metal oxo may benefit from the contribution of ionic resonance structures, which could compensate the penalty of opening the M–O π bond. We believe that these findings can help to design more effective catalysts for the activation of light alkanes.

© 2016 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. and Science Press. All rights reserved.

1. Introduction

Hydrogen abstraction (H–Ab), or hydrogen atom transfer (HAT) reaction, is a fundamental process in both chemistry and biochemistry [1–6]. It is generally recognized as the rate determining step in some important heterogeneous catalytic processes such as the oxidative coupling of methane to the C₂ products (ethane and ethylene), the selective oxidation of methane to oxygenates (e.g. methanol, formaldehyde) or the oxidative dehydrogenation of ethane and propane [7–9]. These processes offer promising alternatives for the economical utilization of natural gas.

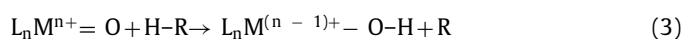
In terms of organic radical chemistry, H–Ab is a typical property of radicals, which has at least one unpaired electron on the abstracting agent, e.g. oxygen radicals.



Nomenclaturally, the term “oxo” denotes a terminal oxygen coordinated to a transition metal, i.e., M=O. Transition-metal oxo

complexes are well known to be active oxidants for hydrocarbons in a broad range from metalloenzyme families to heterogeneous metal oxide catalysts and homogeneous oxidative reagents. For instance, cytochromes P₄₅₀ with an Fe^{IV}=O unit show high activity and selectivity to hydroxylate C–H bonds [10]. Heterogeneous catalysis often employs high valence metal oxoes, e.g. V⁵⁺=O and Mo⁶⁺=O, as the active components [11,12]. Moreover, simple metal oxo compounds, such as MnO₄[−], CrO₂Cl₂ and OsO₄, are applied extensively in the partial oxidation of C–H bonds [13,14]. All these highlight the importance of high valence d⁰ metal oxoes in C–H bond oxidation.

Similar to oxyradicals, the initial abstraction of a hydrogen atom has also been proposed as the key step in the oxidation of the C–H bond.



Although it is common to assume that unpaired spin density at the terminal oxygen is necessary for accepting the H atom, it is not clear how H–Ab really happens on a closed-shell high valence oxidant, such as permanganate MnO₄[−] or CrO₂Cl₂, which has a d⁰ configuration with no unpaired electrons.

A number of mechanistic studies concerning the C–H bond oxidation by MnO₄[−] have been reported. Wiberg and coworkers [15],

* Corresponding author.

** Corresponding author.

E-mail addresses: hlwan@xmu.edu.cn (H. Wan), xxchem@fudan.edu.cn (X. Xu).

as well as Brauman and Pandell [16], have pointed out that the tertiary C–H bond oxidation by MnO_4^- utilized the initial hydrogen atom abstraction. Kinetic experiments by Mayer [13] and Gardner et al. [17] revealed that the rate of H-Ab by ${}^n\text{Bu}_4\text{NMnO}_4$ or CrO_2Cl_2 correlates well with the rate of abstraction by a series of alkoxy radicals. Thus they suggested that the unpaired spin density is not a prerequisite for a species to enter a radical reaction; it is the hydrogen affinity that determines the ability of a species to abstract an H atom.

Experimentally, the strongest evidence that the reactivity of closed-shell MnO_4^- or CrO_2Cl_2 is reminiscent of oxygen radicals is the Polanyi relationship of rates and the activation energies (E_a) correlating with the forming O–H bond strength ($D_e(\text{O–H})$) for a given H–R (see Eqs. (1)–(3)).

$$E_a = \alpha D_e(\text{O–H}) + \beta \quad (4)$$

Previously, we have carried out a systematic density functional theory (DFT) study to explore the H abstraction process from light alkanes using trinuclear or tetranuclear clusters as model catalysts [18–21]. In this contribution, we compare the H-Ab mechanisms by various abstracting agents (oxyradicals ($\text{RO}\cdot$), peroxyradicals ($\text{ROO}\cdot$) and mononuclear high valence metal oxo compounds). We show that although H-Ab from hydrocarbons by metal oxoes can be satisfactorily fitted into the Polanyi correlation on the basis of H-Ab by oxygen radicals, the underlying mechanisms are different. Detailed frontier molecular orbital (FMO) analyses reveal that there are three electrons and three active orbitals ($3e,3o$) involved in H-Ab by $\text{RO}\cdot$; whereas H-Ab by M=O is a ($4e,4o$) process. In the latter case, additional energy is required to open the M–O π bond. In terms of valence bond state correlation diagram (VBSCD), we find that H-Ab by a metal oxo may benefit from the contribution of ionic valence bond resonance structures, such as $[\text{MO}\cdot\text{H}^+\text{R}^-]$ and $[\text{MO}^-\text{H}^+\text{R}]$.

2. Computational details

All calculations were carried out using the Gaussian 09 package [22]. Spin unrestricted DFT method was employed which used Becke's three parameter hybrid functional [23,24] combined with the correlation functional of Lee et al. [25], i.e., UB3LYP. The 6-311+G (d,p) basis set [26] was used to represent all other atoms, while the late transition metal atoms were described using Stuttgart RSC97 ECP basis set plus effective core potentials [27]. Geometries were fully optimized and vibrational frequencies were analytically computed in order to confirm that a local minimum had no imaginary frequency or a transition state (TS) had only one imaginary frequency. Zero point energy (ZPE) corrections were included with no empirical scaling.

3. Results and discussion

Fig. 1 (black squares) shows a plot of the theoretical Polanyi correlation of E_a versus $D_e(\text{O–H})$ for oxyradicals ($\text{RO}\cdot$, $\text{CH}_3\text{O}\cdot$, and $\text{t-BuO}\cdot$) as well as for peroxy radicals ($\text{ROO}\cdot$, $\text{CH}_3\text{OO}\cdot$, and $\text{t-BuOO}\cdot$) abstracting H from methane. We find a good linearity (correlation coefficient $R^2 = 0.997$) with a slope of -0.678 and an interception of 78.12 kcal/mol (dashed line in Fig. 1). Indeed our calculations show that closed-shell metal oxo CrO_2Cl_2 or MnO_4^- (red triangles in Fig. 1) can be fitted satisfactorily into the Polanyi relation drawn by $\text{RO}\cdot$ and $\text{ROO}\cdot$ radicals ($\alpha = -0.672$, $\beta = 77.43$ and $R^2 = 0.994$), in agreement with Mayer's experimental observations.

We have extended the calculations to include other high valence transition metal oxoes with closed-shell electronic structures. The calculated numbers for metal oxoes (blue circles in Fig. 1) scatter around the Polanyi correlation determined by oxygen radicals

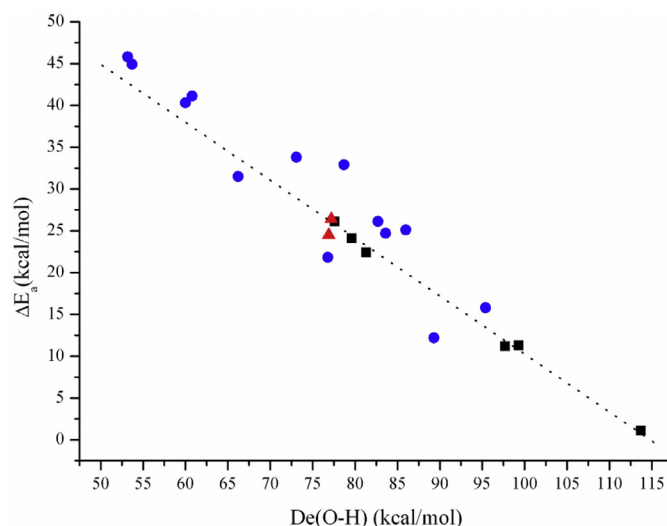


Fig. 1. Polanyi relationship for the activation energy (E_a) versus the forming O–H bond strength ($D_e(\text{O–H})$) for H-abstraction from methane by various abstracting agents. Keys: black squares for $\text{RO}\cdot$, $\text{CH}_3\text{O}\cdot$, and $\text{t-BuO}\cdot$ and $\text{ROO}\cdot$, $\text{CH}_3\text{OO}\cdot$, and $\text{t-BuOO}\cdot$; red triangles for CrO_2Cl_2 or MnO_4^- ; and blue circles for other closed-shell metal oxo compounds VO_2Cl , NbO_2Cl , TaO_2Cl , MoO_2Cl_2 , VOCl_3 , MnO_3Cl , TeO_3Cl , ReO_3Cl , CrO_3 , MoO_3 , WO_3 , and RuO_4 . Dotted line is based on $\text{RO}\cdot$ and $\text{ROO}\cdot$ whose Polanyi relationship is $E_a = -0.678 D_e(\text{O–H}) + 78.12$ with correlation coefficient $R^2 = 0.997$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

($\text{RO}\cdot$, $\text{ROO}\cdot$), reinforcing the idea that a metal oxo is a 'reminiscent' of oxygen radicals [13,17], even though it is not a radical; while at the same time demonstrating that there are intrinsic factors other than 'hydrogen affinity' which contribute to the reaction barrier.

Table 1 lists the H-Ab barriers from methane (E_a) versus the forming O–H bond strengths ($D_e(\text{O–H})$). Also listed are the singlet and triplet excitation energies ($\Delta E_{\text{ST}}(\text{M=O})$), and the key geometric parameters in the TS. Inspection of data in Table 1 indicates that E_a may not only be correlated with hydrogen affinity ($D_e(\text{O–H})$), but also be correlated with such property as the singlet and triplet excitation energies ($\Delta E_{\text{ST}}(\text{M=O})$), which measure the π bond strengths in M=O . A stronger metal oxo π bond would generally lead to a higher H-Ab barrier accompanied with a weaker O–H bond. In view of the metal oxo π bond strength, MnO_4^- is actually one of special cases with an extraordinary weak metal oxo π bond.

To gain deeper insight on the H-Ab process, we perform FMO analyses. Table 2 summarizes the active orbitals involved in H-Ab from CH_4 by $\text{RO}\cdot$ and M=O . For H-Ab from CH_4 by $\text{RO}\cdot$, the key frontier orbitals in the reactants are $(n_{\text{O}})^1$, $(\sigma_{\text{C–H}})^2$, $(\sigma_{\text{C–H}}^*)^0$, while those in the products are $(n_{\text{C}})^1$, $(\sigma_{\text{O–H}})^2$, $(\sigma_{\text{O–H}}^*)^0$. Hence a $\sigma_{\text{C–H}}$ bond is breaking and a $\sigma_{\text{O–H}}$ bond is forming, with the net result that the singly occupied radical orbital changes its location from oxygen of methoxyl (n_{O}) to carbon of methyl (n_{C}). Thus this is a (3 electrons, 3 orbitals) process, denoted as ($3e,3o$). On the other hand, H-Ab by M=O is similar to H-Ab by $\text{RO}\cdot$ in that a pair of $\sigma_{\text{C–H}}$ and $\sigma_{\text{C–H}}^*$ is transformed to a pair of $\sigma_{\text{O–H}}$ and $\sigma_{\text{O–H}}^*$, but differ in that $(n_{\text{O}})^2(\pi_{\text{M–O}}^*)^0$ of M=O are involved, which are transformed to $(n_{\text{M}})^1(n_{\text{C}})^1$ in the products. Thus this is a (4 electrons, 4 orbitals) process, denoted as ($4e,4o$).

Fig. 2 shows the orbital mixing diagram that generates the key frontier orbitals of the TS for H-Ab by $\text{RO}\cdot$. Using the active orbitals in Table 2, we have three resulting orbitals as shown in Eqs. (5)–(7).

$$\Psi_1(\sigma_{\text{O–H}}) = \sigma_{\text{C–H}} + (n_{\text{O}}) + [\sigma_{\text{C–H}}^*] \quad (5)$$

$$\Psi_2(n_{\text{C}}) = n_{\text{O}} - (\sigma_{\text{C–H}}) + (\sigma_{\text{C–H}}^*) \quad (6)$$

$$\Psi_3(\sigma_{\text{O–H}}^*) = \sigma_{\text{C–H}}^* - (n_{\text{O}}) + [\sigma_{\text{C–H}}] \quad (7)$$

Download English Version:

<https://daneshyari.com/en/article/6530421>

Download Persian Version:

<https://daneshyari.com/article/6530421>

[Daneshyari.com](https://daneshyari.com)