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# Trimethyl-phosphite dissociative adsorption on iron by combined *first-principle* calculations and XPS experiments

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*The reaction of trimethyl-phosphite, TMPi, with the clean Fe (110) surface has been investigated by ab initio calculations. The most stable configurations and energies are identified for both molecular and dissociative adsorption. The calculated reaction energies indicate that dissociation is energetically more favored than molecular adsorption and we provide a description of the dissociation path and the associated energy barrier. In-situ XPS analysis of adsorbed TMPi on metallic iron confirmed molecular chemisorption and dissociation at high temperature. These results shed light into the mechanism of phosphorus release from organophosphites at the iron surface, which is important for the functionality of these phosphorus-based additives included in lubricants for automotive applications.*

## I. Introduction

Phosphites compounds are widely used in engine oils, especially for gearbox components as extreme pressure (EP), anti-wear (AW) and friction modifier (FM) additives. Nevertheless, few studies were dedicated to phosphites [1-7] and little it is known on the mechanisms by which these compounds decompose and modify the chemical composition of the metal surface, and consequently reduce friction. Among all types of phosphite additives, trimethyl-phosphite,  $(\text{CH}_3\text{O})_3\text{P}$ , is probably the simplest compound containing alkoxy groups, thus it has been chosen as a model to provide a basis understanding on how these molecules interact with the iron surface.

The reaction of trimethyl-phosphite (TMPi) with the clean Fe (110) has been studied by temperature-programmed reaction spectroscopy (TPRS), X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED) [7]. In this experiment, it is observed that TMPi decomposes into adsorbed phosphorous and gaseous CO and H<sub>2</sub> via methoxy (CH<sub>3</sub>O) intermediate on the clean Fe(110), leaving behind a phosphide film. The phosphorus release from TMPi dissociative adsorption is a thermally activated and self-limiting process. Experiments on other metal surfaces revealed a similar decomposition mechanism [8-9].

The dissociation of TMPi has been also studied under boundary lubrication conditions [10-12] and the formation of iron phosphide has been observed after the tribo-test. A detailed reaction mechanism of TMPi on the iron surface has been proposed [10] and the role of nascent surfaces in promoting tribochemical reactions has been highlighted through *in situ* XPS analysis [12]. Gas Phase

Lubrication (GPL) using an environmentally controlled analytical tribometer (ECAT) is able to simulate the boundary lubrication regime, where the additive molecules interact with the surfaces in contact without any external contamination [13]. This simplified experimental approach opens the way to combined theoretical analysis based on atomistic simulations. Indeed, we have recently coupled first principles calculations and gas phase lubrication experiments to elucidate the effects of the surface termination on the adhesion and friction of nanocrystalline diamond (NCD) coatings [14] and iron interfaces [15].

The use of first principles calculations in tribology has been traditionally very scarce, especially in the field of lubricant additives. However a parameter-free, fully quantum-mechanical approach is very important to provide an accurate description of the surface chemical processes involving additive molecules and understand their functionality. By means of this approach, we have recently showed that elemental phosphorus plays a key role in reducing the adhesion and ideal shear strength between two iron surfaces. This may explain the low friction coefficient observed when the iron phosphide tribofilm is formed [15]. Here we apply first principles calculations based on density functional theory (DFT) to elucidate the mechanism of P release from TMPi decomposition at the iron surface. To our knowledge, no theoretical study of TMPi reaction with iron has been reported so far in the literature, and there are very few investigations on P adsorption on the Fe surface. The previous theoretical works are limited to the study of P diffusion into bulk iron [16] and the adsorption of different elements such as H, C, O atoms and CO, H<sub>2</sub>, O<sub>2</sub>, CH<sub>x</sub> molecules on Fe (110) and/or Fe(100) surfaces [17-22]. In the present study, we describe TMPi adsorption and calculate the reaction path and the energy barriers for dissociation. The numerical results are discussed in relation to *in situ* XPS analysis performed on metallic iron after TMPi thermally-controlled adsorption.

## II. Systems and methods

### 2.1. First-principles calculations

We perform spin-polarized DFT calculations [23]. The electronic wave-functions are expanded on a plane waves basis and the ionic species are described by pseudopotentials. The generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) parametrization [24] is used to describe the exchange correlation functional. The Fe 3s and 3p states are considered in the Fe valence, which thus consists of 16 electrons. On the basis of tests carried out for Fe bulk, a 30 Ry (240 Ry) cutoff is used to truncate the plane-wave expansion of the electronic wave-functions (charge density) and a Monkhorst Pack grid [25] equivalent to (8x8) in the surface unit cell is employed to sample the supercell Brillouin zone. A Gaussian smearing of 0.02 Ry is also used.

We considered the Fe (110) surface since it is the most stable among densely packed iron surfaces [26]. It is known that this surface does not reconstruct, but presents relaxation. The surface is modeled by means of periodic supercells containing an iron slab with (4x4) in-plane size, e.g. 16 atoms per layer, and a vacuum region 20 Å thick. It has been verified that the choice of the (4x4) in-plane size is sufficient to avoid lateral interaction of TMPi with its periodic replicas. The slab thickness has been chosen of three-layers, the bottom one was kept fixed during the relaxation process. This choice represents a good compromise between calculation accuracy and computational efficiency: We studied P adsorption at the Fe (110) surface both by using three-layer and five-layer thick slabs,

the geometries obtained in the two cases are similar and the energy differences preserved. Therefore, three-layer thick slabs are considered in the present study.

To identify the microscopic mechanisms that govern the release of P and its adsorption on the Fe (110) surface by TMPi dissociation, we perform a twofold analysis: first, we study the molecular and dissociative adsorption of TMPi, then we calculate the reaction paths and the energy barriers for molecular dissociation by means of the Nudged elastic band (NEB) method [27]. The NEB method allows to obtain the minimum energy path (MEP), which is the path with the greatest statistical weight, followed by the system in a transition from an initial to a final stable configuration. In the present study, the initial and final states correspond to the adsorbed and dissociated configurations previously identified as the most stable ones. Intermediate images of the system are generated by interpolation between these two configurations. The images are connected by springs thus forming an elastic band in the 3N-dimensional space. The band is driven into the MEP by orthogonal forces, while spring tangential forces keep the images connected to each other. The highest energy image along the path is the transition state that defines the energy barrier. The 'climbing image' scheme is adopted in the present study [28].

## 2.2 Thermally-controlled adsorption experiment and *in-situ* XPS analysis

To perform thermally-controlled adsorption experiment and *in-situ* XPS analysis, a specific apparatus ECAT dedicated to gas phase lubrication is used. It is composed of two UHV chambers : the first chamber is dedicated to adsorption and tribological experiments under controlled gas phase and the second to *in situ* XPS surface analysis. Additional details on the operation of the ECAT device are given elsewhere [10, 13].

Heavy molecular weight compounds like triphenyl-phosphite are used as additives in commercial lubricants due to their solubility in oil provided by the presence of long carbon chains. However, it is difficult to evaporate such heavy molecular weight additives in UHV,  $10^{-9}$  hPa. Smaller molecules as trimethyl-phosphite, having similar chemical function, are used as model compound for adsorption experiment. Liquid TMPi was provided from Aldrich Chemical Co and has a purity >99%. It was further purified by freeze pump thaw cycles before being introduced into the UHV chamber by evaporation at ambient temperature. The adsorption experiments are carried out with a TMPi gas pressure of about 5 hPa during one hour.

In order to reproduce as close as possible the conditions modeled in the molecular simulation study, TMPi is adsorbed on metallic iron. This metallic surface is obtained after argon etching of the flat sample made of AISI 52100 steel (96.9Fe–1.04C–1.45Cr–0.35Mn–0.27Si (wt%)) thanks to a VG EXO5 ion gun till no oxide was detectable by XPS. The steel sample was previously polished with a diamond solution and cleaned with n-heptane and 2-propanol ultrasonic baths in order to obtain a surface roughness of about 20-25 nm in Ra. Before the adsorption experiment, the etched sample was first analyzed by XPS analysis to check its purity in iron, e.g. the absence of any adventitious carbon and oxides layers. The temperature of the steel sample can be controlled and adsorption was conducted at 30, 100, 200 and 300 °C.

After the thermally-controlled adsorption experiments, the excess of TMPi gaseous vapor in the chamber is pumped until an ultra low pressure of  $10^{-9}$  hPa before the sample was transferred in an analytical chamber for *in-situ* XPS analysis. This surface analysis is carried out with a focus (250  $\mu\text{m}$ ) and monochromatic Al X-ray source. The photoelectrons emitted by the surface during analyses are detected by a VG 220i spectrometer.

### III. Results and discussion

#### 3.1 Molecular and dissociative adsorption of TMPi on Fe (110) surface

The optimized geometry obtained for TMPi ( $\text{P}(\text{OCH}_3)_3$ ) molecule in vacuum is shown in Fig. 1, the bond lengths and angles, which are reported in Tab. 1, are in good agreement with experimental data [29]. The Löwdin population analysis reveals that the P atom is positively charged as bonded to three oxygen atoms that are more electronegative. Indeed, the O atoms present an excess of electronic charge  $\delta^{\ominus} = 0.52e$ .

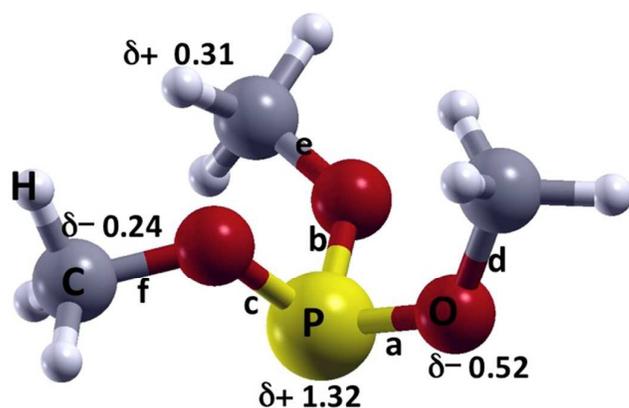


Fig. 1 Optimized structure of TMPi molecule. The Löwdin partial charges on different elements are also reported: the negative (positive) sign indicates an excess (lack) of electrons with respect to the number of valence electrons.

We study the adsorption of the whole TMPi molecule and of its possible fragments, *i.e.*,  $\text{P}(\text{OCH}_3)_n$  with  $n = 1, 2, 3$  and the methoxy group,  $\text{OCH}_3$ , on the Fe (110) surface. Each fragment is considered isolated on the surface, *i. e.*, one fragment per (4x4) cell is considered at this stage of the study. The most stable adsorption site is identified by comparing the adsorption energy of each fragment in different sites. The considered adsorption sites, shown in the inset of Fig 2, are labeled as top (TO), short bridge (SB), threefold (TF) and long bridge (LB). The optimized adsorption geometries are shown in Figure 2, where the partial charges and the bond lengths are also reported.

The optimized configuration of the TMPi molecule adsorbed on the Fe (110) surface is represented in Figure 2a. The most favorable adsorption site is the TO site, where the molecule is attached to the surface with a Fe-P bond 2.13 Å long. During adsorption, the P atom is subject to slight electron depletion in favor of the Fe atom to which it is attached ( $\delta^{\text{Fe}} = -0.46e$ ). The molecule adsorption

energy,  $E_a$ , in this configuration is calculated as the difference between the energy of the adsorbate system and the sum of the energies of the molecule in vacuum and the clean surface. The calculated value,  $E_a = -1.99$  eV, indicates chemisorption of TMPi molecule on the surface. In Figure 2b, we report the optimized configuration of the  $P(OCH_3)_2$  fragment, obtained after removing one of the methoxy groups from the TMPi molecule. The most favorable adsorption site is the SB site where the P atom is bonded to two Fe atoms. Because of the removal of the P-O bond, the P atom is slightly less positively charged than in the adsorbed TMPi molecule ( $\delta^P = +1.32e$  instead of  $\delta^P = +1.43e$ ).

In Figure 2c, it is displayed the optimized configuration of the  $POCH_3$  fragment, obtained by removing an additional methoxy group. The most favorable adsorption site is the LB site where the P atom is bonded to four Fe atoms with two non equivalent P-Fe bonds of 2.17 Å and 2.38 Å lengths. Because of the removal of two P-O bonds from TMPi molecule, the partial charge of P is further decreased ( $\delta^P = +1.02e$ ).

The stable adsorption site for a methoxy group is a TF site where three O-Fe bonds are established (Fig. 2d). Finally, the most stable adsorption configuration obtained for the P atom is the LB site, where the P atom is bonded to four Fe atoms with two non equivalent P-Fe bonds of 2.19 Å and 2.44 Å lengths, respectively. The partial charge is reduced to  $\delta^P = +0.48e$ .

Figure 3 shows the energy gain in adsorption with respect to the energy of an isolated gaseous TMPi molecule. The negative sign of energy indicates that the adsorbed configurations are more stable than the gaseous one and dissociation is highly exothermic. The energy gain increases with the number of broken P-O bonds. In particular, the situation of an isolated P atom and three methoxy groups is the most favorable adsorption configuration. Phosphide formation from TMPi dissociation on Fe (110) surface is therefore highly energetically favorable.

Table 1: Calculated geometrical parameters (see Fig. 1) for the TMPi molecule. Data from experiments [29] are reported in brackets for comparison.

Bond length (Å)		Valence Angles		Dihedral Angles	
P-O (a)	1.632 (1.609)	OPO (ab)	98.27 (98.2)	COPO (dab)	47 (45)
P-O (b)	1.655 (1.632)	OPO (bc)	96.24 (96.1)	COPO (dac)	51 (54)
P-O (c)	1.673 (1.651)	OPO (ac)	104.01 (103.8)	COPO (ebc)	76 (84)
O-C (d)	1.451 (1.431)	POC (ad)	122.95 (121.6)	COPO (eba)	179 (171)
O-C (e)	1.441 (1.421)	POC (be)	117.48 (116.9)	COPO (fca)	90 (93)
O-C (f)	1.442 (1.422)	POC (cf)	116.6 (116.2)	COPO (fcb)	169 (167)

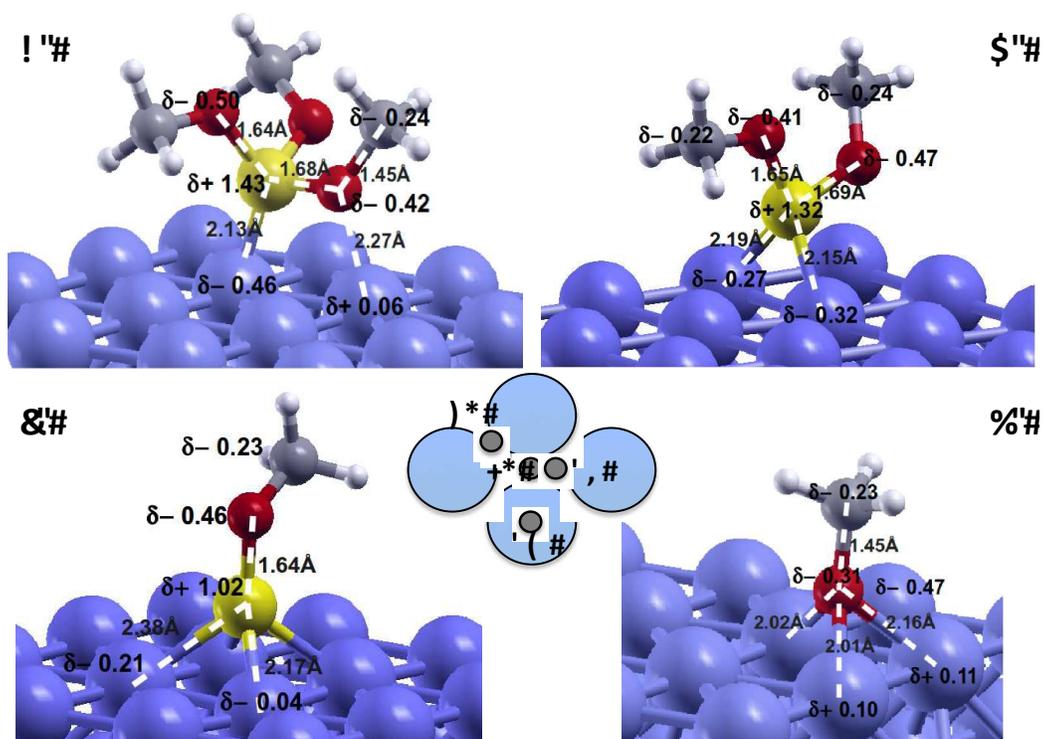


Figure 2 : Optimized adsorption geometries for TMPi molecule (a), P(OCH<sub>3</sub>)<sub>2</sub>,1 fragments (b, c), methoxy group (d) on Fe (1 1 0). The inset shows the symmetry sites within the Fe (110) unit cell.

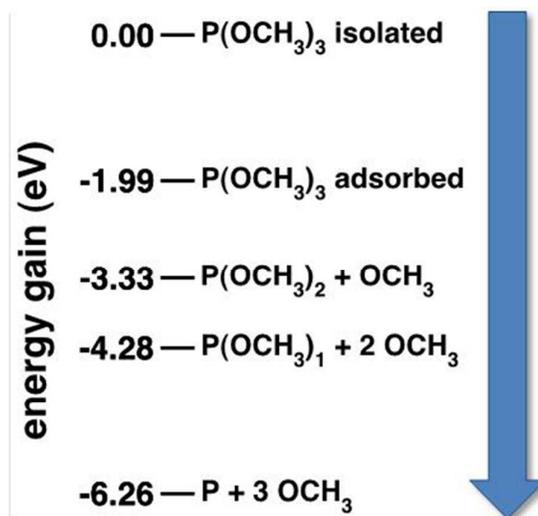


Figure 3 : Differences between energy of an isolated gaseous TMPi molecule taken as reference and the energy of adsorbed configurations with an increasing number of detached fragments up to full dissociation into elemental P and three isolated methoxy groups. The energy of the adsorbed fragments is obtained by considering one fragment per (4x4) cell, i.e., without interaction with any other adsorbates.

### 3.2 Reaction paths and energy barriers for TMPi dissociation

Having identified the adsorption site for each isolated fragment, the most favorable arrangement of co-adsorbed fragments on the surface is then considered in order to identify the final state of each reaction of methoxy detachment. In particular, all the possible arrangements for a methoxy in the neighborhood of each fragment  $P(OCH_3)_n$ , with  $n=1$  or  $2$ , have been modeled by using the same  $4 \times 4$  cell adopted for the study of isolated fragments and the most energetically favored configuration has been selected. The analysis of the adsorption energies associated to the considered configurations reveals that the adsorption of methoxy group is never energetically favored when it involves Fe atoms already involved in P-Fe bonds, indicating that open Fe sites are necessary for methoxy detachment. A schematic representation of the identified configurations for the products of the three subsequent reactions is presented in the left panel of Figure 4. The first reaction (in red) consists in the detachment of a methoxy group from the TMPi molecule, in the second reaction (in blue) a methoxy detaches from the  $P(OCH_3)_2$  fragment, the third reaction (in green) is the splitting of the  $P(OCH_3)$  fragment into a P atom and a methoxy. It is interesting to see that the fully dissociated configuration, which consists in one adsorbed P atom plus three methoxy groups, occupies a  $(5 \times 3)$  surface area. Therefore, in order to have this fragmentation of TMPi, a large number of free iron sites should be available. The right panel of Figure 4 shows the optimized structures of the initial and final state of each reaction.

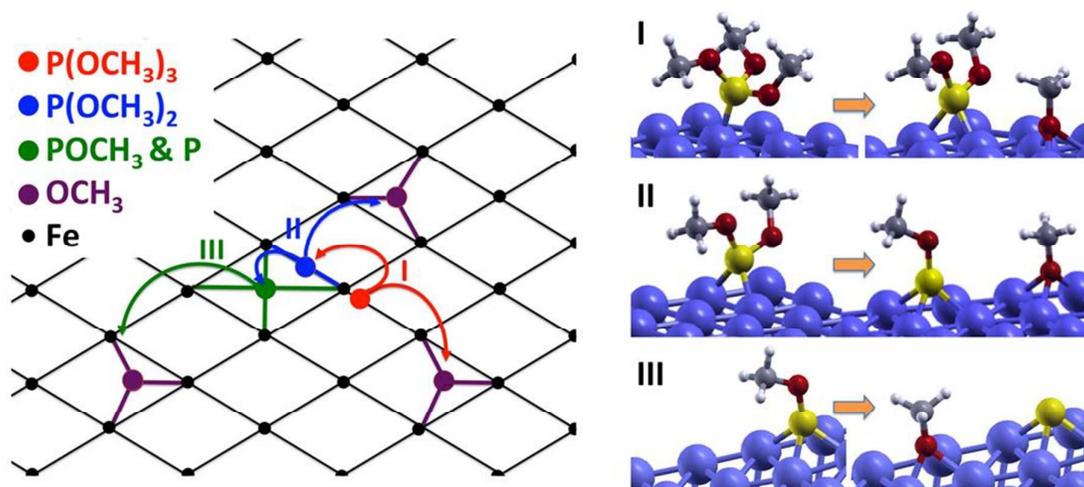


Figure 4: Schematic representation of TMPi dissociation into atomic phosphorus and adsorbed methoxy groups on the Fe(110) surface (left). Initial and final states for each methoxy detachment process (right).

The corresponding reaction energies denoted  $E_R$  and activation barriers denoted  $E_A$  are listed in Table 2.  $E_R$  is calculated as the energy difference between the final state and the initial state of the reaction. All the considered reactions are exothermic as indicated by the negative values of  $E_R$  and the highest energy gain is obtained for methoxy detachment from the  $P(OCH_3)_2$  fragment, suggesting a lower stability of this reactant.

Table 2: Reaction energies,  $E_R$ , and the activation energies,  $E_A$ , for the three subsequent processes of methoxy detachment described in Fig. 4.

Reaction	Initial state	Final state	$E_R$ (eV)	$E_A$ (eV)
I	$P(OCH_3)_3$	$P(OCH_3)_2 + OCH_3$	- 0.73	0.75
II	$P(OCH_3)_2$	$POCH_3 + OCH_3$	- 1.20	0.23
III	$P(OCH_3)$	$P + OCH_3$	- 0.78	0.85

The reaction energy for the first methoxy detachment, e.g.  $E_R = -0.73$  eV, can be compared with that obtained for isolated fragments, e.g.  $E_R = -1.34$  eV. It appears evident that separated fragments are more stable than adjacent fragments. This is a further evidence that TMPi dissociative adsorption is favored in the presence of open Fe sites, in agreement with the key role played by the nascent metallic surfaces on the tribochemistry of phosphites evidenced by the experiments [12].

Once the initial and final states of each reaction have been identified, the NEB algorithm is adopted to calculate the minimum energy path followed by the system in its transition between the two states. The highest energy configuration assumed by the system along the path corresponds to the transition state that defines the activation energy ( $E_A$ ) for the reaction. The activation energy,  $E_A$ , for the detachment of the first methoxy is higher than that for the second one because the reaction energy associated to the first reaction is lower than the reaction energy associated to the second reaction. The dissociation of the third methoxy from the  $POCH_3$  fragment requires almost the same energy as the first methoxy dissociation. Therefore, if thermal energy is enough to activate the detachment of the first methoxy, the subsequent methoxy detachments may be activated as well.

### 3.3 *In situ* XPS analysis after TMPi thermally-controlled adsorption

The above described first principles calculations revealed that the thermally activated molecular dissociation leads to the phosphorus release at the iron surface, i.e., the formation of iron phosphide. It is interesting to combine the theoretical study with experimental analyses. The formation of iron phosphide from TMPi adsorption on metallic iron at different temperatures has been investigated thanks to *in situ* surface analyses. Figure 5 shows the  $P_{2p}$  XPS spectra of phosphorous obtained *in situ* after adsorption of TMPi on an etched steel surface at various temperatures. The chemisorption of TMPi molecules is evidenced by the appearance of the  $P_{2p}$  XPS peak at 133.2 eV at 100 °C. The characteristic peak of iron phosphide appears clearly at temperature of 300 °C with a distinct characteristic binding energy of 130 eV. These results strongly suggest that the formation of iron phosphide is thermally-activated. In fact, temperatures above 200 °C increase the formation of phosphide to a large extent, providing sufficient energy to dissociate the TMPi molecule. Although iron phosphide formation is evidenced, undissociated TMPi molecules are also observed on the surface as shown by the characteristic binding energy at 133.5 eV. It is difficult to differentiate the phosphide chemical state from the phosphate one that is also probable at this temperature that can explain the small energy shift noticeable in this contribution at higher temperature (133.5 eV instead of 133.2 eV). Of course metallic iron surface produced by the argon etching of an oxidized steel

surface is certainly different from a single crystal of iron. Furthermore, previous studies showed that the nascent metallic iron surface created by friction in a contact under severe sliding conditions is highly reactive in comparison with an etched steel surface [12]. Indeed adsorption experiments carried out in vacuum on nascent metallic iron surfaces created by friction have shown to promote the decomposition of EP additives, like polysulfides compounds, without any thermal activation, contrary to etched metallic iron surfaces. Therefore, the activation energy at the origin of the TMPi decomposition on an iron surface appears to be induced either by thermally or mechanically way.

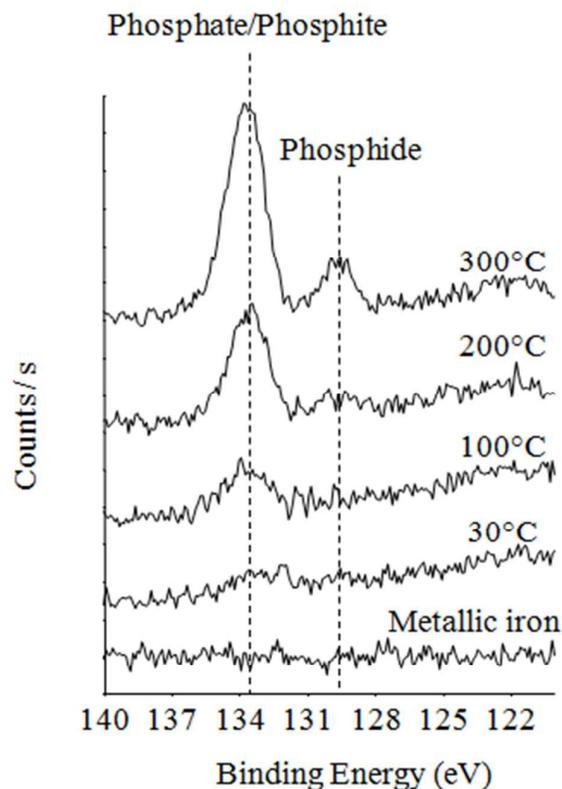


Figure 5: *in situ* X-ray photoelectron spectroscopy P2p lines recorded after TMPi thermally-controlled adsorption on an etched steel, e.g. metallic iron [10]

#### IV. Conclusions

We applied spin-polarized density functional theory calculations to shed light into the functionality of phosphite additives. Since the boundary lubrication of steel surfaces has been shown to be connected to the formation of iron phosphide,[12] we studied the mechanisms of phosphorus release at the iron surface through the dissociative adsorption of the TMPi molecule, which is a model molecule for phosphite chemistry.

We first considered the molecular and dissociative adsorptions of TMPi at the Fe(110) surface and found that the  $\text{P}(\text{OCH}_3)_3$  molecule binds to the surface forming one P-Fe bond. Via methoxy detachment, the number of P-Fe bonds increases until the P atom is adsorbed in a LB site where it is bonded to four Fe atoms. The energy of the dissociated adsorption configurations decreases with the number of detached methoxy, and the most stable adsorption configuration is obtained when all the methoxy groups got detached and atomic P is released at the surface. The passivation of the Fe surface with phosphorus through TMPi dissociation is thus an energetically favorable process.

Then, the NEB method has been applied to identify the reaction paths and the energy barriers for the processes of TMPi dissociation through subsequent methoxy detachments. The result of this analysis suggests that the dissociation of the second methoxy group occurs almost instantaneously once the first PO bond is broken. An activation energy of 0.75 eV is predicted as necessary to start the TMPi dissociation process.

In a second step, thermally-controlled adsorption of TMPi molecule on a metallic iron surface followed by *in situ* XPS analysis was performed in order to confirm the dissociative decomposition. The iron surface has been obtained by ion etching of a steel surface with removal of carbon contamination and oxides layers. The *in situ* XPS analysis confirmed molecular chemisorption and that the formation of iron phosphide is thermally activated at high temperatures, above 300 °C. However, we also observed adsorption of intact TMPi molecules at such high temperatures, although the formation of phosphate cannot be excluded. The TMPi dissociation on the iron surface in static conditions is a thermally activated process. The analysis of the effects of tribological conditions (load and shear) on the reaction kinetics of TMPi at the Fe(110) surface is the subject of a forthcoming publication.

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