Supplementary Information: Oxidative Decomposition of Dimethyl Mehylphosphonate on

rutile TiO₂(110): the role of oxygen vacancies

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Surface Thickness Convergence test

In order to see the impact of the size of the surface model on the calculated reactivity of DMMP with the pristine surface and the defective surface with vacancies, tests with a larger surface unit cell (3x6 vs 2x4) and a larger number of layers (6 O-Ti-O trilayers vs 4) were conducted (Fig. S1). We found that the 3x6 surface model yields the same adsorption energy of DMMP on the pristine TiO₂(110) surface compared to the smaller 2x4 surface model. Similarly, increasing the number of O-Ti-O trilayers for the 2x4 unit cell from 4 to 6 provides no effect on DMMP adsorption energy for the pristine surface, and only a very small difference for the defective surface (0.03 eV) (Table S1). We further calculated a decomposition step (P-O bond cleavage) on the thicker (6 trilayers) model of the defective surface. The energy of the TS is only modified by 0.05 eV, and the energy of the first decomposition intermediate by 0.02 eV (Table S2). Thus, we conclude that the 4 trilayer model can capture the reactivity (barrier and relative energy) of DMMP very well compared to the thicker 6 trilayer model. As a result, we performed all further calculations using the 2x4 unit cell with 4 trilayers.



Figure S1 (i) Larger surface unit cell model (3x6). (ii) thicker model (6 O-Ti-O trilayer).

Table S1 Convergence of the DMMP adsorption energy with the number of layersin the 2x4 unit cell model for the pristine surface and the case with one O vacancy(defective). Models with 4 and 6 O-Ti-O trilayers are compared.

Surface	Adsorption Energy (eV)				
	Thin Model	Thick Model			
	4 trilayers	6 trilayers			
Pristine	-2.35	-2.35			
Defective	-2.29	-2.32			

Table S2 Convergence of transition state energy/barrier and intermediate
energy/energy difference for DMMP decomposition initiated via P-O_{II} bond
cleavage on r-TiO2(110) with one O vacancy. Models with 4 and 6 O-Ti-O trilayers
are compared. Notations refer to Figure 10 in the main text. All energies are given
in eV.

Model	steps	Molecular Adsorption	TS1gr	S2gr
4 trilayers	Е	-2.29	-0.88	-2.25
	barrier/dE	-	1.41	0.04
6 trilayer	Е	-2.32	-0.83	-2.23
	barrier/dE	-	1.49	0.08



Figure S2: Temperature-programmed desorption of 2 ML H₂O on the reduced TiO₂(110) surface with a heating rate of 1 K/s. Water is molecularly desorbing from bridge-bonding oxygen and Ti_{5c} sites. A bridge-bonding oxygen vacancy feature is discernable at 430 K, indicating bridge-bonding oxygen vacancy concentration of 1.5% $\pm 0.5\%$. In further analogy with literature, the feature at 275 K corresponds to desorption of water from Ti_{5c} sites, while the feature at 180 K stems from desorption from bridging oxygen atoms of the surface. A very light blue color shade is observed looking onto the titania crystal.¹



Figure S3: Temperature programmed desorption/reaction of DMMP on reduced $TiO_2(110)$ shows that DMMP desorbs intact from the titania surface between 200 K and 500 K, while only minor amounts of methanol and formaldehyde are detected. No other reaction products were detected. The traces are not corrected for fragmentation and as evidenced by the ratio of the mass 29 to 30, formaldehyde desorption is indeed observed in addition to methanol desorption. For formaldehyde, a 30/29 ratio of about 0.6 is expected, while the methanol fragmentation pattern shows normalized ratios of (0.47, 0.1 and 1) for the mass 29, 30 and 31.



Figure S4: The Auger electron spectrum of the $TiO_2(110)$ single crystal after a temperature-programmed desorption experiment shows that phosphorous and carbon are present on the surface indicating a residual P-containing species on the surface that is assigned to a DMMP reaction product in agreement with other studies on oxides. The elements are identified by their characteristic Auger peak energies: P at 110 eV, C at 272 eV, Ti at 387 and 418 eV and O at 503 eV

Influence of DMMP coverage on DMMP adsorption/desorption energy

To demonstrate the influence of high coverage on DMMP adsorption energy, we simulated the adsorption of DMMP at different coverages (2-4 molecule) on 2x4 and 2x3 TiO_2 surfaces.

Fig S5 shows different possible DMMP packing at 3/8ML (3 DMMP per 8 Ti sites) coverage on the 2x4 surface. The most stable packing structure is structure A with all three DMMP interacting with two surface Ti (η_2) with average adsorption energy of -2.03 eV. We immediately see the destabilizing effect of having 2 DMMP on one Ti rows back to back as the adsorption energy decreases from -2.35 eV (in the case of 1/8 ML coverage) to -2.03 eV. The least stable structure is structure D with all three DMMP interacting with only one Ti site, hence η_1 , with an average adsorption energy of -1.74 eV per DMMP molecule. We then estimated the differential adsorption energy of the DMMP molecule, considering the weakest bound molecule, within selected packing geometries (A, B, and D).

$$E_{ads,diff} = E_{surf+x*DMMP} - E_{surf+(x-1)DMMP} - E_{DMMP(a)}$$

Figure S6 showcases the optimized geometries of packing configuration A, B and D upon the removal of 1 DMMP. We found that DMMP binds the weakest when it is on the same Ti row with another DMMP η_2 and is interacting with only 1 Ti (Fig S6, B minus 1). The binding energy of this DMMP is only -1.39 eV.



Figure S5 Various DMMP packing configuration at 3/8ML coverage on 2x4 TiO₂(110). DMMP which adsorb via two O-Ti bonds are denoted as DMMP η_2 and DMMP which adsorb via only one O-Ti bond are denoted as DMMP η_1 . Stars indicate the location of DMMP η_1 . The calculated adsorption energy averaged per DMMP molecule ($E_{ads/DMMP}$) is indicated in eV.



Figure S6 Optimized structure from fig S4 after the removal of 1 DMMP (1/4ML). The differential adsorption energy ($E_{ads,diff}$ in eV) corresponds to that of the removed molecule in each case.

This effect is more prominent as we add another DMMP to the system (1/2 ML coverage).

Figure S7 shows a 4 DMMP adsorption packing geometry with 3 DMMP η_2 and 1 DMMP

 η_1 . Upon removal of the DMMP η_1 , we found that the differential adsorption energy is only 1.21 eV.



Figure S7 (Left) Optimized adsorption structure with four DMMP molecules (3 η_2 and 1 η_1) on 2x4 TiO₂(110) (coverage ½ ML) with the average adsorption energy. (Right) optimized structure after removal of the η 1 DMMP molecule and calculated differential absorption energy. All energies in eV.

Figure S8 shows 2/3ML DMMP adsorption on a 2x3 TiO₂(110) surface (3 Ti sites per row with 2 DMMP adsorbed on each row) and the corresponding differential adsorption energy for the least stable DMMP molecule. Two DMMP adsorb on each Ti row. The first DMMP is adsorbed as η_2 , whereas the second one is adsorbed as η_1 . The average adsorption energy of DMMP decreases to -1.36 eV at 2/3ML coverage. Due to the repulsive interaction between DMMP molecules, the n_1 molecules is further away from the surface, developing non-covalent interactions. The differential adsorption energy is - 0.70 eV.



Figure S8 (A) 2x3 TiO₂(110) surface with 6 available 5 coordinated Ti sites. (B) 2/3ML DMMP adsorption on 2x3 TiO₂(110) surface. On each Ti row, 2 DMMP adsorbs (1 η_2 , 1 η_1). The average adsorption energy Eads/DMMP is given (eV) (C) Same structure as B with 1 η_1 DMMP removed (1/2ML). The differential adsorption energy E_{ads,diff} of the removed DMMP is -0.70 eV.

Thermodynamic analysis of DMMP decomposition via P-C bond cleavage on pristine surface

We have also investigated the possibility that DMMP would adsorb dissociatively via the breaking of the P-CH₃ bond, yielding an adsorbed methyl on a surface bridging oxygen. Our thermodynamic analysis on possible intermediates showed that the P-CH₃ bond cleavage from the most stable adsorption geometry position yields an intermediate which is 1.14 eV less stable (Figure S9b). This geometry can be stabilized further by having P interacting with an O_{2c} (Fig S9c), but the structure is still less stable than chemisorbed DMMP by 0.39 eV. We then cleaved an additional P-OCH₃ bond (fig S9d). Our calculations showed that the cleavage of an additional P-OCH₃ bond yields an intermediate that has higher energy by about 1.49 eV from the initial molecular adsorption. There seems to be no tendency for P to interact with surface basal O_{3c} , which causes P to be undercoordinated. Hence further decomposition proceeding via this intermediate is very much unlikely. Therefore, decomposition structures of DMMP initiated by P-CH₃ bond cleavage are not thermodynamically favored and we did not explore the pathways further.



Figure S9 Dissociative DMMP adsorption on the pristine TiO_2 surface via cleavage of the P-C bond, leaving a methyl group on surface O2c, is not thermodynamically favored: (a) Initial DMMP adsorption geometry, (b) P-C bond cleavage, (c) stabilization by P-O bond formation (process remains endothermic) (d) intermediate upon additional cleavage of a P-O bond. This structure is less stable since P is undercoordinated.



Figure S10 Transition State for the 1st P-OCH₃ bond cleavage of DMMP on pristine TiO₂ (110). Bond distances are: P-O_{2c} =1.69 Å, P-O₁ =1.60 Å, P-O₁₁ =2.02 Å, Ti-O₁₁=2.16 Å and Ti-O₁ =1.89 Å.

Table S3: Calculated energies and kinetic rate constants for DMMP
decomposition on the pristine r-TiO ₂ (110) surface via P-OCH ₃ cleavage. Labels
refer to Fig. 6

Structure	S1	TS 1	S2	TS 2	S3	TS 3	S4
Relative Energy	-2.35	-0.17	-2.72	-1.28	-1.77	-0.51	-2.48
[eV, (kJ/mol)]	(-227)	(-16)	(-262)	(-123)	(-171)	(-49)	(-239)
Rate constant at		2.35E-24		5.31E-12		9.87E-25	
300K [1/s]							
Rate constant at		7.66E-06		1.15E+01		4.97E-06	
600K [1/s]							

Table S4 Calculated energies and kinetic rate constants for DMMP decompositionon the pristine r-TiO2(110) surface via O_{II} - C_{II} cleavage (path a/green)

Structure	S1	TS 1a	S2a	TS 2a	S3a
Relative Energy	-2.35	-0.18	-3.28	-1.51	-2.97
[eV, (kJ/mol)]	(-226)	(-17)	(-316)	(-145)	(-286)
Rate constant at		3.35E-24		1.48E-17	
300K [1/s]					
Rate constant at		5.58E-06		1.92E-02	
600K [1/s]					

Table S5 Calculated energies and kinetic rate constants for DMMP decompositionon the pristine r-TiO2(110) surface via O_{III} -CIII cleavage (path b/red)

Structure	S1	TS 1b	S2b	TS 2b	S3b
Relative Energy	-2.35	-1.05	-2.64	-0.91	-2.65
[eV, (kJ/mol)]	(-226)	(-101)	(-254)	(-88)	(-255)
Rate constant at		2.36E-09		7.90E-17	
300K [1/s]					
Rate constant at		2.43E+02		2.31E+00	
600K [1/s]					



Figure S11 The release of methanol and formaldehyde from two O_SCH_3 is not possible even at high temperatures due to the step being highly endothermic. This uphill step is attributed to the creation of two oxygen vacancy sites upon the creation of gas products.



Figure S12 Thermodynamic analysis of the release of gaseous methanol and formaldehyde from O_SCH_3 an O_DCH_3 groups. The release of methanol and formaldehyde is thermodynamically favorable only above 700 K.

Thermodynamic analysis of DMMP decomposition via P-C bond cleavage on defective surface

Finally, we also investigated the P-CH₃ bond cleavage-initiated pathway on the surface with O vacancy. The thermodynamic analysis showed that the oxygen vacancy does not help to stabilize the intermediate after P-CH₃ bond cleavage (fig. S15). This intermediate is 0.91 eV less stable than the adsorbed state. Again, there seems to be no tendency for P to interact with surface basal O_{3c} , which causes P to be undercoordinated. Even with an additional P-OCH₃ bond cleaved and with a P-O3c interaction, the stability does not seem to improve (adsorption energy 1.08 eV higher with respect to most stable molecularly adsorbed DMMP). We conclude that the P-CH₃ bond cleavage is unlikely on defective r-TiO₂.



Figure S13 Intermediate resulting from P-C bond cleavage on defective surface. P=O occupies the vacancy. P-C bond cleavage leaves the phosphor center undercoordinated.



Figure S14 (Left) Transition state of P-O cleavage for green isomer, (right) transition state for blue isomer. Bond distances are: P--- $O_{2c} = 1.65$ Å, P- $O_{II} = 2.10$ Å, Ti- $O_{II} = 2.06$ Å and Ti- $O_{I} = 1.89$ Å.



Figure S15 (left) green pathway intermediate (S3gr) upon second P-O bond cleavage. (right) S3bl isomer in blue pathway. Labels refer to Fig. 10.

Table S6 Calculated energies and kinetic rate constants for DMMP decomposition on the defective r-TiO₂(110) surface via O-P bond cleavage (2 -OCH₃ transferred to the same Ti_{5c} row. Labels refer to Fig. 10.

Structure	Molecular	TS 1 blue	S2 blue	TS 2 blue	S3 blue
	adsorption				
Relative Energy	-2.29	-0.82	-2.37	-1.16	-1.84
[eV, (kJ/mol)]	(-220)	(-79)	(-228)	(-111)	(-177)
Rate constant at		1.70E-12		2.90E-08	
300K [1/s]					
Rate constant at		6.51E+00		8.52E+02	
600K [1/s]					

Table S7 Calculated energies and kinetic rate constants for DMMP decomposition on the defective r-TiO₂(110) surface via O-P bond cleavage (2 -OCH₃ transferred to different Ti_{5c} rows). Labels refer to Fig. 10.

Structure	Molecular	TS 1 green	S2 green	TS 2 green	S3 green
	Adsorption				
Relative Energy	-2.29	-0.88	-2.25	-0.82	-2.05
[eV, (kJ/mol)]	(-220)	(-84)	(-217)	(-79)	(-198)
Rate constant at		1.43E-11		9.24E-12	
300K [1/s]					
Rate constant at		1.89E+01		1.52E+01	
600K [1/s]					



Figure S16 Intermediates from P-O bond cleavage after O-C bond cleavage on defective surface. (Left) PO_{III} bond dissociation from S2a. (Right) PO_{II} bond dissociation from S2b. In both cases, the P-OCH₃ bond cleavage is thermodynamically unfavorable. From S2a (after O_{II} - C_{II} bond cleavage), cleaving P- O_{III} (left) yields an intermediate that is 1.6 eV less stable than S2b. From intermediate S2b (after O_{III} - C_{III} bond cleavage), cleaving P- O_{III} (left) yields an intermediate that is 0.29 eV less stable than S2a. The barrier for this step is 2.22 eV. Since these intermediates are not thermodynamically stable, we did not calculate the barriers for these steps.

Table S8 Calculated energies and kinetic rate constants for DMMP decomposition on the defective r-TiO₂(110) surface via O-C bond cleavage (initiated via O_{II} - C_{II} bond cleavage, black pathway). Labels refers to Fig. 12.

Structure	S1	TS 1a	S 2a	TS 2a	S3
Relative Energy	-2.29	-0.87	-3.51	-1.73	-3.66
[eV, (kJ/mol)]	(-220)	(-83)	(-338)	(-167)	(-353)
Rate constant at		1.14E-11		1.35E-17	
300K [1/s]					
Rate constant at		1.69E+01		1.83E-02	
600K [1/s]					

Table S9 Calculated energies and kinetic rate constants for DMMP decompositionon the defective r-TiO₂(110) surface via O-C bond cleavage (initiated via Ol_{II}-C_{III}bond cleavage, blue pathway). Labels refers to Fig. 12.

Structure	S1	TS 1b	S2b	TS 2b	S3
Relative Energy	-2.29	-1.04	-3.20	-1.24	-3.66
[eV, (kJ/mol)]	(-220)	(-100)	(-318)	(-119)	(-353)
Rate constant at		7.39E-09		1.06E-20	
300K [1/s]					
Rate constant at		4.30E+02		5.14E-04	
600K [1/s]					



Figure S17 Reaction pathway for methoxy disproportionation reaction between 2 O_DCH_3 resulting from DMMP decomposition on the defective TiO₂(110) surface with one O vacancy, forming gas phase formaldehyde and methanol.



Figure S18 Thermodynamic analysis of the release of methanol and formaldehyde as gas products from two O_DCH_3 adsorbed on neighboring Ti_{5c} sites on the defective $TiO_2(110)$ surface with one O vacancy. The release of gas products is possible at 500K, agreeing quite well with the TPD result.

References

 Li, Z.; Scott Smith, R.; D. Kay, B.; Dohnálek, Z. Determination of Absolute Coverages for Small Aliphatic Alcohols on TiO2(110). *J. Phys. Chem. C* 2011, *115* (45), 22534–22539. https://doi.org/10.1021/jp208228f.