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Mo(VI) dithiocarbamate with no pre-existing Mo-S-Mo core as an active lubricant additive

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Abstract (100 words)

MoDTC molecular additives reduce friction in boundary lubricated steel-steel contacts through formation of MoS₂ sheets. The chemical pathway from MoDTC to MoS₂ is investigated for optimizing MoS₂ formation. Our experiments show that a MoDTC molecule containing sulfur only in its thiocarbamate ligands forms MoS₂ sheets during friction, demonstrating that the presence of peripheral thiocarbamate ligands can be sufficient to provide the required sulfur source. This molecule is not only competitive with MoDTC containing sulfur in the core of the molecule but also more efficient at high contact pressures. Mechanistic investigations on the chemical transformation of MoDTC to MoS₂ reveal that thermal activation alone is not sufficient thus suggesting that pressure and/or shear are necessary for MoS₂ generation in this system.

22 1 Introduction

23 Energy saving has become a critical societal stake that stimulates drastic technological
24 changes in the transportation and energy sectors [1]. In the field of tribology, reducing friction
25 losses over extended durations is a key challenge. Several solutions have been developed, in
26 particular Transition Metal Dichalcogenides (TMDs), like MoS₂, have been known as efficient
27 solid lubricants for more than fifty years [2–4]. MoS₂ is used in tribological contacts as coating
28 but it can also be formed *in situ* through tribochemical reactions from molecular lubricant
29 additives [5–10]. Among molecular lubricant additives effective under boundary lubrication for
30 steel-steel contacts, the “all-in-one” types of molecules, that is the ones which provide the
31 molybdenum and the sulfur atoms within a single molecule, are commonly used. Molybdenum
32 DiThioCarbamates (MoDTC) are representative examples of these types of molecules (Figure
33 1).

34 Even if the mechanism of action of MoDTC has been widely studied, [7–9,11–15] the
35 understanding of the chemical pathway allowing the generation of MoS₂ sheets from the
36 MoDTC molecule is still attracting substantial interest because of the potential insight in novel
37 molecule design. Concerning the elementary steps of MoDTC decomposition, several
38 approaches are found in literature. Initially, only the sulfur atoms present in the core of dimeric
39 molecules, that is as bridging atoms across molybdenum two centers as in (R₂NCS₂) [Mo(O)(μ-
40 S)₂Mo(O)] (S₂CNR₂) were considered able to contribute to the formation of MoS₂ sheets [8,13].
41 Later on, it was also proposed that the sulfur atoms from the thiocarbamate ligand, (R₂NCS₂)
42 [Mo(O)(μ-S)₂Mo(O)] (S₂CNR₂) could be involved in the generation of MoS₂ sheets, either by
43 prior linkage isomerism, as in (R₂NCOS) [Mo(S)(μ-S)₂Mo(O)] (S₂CNR₂) [11,12] or by cleavage
44 of carbon-sulfur bonds of the ligand, schematized as (R₂NC) [(S₂Mo(O)(μ-S)₂Mo(O)S₂)] (CNR₂)
45 [7,16]. All these approaches suggest that core [Mo_nS_m] fragments called MoS_x intermediate
46 products [7] are needed at some stage in generating well-organized MoS₂ lamellar sheets
47 during friction.

48 In this work, the performance of a molecular precursor MoDTC **1**, containing only one
49 molybdenum atom and no pre-formed core [Mo_nS_m], is compared with that of a well-established
50 “all-in-one” MoDTC **2** molecule, which contains preformed [Mo(μ-S)₂Mo] core classically used
51 in engine lubrication. We show that the tribological properties of molecule MoDTC **1** are
52 competitive with those of well-established MoDTC **2** and show better performances at high
53 contact pressures.

54

55 2 Experimental methods

56 2.1 Lubricant additive synthesis

57 Two different MoDTC molecules were synthesized (Figure 1). MoDTC 1 has no pre-existing
58 core $[\text{Mo}-(\mu\text{-S})\text{-Mo}]$, nor terminal sulfur atoms ($\text{Mo}=\text{S}$) and is in oxidation state $\text{Mo}(+\text{VI})$.
59 MoDTC 2 contains the $[\text{Mo}(\mu\text{-S})_2\text{Mo}]$ sulphided core and is in oxidation state $\text{Mo}(+\text{V})$. Molecule
60 MoDTC 2 is used here as a representative example of the classical molecules used in engine
61 lubrication.

62 The lubricant composition is prepared in a beaker on a stirrer hot plate by adding a weight
63 percentage of 0.3 w% of each molecule of MoDTC in the synthetic base oil PAO4 at a
64 temperature of 50°C , whilst stirring for 30 min. Solutions were transparent after this mixing
65 procedure showing the good solubility of the additives in base oil.

66 Note that the atomic concentration of Mo in lubricants containing MoDTC 1 or MoDTC 2 is in
67 the same range since the contribution of Mo to the mass of MoDTC1 (23 wt%) is extremely
68 close to that in MoDTC2 (21 wt%). Thus the difference in molybdenum atomic content in both
69 lubricants is not significant enough to explain potential differences in tribological behaviors.
70 The content of sulfur atoms is a bit larger in MoDTC 1 than in MoDTC 2. As both molecules
71 don't have the same atomic S/Mo ratio (4 for MoDTC 1 and 3 for MoDTC 2), it is anyway not
72 possible to have the exact same content of molybdenum and sulfur in each lubricant.

73

74 • Synthesis method of MoDTC 1:

75 The complex was prepared according to literature [17]. Under air, ammonium molybdate
76 tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}] \cdot 4 \text{H}_2\text{O}$ (3.20 g, 2.59 mmol) was dissolved in 25 mL of distilled
77 water. 3.05 g (13.54 mmol) of sodium diethyldithiocarbamate trihydrate, dissolved in 10 mL of
78 distilled water, were then slowly added over the course of 30 min under vigorous stirring, during
79 which time the colour of the solution gradually turned from yellow to orange and then red with
80 the formation of a precipitate. The red precipitate was isolated on a fritted glass connected to
81 a vacuum Erlenmeyer flask then washed with distilled water (3x10 mL). After washing, the
82 sample was dried under vacuum. Yield, 2.10 g (56 %). Anal. Calcd for $\text{MoC}_{10}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_4$ (MW=
83 $424.48 \text{ g}\cdot\text{mol}^{-1}$): C 28.30, H 4.75, N 6.60; Found C 27.94, H 5.09, N 6.51%.

84

85 • Synthesis method of MoDTC 2:

86 The complex was prepared according to the literature [17]. Ammonium molybdate tetrahydrate
87 $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}] \cdot 4 \text{H}_2\text{O}$ (4.22 g, 3.41 mmol) was dissolved in 20 mL of distilled water. 30 mL
88 of dimethylformamide (DMF) were poured into the solution and stirred vigorously. Then 9 g of
89 dioctylamine (37.27 mmol) and 30 mL of DMF were added at room temperature. The reaction

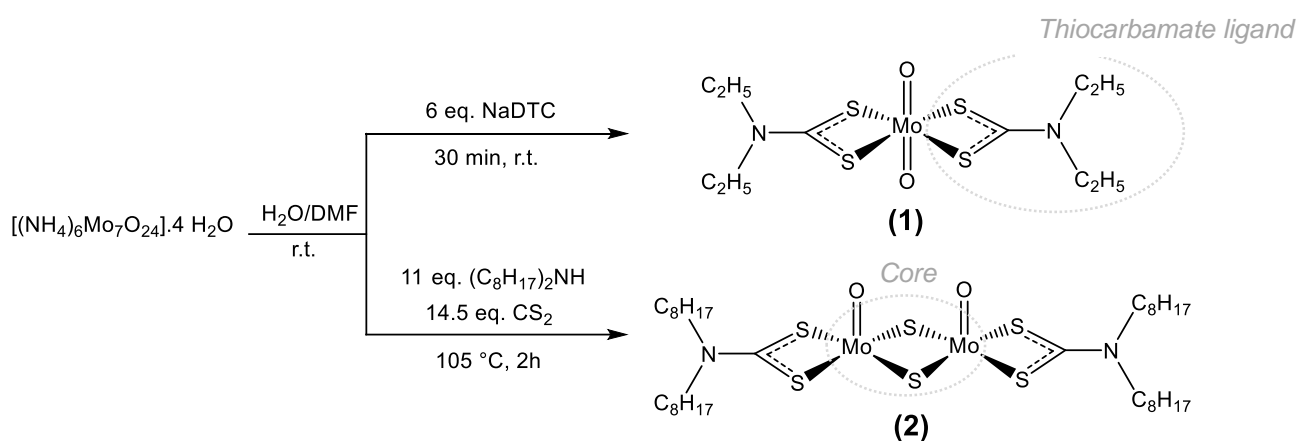
90 medium was cooled in an ice-water bath and finally, 3 mL of carbon disulphide CS₂ (49.65
91 mmol) were added dropwise over a period of 15 min.

92 The addition of CS₂ resulted in a gradual colour change of the suspension from white to yellow,
93 then orange and finally purple-red. The solution was then refluxed at 105°C under argon until
94 the colour changed from purple-red to green. The resulting viscous residue was collected on
95 a fritted glass connected to a vacuum Erlenmeyer flask, then washed with acetone (3x50 mL).
96 After washing, a yellow precipitate appeared. After washing, the sample was dried under
97 vacuum Yield, 1.10 g (10 %). Anal. Calcd for Mo₂C₃₄H₆₈N₂O₂S₆ (MW = 921.19 g.mol⁻¹): C
98 44.33, H 7.44, N 3.04; Found C 41.13, H 7.10, N 3.78%.

99

100 The XPS characterizations of MoDTC **1** and MoDTC **2** are reported in supplementary
101 information (SI 1) and corroborate the structures reported in Figure 1.

102



105 **Figure 1: Synthesis of the MoDTC derivatives 1 and 2 (only one linkage isomer**
106 **represented).**

107

108 2.2 Friction experiments

109 Balls and flats counterfaces used for tribotests are both in steel AISI52100. The hardness is
110 around 800 HV. The roughness of the flats and balls are respectively Ra = 12 ± 5 nm and Ra
111 = 40 ± 1 nm. The base oil used is a PAO4. A reciprocating ball-on-flat tribometer [18] was used
112 for tribotests. No external sulfur supply was added to the system. During the test, normal force
113 (strain gage), tangential force (piezoelectric sensor and bi-blades) and temperature
114 (thermocouple type K) were recorded.

115 Standard conditions of boundary lubrication were as follow: average sliding speed of 56 mm/s,
116 temperature of 100°C and an initial Hertz maximum pressure of 1 GPa (Load of 17 N).

117 For other tests, the temperature was varied as well as load in order to vary the initial Hertz
118 maximum contact pressure. The contact conditions are summed up in Table1.

Contact conditions	
Samples	Flat ball (R = 6.7 mm)
Load	4 N → 180 N
Speed	56 mm/s
Temperature	20°C, 100°C, 180°C
Stroke length	7 mm
Kinematic	Linear
Frequency	4 Hertz
Maximum Hertz pressure	0.62 GPa → 2.3 GPa
Number of cycles	18000
Immersion volume	80 µL

119

120

Table 1: Contact conditions of reciprocating ball-on-flat tribotests.

121

122 Representative curves of the friction coefficient as the function of number of cycles are
 123 reported. Steady state friction coefficient are calculated from the last 8000 cycles of each test.
 124 As tests were repeated at least four times, average steady state friction coefficients and their
 125 standard deviations were calculated from the values obtained from the different repeatability
 126 tests.

127 After each test, wear scar diameters were measured by optical microscopy.

128

129 **2.3 Characterization of tribofilms**

130 All samples were cleaned with *n-heptane* for 10 min in ultrasonic bath before characterization
 131 by XPS, Raman spectroscopy and FIB-TEM.

132 XPS analyses were carried out on a PHI 5000 Versaprobe II apparatus from ULVAC-PHI Inc.
 133 A monochromatized AlK_α source (1486.6 eV) was used with a spot size of 20 µm. A charge
 134 neutralization system is used to limit charge effect. The remaining charge effect was corrected
 135 fixing the C-C bond contribution of C1s peak at 284.8 eV. Spectra of Mo_{3d5/2} and S_{2p} regions
 136 were obtained using a pass energy of 23.5 eV. All the peaks were fitted with CasaXPS software
 137 using a Shirley background. Quantification was carried out using the transmission function of
 138 the apparatus and angular distribution correction for a 45° angle. Sensitivity factors were
 139 extracted from [19], they integrate cross section and escape depth correction.

140 Raman spectra were collected using a LabRam HR800 spectrometer from Horiba Scientific.
 141 Two different laser wavelengths were used 785 nm (MoDTC 1) and 532 nm (MoDTC 2 and
 142 tribofilms). Typical laser powers of 5 mW were used.

143 FIB sections were performed across tribofilms for TEM observations. A platinum layer was
144 deposited as a protective layer on tribofilm before nanomachining with Ga⁺ ions. Subsequent
145 thinning was carried out to ensure that lamella is thin enough for TEM observations.

146 The TEM observations were carried out on JEOL2010F equipped with EDS and operating at
147 an accelerating voltage of 200 kV.

148 Tribofilm compositions could slightly vary in terms of composition regarding position on the
149 wear track. Because of reciprocating oscillatory motion, the contact conditions are most severe
150 at the extremity of wear tracks, where the change of friction directions occurs. The Raman and
151 XPS analyses were done close to these areas as the amount of MoS₂ was the most important.
152 Then, some discrepancies in the results between XPS and Raman analyses could be related
153 to the fact that the size of the analyzed area was slightly different for each technique (20 μm of
154 diameter for XPS analyses and around 1 μm for Raman analyses) and to the fact that XPS
155 spectroscopy is more surface sensitive than Raman.

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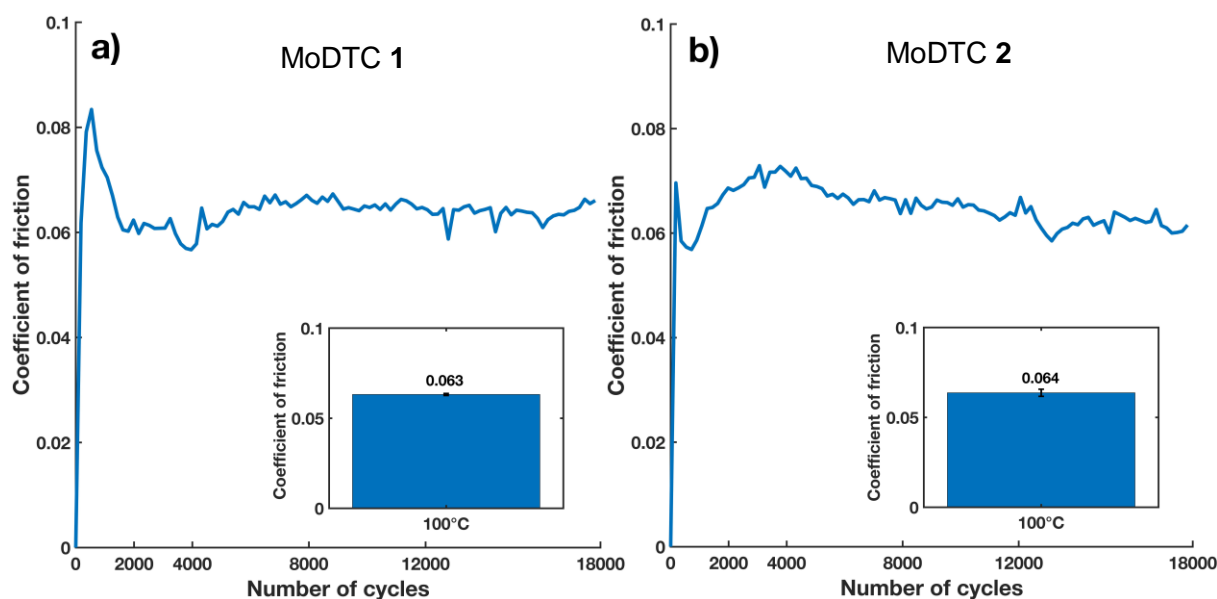
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159 3 Results

160 3.1 Low friction with MoDTC (1) under standard boundary lubricated 161 conditions

162 3.1.1 Friction results with MoDTC (1)

163 MoDTC 1 has been tested under our standard conditions of boundary lubrication ($T = 100^{\circ}\text{C}$,
164 $V = 56 \text{ mm/s}$, $P_{\text{Hertzmax}} = 1 \text{ GPa}$, 18 000 cycles). The evolution of the friction coefficient as
165 function of the number of cycles is presented in Figure 2.a as well as statistical data processing
166 from several measurements. The average steady state friction coefficient for MoDTC 1 is 0.063 ± 0.001
167 that is within the range obtained with the reference molecule MoDTC 2 (Figure 2.b -
168 $\mu_{\text{MoDTC 2}} = 0.0644 \pm 0.009$). The values for the two molecules are statistically similar and in the
169 expected range for the formation of MoS_2 in a boundary lubricated contact [6,15]. It can be
170 also noticed that MoDTC 1 requires longer induction time to reach the low friction steady state
171 regime than MoDTC 2. No loss of friction reduction capabilities is observed over the full
172 experiment (18000 cycles) for each molecule.



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174
175 **Figure 2: Coefficient of friction at 100°C for a) molecule MoDTC 1 b) molecule MoDTC 2.**
176 **The tests were performed at an initial maximum Hertz pressure of 1 GPa and an average**
177 **sliding speed of 56 mm/s. Representative curves of the friction coefficient as the**
178 **function of number of cycles are shown as well as average steady state friction**
179 **coefficients calculated from several tests with the related standard deviation.**
180

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182 3.1.2 MoDTC 1 Tribofilm characterization

183 TEM tribofilm characterizations (Figure 3) confirm the presence of MoS₂ in the tribofilm (flat
184 sample) obtained with MoDTC 1 in the absence of external sulfur supply. In TEM images of
185 tribofilm obtained with MoDTC 1 in standard conditions, MoS₂ sheets are found at the top of
186 the tribofilm of thickness between 30 and 40 nm. The presence of sheets is confirmed by EDS
187 analyses with prominent molybdenum and sulfur peaks, and by interlayer distance around 0.6
188 nm on HRTEM images, consistent with MoS₂ lamellar sheets observed in tribofilms [15].

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207 **Figure 3: a) and b) TEM images of FIB-cross section of tribofilm (flat) obtained with**
208 **MoDTC 1 after 18 000 cycles of rubbing under standard contact conditions c) EDX**
209 **spectrum recorded on the MoS₂ sheets area.**

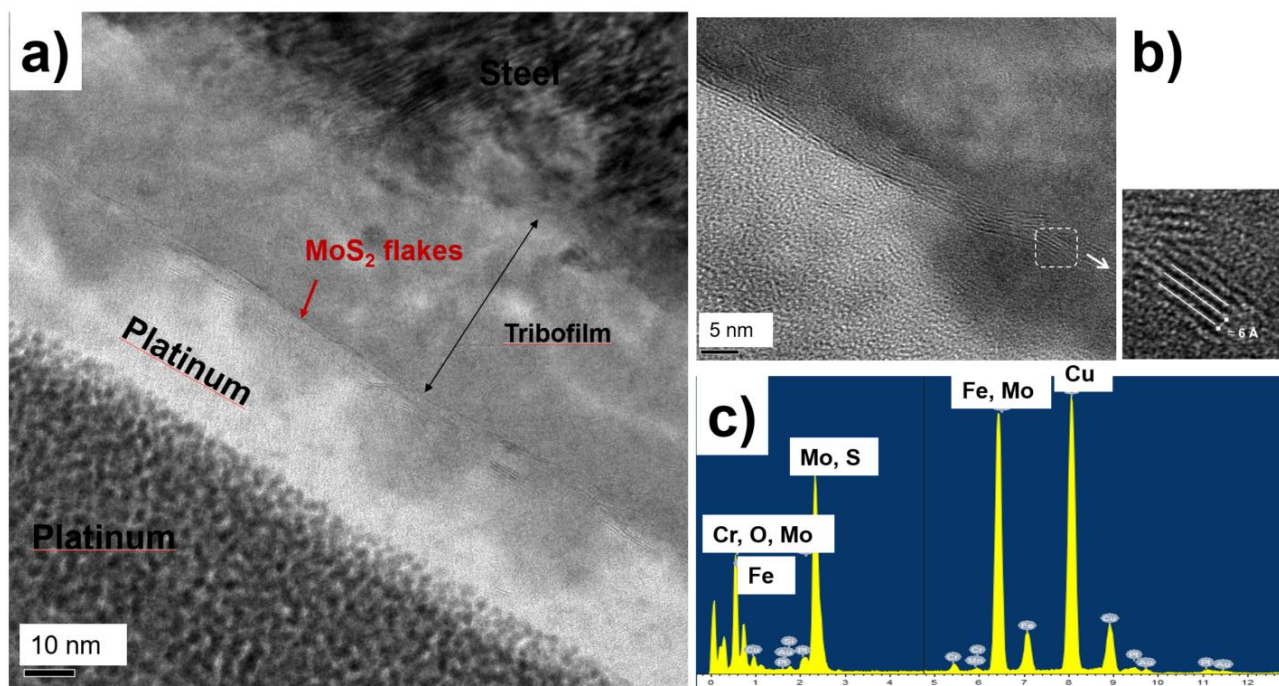
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215 The XPS analysis of the Mo_{3d} and the S_{2p} transitions carried out on the tribofilms obtained after
216 18 000 cycles with MoDTC 1 at 100°C is reported in Figure 4; details of the fits can be found
217 in Table 2.

218 Two main molybdenum contributions are found: one with a Mo_{3d5/2} peak around 232.1 eV (Mo_{3d}
219 (C), pink) corresponding to a Mo(+VI) environment related to MoO₃ or FeMoO₄ [7,20,21] and
220 another one with a Mo_{3d5/2} peak around 229.0 eV (Mo_{3d} (B), blue) attributed to a Mo(+IV)
221 environment that could correspond to MoS₂ [6,20] or MoS₃ [22,23]. One minor Mo contribution
222 is found at lower binding energy (228.2 eV, Mo_{3d} (A), light blue). This Mo_{3d} (A) contribution at
223 low binding energy is related to a reduced molybdenum species. Such a contribution has been
224 observed on sulfided molybdenum oxide thin films [21,22,24]. It has been proposed to be a
225 defective Mo environment possibly formed in the present context by friction. The peaks near
226 226 eV (yellow/brown) correspond to sulfur S_{2s} contributions related to S_{2p} contributions
227 discussed in the following paragraph.

228 The S_{2p} spectrum shows sulfide-type environment at binding energies near 161 eV. The shape
229 and width of the sulfide part of the spectrum leads to the deconvolution of 3 separate
230 contributions. The main S_{2p} (B) contribution at 161.8 eV matches with S²⁻ anion in MoS₂ or in
231 MoS₃. This contribution is consistent with the Mo_{3d} results. A lower binding energy contribution
232 around 161.0 eV S_{2p} (A) would correspond to a more electron-rich sulfur. Such a contribution
233 has been ascribed to sulfur depleted MoS₂ environments that could correspond to the reduced
234 S_{2p} (A) species films [21]. S_{2p} (C) at around 163.1 eV matches either with FeS₂, with
235 thiomolybdate or (S₂)²⁻ in MoS₃ [22].

236 To summarize, XPS analyses performed at 100°C after tribotest under standard conditions in
237 presence of MoDTC 1 suggest that MoS₂ is the main Mo based compound present at the top
238 surface of the tribofilm. This is supported by quantification of sulfur (S_{2p} (A) and (B)) over
239 molybdenum (Mo (B)) species characteristic of MoS₂ yielding a S/Mo ratio close to 2. MoS₃
240 could be also considered as peak position of Mo_{3d} (B), S_{2p} (B) and S_{2p} (C) are in agreement
241 with [22], but in much lower amount compared to MoS₂ regarding the at% of S_{2p}(C) peak
242 (Figure 4 and Table 2).

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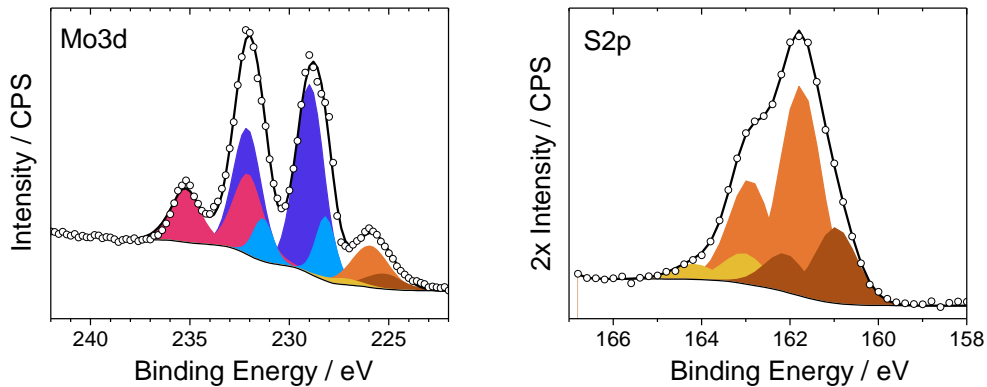
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Sample Id.	Element/Transition	Peak energy (eV)	FWHM (eV)	Atomic concentration (at %)	Assignment
MoDTC 1	$Mo_{3d5/2 - 3/2}$				
	Mo _{3d} - (A)	228.2 - 231.4	1.2	6.1	Reduced MoS ₂
	Mo _{3d} - (B)	229.0 - 232.2	1.7	25.3	MoS ₂ ou MoS ₃
	Mo _{3d} - (C)	232.1 - 235.3	1.7	11.9	MoO ₃ / FeMoO ₄
	$S_{2p3/2 - 1/2}$				
	S _{2p} - (A)	161 - 162.1	1.1	13.6	S ²⁻ in reduced MoS ₂
	S _{2p} - (B)	161.8 - 162.9	1.1	37.7	S ²⁻ in MoS ₂ or in MoS ₃
	S _{2p} - (C)	163.1 - 164.2	1.1	5.4	(S ₂) ²⁻ in FeS ₂ or thiomolybdate or MoS ₃

248

249 **Table 2: Peak fitting details related to Figure 4 e.i. XPS analyses of tribofilms obtained**
 250 **with MoDTC 1 after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz**
 251 **pressure of 1 GPa and an average sliding speed of 56 mm/s.**

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255 **Figure 4: XPS analyses (Mo3d) carried out of tribofilms (flats) obtained with MoDTC 1**
 256 **after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz pressure of 1 GPa**
 257 **and an average sliding speed of 56 mm/s.**

258

259

260 The characteristic Raman analyses of the tribofilm obtained at 100°C under standard
261 conditions with MoDTC 1 are presented in Figure 5. The two MoS₂ characteristic Raman shifts
262 E_{2g}^1 and A_{1g} at 373 cm⁻¹ and 405 cm⁻¹, respectively, are detected, in agreement with Raman
263 analyses of MoDTC tribofilms [10,14,25]. The presence of amorphous MoS₃ compound [26]
264 could explain the background shape near E_{2g}^1 and A_{1g} . The presence of Fe(MoO₄) is suggested
265 by the presence of the Raman peak at 925 cm⁻¹ [7] and is consistent with the Mo (+VI) oxide
266 contribution detected by XPS at 232.3 eV on Mo_{3d} peak.

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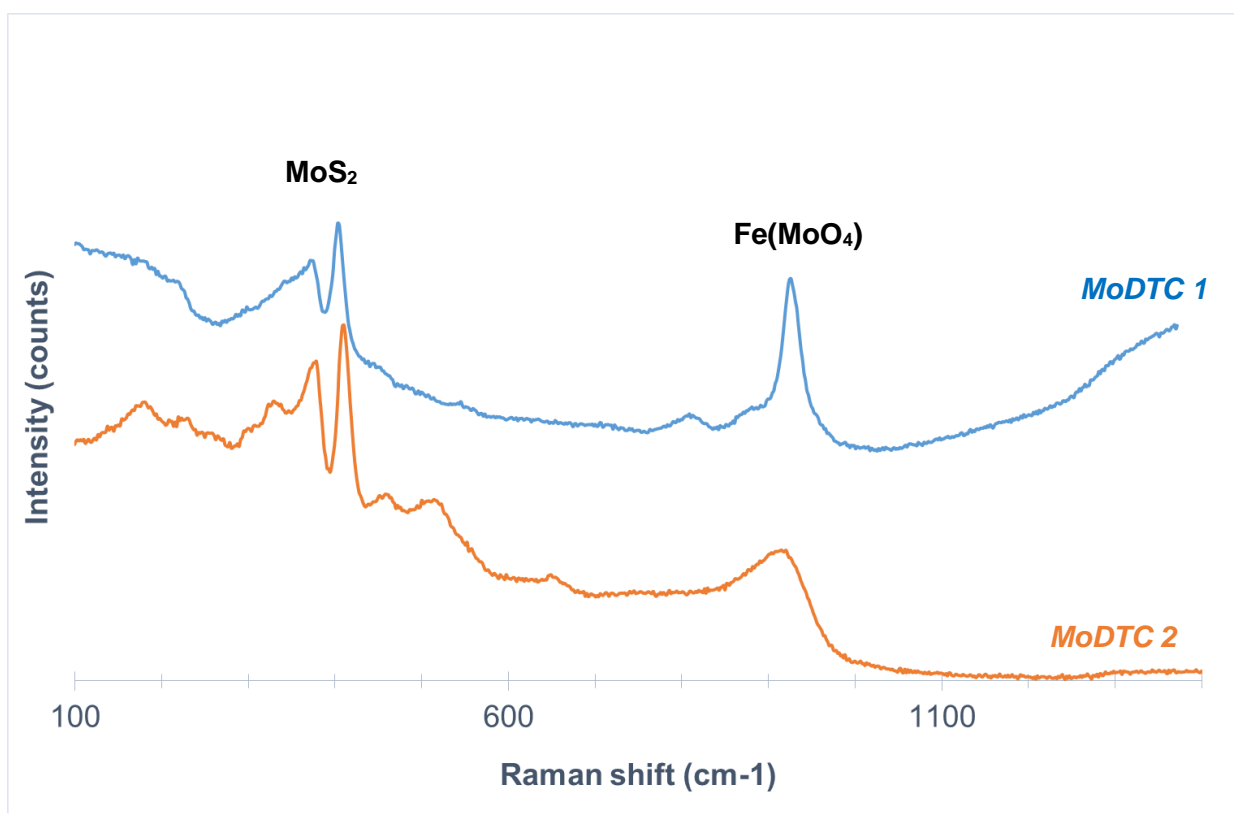
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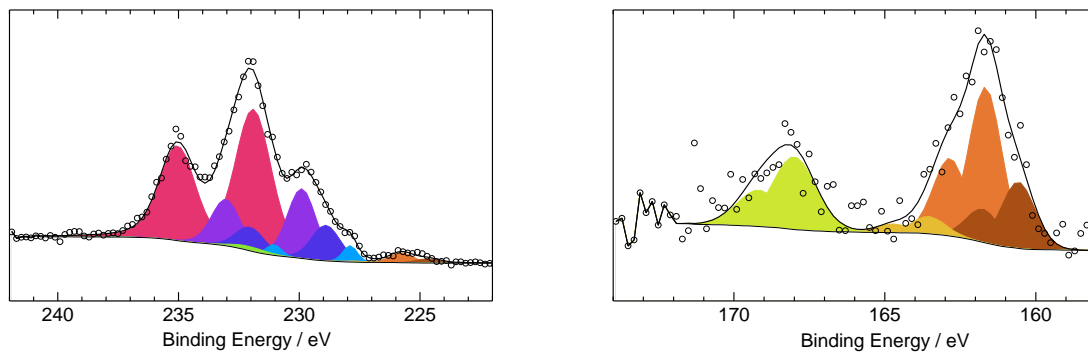
281 **Figure 5: Raman analyses on tribofilms (flats) obtained with MoDTC 1 and MoDTC 2**
282 **after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz pressure of 1 GPa**
283 **and an average sliding speed of 56 mm/s.**

284

285

286 **3.1.3 MoDTC 2 Tribofilm characterization**

287 Raman (Figure 5) and XPS (Figure 6 and Table 3) characterizations were also performed on
 288 tribofilm obtained with MoDTC 2 at 100°C and 1 GPa for comparison with MoDTC 1. Both
 289 results show the presence of MoS₂ and FeMoO₄ for MoDTC 2 tribofilm, like for MoDTC 1. This
 290 is in accordance with literature works since XPS analyses of tribofilm obtained with MoDTC
 291 often propose the presence of two main contributions attributed to Mo+IV and Mo+VI [15,27].
 292 The presence of molybdenum oxysulfide (purple contribution B' in Figure 6 and table 3) is also
 293 detected for MoDTC 2 tribofilm by XPS and was previously suggested in literature [6,20].



294

295 **Figure 6: XPS analyses (Mo3d) carried out of tribofilms (flats) obtained with MoDTC 2**
 296 **after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz pressure of 1 GPa**
 297 **and an average sliding speed of 56 mm/s.**

Sample Id.	Element/Transition	Peak energy (eV)	FWHM (eV)	Atomic concentration (at%)	S (at%) /Mo (at%) ratio	Assignment
MoDTC 2	Mo_{3d5/2 - 3/2}				0.5	
	Mo _{3d} - (A)	227.9- 231.0	0.7	1.7		Reduced MoS ₂
	Mo _{3d} - (B)	228.9 - 232.0	1.4	7.4		MoS ₂ or MoS ₃
	Mo _{3d} - (B')	229.9- 233.0	1.4	14.6		MoO _x S _y
	Mo _{3d} - (C)	231.9 – 235.0	1.8	42.0		MoO ₃ / FeMoO ₄
	S_{2p3/2 - 1/2}					
	S _{2p} - (A)	160.6 – 161.8	1.3	6.7		S ²⁻ in reduced MoS ₂
	S _{2p} - (B)	161.7 - 162.9	1.3	15.8		S ²⁻ in MoS ₂ or in MoS ₃
	S _{2p} - (C)	163.6 - 164.9	1.3	1.9		(S ₂) ²⁻ in FeS ₂ , thiomolybdate MoO _x S _y or MoS ₃
	S _{2p} - (E)	168.0 – 169.2	1.3	10		Sulfate

298 **Table 3: Peak fitting details related to Figure 6 e.i. XPS analyses of tribofilms obtained**
 299 **with MoDTC 2 after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz**
 300 **pressure of 1 GPa and an average sliding speed of 56 mm/s.**

301

302

303 3.2 Effect of temperature

304 3.2.1 Friction and wear results

305 The friction performances of molecules MoDTC **1** and MoDTC **2** have been studied at three
306 different temperatures ($T = 20^{\circ}\text{C}$, 100°C and 180°C at $V = 56 \text{ mm/s}$, $P_{\text{Hertzmax}} = 1 \text{ GPa}$, Figure
307 7).

308 The optimal tested temperature for both molecules is 100°C as a durable and low friction
309 regime is achieved in both cases (cf §3.1.1).

310 At 20°C , MoDTC **2** performs only marginally worse than at 100°C , while MoDTC **1** significantly
311 underperforms ($\mu = 0.074$ vs 0.099 , respectively). Considering the overall monotonous
312 decrease of the friction coefficients over the whole experiment (Total number of cycles = 18
313 000) for both molecular lubricants, it might be possible that neither system has reached steady
314 state by the end of the experiment. Given the more pronounced decrease of the friction
315 coefficient (both in terms of starting absolute value and in terms of overall drop) for MoDTC **1**
316 than for MoDTC **2**, the induction process seems more pronounced for MoDTC **1** than for
317 MoDTC **2**.

318 At 180°C , the loss of friction reduction capabilities is observed after a few thousand cycles for
319 both MoDTC **1** and MoDTC **2** and very high friction coefficient are observed for most of the
320 experiment, leading to high (apparent) steady state coefficients.

321 The wear behaviors obtained with the two molecules over the three temperatures appear to
322 follow the same trend as the apparent steady state coefficients described above (cf Figure 8).
323 The lowest wear is found at 100°C for both molecules MoDTC **1** and MoDTC **2**, with MoDTC
324 **1** still marginally outperforming MoDTC **2** (width of the wear = $180 \mu\text{m}$ vs. $222 \mu\text{m}$,
325 respectively). Both wear (MoDTC **1** and MoDTC **2** at 100°C) are just slightly superior to Hertz
326 diameter (red line) which represent the size of the contact before friction without any wear. The
327 loss in performance at 20°C is more noticeable for MoDTC **1** than for MoDTC **2** (width of the
328 wear = $558 \mu\text{m}$ vs. $299 \mu\text{m}$, respectively). The poorest performances are observed at 180°C
329 for both lubricants (width of the wear = $620 \mu\text{m}$ for MoDTC **1** and $650 \mu\text{m}$ for MoDTC **2**).

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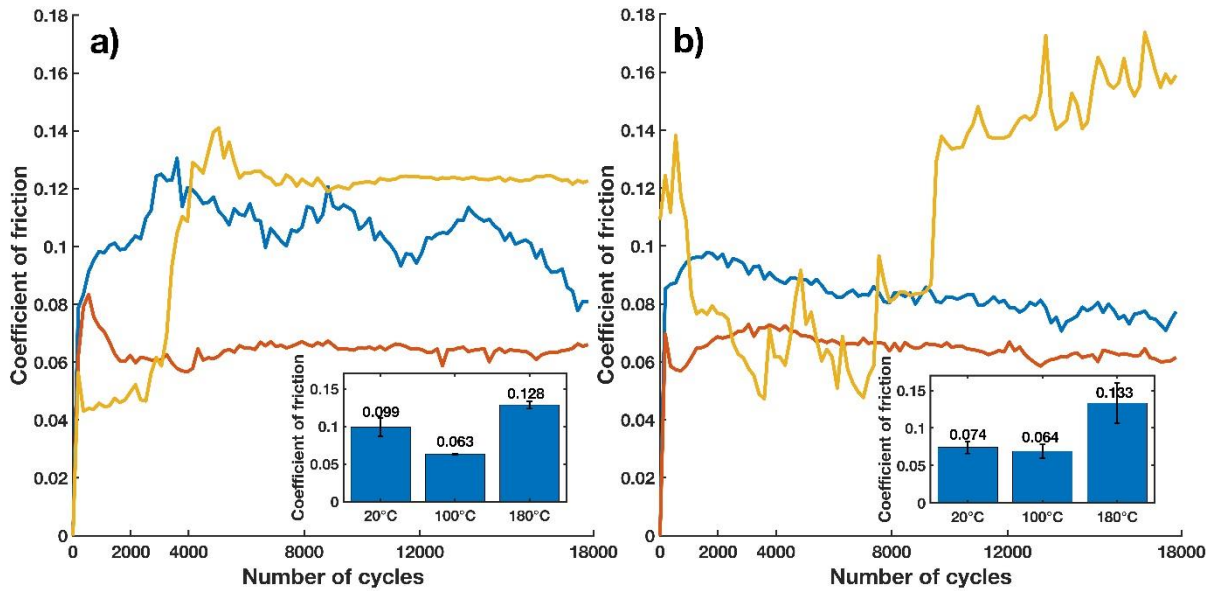
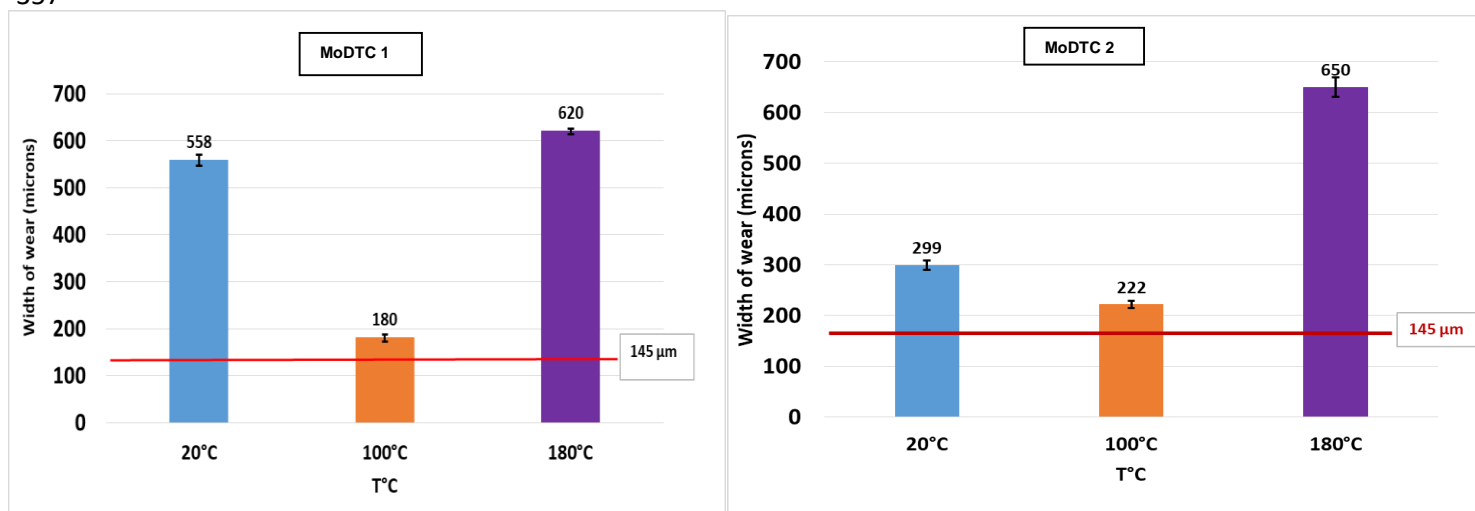


Figure 7: Coefficient of friction at 20°C (blue), 100°C (orange) and 180°C (yellow) for a) molecule MoDTC 1 b) molecule MoDTC 2. The tests were performed at an initial maximum Hertz pressure of 1 GPa and an average sliding speed of 56 mm/s. Representative curves of the friction coefficient as the function of number of cycles are shown as well as average steady state friction coefficients calculated from several tests with the related standard deviation.

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357



365 **Figure 8: Width of ball wear obtained at 20°C, 100°C and 180°C for a) molecule MoDTC**
366 **1 b) molecule MoDTC 2. The tests were performed at an initial maximum Hertz pressure**
367 **of 1 GPa and an average sliding speed of 56 mm/s. The red line represents the Hertz**
368 **diameter (size of the contact before friction).**

369

370 3.2.2 Tribofilm characterizations with MoDTC 1 at 20°C, 100°C and 180°C (XPS and 371 Raman)

372 The XPS analyses of the Mo_{3d} and the S_{2p} transitions carried out on the tribofilms obtained
373 with MoDTC 1 at different temperatures after 18 000 cycles are reported in Figure 9; details of
374 the fits can be found in Table 4.

375 The fit explanation of the tribofilm obtained at 100°C is detailed in § 3.1.2.

376 For the tribofilm at 20°C, only one Mo environment is found around 232.1 eV (Mo_{3d} (C), pink)
377 corresponding to a Mo(+VI) environment related to MoO₃ or FeMoO₄. Significant amount of
378 SO_x species is found but no evidence of MoS₂ is detected.

379 For the tribofilm at 180°C, two Mo environments are found. The main one with a Mo_{3d5/2} peak
380 around 232.1 eV (Mo_{3d} (C), pink) corresponds to a Mo(+VI) environment related to MoO₃ or
381 FeMoO₄. The Mo_{3d} (B') contribution (229.9 eV, purple) at binding energy higher than MoS₂ but
382 lower than a typical Mo(+VI) signal could correspond to oxysulfide species MoO_xS_y [6,20]. SO_x
383 species are also detected.

384

Sample Id.	Element/Transition	Peak energy (eV)	FWHM (eV)	Atomic concentration (at%)	Assignment
MoDTC 1 20°C	MO_{3d5/2} - 3/2				
	Mo _{3d} - (C)	232.2 - 235.4	1.3	54.0	MoO ₃ / FeMoO ₄
	S_{2p3/2} - 1/2				
	S _{2p} - (B)	162.1 - 163.2	1.7	8.3	(S ₂) ²⁻ in FeS ₂ or Fe thiomolybdate
	S _{2p} - (D)	166.4 - 167.5	1.5	12.4	SO ₃ species
	S _{2p} - (E)	168.3 - 169.4	1.5	25.3	Sulfate
MoDTC 1 100°C	MO_{3d5/2} - 3/2				
	Mo _{3d} - (A)	228.2 - 231.4	1.2	6.1	Reduced MoS ₂
	Mo _{3d} - (B)	229.0 - 232.2	1.7	25.3	MoS ₂ ou MoS ₃
	Mo _{3d} - (C)	232.1 - 235.3	1.7	11.9	MoO ₃ / FeMoO ₄
	S_{2p3/2} - 1/2				
	S _{2p} - (A)	161 - 162.1	1.1	13.6	S ²⁻ in reduced MoS ₂
	S _{2p} - (B)	161.8 - 162.9	1.1	37.7	S ²⁻ in MoS ₂ or in MoS ₃
	S _{2p} - (C)	163.1 - 164.2	1.1	5.4	(S ₂) ²⁻ in FeS ₂ or thiomolybdate or MoS ₃
MoDTC 1 180°C	MO_{3d5/2} - 3/2				
	Mo _{3d} - (B')	229.9 - 233.0	1.9	26.2	MoO _x S _y
	Mo _{3d} - (C)	232.0 - 235.1	1.3	46.2	MoO ₃ / FeMoO ₄
	S_{2p3/2} - 1/2				
	S _{2p} - (B)	163.0 - 164.1	1.7	9.0	(S ₂) ²⁻ in FeS ₂ or thiomolybdate
	S _{2p} - (E)	168.3 - 169.4	1.7	18.6	Sulfate

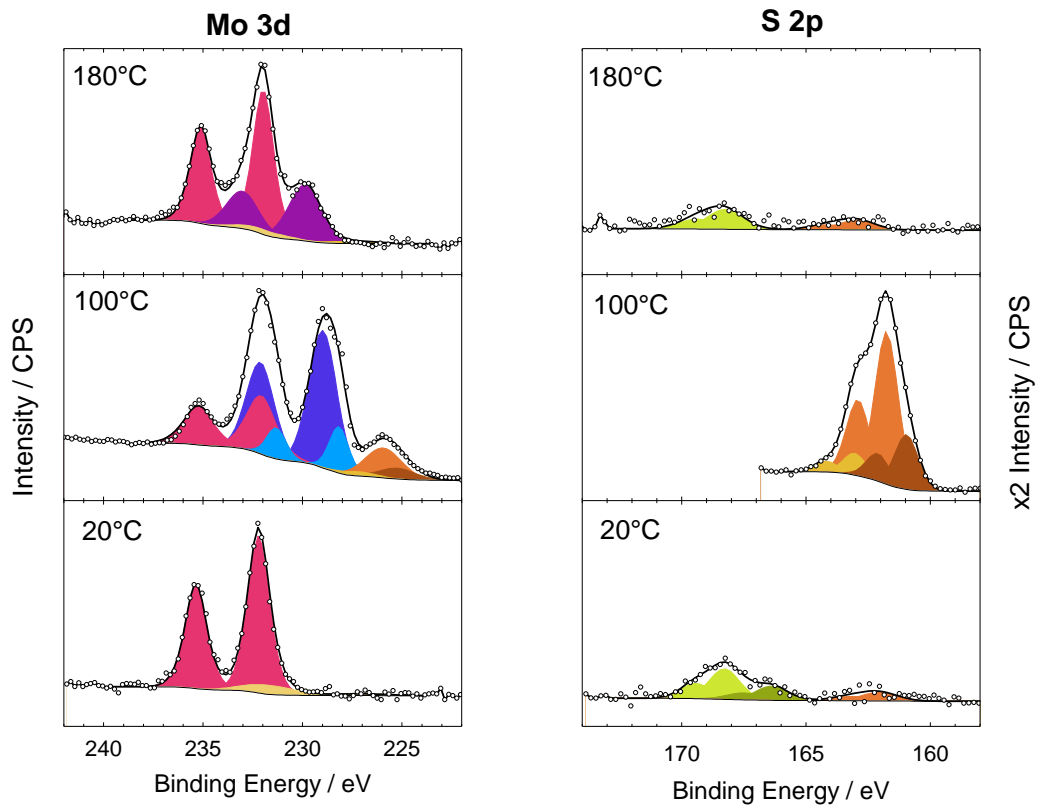
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387 **Table 4: Peak fitting details related to Figure 9 e.i. XPS analyses of tribofilms obtained**
388 **with MoDTC 1 after 18 000 cycles of rubbing at 20°C, 100°C and 180°C at an initial**
389 **maximum Hertz pressure of 1 GPa and an average sliding speed of 56 mm/s**

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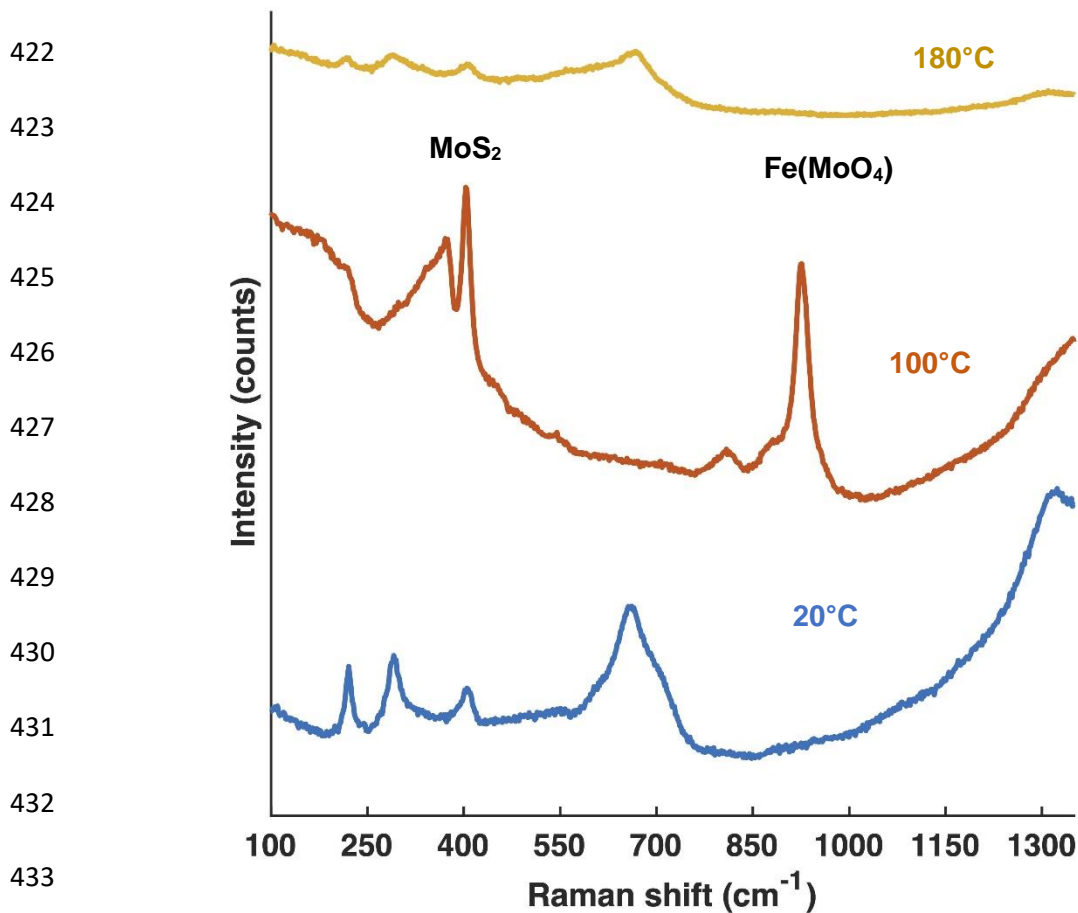
404 **Figure 9: XPS analyses (Mo3d) carried out of tribofilms (flats) obtained with MoDTC 1**
405 **after 18 000 cycles of rubbing at 20°C, 100°C and 180°C at an initial maximum Hertz**
406 **pressure of 1 GPa and an average sliding speed of 56 mm/s (see text for further details).**

407

408 The Raman analyses of the MoDTC 1 tribofilms obtained at 20°C, 100°C and 180°C are
409 presented in Figure 10.

410 At 20°C, the observed peaks are mostly related to iron oxides (Fe_2O_3 and Fe_3O_4), like at 180°C
411 [28] and molybdenum based species like MoO_3 are poorly detected [29]. Atomic ratio Mo/Fe
412 calculated from XPS data ($\text{Mo/Fe}_{20^\circ\text{C}} = 0.5$ - $\text{Mo/Fe}_{100^\circ\text{C}} = 2.9$ - $\text{Mo/Fe}_{180^\circ\text{C}} = 0.9$) suggests that
413 the amount of molybdenum compared to iron in tribofilms is much smaller at 20°C and 180°C
414 than at 100°C. As Raman technic is much less surface sensitive than XPS, it could explain
415 why such molybdenum-based compounds are poorly detected by Raman technics at 20°C and
416 180°C.

417 At 100°C, the two MoS_2 characteristic peaks E_{2g}^1 and A_{2g} at 373 cm^{-1} and 405 cm^{-1} ,
418 respectively are detected. The presence of amorphous MoS_3 compound could explain the
419 background shape near E_{2g}^1 and A_{2g} . The presence of $\text{Fe}(\text{MoO}_4)$ at 100°C is suggested by the
420 presence of the Raman peak at 925 cm^{-1} and is consistent with the Mo (+VI) oxide contribution
421 detected by XPS at 232.3 eV on Mo3d peak.



434 **Figure 10: Raman analyses on tribofilms (flats) obtained with MoDTC 1 after 18 000**
 435 **cycles of rubbing at 20°C, 100°C and 180°C at an initial maximum Hertz pressure of 1**
 436 **GPa and an average sliding speed of 56 mm/s.**

437 3.2.3 Tribofilm characterizations with MoDTC 2

438 XPS and Raman analyses of tribofilms obtained with MoDTC 2 at 20°C are reported in Figures
 439 SI 2-1 and SI 2-2 for comparison. Like for tribofilm obtained with MoDTC 1 at 20°C, Mo+VI
 440 contribution is mostly detected by XPS on Mo3d peak as well as sulfate on S2p peak. The
 441 composition of the tribofilm dominated by molybdenum oxide at temperatures around 20°C-
 442 30°C was already observed in literature for such type of MoDTC [15,27].

443 The comparison of tribofilm composition of MoDTC 1 and MoDTC 2 at 100°C was presented
 444 in §3.1.3. As found in literature [15,27], the Mo+IV contribution (MoS₂) increases in tribofilms
 445 obtained at higher temperatures, up to 80°C-100°C. Rai *et al.* [14] and Komaba *et al.* [15] have
 446 also suggested that such temperatures have an effect on the structural organization of the
 447 MoS₂ layers.

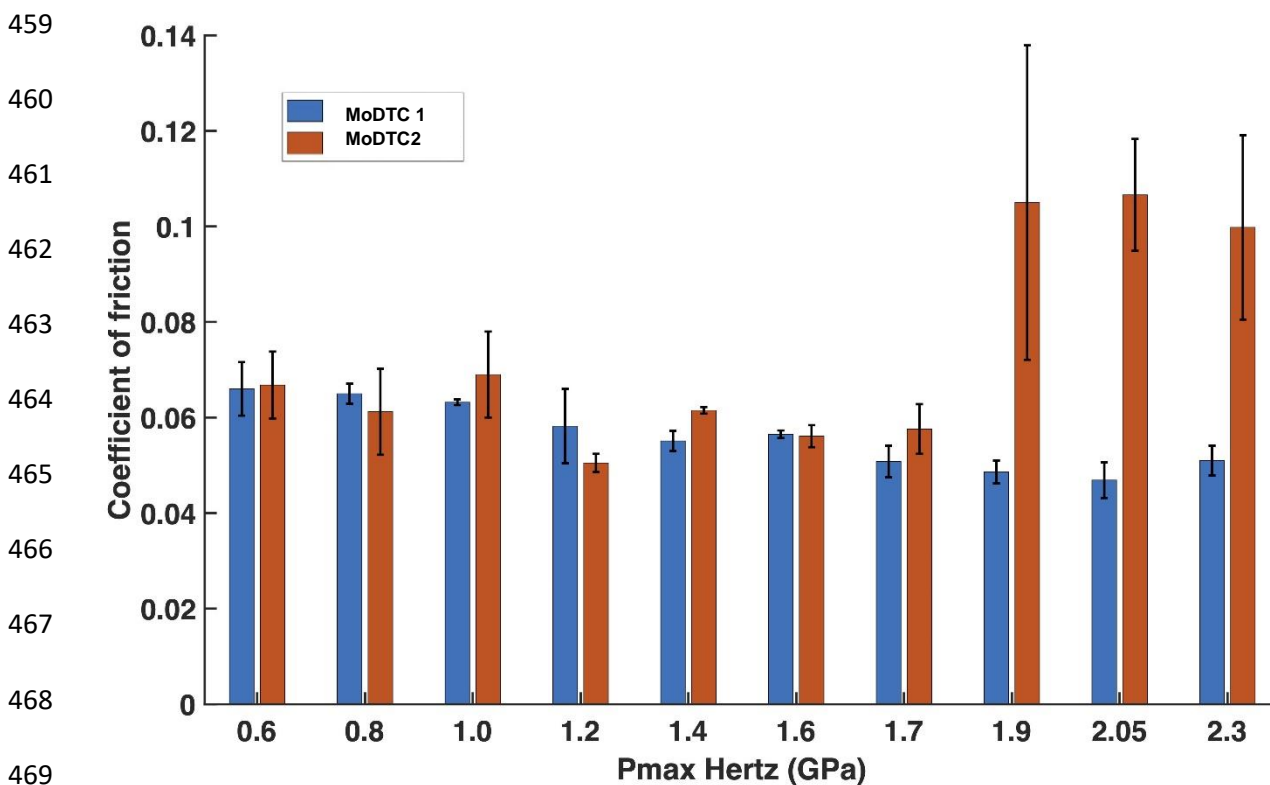
448 For temperatures higher than 100°C, only few data are found in literature [27].

449 **3.3 Effect of contact pressure**

450 **3.3.1 Friction results**

451 Friction results obtained at 100°C for the two molecules MoDTC 1 and MoTDC 2 at different
452 initial maximum Hertz pressures (from 0.6 to 2.3 GPa) are reported in Figure 11 ($V = 56$ mm/s.
453 $T = 100^\circ\text{C}$, 18 000 cycles). Average steady state friction coefficients obtained from repeated
454 tests and observed standard deviations are reported.

455 At low contact pressures, the friction behavior at the steady state is similar for the two
456 molecules within standard deviations. Above an initial maximum Hertz contact pressure of 1.9
457 GPa, significant differences in friction behavior appear between the two molecules: MoDTC 1
458 still achieves a low friction regime whereas MoDTC 2 does not.



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472 **Figure 11: Average steady state friction coefficient for different Initial Hertz maximum**
473 **contact pressures for molecule MoDTC 1 and molecule MoDTC 2. The tests were**
474 **performed at a temperature of 100°C and an average sliding speed of 56 mm/s. Average**
475 **steady state friction coefficients are calculated from several tests with the related**
476 **standard deviation.**

477

478

479 3.3.2 Tribofilms characterization

480 The XPS and Raman characterizations performed on tribofilms obtained with MoDTC 1 at
481 different contact pressures are shown respectively in Figure 12/Table 5 and Figure 13.

482 The interpretation of the XPS data follows the results presented in §3.1.2. For all tested contact
483 pressures, beside the main contributions (Mo_{3d} (B), blue) attributed to MoS_2 or MoS_3 , Mo (+VI)
484 oxide contributions attributed to $\text{Fe}(\text{MoO}_4)$ is also found in significant amount (namely, Mo_{3d}
485 (C), pink and 925 cm^{-1} Raman peak). At high contact pressures, Mo_{3d} (B) is the main
486 contribution, and Mo_{3d} (C) dominates at low contact pressure (0.8 GPa). The low binding
487 energy Mo_{3d} (A) contribution is detected mainly at low contact pressures (0.8 GPa and 1 GPa)
488 and would correspond to defective MoS_2 . No oxysulfide-type molybdenum is evidenced
489 (binding energies expected between Mo_{3d} (B) and Mo_{3d} (C)) [6,20,22].

490 Concerning the S_{2p} spectra, two main characteristic sulfur environments are found with no
491 clear dependence on contact pressure: a sulfide-type environment at low binding energies
492 ($\text{S}_{2p_{3/2}} < 164\text{ eV}$) and a SO_x type environment at higher binding energies ($\text{S}_{2p_{3/2}} > 166\text{ eV}$)
493 characteristic of oxidized sulfur.

494 In Raman spectra, different components, MoS_2 , $\text{Fe}(\text{MoO}_4)$, amorphous MoS_3 and
495 carbonaceous matrix [30] are identified. It is difficult to further interpret the observed
496 differences as they may be related to the localization of the analyzed area within the
497 heterogeneous wear track, rather than to systematic dependence on contact pressure.

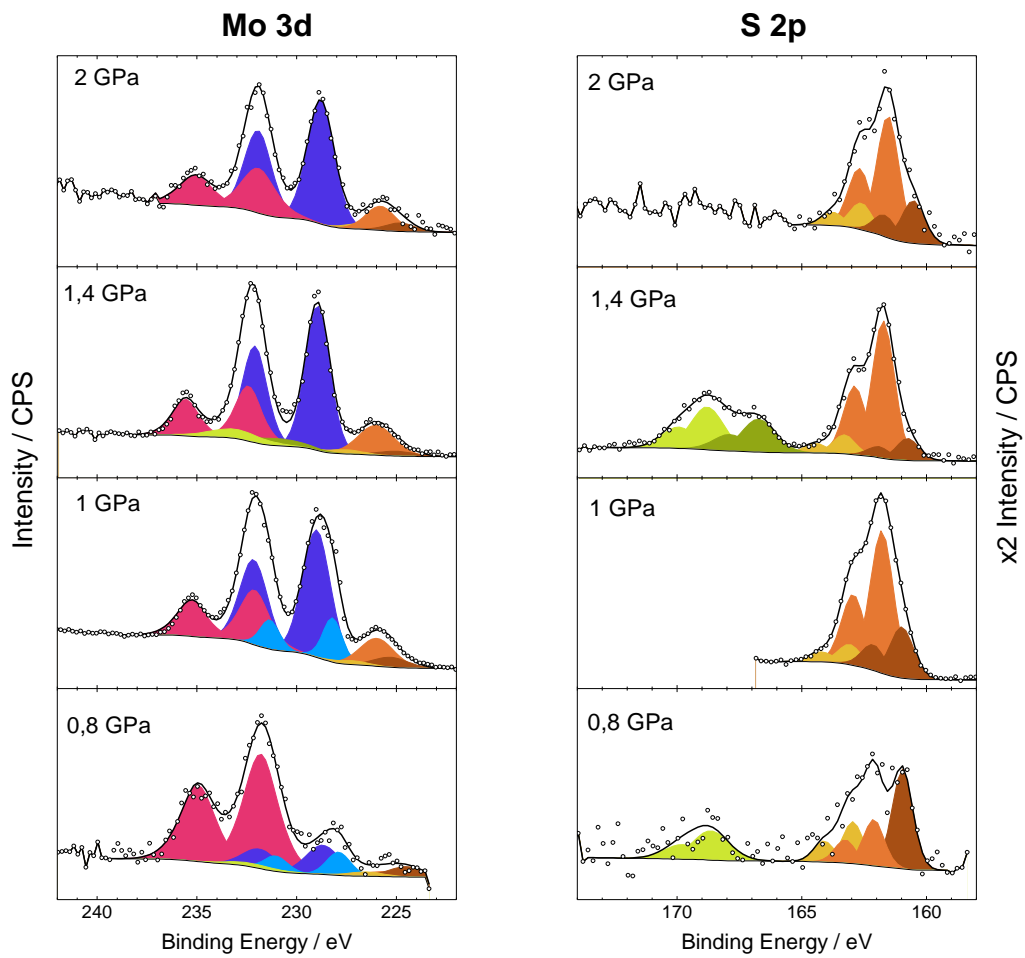
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Sample Id.	Element/Transition	Peak energy (eV)	FWHM (eV)	Atomic concentration (at%)	S (at%) /Mo (at%) ratio	Assignment
MoDTC 1 0.8 GPa	$MO_{3d5/2} - 3/2$				1.6	
	Mo _{3d} - (A)	227.9 - 231.1	1.4	3.7		Reduced MoS ₂
	Mo _{3d} - (B)	228.7 - 231.9	2.0	6.7		MoS ₂ or MoS ₃
	Mo _{3d} - (C)	231.8 - 235.0	2.0	28.2		MoO ₃ / FeMoO ₄
	$S_{2p3/2} - 1/2$					
	S _{2p} - (A)	161.0 - 162.1	1.0	25.6		S ²⁻ in reduced MoS ₂
	S _{2p} - (B)	162.1 - 163.3	1.0	11.9		S ²⁻ in MoS ₂ or in MoS ₃
	S _{2p} - (C)	163.0 - 164.1	1.0	10.8		(S ₂) ²⁻ in FeS ₂ or thiomolybdate or MoS ₃
S _{2p} - (E)	168.6 - 169.8	1.7	13.1	Sulfate		
MoDTC 1 1 GPa	$MO_{3d5/2} - 3/2$				1.3	
	Mo _{3d} - (A)	228.2 - 231.4	1.2	6.1		Reduced MoS ₂
	Mo _{3d} - (B)	229.0 - 232.2	1.7	25.3		MoS ₂ or MoS ₃
	Mo _{3d} - (C)	232.1 - 235.3	1.7	11.9		MoO ₃ / FeMoO ₄
	$S_{2p3/2} - 1/2$					
	S _{2p} - (A)	161 - 162.1	1.1	13.6		S ²⁻ in reduced MoS ₂
	S _{2p} - (B)	161.8 - 162.9	1.1	37.7		S ²⁻ in MoS ₂ or in MoS ₃
	S _{2p} - (C)	163.1 - 164.2	1.1	5.4		(S ₂) ²⁻ in FeS ₂ or thiomolybdate or MoS ₃
MoDTC 1 1.4 GPa	$MO_{3d5/2} - 3/2$				2.3	
	Mo _{3d} - (B)	229.0 - 231.1	1.4	21.2		MoS ₂ or MoS ₃
	Mo _{3d} - (C)	232.4 - 235.6	1.6	9.1		MoO ₃ / FeMoO ₄
	$S_{2p3/2} - 1/2$					
	S _{2p} - (A)	160.8 - 161.9	1.1	5.3		S ²⁻ in reduced MoS ₂
	S _{2p} - (B)	161.7 - 162.9	1.1	33.0		S ²⁻ in MoS ₂ or in MoS ₃
	S _{2p} - (C)	163.3 - 164.4	1.1	4.6		(S ₂) ²⁻ in FeS ₂ or thiomolybdate or MoS ₃
	S _{2p} - (D)	166.7 - 167.9	1.6	11.7		SO ₃ species
S _{2p} - (E)	168.8 - 170.0	1.6	15.1	Sulfate		
MoDTC 1 2 GPa	$MO_{3d5/2} - 3/2$				1.55	
	Mo _{3d} - (B)	228.8 - 231.9	1.6	26.5		MoS ₂ or MoS ₃
	Mo _{3d} - (C)	231.9 - 235.1	2.0	12.6		MoO ₃ / FeMoO ₄
	$S_{2p3/2} - 1/2$					
	S _{2p} - (A)	160.5 - 161.7	1.1	13.6		S ²⁻ in reduced MoS ₂
	S _{2p} - (B)	161.5 - 162.7	1.1	38.8		S ²⁻ in MoS ₂ or in MoS ₃
S _{2p} - (C)	162.6 - 163.8	1.1	8.5	(S ₂) ²⁻ in FeS ₂ or thiomolybdate or MoS ₃		

500

501 **Table 5: Peak fitting details related to Figure 12 e.i. XPS analyses of tribofilms obtained**
502 **with MoDTC 1 after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz**
503 **pressure of 0.8 GPa, 1 GPa, 1.4 GPa, 2 GPa and an average sliding speed of 56 mm/s**

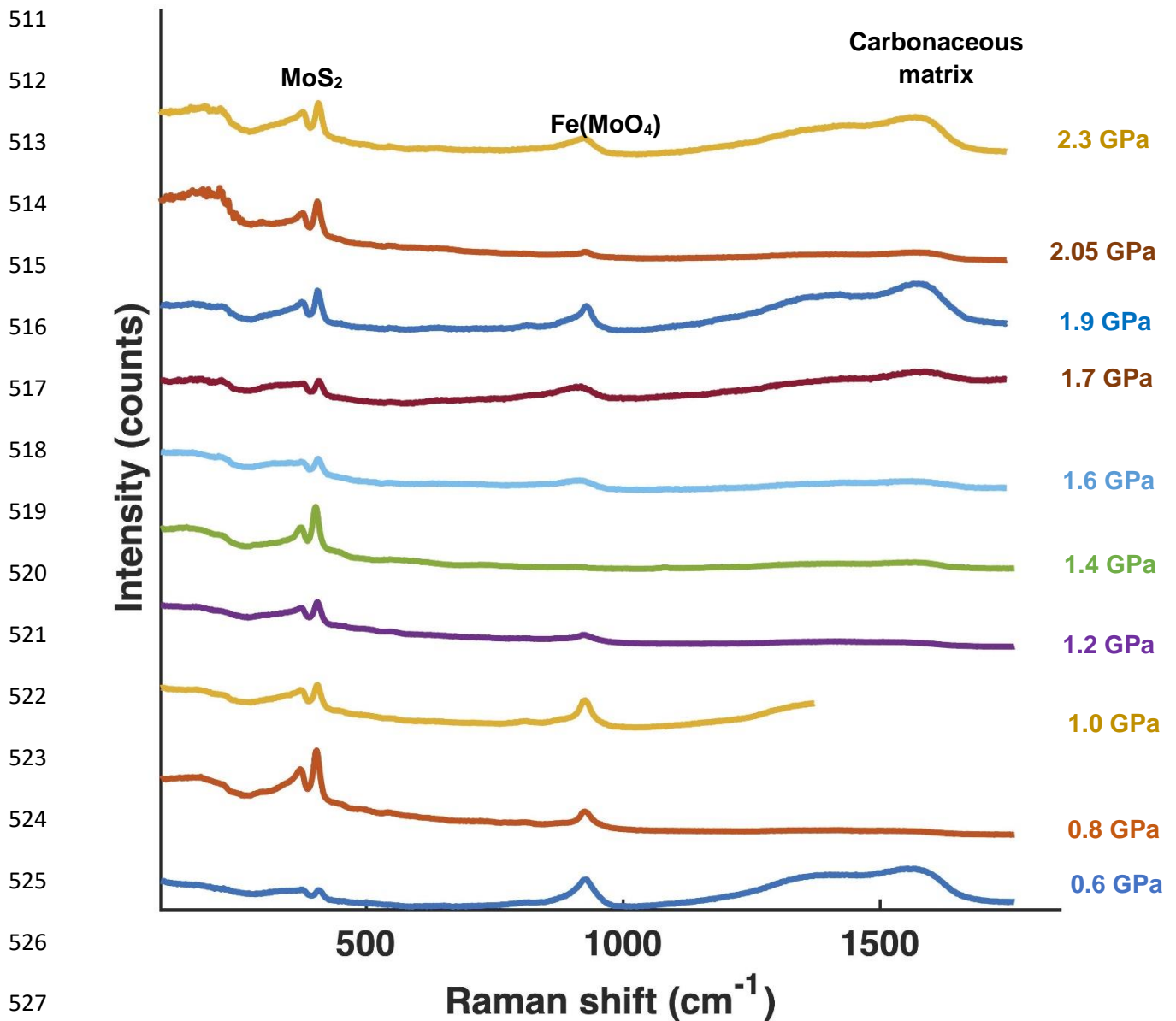
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507 **Figure 12: XPS analyses (Mo3d peak) carried out of tribofilms (flats) obtained with**
 508 **MoDTC 1 at various initial maximum Hertz pressure after 18 000 cycles of rubbing at**
 509 **100°C and an average sliding speed of 56 mm/s.**

510



528 **Figure 13: Raman analyses on tribofilms (flats) obtained with MoDTC 1 after 18 000**
 529 **cycles of rubbing at different initial maximum Hertz pressure, at 100°C and at an average**
 530 **sliding speed of 56 mm/s.**

531 XPS and Raman analyses of tribofilms obtained with MoDTC 2 at 0.8 GPa and 1.2 GPa are
 532 reported in Figures SI 2-3, SI 2-4 and SI 2-5 for comparison with MoDTC 1. Like for tribofilms
 533 obtained with MoDTC 1, MoS₂ is mainly detected by Raman and XPS. The low binding energy
 534 Mo_{3d} (A) contribution detected by XPS and that would correspond to defective MoS₂ analyses
 535 is also mainly detected at low contact pressures (0.8 GPa) like for MoDTC 1. The peak at 925
 536 cm⁻¹ on Raman spectra attributed to Fe(MoO₄) seems more significant in case of MoDTC 1
 537 than for MoDTC 2.

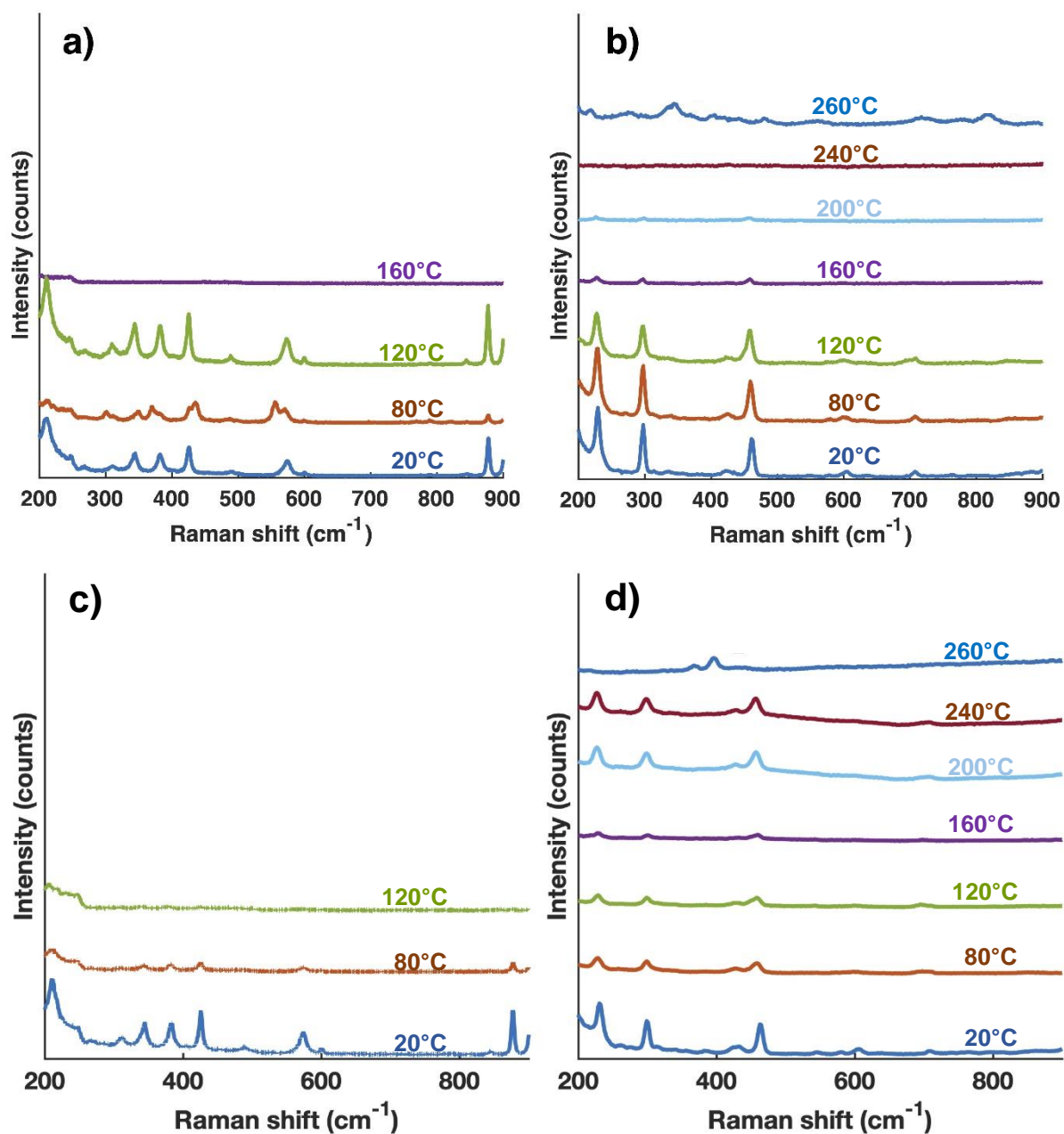
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539 **3.4 Effect of temperature without contact pressure and shear**

540 To test if the decomposition of both MoDTC molecules toward MoS₂ can be thermally induced
541 (with no other concurrent reagent), we performed Raman analyses after thermal degradation
542 for both molecules at different temperatures in air and under argon atmosphere (Figure 14) in
543 the absence of steel material. At high temperature (160°C for open air tests and 120°C for
544 argon atmosphere tests), the molecule MoDTC **1** is decomposed but no MoS₂ formation is
545 observed. In contrast, Raman spectra obtained from 260°C both in air and Ar atmosphere with
546 MoDTC **2** exhibits Raman peaks around 400 cm⁻¹. This is not compatible with MoO₃ and MoO₂
547 [31] but that could be related to Mo-S vibrations. The E_{2g}^1 and A_{1g} peaks are found at slightly
548 lower positions than standard MoS₂ analyzed at ambient temperature, but this may be due the
549 temperature dependence of the peak position with temperature [32] or to the fact that it is more
550 a MoS_x compound rather than MoS₂ [33]. The decomposition in MoS₂ of MoDTC closed to
551 MoDTC **2** structure by thermal degradation was already found in literature [34].

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Figure 14: Raman analyses performed on pure additives in different atmosphere and at different temperatures: a) MoDTC 1 in air (laser wavelength 784 nm) and b) MoDTC 2 in air (laser wavelength 532 nm) c) MoDTC 1 under argon atmosphere (laser wavelength 784 nm) and d) MoDTC 2 under argon atmosphere (laser wavelength 532 nm).

572 4 Discussion

573 The achievement of low friction coefficients (0.05 to 0.07) under boundary lubrication in steel-
574 steel contact was observed for both molecules MoDTC **1** and MoDTC **2**, and is concurrent with
575 the formation of MoS₂. The originalities of MoDTC **1** are to outperform MoDTC **2** at high contact
576 pressures, and to allow MoS₂ formation without a preformed dimeric core in the molecule,
577 external sulfur supply, and with a high starting oxidation number (Mo(+VI)). Such distinctive
578 chemical properties open mechanistic questions on how such MoDTC molecules can lead to
579 the formation of MoS₂.

580 Concerning the oxidation state of molybdenum atom within the molecule, systems with a
581 Mo(+VI) molybdate core have been described but they need to be blended with other additives
582 to form MoS₂ sheets [26]. Among the potential reductive sources, the organic oil or the organic
583 ligands could play a chemical reducing role, but the formation of iron-molybdate involving both
584 iron coming from the steel surface and molybdenum from the additive supports the idea of an
585 active role of steel in these phenomena. This is further corroborated by the fact that MoS₂ is
586 not observed upon thermal heating of MoDTC powder in the absence of steel (results §3.4)
587 and by the fact that molybdate is the main detected phase under less severe conditions at low
588 contact pressure (Figures 12 and 13). Therefore, it can be suggested that the steel-steel
589 contact lubricated with oil environment is reducing enough to reduce Mo(+VI) in MoDTC **1** into
590 Mo(+IV), in the absence of other additives.

591 The two MoDTC molecules display a very different response during thermal degradation.
592 Additive MoDTC **2** seems to degrade into MoS_x compounds in both air and argon atmospheres
593 near 260°C. This is in agreement with reported mechanism on thermal degradation of such
594 molecules containing the [Mo(μ-S)₂Mo] sulphided core as MoDTC **2** [34]. Conversely, as
595 shown on Figures 14, MoS₂ is not formed from MoDTC **1** during thermal degradation. This
596 suggests a strong role of mechanical stresses and a chemical role of iron. Consistently, we
597 have evidenced the formation of MoS₂ from MoDTC **1** only in wear tracks of tribotests (Figures
598 3 and 4). As shown above, mechanical stresses for MoDTC **2** action does not seem necessary
599 for forming MoS₂, as it seems to form in thermal degradation experiments, but they may
600 positively add to thermal degradation and/or chemical role of steel surface.

601

602 To summarize, MoDTC **1** is an interesting molecular additive to reduce friction in boundary
603 lubricated steel-steel contacts. This efficient molecule achieves high performance up to high
604 contact pressures by accessing mechanistic pathways that could be distinct from those of
605 classical molecules such as MoDTC **2** or molybdate [26]. We ruled out the formation of MoS₂
606 by a mechanism based solely on the thermal degradation of MoDTC **1**. The absence of core

607 sulfur in molecule MoDTC **1** also rules out (at least in the initial stages) the chemical
608 degradation mechanism proposed by Grossiord *et al.* [8] where only sulfur atoms present in
609 the core of the molecule contribute to the MoS₂ generation. The necessary involvement of the
610 sulfur atoms in the ligands of MoDTC **1** remains compatible with at least two proposed
611 mechanisms: the formation of a Linkage Isomer - MoDTC [11,12], or the cleavage of carbon-
612 sulfur bonds of the ligand [7,16]. Then, MoS_x intermediate products seems needed before
613 generating well-organized MoS₂ lamellar sheets during friction as it was proposed previously
614 [7,26].

615

616 **5 Conclusion**

617 In this work, the tribological properties and factors influencing the formation of MoS₂ from
618 {[MoO₂](S₂CNEt₂)₂} (MoDTC **1**) and {[Mo₂(S/O)₄](S₂CNOc₂)₂} (MoDTC **2**) were investigated.
619 Unexpectedly, MoDTC **1**, comprising Mo(+VI) and containing sulfur atoms only in its
620 thiocarbamate ligands, is able to form MoS₂ sheets in lubricated steel/steel contacts under
621 boundary lubrication conditions. This experimental study therefore demonstrates that, contrary
622 to what was classically assumed, the presence of peripheral thiocarbamate ligands can be
623 sufficient to provide the required sulfur source in these “all-in-one” types of molecules. This
624 molecule is not only competitive with “classical” MoDTC used in engine lubrication, containing
625 sulfur in the core of the molecule, but is even more powerful at high contact pressures.

626 On the mechanistic point of view, this work confirms that the chemical pathway from MoDTC
627 to MoS₂ is not only thermal. Pressure and shear take an important role in the tribochemical
628 reactions route leading to the formation of MoS₂. A substantial contribution of the surface, as
629 mentioned in the discussion section, remains an important parameter to consider as well.

630 Those results give insights in molecule design and lubricant formulation to improve MoS₂
631 sheets generation from several types of contact conditions

632

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640 of the French government operated by the National Research Agency (ANR).

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