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Dithiocarbamate transfer reaction from methylene-bis(dithiocarbamates) to molybdenum dithiocarbamates in engine lubricants investigated using laboratory experiments†

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Elaboration of new engine oil specifications and growing level of environmental awareness have been calling for better fuel efficiency and reduction of carbon emissions. In this context, molybdenum dithiocarbamates (MoDTC) are important lubricant additives used to reduce friction coefficients and hence to improve fuel economy. It has been recently shown that under engine test conditions, the combined use of MoDTC and methylene-bis(dithiocarbamates) (MBDTC) leads to the prolonged existence of MoDTC complexes at useful levels in formulated engine oil due to ligand transfer reactions, resulting in the synergistic enhancement of tribological performances. In order to investigate the process of this ligand transfer at the molecular level in detail, laboratory ageing experiments involving MoDTC, MBDTC and zinc dithiophosphates (ZnDTP) – a combination of additives frequently used in formulated lubricants – in solution in hydrocarbon base oils were performed under thermal and thermo-oxidative conditions. The evolution of the concentrations of the substrates and of their transformation products were followed using HPLC-MS, Probe-MS analyses and NMR spectroscopy. It could be shown that Zn(II) complexes such as ZnDTP are able to induce dithiocarbamate (DTC) transfer reactions from MBDTC to MoDTC through a mechanism involving activation of carbon-sulfur bonds on MBDTC. Zn(II) ions act as a Lewis acid inducing the release of DTC from MBDTC. Oxidative conditions (NO_2 in air) were also shown to induce the release of DTC from MBDTC, even in the absence of Zn(II) ions, which then become available for ligand exchange with MoDTC or for re-complexation of the metal core of Mo complexes ($Mo_2O_2S_2$ or Mo oxysulfides) after partial oxidative degradation of the genuine MoDTC ligands.

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1. Introduction

Energy saving, worldwide concerns over CO_2 emission and the introduction of new engine oil specifications are among the major driving forces to increase fuel economy in internal combustion engines.[1–3] The development of new engine technologies[4] and lubricants[5] plays a significant role in attempting to achieve this goal. Over the past decades, different families of additives have been widely employed in lubricant oils to protect the engine metallic parts from thermal, chemical and mechanical degradation as well as to improve the overall lubricating performances.[5] One of the most general trend to improve fuel efficiency is the use of molybdenum dithiocarbamates (MoDTC) as effective friction modifiers in lubricants since they lower significantly the friction coefficient at the tribological contacts under boundary lubrication conditions.[6–10]

However, MoDTC undergo thermo-oxidative degradation during engine functioning, resulting in the progressive loss of the ability of lubricants to reduce friction.[11–14] To date, only a few studies have been carried out to follow at the molecular level the progressive degradation of MoDTC, as well as their chemical transformation pathways. Fourier transform infrared spectroscopy (FT-IR),[12–14] mass spectrometry (MS),[13–17] UV-vis spectrophotometry,[18] and NMR spectroscopy[15,19] are among the main analytical techniques reported in the literature to investigate the evolution and chemical behaviour of MoDTC in lubricants. A better understanding of their degradation pathways in engine oil when subjected to thermo-oxidative degradation is still important since it might potentially lead to the design of novel molecules with improved tribological properties and enhanced resistance to alteration.

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Despite the excellent efficiency of MoDTC to reduce friction coefficient to relatively low values, the tribological performances of MoDTC in engine oils still highly depend on the nature and chemistry of the other additives present in formulated oils. The occurrence of synergistic or antagonistic interactions between MoDTC and other lubricant additives plays an important role in minimizing the friction in automobile engines. For example, zinc dithiophosphates (ZnDTP), which are amongst the most widely used multifunctional additives in engine oils,[20] have been shown to promote the formation of MoS_2 and to enhance the persistence of the MoS_2 tribofilm when used in combination with MoDTC.[21,22] In this respect also, the synergistic interactions between MoDTC and methylene-bis(dithiocarbamates) (MBDTC) have been recently shown to increase the durability of MoDTC and to extend the friction reducing capability of formulated engine lubricants to longer periods under engine test conditions.[23] Since the MoDTC remaining after prolonged functioning of the engine were shown to exclusively bear ligands corresponding to DTC moieties from MBDTC – the genuine MoDTC species having been completely degraded –, it was concluded that the prolonged existence of MoDTC was due to the progressive and constant replacement of the degraded DTC ligands from MoDTC educts by DTC released from MBDTC during engine functioning.[23]

The present study aimed to deepen the knowledge of the interactions between MoDTC and MBDTC and to explore their synergy at the molecular level in the presence of different lubricant additives. For this purpose, laboratory ageing experiments under thermal (non-oxidizing) and thermo-oxidative conditions reproducing those undergone by lubricants in operating engines have been performed on mixtures involving MoDTC, MBDTC and eventually Zn(II) complexes in solution in a hydrocarbon base oil or in fully formulated lubricants. The evolution of the substrates and of their transformation products formed upon alteration was followed using HPLC-MS, Probe-MS analyses and NMR spectroscopy. Focus has been put on the evaluation of the effect of ZnDTP and oxidative conditions on the interactions between MoDTC and MBDTC. Interactions of MBDTC with other lubricant additives have, to our knowledge, not been investigated at a molecular level so far using such an approach, MBDTC being postulated to mainly act as an antioxidant in additivated lubricants.[24] A comprehensive understanding of the underlying chemical processes involved in the interaction between MoDTC and MBDTC in lubricants is indeed expected to offer new strategies for molybdenum tribochemistry optimization in real engine systems.

2. Experimental section

2.1. Materials (oils and additives)

The mineral base oil used in this work was provided by TotalEnergies Marketing Services. The two fully formulated oils (referred to as "oil A" and "oil A_{MBDTC}") were also provided by TotalEnergies Marketing & Services and have globally a similar composition comprising, notably, alkylated aryl amine antioxidants and secondary zinc dithiophosphates **2b** (bold numbers refer to the chemical structures shown in Fig. 1). The sole difference between oil A and oil A_{MBDTC} is the additional presence

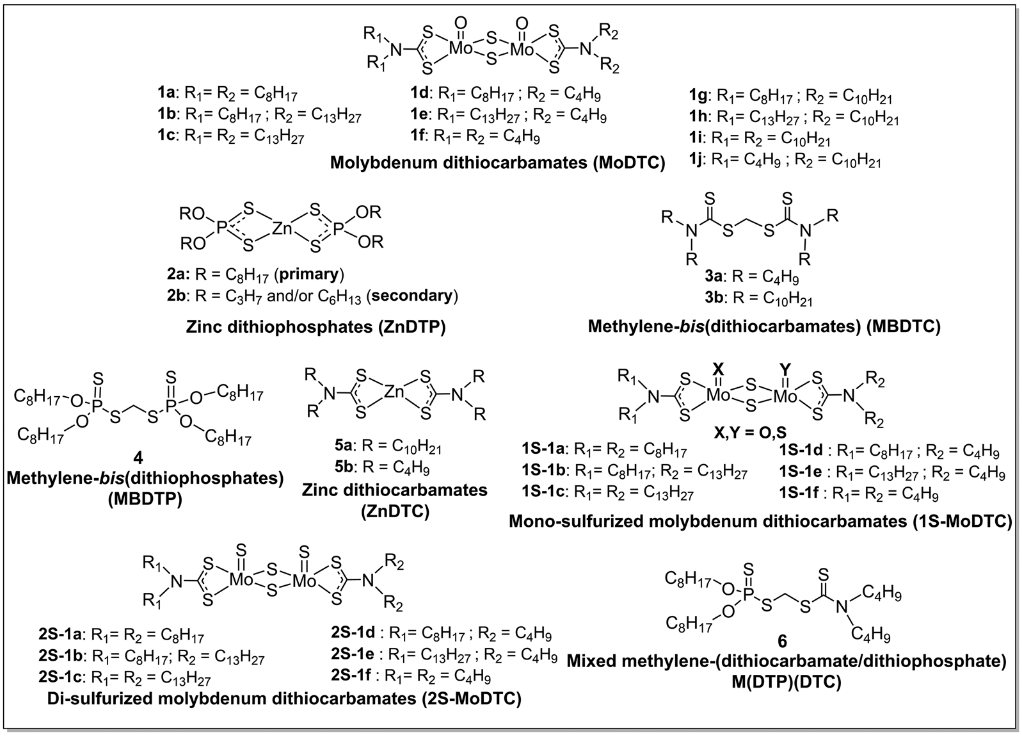

Fig. 1 Chemical structures of the compounds mentioned in this work.

of MBDTC **3a** (2 wt%) in the oil A_{MBDTC}. The commercial product Sakuralube S525 (mixture of MoDTC **1a–1c**; 10 wt% Mo in hydrocarbon base oil) was purchased from Adeka. The primary ZnDTP complexes **2a** with (ethylhexyl) alkyl chains (7.3 wt% P in base oil, trade name: OLOA 269R) and the secondary ZnDTP **2b** (mixture of compounds with C_3 and C_6 alkyl chains; 7.0 wt% P in base oil, trade name: Infineum C9426) were both purchased from Infineum. MBDTC **3a** (Vanlube 7723) was obtained from Vanderbilt Chemicals. Unless otherwise indicated, all the purchased additives were used without prior purification. ZnDTC **5a**, MBDTC **3b** and methylene-bis(dithiophosphate) (MBDTP) **4** were obtained by synthesis (*cf.* § 2.2, § 2.3 and Kiw *et al.*[15]).

2.2. Synthesis of methylene-bis(di-*n*-decyl-dithiocarbamate) 3b

MBDTC **3b** was prepared according to a published procedure.[25] NaOH (1.6 g, 40 mmol, 2.4 eq.) and *n*-didecylamine (5.0 g, 16.8 mmol, 1 eq.) were mixed and dissolved in water (15 mL) at 5 °C. Carbon disulfide (2.3 mL, 38 mmol, 2.3 eq.) was added dropwise under stirring into the reaction mixture and the temperature was kept below 15 °C. Stirring was continued for a further 30 min ($T < 15$ °C). A large excess of methylene chloride (20 mL) was added and the mixture was stirred for 1 h. The crude mixture was then transferred into a separatory funnel and ethyl acetate (100 mL) and water (100 mL) were added. The organic phase was recovered, and the mixture was re-extracted with ethyl acetate (100 mL). The combined organic layers were dried over magnesium sulfate, filtrated and concentrated *in vacuo*. Purification on silica gel using cyclohexane/methylene chloride (90 : 10 v/v) as eluent yielded methylene-bis(di-*n*-decyl-dithiocarbamate) **3b** (5.29 g, 83%) as a red-orange oil.

^{1}H-NMR (500 MHz; $CDCl_3$): 5.40 (2H, s), 3.91 (4H, t, J = 7.8 Hz), 3.60 (4H, t, J = 8.0 Hz), 1.75–1.63 (8H, m), 1.2–1.33 (56H, m), 0.88 (12H, t, J = 6.0 Hz).

^{13}C-NMR (126 MHz; $CDCl_3$): 195.09, 55.78, 53.06, 46.26, 32.03, 29.71, 29.69, 29.66, 29.48, 29.45, 29.37, 27.46, 27.03, 26.98, 26.37, 22.84, 14.28.

Probe-MS (EI, 70 eV): *m*/*z* (relative intensity) 418 (100%), 386 (4), 340 (15), 308 (9), 200 (9), 170 (23), 85 (23). See also Fig. S1 and S2 (ESI†) for detailed ^{1}H- and ^{13}C-NMR spectra of **3a** and **3b** respectively, and Fig. S3 (ESI†) for the mass spectrum of **3b** under EI ionization mode (probe MS).

2.3. Synthesis of methylene-bis(dithiophosphate) 4

The synthesis of MBDTP **4** was carried out to obtain a reference compound for identification purposes (*cf.* § 3.2) because this compound is currently not commercially available. Prior use, ZnDTP **2a** was purified by column chromatography on silica gel eluting first with cyclohexane (2 dead volumes) to remove the base oil, and then with methylene chloride (3 dead volumes) to recover pure ZnDTP **2a**.

Purified ZnDTP **2a** (78 mg, 101 μmol), NaI (14 mg, 93 μmol), CH_2ClBr (100 μL, 193 mg, 1.52 mmol) and MeOH (250 μL) were mixed in a vial which was closed and heated at 60 °C for 6 h, after which CH_2ClBr and MeOH were removed under a flux of argon. NaI (14 mg, 93 μmol), MeOH (250 μL) and toluene (250 μL) were added to the crude mixture which was heated for a further 14.3 h. After cooling to room temperature and addition of water (20 mL), the organic phase was extracted with methylene chloride (20 mL) and washed with water (20 mL), dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The crude extract (66 mg) was purified on silica gel by eluting with a mixture of methylene chloride/cyclohexane (1 : 3 v/v; 25 mL), yielding a fraction (50 mg) containing MBDTP **4** as the predominant constituent as shown by MS analysis. For characterization purposes, an aliquot (14 mg) of this fraction was fractionated by thin layer chromatography (TLC) on silica gel (20 cm × 20 cm; 0.5 mm silica gel thickness) using ethyl acetate/cyclohexane (2.5 : 97.5 v/v) as eluent. The TLC plate was developed twice and the main fraction ($R_f \approx 0.8$) was scrapped off from the plate, yielding *ca.* 7 mg of pure MBDTP **4**.

^{1}H-NMR (500 MHz; $CDCl_3$): 4.27 (2H, t, J = 17.3), 4.06 (4H, m), 3.96 (4H, m), 1.62 (4H, m), 1.39 (8H, m), 1.30 (22H, m), 0.91 (26H, m).

^{13}C-NMR (126 MHz; $CDCl_3$): 70.38, 70.36, 70.32, 70.30, 39.90, 39.88, 39.83, 39.81, 37.17, 37.13, 37.10, 30.07, 30.00, 28.92, 28.89, 23.47, 23.40, 22.97, 14.07, 10.99, 10.96.

Note that there are several signals comprised within a small ppm range for a given carbon atom because the synthesized MBDTP **4** corresponds to a mixture of diastereomers due to the occurrence of an asymmetric centre on the ethylhexyl alkyl chains.

^{31}P-NMR (121 MHz; $CDCl_3$): 93.0 (2P, s) HPLC-MS (APPI, positive mode), *m*/*z* (relative intensity) 721 (100%; $[M + H]^+$), 609 (62), 497 (44), 385 (12), 273 (7). Probe-MS (EI, 70 eV): *m*/*z* (relative intensity) 609 (10%), 497 (48), 385 (92), 273 (100) see also Fig. S4 (ESI†) for ^{1}H- and ^{13}C-NMR spectra of **4**, Fig. S5 and S6 (ESI†) for HPLC-MS chromatogram and mass spectra of **4** under APPI and EI ionization mode (probe MS).

2.4. Laboratory oil ageing experiments

Table 1 shows the starting products and experimental conditions used for the different laboratory oil ageing experiments. 50 g of hydrocarbon base oil containing MoDTC and other additives (1 or 2 wt%, wt% refers to weight percent of the commercial additives) were heated under stirring (1500 rpm) to insure a good homogenization of the temperature within the reaction medium at 135 °C in a multi-necked round-bottomed flask with a constant flow of gas (100 mL min^{-1}) bubbling within the reaction medium using argon or NO_2 in air (2000 ppm) for non-oxidative and thermo-oxidative experiments, respectively. Additionally, thermo-oxidative ageing experiments (NO_2, 2000 ppm in air) were performed on formulated engine oils (oils A and A_{MBDTC}) at 135 °C under stirring (1000 rpm) to insure homogenization of the temperature within the reaction mixture and a good mixing of the oil and the reactive gases during the thermo-oxidative experiments.

In combustion engines, the internal temperature of the lubricating oil is in the range 90–105 °C[26] with significantly higher temperatures at certain zones of the engine lubricating system. The temperature of 135 °C selected for the laboratory

Table 1 Starting products and experimental conditions used for the oil ageing experiments

Experiment	Starting products	Atmosphere	Temperature (°C)
1	MoDTC **1a–1c** + MBDTC **3a**[a]	Argon	135
2	MoDTC **1a–1c** + MBDTC **3a** + ZnDTP **2a**[a]	Argon	135
3	MoDTC **1a–1c** + MBDTC **3a** + ZnDTP **2b**[a]	Argon	135
4	MoDTC **1a–1c** + MBDTC **3b** + ZnDTP **2a**[a]	Argon	135
5	MoDTC **1a–1c** + MBDTC **3a** + ZnDTC **5a**[a]	Argon	135
6	MoDTC **1a–1c** + MBDTC **3a**[a]	NO_2[b]	135
7	Formulated oil A	NO_2[b]	135
8	Formulated oil A_{MBDTC}	NO_2[b]	135

[a] In hydrocarbon base oil. [b] 2000 ppm NO_2 in air.

experiments thus corresponds to a compromise taking into account the occurrence of hot spots in the engine. In this respect, temperatures up to 160 °C are generally reported in the literature for lubricant ageing experiments.[14,27,28]

For the different experiments, the starting products were dissolved in the hydrocarbon oil base (50 g). Aliquots of oil samples (1 mL) were collected at 1 h intervals through a septum using a syringe for analysis by HPLC-MS and for tribological tests. The first sample was collected when the oil mixture reached 135 °C (defined as $T = 0$ h). In the case of the experiments carried out under NO_2 in air, the oil mixtures were first heated up to 135 °C under argon bubbling, and then argon was replaced by 2000 ppm of NO_2 in air.

2.5. Reaction between MBDTC 3a and ZnDTP 2a (neat mixture)

A mixture of MBDTC **3a** (275 mg, 0.65 mmol) and purified primary ZnDTP **2a** (500 mg, 0.65 mmol; see § 2.3 for the purification of **2a**) was vacuum-sealed in a glass tube which was heated at 150 °C for 8 h. An aliquot (5 mg) of the mixture was dissolved in $CDCl_3$ for NMR analysis (^1H, ^{13}C, ^{31}P) and another aliquot (*ca.* 1 mg) of the reaction mixture was dissolved in *n*-heptane/isopropanol (95 : 5 v/v; 1 mL) for HPLC-MS analysis.

2.6. High pressure liquid chromatography-mass spectrometry (HPLC-MS) analyses

MoDTC involved in oil ageing experiments were analyzed by HPLC-MS using an Agilent HP 1100 series HPLC instrument equipped with an auto-injector and connected to a Bruker Esquire 3000^{Plus} ion trap mass spectrometer with an atmospheric pressure photoionization (APPI) source operating in the positive mode as described in Kiw *et al.*[15] Sample preparation and quantification of MoDTC derivatives were carried out as described in Kiw *et al.*[15] It is worth noting that under the analytical conditions developed by Kiw *et al.*,[15] ZnDTP derivatives could not be detected.

3. Results

3.1. Interactions between MoDTC and MBDTC

DTC transfer reactions were investigated by means of laboratory oil ageing experiments involving MBDTC **3a** (2 wt%) and MoDTC **1a–1c** (1 wt%) in solution in a hydrocarbon base oil under argon bubbling at 135 °C for 18 h (Experiment 1, Table 1). Complementary experiments were performed using primary and secondary ZnDTP (**2a** and **2b**, respectively, 1 wt%; experiments 2 and 3, Table 1) in order to evaluate the role of Zn species in the interactions between MBDTC **3a** and MoDTC **1a–1c**. An experiment was also performed using the synthesized MBDTC **3b** bearing C_{10} alkyl chains instead of the commercial MBDTC **3a** bearing C_4 alkyl chains (Experiment 4, Table 1). In addition, DTC exchange reactions between MoDTC **1a–1c** and MBDTC **3a** were investigated in the presence of ZnDTC **5a** (Experiment 5, Table 1) and under NO_2 in air (Experiment 6, Table 1). Experiments were also carried out with fully formulated engine oils (oils A and A_{MBDTC}; see § 2.1) under thermo-oxidative conditions (Experiments 7 and 8, Table 1). Identification and monitoring of the evolution of the concentration of the various MoDTC derivatives and of the newly-formed products were performed by HPLC-MS.

3.1.1. Reaction between MoDTC and MBDTC. For the experiments involving MoDTC **1a–1c** and MBDTC **3a**, ligand transfer reactions only took place to a limited extent, resulting in the moderate formation of MoDTC **1d** and **1e** after 18 h and a slight decrease of the concentration of the MoDTC substrates **1a–1c** (Fig. 2). According to their protonated $[M + H]^+$ ions in HPLC-MS analysis, compounds **1d** and **1e** were shown to correspond to "mixed" MoDTC species bearing one DTC ligand with C_8 or C_{13} alkyl chains from the genuine MoDTC substrates **1a–1c** and a second DTC ligand bearing C_4 alkyl chains

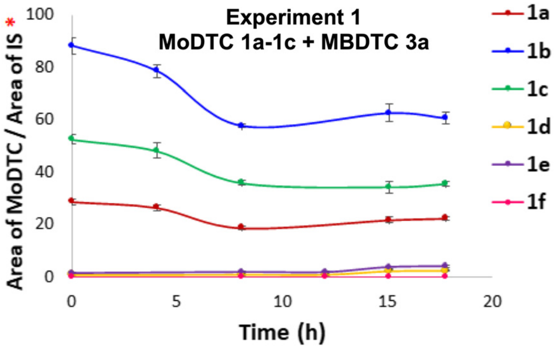

Fig. 2 Evolution of the concentrations of MoDTC **1a–1c** and of the newly formed MoDTC **1d–1f** bearing DTC ligands with C_4 chains in an experiment involving MoDTC **1a–1c** and MBDTC **3a** in hydrocarbon base oil under argon bubbling (Experiment 1, Table 1). IS: internal standard. **Y*-axis: arbitrary units. Error bars correspond to triplicate HPLC-MS analyses for each sample.

originating from MBDTC **3a** (*cf.* Fig. S7, ESI† for the HPLC chromatograms and mass spectra of MoDTC **1d** and **1e**). In contrast to the results obtained by Kiw *et al.*[23] during engine tests involving MoDTC **1a–1c** and MBDTC **3a** in a formulated oil, the MoDTC species bearing two DTC ligands with C_4 alkyl chains (**1f**) was not detected, thus showing that, under these conditions, the transfer of DTC from MBDTC to MoDTC was rather limited.

3.1.2. Reaction between MoDTC and MBDTC in the presence of ZnDTP.

The potential role of ZnDTP – a widely used anti-wear additive in formulated engine oils – in the interactions between MoDTC and MBDTC was investigated by heating MoDTC **1a–1c** (1 wt%), MBDTC **3a** (2 wt%) and ZnDTP (**2a** or **2b**, 1 wt%) in hydrocarbon base oil at 135 °C under argon atmosphere (Experiments 2 and 3, Table 1).

In contrast to the experiment carried out without ZnDTP (*cf.* § 3.1.1.), the progressive formation of a yellowish precipitate in the reaction mixture over time was observed in the presence of both primary and secondary ZnDTP (see Fig. S8, ESI† for the visual aspect of the reaction mixture for the experiment with primary ZnDTP **2a**). This precipitate was retrieved by filtration from the reaction mixture, dissolved in *n*-heptane/isopropanol (95 : 5 v/v; 1 mL) and analysed using APPI-MS and Probe EI-MS in the case of the reaction with primary ZnDTP **2a** (Fig. S9, ESI†). It could be determined that the precipitate corresponded predominantly to MoDTC **1f** and MoDTC **1d–1e** to a minor extent. The shorter alkyl chains (C_4H_9) of the DTC ligands as compared to those from the starting MoDTC **1a–1c** are likely to be responsible for the lower solubility of the newly-formed MoDTC complexes **1d–1f** (notably in the case of **1f**) in the hydrocarbon base oil and thereby explaining their progressive precipitation in the hydrocarbon base oil. These complexes (**1d–1f**) result from DTC exchange reactions between MoDTC **1a–1c** and MBDTC **3a**. In the present experiment, the formation of a precipitate suggests that the yield of this exchange was obviously significantly increased as compared to the experiments performed without ZnDTP and could be explained by the fact that ZnDTP species is involved in the DTC exchange reaction between MBDTC and MoDTC.

In parallel, based on HPLC-MS analysis, the formation of mono- and di-sulfurized analogues of all the MoDTC species present in the reaction mixture was observed (compounds **1S-1a–1f** and **2S-1a–1f**; see Fig. S10, ESI† for the quantification results of **1S-1d–1f** and **2S-1d–1f**). They result from the sulfurization of MoDTC induced by ZnDTP, their occurrence and mode of formation being described in Kiw *et al.*(2022).[16] In the following discussion, since DTC exchange reaction is the focus of the present article, the sulfurized analogues of MoDTC will not be considered further, although they can represent up to 47% and 18% of the transformation products of the initial MoDTC in the case of the experiments involving secondary ZnDTP **2b** and primary ZnDTP **2a**, respectively (see Fig. S11, ESI†).

As a result, the relative concentrations of the MoDTC substrates **1a–1c** significantly decreased with time in the presence of both primary and secondary ZnDTP (Fig. 3). Meanwhile, the concentration of the newly formed MoDTC complexes **1d** and **1e** increased during heating but tended to slowly decrease afterwards (Fig. 3), whereas those of the MoDTC complex **1f** increased initially with time and seemed to reach a plateau between 15 and 18 h (Fig. 3).

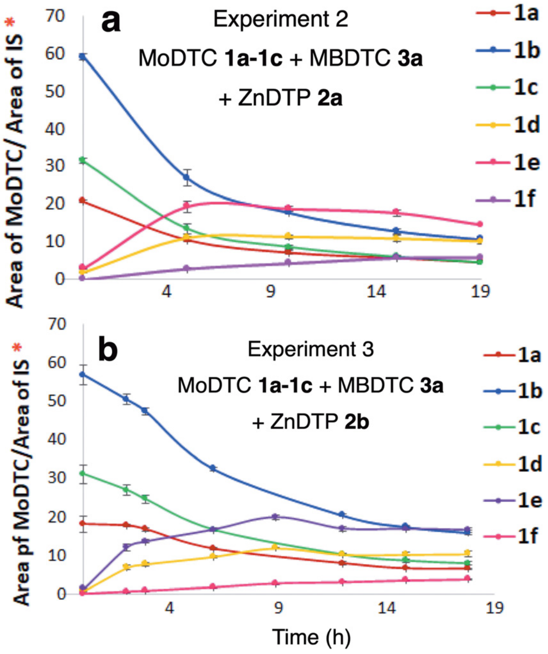

Fig. 3 Evolution of the concentrations of MoDTC **1a–1c** and of the newly formed MoDTC **1d–1f** during the experiments involving MoDTC **1a–1c** and MBDTC **3a** in the presence of (a) primary ZnDTP **2a** (Experiment 2, Table 1) and (b) ZnDTP **2b** (Experiment 3, Table 1). IS: internal standard. **Y*-axis: arbitrary units. Error bars correspond to triplicate HPLC-MS analyses for each sample.

The progressive decrease of the concentration of MoDTC **1d** and **1e** can be partly explained by the fact that these species correspond to the intermediate MoDTC species that are ultimately transformed into MoDTC **1f.** In addition, it could be shown that the precipitate formed during the experience corresponded to a mixture of MoDTC **1d–1f** (see above), which indicates that a noticeable part of the newly-formed MoDTC bearing C_4-alkyl chains – and notably MoDTC **1f**- escaped from the pool of the samples collected (in solution) for quantitative analysis throughout the experiment.

3.1.3. Comparison between secondary and primary ZnDTP.

The formation rates of MoDTC **1d** and **1e** were similar in the experiments involving primary (**2a**) and secondary (**2b**) ZnDTP (Fig. 4a and b; red and blue colours) whereas the formation of the MoDTC complex **1f** after 18 h was slightly slower in the experiment involving secondary ZnDTP **2b** (Fig. 4c).

However, as pointed out previously, it is worth noting that the formation of a precipitate containing predominantly the MoDTC **1f** (*cf.* Fig. S9, ESI†) during the experiments prevented a precise quantification to be made. By comparison, in the absence of ZnDTP, the MoDTC complexes **1d** and **1e** were formed at a significantly slower rate (Fig. 4a and b, green colour), and MoDTC **1f** was not formed at all (Fig. 4c, green colour). It should be noted that an oil ageing experiment involving MoDTC **1a–1c**, MBDTC **3a**,

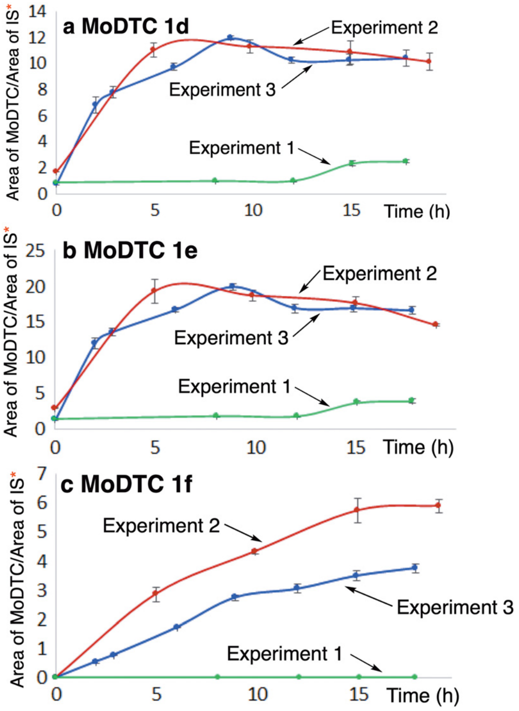

Fig. 4 Evolution of the concentrations of the newly formed MoDTC (a) **1d** (b) **1e** and (c) **1f** during the experiments involving: (i) green colour: MoDTC **1a–1c** and MBDTC **3a** (Experiment 1, Table 1); (ii) blue colour: MoDTC **1a–1c**, MBDTC **3a** and secondary ZnDTP **2b** (Experiment 3, Table 1); (iii) red colour: MoDTC **1a–1c**, MBDTC **3a** and primary ZnDTP **2a** (Experiment 2, Table 1). IS: internal standard. *Y-axis: arbitrary units. Error bars correspond to triplicate HPLC-MS analyses for each sample. The initial concentrations of the substrates for the experiments were: MoDTC: 1 wt%; MBDTC: 2 wt%; ZnDTP: 1 wt% (if present).

and Zn(acac)$_2$ – another Zn(II) species – in a hydrocarbon base oil under argon atmosphere at 135 °C also resulted in the formation of the new MoDTC complexes **1d**-**1f** (results not shown).

3.1.4. Role of the alkyl chain length of MBDTC on the DTC transfer reactions between MBDTC and MoDTC. Since the formation of MoDTC complexes with C$_4$ alkyl chain substituents resulted in their partial precipitation in the reaction mixture –thus distorting the quantification results – (*cf.* § 3.1.2.), a similar oil-ageing experiment involving MoDTC **1a–1c** (1 wt%) and primary ZnDTP **2a** (1 wt%) in the presence of the C$_{10}$-substituted MBDTC **3b** (see § 2.2.) instead of MBDTC **3a** (Experiment 4, Table 1) was performed, longer alkyl chains on MBDTC **3b** as compared to those from MBDTC **3a** likely resulting in a better solubilisation of the newly-formed MoDTC species in the hydrocarbon base oil. Again, the neoformation of MoDTC complexes bearing C$_{10}$ alkyl chains **1g–1i** was evidenced using HPLC-MS analysis (Fig. 5 and Fig. S12, ESI†) as a result of DTC transfer reactions from MBDTC **3b** to MoDTC **1a–1c**.

As expected, no precipitate was formed during the experiment (Fig. S13, ESI†), and HPLC-MS quantification showed the concomitant decrease of the concentration of the MoDTC substrates **1a–1c** (Fig. 5c) together with the progressive increase in concentration of the MoDTC complexes **1g–1i** over time (Fig. 5d) as was observed in the case of the experiment with MBDTC **3a** (Fig. 5a and b).

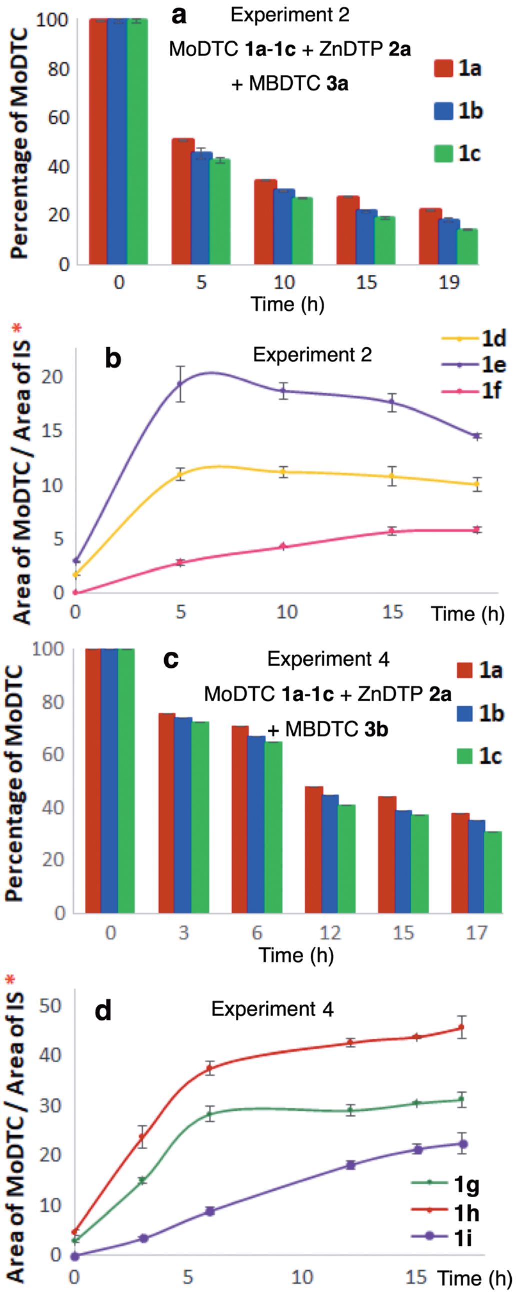

Fig. 5 Evolution (a and c) of the relative abundance of MoDTC substrates **1a–1c** and (b and d) of the concentrations of the newly formed MoDTC complexes **1d–1i** during the experiments involving MoDTC **1a–1c**, MBDTC **3a** and primary ZnDTP **2a** (Experiment 2, Table 1) and MoDTC **1a–1c**, MBDTC **3b** and primary ZnDTP **2a** (Experiment 4, Table 1). IS: internal standard. *Y-axis: arbitrary units. Error bars correspond to the triplicate HPLC-MS analyses of each sample.

3.1.5. Interactions between MoDTC, ZnDTC and MBDTC. The role of zinc dithiocarbamates (ZnDTC) – another type of Zn complex bearing DTC ligands – in the DTC transfer reactions between MBDTC **3a** and MoDTC **1a–1c** was also investigated. For this purpose, an oil ageing experiment involving MoDTC **1a–1c** – with C$_8$ and C$_{13}$ DTC ligands – (1 wt%), MBDTC **3a** – with C$_4$ DTC moieties – (2 wt%) and ZnDTC **5a** – with C$_{10}$ DTC

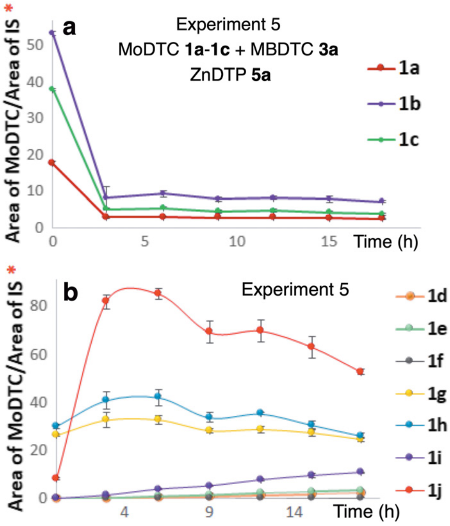

Fig. 6 Evolution of the concentrations of (a) MoDTC substrates **1a–1c**; (b) newly formed MoDTC complexes **1d–1j** during an experiment involving MoDTC **1a–1c**, MBDTC **3a** and ZnDTC **5a** (Experiment 5, Table 1). IS: internal standard. **Y*-axis: arbitrary units. Error bars correspond to triplicate HPLC-MS analyses for each sample.

ligands – (1 wt%) in a hydrocarbon base oil was carried out under argon atmosphere at 135 °C for a period of 18 h (Experiment 5, Table 1). As a result, new MoDTC complexes with DTC ligands bearing C_4 alkyl chains (MoDTC **1d–1f**), C_{10} alkyl chains (MoDTC **1g–1i**) and a mixture of both (MoDTC **1j**) were detected by HPLC-MS (Fig. 6 and Fig. S14, ESI†).

These compounds were formed by DTC exchange reactions between the MoDTC **1a–1c**, MBDTC **3a** and ZnDTC **5a**. Accordingly, during the first 3 h of experiment, a rapid decrease of the concentrations of the MoDTC substrates **1a–1c** over time was observed (Fig. 6a) paralleling the progressive formation of the ligand exchange products **1g–1i** (Fig. 6b).

3.2. Investigation of the interactions between MBDTC 3a and ZnDTP 2a

In order to get a better understanding of the role of ZnDTP in accelerating the DTC transfer reactions between MBDTC and MoDTC species, the interactions between MBDTC and ZnDTP were investigated by ^{1}H- and ^{13}C-NMR spectroscopy as well as by HPLC-MS. For this purpose, MBDTC **3a** was mixed with ZnDTP **2a** in a 1 : 1 molar ratio without further dilution, vacuum sealed in a glass tube and heated at 150 °C for a period of 8 h prior analysis.

NMR analysis of the reaction mixture after 8 h at 150 °C showed that the ^{1}H chemical shifts of the protons on the methylene groups adjacent to the functional groups (α-OP or α-N) of the substrates ZnDTP **2a** and MBDTC **3a**, and of the compounds postulated to be formed during the DTC exchange reaction (*i.e.*, ZnDTC **5b**, methylene-bis(dithiophosphate) (MBDTP) **4** and the mixed species with DTP/DTC ligands or moieties; Fig. 7) are all in a range comprised between 3.0–5.5 ppm (Fig. 8).

Since MBDTP **4** was not commercially available, it was specifically synthesized (*cf.* § 2.3) in order to obtain reference ^{1}H- and ^{13}C-NMR spectra. The differences in the ^{1}H chemical shifts of the signals of these compounds in the 3.0–5.5 ppm range as well as the interpretation of their integral values allowed the educts and the various products formed by reaction between ZnDTP **2a** and MBDTC **3a** to be distinguished. The 4 methylene groups adjacent to the functional groups of ZnDTP **2a** (resp. ZnDTC **5a**) have the same chemical shift due to symmetry reason and only 1 multiplet is observed for these protons at 4.07 ppm for **2a** (resp. 3.75 ppm for **5b**) (Fig. 8a and b). In the case of MBDTC **3a**, the two alkyl chains on the same DTC moiety are not equivalent because of the limited rotation around the C–N bond. As a result, two signals at 3.93 and 3.61 ppm are observed for the methylene groups adjacent to the N–CS_2 bonds of **3a**. The signal observed at 5.37 ppm (Fig. 8c) corresponds to the protons from the central methylene group.

In the case of MBDTP **4**, all the methylene groups located α to the O–P bond are identical. The two protons on these methylenes are however not equivalent because of the presence of an asymmetric center at C-2 (2-ethylhexyl alkyl chains), thus explaining the presence of two multiplet signals (H_b and H_c, Fig. 8d) at 3.96 and 4.05 ppm. The complexity of the coupling pattern can be explained by the occurrence of ^3J P–H couplings in addition to the ^2J and ^3J H–H couplings. Similarly, the signal at 4.30 ppm (H_a, Fig. 8d) which corresponds to the methylene linked to the two dithiophosphate moieties appears as a triplet because of the ^3J couplings with both P atoms (see Fig. S15, ESI† for the partial P-decoupled ^{1}H-NMR spectrum of MBDTP **4**).

The partial disappearance of the substrates ZnDTP **2a** and MBDTC **3a**, and the formation of new compounds was observed on the ^{1}H-NMR spectrum of the mixture after 8 h of heating at 150 °C (Fig. 9).

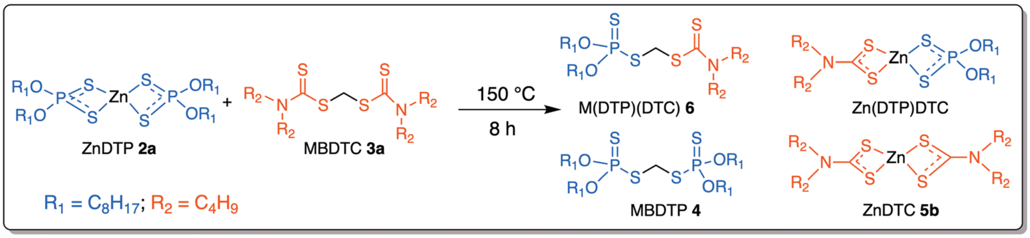

Fig. 7 Ligand exchange reactions between ZnDTP **2a** and MBDTC **3a** potentially leading to the formation of different compounds bearing DTP and DTC moieties or ligands.

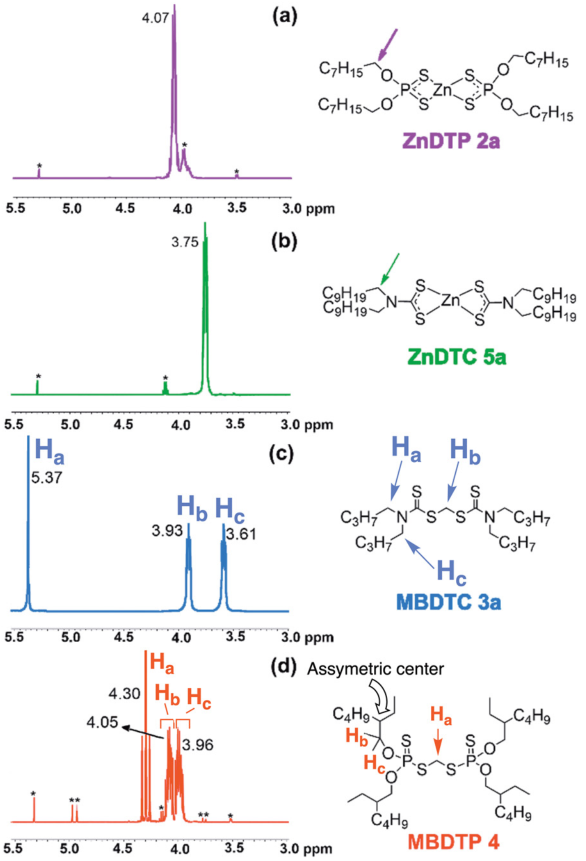

Fig. 8 Partial ^1H-NMR spectra (3.0–5.5 ppm, 500 MHz, $CDCl_3$) of reference compounds (a) ZnDTP **2a**, (b) ZnDTC **5a**, (c) MBDTC **3a** and (d) MBDTP **4**. *: impurities.

The newly formed compounds could be identified based on the comparison of the ^1H-NMR spectra of the reaction mixture (Fig. 9) and of reference compounds (Fig. 8 and Kiw *et al.*[15] – Fig. S5, ESI†). Thus, the signal at 3.75 ppm (Fig. 9, green colour) presents chemical shifts and a coupling pattern comparable with that of the methylene groups located on α position to the N–CS_2 bonds of ZnDTC **5a** bearing *n*-decyl alkyl chains (Fig. 8b and Kiw *et al.*[15] – Fig. S5, ESI†). It is, therefore, most likely that it corresponds to ZnDTC **5b** with DTC ligands bearing C_4 alkyl chain originating from MBDTC **3a**. The formation of MBDTP **4** was evidenced by the appearance of a triplet at 4.27 ppm (Fig. 9, red colour) which is similar to that of the central methylene group of the reference synthetic compound (Fig. 8d and Fig. S4, ESI†). In addition, the signals at 4.02 and 3.93 ppm are also compatible with those of the methylene groups adjacent to the O–P bonds of MBDTP **4**. However, integration of these signals suggests that they are superimposed with the signals of other compounds present in the mixture as discussed below.

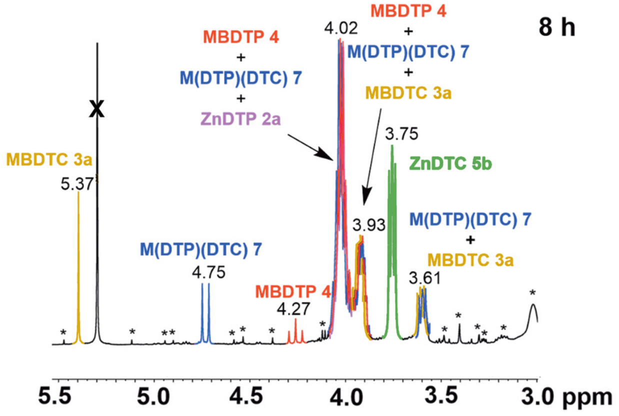

Fig. 9 Partial ^1H-NMR spectrum (3.0–5.5 ppm, 500 MHz, $CDCl_3$) of the mixture obtained after 8 h of heating at 150 °C of MBDTC **3a** and ZnDTP **2a** in a 1 : 1 molar ratio. *: impurities.

The signal at 4.75 ppm (Fig. 9, blue colour), which is absent in the ^1H-NMR spectra of reference compounds (Fig. 8), was attributed to the central methylene group of M(DTP)(DTC) **6** bearing mixed DTP/DTC moieties. Indeed, this chemical shift has an intermediate value between that of the methylene group from MBDTC **3a** and MBDTP **4**. In addition, this signal appears as a doublet due to the coupling of the protons from the central methylene group with one P atom from the dithiophosphate moiety. The chemical shifts of the methylene groups located on α position to the N–CS_2 and O–P bonds of M(DTP)(DTC) **6** are expected to be similar or even identical to those of the MBDTC **3a** and MBDTP **4**, respectively, and most likely contribute to the signals at 4.02, 3.93 and 3.61 ppm (Fig. 9, blue colour). By interpreting the integrated areas of the signals at 5.37, 4.75 and 4.27 ppm in (Fig. 9), around 45% of MBDTC **3a**, 38% of M(DTP)(DTC) **6** and 16% of MBDTP **4** were formed after 8 h of reaction between MBDTC **3a** and ZnDTP **2a**. The mixed Zn(DTC)(DTP) complex was also expected to be formed during the reaction, but was however not detected by NMR at room temperature because the ligand exchange between the different forms of Zn complexes is too rapid on the NMR time scale.[16]

In addition to this NMR study, HPLC-MS analysis of the mixture recovered after 8 h revealed the presence of a newly-formed compound showing a mass spectrum with $[M + H]^+$ at *m*/*z* 721 identified as MBDTP **4** based on the comparison with the mass spectrum and retention time of synthetic MBDTP **4** (see § 2.3). As mentioned earlier (*cf.* § 2.6), it is worth noting that under the currently used HPLC-MS analytical conditions, ZnDTP, ZnDTC and Zn(DTP)(DTC) species cannot be detected.

By combining the ^1H, ^{13}C NMR and HPLC-MS results, it clearly appears that partial DTC/DTP exchange reactions took place between MBDTC **3a** and ZnDTP **2a** at high temperatures (150 °C), leading to the formation of ZnDTC **5b**, MBDTP **4** and mixed M(DTP)(DTC) **6**. In this respect, the formation of the intermediate ZnDTC species in this process may be central to the transfer of DTC from MBDTC to MoDTC in the presence of ZnDTP since ZnDTC have been shown to exchange ligands with MoDTC (see above and Kiw *et al.*[15]). Possibly due to the relative inertness of MoDTC, this exchange is extremely slow at room temperature. The reaction is faster (although not immediate) at 135 °C, the equilibrium between MoDTC and ZnDTC being reached relatively rapidly.[15]

3.3. Effect of NO_2 on the interactions between MoDTC and MBDTC under laboratory conditions

The interactions between MoDTC and MBDTC in the absence of ZnDTP was also investigated under thermo-oxidative conditions at the laboratory scale. To this aim, an oil ageing experiment was carried out using MoDTC **1a–1c** and MBDTC **3a** under a flow of NO_2 in air (2000 ppm) at 135 °C. Monitoring of the evolution of the reaction mixture with time by HPLC-MS showed that the relative concentrations of the initial MoDTC **1a–1c** decreased, mainly due to thermo-oxidative degradation and to DTC transfer reactions with MBDTC **3a** (Fig. 10a).

Indeed, MoDTC **1d–1f** bearing C_4 DTC ligands originating from MBDTC were formed and their concentrations increased gradually during the oil ageing experiment despite the absence of Zn derivatives (Fig. 10b). As pointed out in Section 3.1.1, when a similar reaction medium was used, but under inert atmosphere (Experiment 1, Table 1), MoDTC **1d–1e** were formed in extremely low amounts, MoDTC **1f** being even undetectable under these conditions. These results suggest that, in the absence of ZnDTP, the DTC transfer reactions between MBDTC and MoDTC take place at a faster rate under oxidative conditions than under non-oxidative conditions. The former conditions are thus able to induce the release of DTC from MBDTC which then become available for complexing the metal core of Mo species ($Mo_2O_2S_2$ or Mo oxysulfides) and to replace the ligands from degraded MoDTC upon oxidation.

3.4. Effect of MBDTC on the enhanced persistence of MoDTC in formulated lubricants under thermo-oxidative laboratory conditions

Previous studies have shown that during engine tests, the presence of MBDTC **3a** in a formulated oil (oil A_{MBDTC}) resulted in an enhanced persistence of MoDTC and extended significantly the friction reducing capability of this oil as compared to the same oil devoid of MBDTC 3a (oil A).[23] The predominant MoDTC remaining at the end of the engine test (after 143 h) comprised mainly MoDTC **1d–1f** with C_4 alkyl chains formed by the progressive replacement of the genuine DTC ligands from MoDTC educts by DTC released from MBDTC. In order to determine the mechanisms involved in this enhanced persistence of MoDTC in the presence of MBDTC, a simplified – as compared to an engine complex system – laboratory model was set up. To this aim, the thermo-oxidative conditions undergone by lubricant additives from the same two formulated engine oils (oil A et A_{MBDTC}) were simulated using oil ageing experiments under bubbling with a blend of 2000 ppm NO_2 in air at 135 °C (Experiments 7 and 8, Table 1).

Fig. 11 shows the evolution of the relative concentrations of MoDTC **1a–1c** substrates in the oils A and A_{MBDTC} during the laboratory ageing experiments.

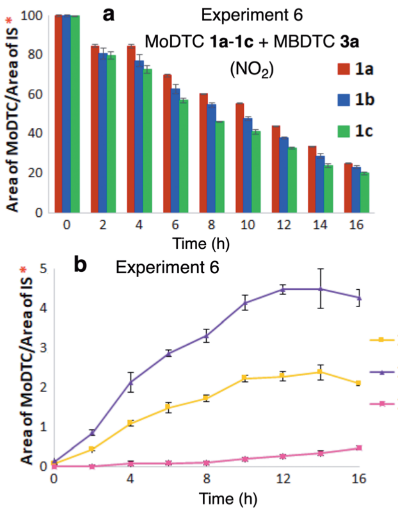

Fig. 10 Evolution of the concentrations of (a) MoDTC **1a–1c** and of (b) the newly formed MoDTC **1d–1f** during the experiment involving MoDTC **1a–1c** and MBDTC **3a** under thermo-oxidative conditions (Experiment 6, Table 1). IS: internal standard. *Y-axis: arbitrary units. Error bars correspond to triplicate HPLC-MS analyses for each sample.

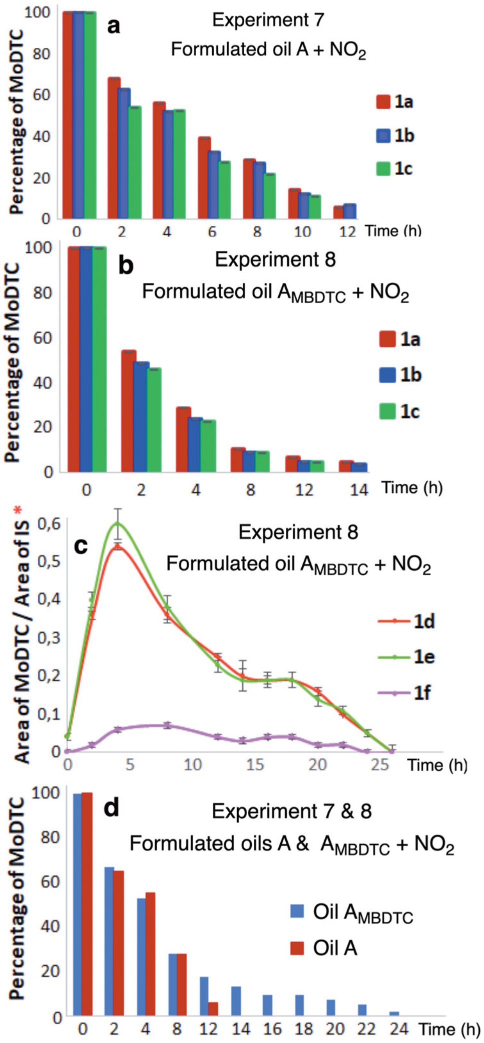

Fig. 11 Evolution of the relative abundance of MoDTC species in formulated engine oils during laboratory ageing experiments (Experiments 7 and 8, Table 1) under thermo-oxidative conditions: (a) MoDTC **1a–1c** in oil A; (b) MoDTC **1a–1c** in oil A_{MBDTC}; (c) newly formed MoDTC complexes **1d–1f** in oil A_{MBDTC}; (d) summed MoDTC **1a–1f** in oil A (red colour) and A_{MBDTC} (blue colour). IS: Internal standard. *Y-axis: arbitrary units. Error bars correspond to triplicate HPLC-MS analyses for each sample.

Upon oil ageing, the MoDTC substrates **1a–1c** decreased progressively over time in both oils, and were completely consumed between 12–14 h in oil A and between 14–16 h in oil A_{MBDTC}. However, in the case of the oil A_{MBDTC}, newly formed MoDTC complexes **1d–1f** were detected, their relative concentrations increasing during the first 4 h (Fig. 11c), and then decreasing gradually before being totally consumed between 24–26 h. The formation of the MoDTC complexes **1d–1f** in oil A_{MBDTC} ascertained the occurrence of ligand transfer reactions between MBDTC **3a** and MoDTC **1a–1c**. The whole MoDTC complex pool in oil A_{MBDTC} (summed MoDTC **1a–1f**) decreased gradually over time, but MoDTC were completely consumed much later than in the case of the oil A (*i.e.*, between 24–26 h *vs.* 12–14 h).

These results clearly show that MoDTC complexes persisted for a longer period of time in oil A_{MBDTC}. Since both oils were of similar composition, except for the additional presence of MBDTC in oil A_{MBDTC}, this enhanced persistence can most likely be attributed to DTC transfer reactions from MBDTC **3a** to the partially degraded MoDTC substrates **1a–1c** or to the metal cores of Mo complexes ($Mo_2O_2S_2$ or Mo oxysulfides) remaining after thermo-oxidative degradation of the initial DTC ligands. The results of these two laboratory experiments are in good agreement with those obtained previously in the case of engine tests involving oils A and A_{MBDTC} under engine operating conditions.[23]

4. Discussion

DTC transfer reactions between MBDTC and MoDTC have been unambiguously evidenced by HPLC-MS analysis and NMR spectroscopy, and laboratory experiments have shown that these reactions appear to be induced by the presence of Zn(II) complexes such as ZnDTP and $Zn(acac)_2$. The Lewis acid properties of Zn(II) complexes as well as the capacity of Zn(II) to bind to sulfur atoms and, in particular, to activate dithioacetals, have been previously reported in other contexts.[29,30] Therefore, in the case of the experiments involving MBDTC and ZnDTP, Zn(II) ions are likely to act as Lewis acids, being able to activate C–S bonds from MBDTC towards nucleophilic attack (Fig. 12). The dithiophosphate ions from ZnDTP **2a**, which are good nucleophilic species, could then attack the central methylene group of MBDTC **3a** and substitute their DTC moieties, thus leading to the release of ZnDTC **5b** and to the formation of methylene-bis(dithiophosphate) **4** together with the mixed methylene-(dithiophosphate)(dithiocarbamate) species **6** (*cf.* § 3.2). In the case of the experiments involving other Zn(II) species such as $Zn(acac)_2$ or ZnDTC **5a**, nucleophiles other than dithiophosphates available in the reaction medium comprising OH^- or DTC could also attack the central methylene group of MBDTC, leading to the release of DTC from MBDTC to form ZnDTC species.

If Zn(II) species, and notably ZnDTP, were shown to efficiently promote the release of DTC from MBDTC and most likely play a significant role in this process in formulated engine lubricants, ZnDTP are highly sensitive to oxidation and dithiophosphates were shown to be rapidly degraded during engine tests or laboratory experiments.[20,31] Therefore, although Zn(II) ions most likely remain available during ageing of lubricants under thermo-oxidative conditions, dithiophosphates progressively disappear and other species such as, for instance, hydroxide ions, thiolates or amines from other additives might intervene as "nucleophilic species" in the release of DTC from MBDTC in the case of altered lubricants as described in Fig. 12.

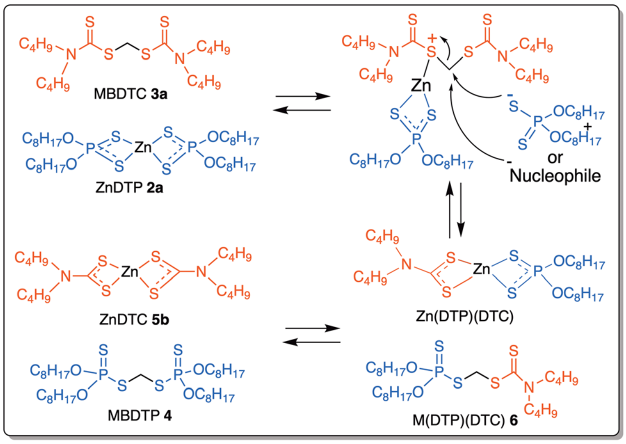

Fig. 12 Proposed mechanism of C–S bond activation of MBDTC by ZnDTP complexes, the latter acting as a Lewis acid that promotes the reaction.

In addition, the results of the laboratory ageing experiments involving MoDTC and MBDTC in a base oil at 135 °C under oxidative conditions (2000 ppm of NO_2 in air) in the absence of any source of Zn(II) (§ 3.3) also showed the progressive formation of MoDTC with ligands originating from MBDTC with the concomitant decrease of the genuine MoDTC species. It therefore seems that the mere thermo-oxidative conditions are capable of inducing the release of DTC from MBDTC which then become available for complexing the metal core of Mo complexes ($Mo_2O_2S_2$ or Mo oxysulfides) and to replace the degraded ligands. The release of DTC from MBDTC under such conditions might proceed *via* a process comprising the oxidation of the sulfur atom from one DTC ligand involved in the dithioacetal bond of MBDTC, followed by the release of the second intact DTC in a process analogous to that described in a different context by Liu and Thayumanavan[32] for dithioacetals under oxidative conditions (Fig. 13).

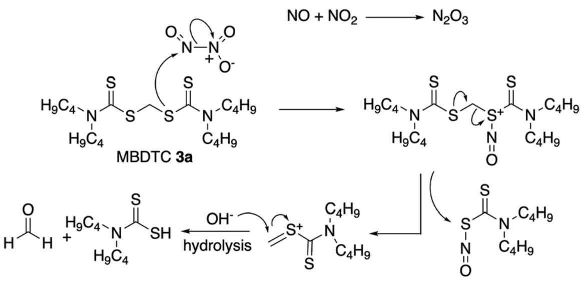

Fig. 13 Proposed oxidative cleavage mechanism of MBDTC under NO_2 (2000 ppm in air). Adapted from Liu and Thayumanavan.[32]

It could thus be demonstrated that the progressive release of DTC from MBDTC induced either by Zn(II) or oxidative conditions insured a progressive supply of ''fresh'' DTC ligand which is potentially able to replace degraded/oxidized DTC ligands on the metal core of Mo complex ($Mo_2O_2S_2$ or Mo oxysulfides) and thus to regenerate the initial structures of MoDTC complexes in lubricants. This process might therefore allow the enhanced persistence of MoDTC ensuring friction reduction properties of engine lubricants for extended periods.

In addition to MBDTC, it appears that ZnDTC also easily exchange their DTC ligands towards altered Mo species. However, MBDTC represent better ''provider'' of DTC ligands than ZnDTC for altered MoDTC in lubricants, since ZnDTC are highly oxidizable and thus decompose easily upon oxidation to form disulfides (thiurams) or other degradation products. Such is not the case with MBDTC, DTC occurring as dithioacetals and being likely more resistant towards oxidative processes. DTC can thus be potentially released in the engine oil following a delayed/controlled process, providing progressively fresh DTC for the regeneration of MoDTC complexes.

5. Conclusion

The extension of friction reducing properties of engine oils for longer periods of time plays an important role in energy saving and in coping with global environmental problems. The control of thermo-oxidative degradation of Mo-based friction modifiers in formulated engine oils upon engine functioning remains a key challenge to achieve this objective. In this context, a preliminary study has shown that the interactions between MoDTC and MBDTC has a beneficial effect on the life time of MoDTC in engine lubricants and on the persistence of their tribological properties. This effect was associated with DTC transfer reactions between MBDTC and MoDTC and it was assumed that the DTC from MBDTC are progressively transferred to the metal core of MoDTC after oxidative degradation of their ligands. As a result, the concentrations of MoDTC could be preserved at a useful level over extended ageing periods, thus maintaining the friction reducing properties of engine oils.

Additionally, the role of Zn(II) complexes (*e.g.*, ZnDTP, $Zn(acac)_2$) on ligand transfer reactions between MBDTC and MoDTC could be clearly demonstrated in the present study. Thus, Zn(II) ions are likely to act as a Lewis acid that is able to activate the C–S bond cleavage of MBDTC, thus inducing the release of DTC from MBDTC as ZnDTC. The latter then become available for ligand exchange with MoDTC or complexation of the metal core of Mo complexes after oxidative degradation of their initial ligands. In the absence of Zn(II) ions, the release of DTC from MBDTC can also be induced by oxidative processes under thermo-oxidative conditions. DTC from MBDTC thus represent potentially a ''stock'' of DTC ligands which can be progressively released during functioning of the engine and replace ligands from MoDTC educts degraded by thermo-oxidative processes following processes promoted by Zn(II) ions and/or oxidative conditions. The MoDTC species remaining after thermo-oxidative degradation of simple mixtures or of fully formulated lubricants containing MoDTC and MBDTC in an oil base consist mainly of newly formed complexes with DTC ligands originating from MBDTC as was also observed during engine tests in a preliminary study.

The results obtained provide insight in future additive design by considering similar delayed DTC transfer mechanisms demonstrated by MBDTC aimed at extending the functional lifetime of MoDTC. One might, notably, envisage to pursue the investigation of potential structures bearing other types of functionalities liable to allow the progressive release of DTC during engine functioning. The present study that investigated the interactions between MoDTC with other additives at the molecular level can also help to predict the friction reduction efficiency of engine oils as well as to provide guidance for the optimization of MoDTC tribological performance for the future development of engine oils.

Conflicts of interest

There are no conflicts of interest to declare.

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Notes and references

1 S. I. Tseregounis, M. L. McMillan and R. M. Olree, *Engine oil effects on fuel economy in GM vehicles – separation of viscosity and friction modifier effects*, SAE Technical Paper No. 982502, 1998.

2 K. Hoshino, H. Kawai and K. Akiyama, *Fuel efficiency of SAE 5W-20 friction modified gasoline engine oil*, SAE Technical Paper No. 982506, 1998.

3 M. D. Johnson, R. K. Jensen, E. M. Clausing, K. Schriewer and S. Korcek, *Effects of aging on frictional properties of fuel efficient engine oils*, SAE Technical Paper No. 952532, 1995.

4 C. M. Taylor, Automobile engine tribology – design considerations for efficiency and durability, *Wear*, 1998, **221**, 1–8.

5 L. R. Rudnick, *Lubricant additives: chemistry and applications*, CRC Press, Boca Baton, FL, 2nd edn, 2009.

6 J. Graham, H. Spikes and S. Korcek, The friction reducing properties of molybdenum dialkyldithiocarbamate additives: Part I – factors influencing friction reduction, *Tribol. Trans.*, 2001, **44**, 626–636.

7 J. Graham, H. Spikes and R. Jensen, The friction reducing properties of molybdenum dialkyldithiocarbamate additives: Part II – durability of friction reducing capability, *Tribol. Trans.*, 2001, **44**, 637–647.

8 G. Spengler and A. Webber, On the lubricating performance of organic molybdenum compounds, *Chem. Ber.*, 1939, **92**, 2163–2171.

9 C. Grossiord, K. Varlot, J. M. Martin, T. L. Mogne, C. Esnouf and K. Inoue, MoS_2 single sheet lubrication by molybdenum dithiocarbamate, *Tribol. Int.*, 1998, **31**, 737–743.

10 K. Kubo, N. Mitsuhiro, T. Shitamichi and K. Motoyama, *The effect of ageing during engine running on the friction reduction performance of oil soluble molybdenum compounds*, Proceeding of the International Tribology Conference, Yokohama, 1995.

11 M. Shekarriz, An investigation of antioxidant properties of zinc and molybdenum dithiocarbamates in hydrocarbons, *Pet. Sci. Technol.*, 2016, **6**, 109–113.

12 M. De Feo, C. Minfray, M. I. De Barros Bouchet, B. Thiebaut, T. L. Mogne, B. Vacher and J. M. Martin, Ageing impact on tribological properties of MoDTC-containing base oil, *Tribol. Int.*, 2015, **92**, 126–135.

13 M. De Feo, *Impact of thermo-oxidative degradation of MoDTC additive on its tribological performances for steel-steel and DLC-steel contacts*, PhD thesis, Université de Lyon, 2015.

14 M. De Feo, C. Minfray, M. I. De Barros Bouchet, B. Thiebaut and J. M. Martin, MoDTC friction modifier additive degradation: Correlation between tribological performance and chemical changes, *RSC Adv.*, 2015, **5**, 93786–93796.

15 Y. M. Kiw, P. Schaeffer, P. Adam, B. Thiébaut, C. Boyer and G. Papin, Ligand exchange processes between molybdenum and zinc additives in lubricants: evidence from NMR (^1H,^{13}C,^{31}P) and HPLC-MS analysis, *RSC Adv.*, 2020, **10**, 37962–37973.

16 Y. M. Kiw, P. Schaeffer, P. Adam, B. Thiébaut and C. Boyer, Molecular evidence for sulfurization of molybdenum dithiocarbamates (MoDTC) by zinc dithiophosphates: a key process in their synergetic interactions and the enhanced preservation of MoDTC in formulated lubricants?, *RSC Adv.*, 2022, **12**, 3545–3553.

17 Y. Sogawa, N. Yoshimura and O. Iwasaki, *R&D on new friction modifier for lubricant for fuel economy improvement*, Japan Petroleum Energy Centre Report, 1999, E1.1.5.

18 T. M. Shea and A. J. Stipanovic, Solution phase reactions of organomolybdenum friction modifier additives for energy conserving engine oils, *Tribol. Lett.*, 2002, **12**, 13–22.

19 R. K. Jensen, M. D. Johnson, S. Korcek and M. J. Rokosz, Friction-reducing and antioxidant capabilities of engine oil additive systems under oxidative conditions. I. Effects of ligand exchange between molybdenum dialkyldithiocarbamate and zinc dialkyldithiophosphate in hexadecane, *Lubr. Sci.*, 1998, **10**, 99–120.

20 H. Spikes, The history and mechanisms of ZDDP, *Tribol. Lett.*, 2004, **17**, 469–489.

21 A. Morina, A. Neville, M. Priest and J. H. Green, ZDDP and MoDTC interactions in boundary lubrication – The effect of temperature and ZDDP/MoDTC ratio, *Tribol. Int.*, 2006, **39**, 1545–1557.

22 A. Neville, A. Morina, T. Haque and M. Voong, Compatibility between tribological surfaces and lubricant additives – How friction and wear reduction can be controlled by surface/lube synergies, *Tribol. Int.*, 2007, **40**, 1680–1695.

23 Y. M. Kiw, P. Adam, P. Schaeffer, B. Thiébaut, C. Boyer and N. Obrecht, Molecular evidence for improved tribological performances of MoDTC induced by methylene-(bisdithiocarbamates) in engine lubricants, *RSC Adv.*, 2022, **12**, 23083–23090.

24 A. Somayaji and P. B. Aswath, The role of antioxidants on the oxidation stability of oils with F-ZDDP and ZDDP, and chemical structure of tribofilms using XANES, *Tribol. Trans.*, 2011, **52**, 511–525.

25 B. Jover, J. Forstner, J. Petro, S. Szoboszlay, I. Fekete, K. Csergo, G. Sztreharszki, G. Raksi, J. Kiss, F. Miko, J. Baladincz and J. Toth, Process for manufacturing methylene-bis(dibutyl-dithiocarbamate) with ASTM colour less than 2, *US Pat.*, 5744629A, 1998.

26 A. F. A. Rasid, T. I. Mohamad, M. J. Ghazali and W. M. F. W. Mahmood, Effect of lubricant temperature in a motorized engine, *World Appl. Sci. J.*, 2012, **20**, 927–930.

27 R. K. Jensen, S. Korcek and M. D. Johnson, Friction-reducing and antioxidant capabilities of engine oil additive systems under oxidative conditions. II. Understanding ligand exchange in a molybdenum dialkyldithiocarbamate zinc dialkyldithiophosphate additive system in various base oils, *Lubr. Sci.*, 2001, **14**, 25–42.

28 A. Ponjavic, T. Lemaigre, M. Southby and H. A. Spikes, Influence of NOx and air on the ageing behaviour of MoDTC, *Tribol. Lett.*, 2017, **65**, 52, DOI: **10.1007/s11249-017-0836-6**.

29 M. H. Salter, J. H. Reibenspies, S. B. Jones and R. D. Hancock, Lewis acid properties of Zinc(II) in its cyclen complex. The structure of $[Zn(Cyclen)(SC(NH_2)_2](ClO_4)_2$ and the bonding of thiourea to metal ions. Some implications for zinc metalloenzymes, *Inorg. Chem.*, 2005, **44**, 2791–2797.

30 L. R. Sutton, W. A. Donaubauer, F. Hampel and A. Hirsch, Tris(thioacetals) from benzene hexathiol: towards covalent self-assembly, *Chem. Commun.*, 2004, 1758–1759.

31 J. J. Dickert Jr. and C. N. Rowe, Thermal decomposition of metal O,O-dialkyl phosphorodithioates, *J. Org. Chem.*, 1967, **32**, 647–653.

32 B. Liu and S. Thayumanavan, Mechanistic investigation on oxidative degradation of ROS-responsive thioacetal/thioketal moieties and their implications, *Cell Rep. Phys. Sci.*, 2020, **1**, 100271.