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Nikola Babic, Simon Pondaven, Herve Vezin. EPR Spin-Trapping Study of Free Radical Intermediates in Polyalphaolefin Base Oil Autoxidation. Polymer Degradation and Stability, 2021, Polymer Degradation and Stability, 192, pp.109687. 10.1016/j.polymdegradstab.2021.109687 . hal-03368449

EPR Spin-Trapping Study of Free Radical Intermediates in Polyalphaolefin Base Oil Autoxidation

Nikola Babić*,[a,b] Simon Pondaven,[a] Hervé Vezin[b]

[a] TotalEnergies, Centre de Recherche de Solaize (CRES), Chemin du canal, BP 22, 69360 Solaize, France

[b] Univ. Lille, UMR CNRS 8516 Laboratoire Avancé de Spectroscopie pour les Interactions, la Réactivité et l'Environnement (LASIRE), F-59000 Lille, France

Abstract

Autoxidation is a set of spontaneous oxygen-mediated radical reactions common to degradation processes of all hydrocarbon-based materials. In this work, EPR (electron paramagnetic resonance) spin-trapping technique was used to study radical species involved in the autoxidation of a sample of synthetic base oil. A sample of polyalphaolefin base oil was aged at 140 °C in the presence of oxygen and the difference in the tendency to generate radical species between the aged and non-aged samples of the same base oil was investigated using DMPO (5,5-dimethyl-1-pyrroline N-oxide) spin-trap. The ageing was performed in such a way that a small amount of hydroperoxides, the primary and key intermediate in autoxidation reactions, accumulated in the sample. Subsequently, the degradation of hydroperoxides was triggered by three different means: thermal treatment, introduction of soluble transition metal ions, and UV irradiation. Radical intermediates were monitored by EPR spin trapping; mixtures of peroxyl, alkoxyl, and carbon-centered radicals were detected and their origin was discussed.

Keywords: autoxidation, hydroperoxide, free radicals, EPR, spin-trapping, polyalphaolefin.

Introduction

Autoxidation is an autocatalyzed process of hydrocarbon oxidation by oxygen. It is a set of spontaneous reactions occurring through a free radical mechanism. Hydrocarbon autoxidation has been the object of studies for over a century due to its high economic impact [1,2]. Many products and materials, including liquid fuels, most lubricants, and plastics are made of hydrocarbons and are subject to similar autoxidative degradation processes under atmospheric conditions.

Lubricants consist of a base oil and additives. Base oil is the main component of a lubricant which, thanks to its high viscosity, reduces friction between moving mechanical parts. Additives have various roles in improving the performance of a lubricant. Engine oils usually consist of 80 to 85 % base oil and 15 to 20 % additives. Most base oils are obtained from highly processed heavy fractions of crude oil and consist of high molecular mass branched alkanes (mineral oils). Base stocks can also be of synthetic origin such as PAO (polyalphaolefins), alkyl branched polymers. Most commonly used PAO lubricant base stocks are synthesized from 1-decene monomer [3]. In the rest of the text we will use term "base oil" to refer to PAO lubricant base stock tested in this study.

Durability is a growing concern for energy companies manufacturing formulated lubricants. Understanding the oxidation pathways involved in the degradation of base oils and additives is key to increase drain intervals in motored vehicles and develop more sustainable products. This challenge is likely to become more critical in the coming years with the increased introduction of "oxygen-rich" products in the formulation of lubricants such as biosourced and recycled base oils (base stocks obtained by refining spent lubricants). In this work, as a preliminary step, we focus on the oxidation and stability behavior of base oil.

Most studies of the autoxidation process rely on the analysis of evolving physical properties of the material during the experiment (viscosity or flash point of lubricants for instance), or macro-chemical parameters (such as consumption of oxygen, monitoring the rate of accumulation of hydrocarbon oxidation products, or conversion of the starting material) [3,4]. On the other hand, EPR spin-trapping technique allows studying hydrocarbon degradation on a more fundamental level, provided the free radical mechanism of autoxidation; it allows studying precursors of later stage oxidation products. To our knowledge, previous EPR spin-trapping studies of liquid-phase autoxidation were done only on oxidation-prone edible oils [5–10], without focusing specifically on the chemistry of hydroperoxides.

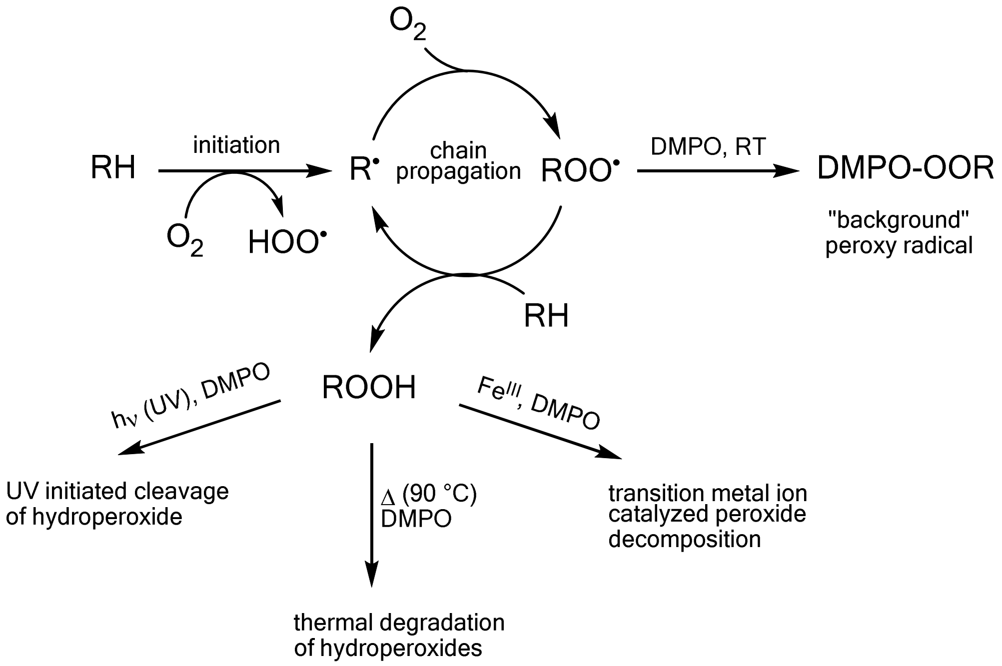
Spin-trapping is a technique used to study free radicals by stabilizing them through the reaction with external probes called spin-traps. A spin-trap is a diamagnetic molecule that upon radical addition reaction with the studied free radical yields a more stable radical product, a paramagnetic species called spin adduct. The higher stability of spin adducts allows EPR detection of otherwise undetectable transient radicals. Spin-trapping also allows unambiguous identification of radicals as each spin adduct has a characteristic EPR spectrum depending on the nature of the trapped species [11]. Many spin-trapping agents were developed, DMPO being the most commonly used for its ability to stabilize a wide range of radicals.

In this work we used EPR spin-trapping to explore reactions involved in the initial stages of PAO base oil autoxidation. The behavior of aged versus non-aged base oil is investigated and discussed.

Results

Autoxidation is the primary means of base oil degradation. Due to its radical mechanism, three stages can be recognized: initiation, propagation, and termination. In the initial stage alkyl radical ($R^{\bullet}$) is generated via hydrogen abstraction by traces of transition metal ions, ionizing radiation, or by oxygen at elevated temperatures. In the propagation of radical chain reaction, alkyl radical reacts very fast with dissolved atmospheric oxygen to produce peroxyl radical ($ROO^{\bullet}$). Peroxyl radicals are less reactive, but still able to selectively abstract secondary or tertiary hydrogen atoms, thus accumulating as hydroperoxides (ROOH). Hydroperoxides are the primary and key oxidation product since they easily decompose to reactive radicals such as alkoxyl ($RO^{\bullet}$) and hydroxyl radicals ($^{\bullet}OH$) enabling chain branching. This autocatalyzed stage is characterized by accelerated oxygen consumption and increased conversion. Until the reaction comes to a standstill – the termination reactions of radicals intercombining prevail – many autoxidation endproducts such as alcohols, aldehydes, ketones, carboxylic acids, and esters accumulate [12–14]. Some of these molecules are corrosive and can combine forming products with a high molecular mass that essentially change the physical properties of the medium [3]. Both these facts lead to a deleterious effect on the lubricant performance.

Scheme 1. Reactions involved in the autoxidation cycle and techniques used in this study to initiate decomposition of peroxides in base oil samples. **R** represents the alkyl chain.



Through the reaction with oxygen, hydrocarbons are activated yielding hydroperoxides, the first relatively stable product. However, hydroperoxides never reach a high concentration in the reaction mixture due to their facile cleavage [13].

All other oxygenated autoxidation products (alcohols, aldehydes, ketones, carboxylic acids, and esters) are formed exclusively from hydroperoxides [13]. Since hydroperoxide production and degradation occur simultaneously during hydrocarbon ageing, to facilitate their studying these two processes were separated. First, a sample of base oil was submitted to ageing and hydroperoxides were formed. Second, hydroperoxide cleavage was intentionally triggered and monitored by EPR spin-trapping. In this way, the complex reaction scheme was simplified.

A sample of pure PAO base oil was aged without catalyst at 140 °C for 1.5 h with constant air flow. Under these accelerated though mild ageing conditions, a small amount of primary oxidation products is formed, namely hydroperoxides and their immediate degradation products: alcohols, ketones, and carboxylic acids [1]. However, the oil oxidation process stays in its initial phase, without a noticeable change in the physical properties of the oil. Under more severe reaction conditions hydrocarbon autoxidation becomes more complex as the increasing number of reaction products gives rise to new reaction pathways [13]. In this study, we intentionally avoided these conditions.

EPR spin-trapping technique using DMPO was used to study the reactions following hydroperoxide cleavage catalyzed by the presence of transition metal ions, triggered by thermal decomposition or by UV light in the aged versus the non-aged sample of the same base oil.

“Background” oxidation signal

Peroxyl radical is the main chain-carrying species in the autoxidation cycle due to its high stability. Consequently, in certain media such as base oil, it may accumulate to a level detectable by EPR spin-trapping. We tested non-aged versus aged base oil for the presence of radicals without triggering radical generation. Immediately after mixing with DMPO, the non-aged sample of base oil showed traces of spin adducts, while in the aged sample slightly higher amounts were detected (**Figure 1**). In both cases, the major trapped radical was peroxyl radical (**Figure 1, red dots**).

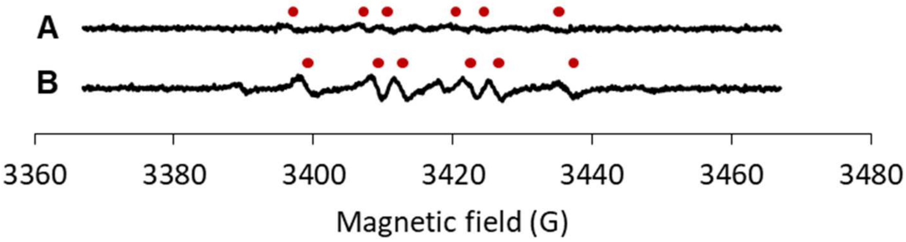


Figure 1. EPR spectra of (A) non-aged and (B) aged samples of base oil immediately after mixing with DMPO (50 mM). In both cases, the adduct of peroxyl radical is dominant (red dots; DMPO-OOR; $A_N \approx 14$ G, $A_H \approx 10$ G,

A_H ≈ 1 G; the signal to noise ratio is too low for a proper simulation). EPR signal intensity obtained by double integration of the spectra (AU): $I_{(A)} = 0.53$, $I_{(B)} = 2.73$.

We presume that the detected peroxyl radicals originate from an already established autoxidation process that takes place in the presence of oxygen, but at a very low rate under ambient conditions; peroxyl radical reaches a low steady-state concentration detectable by EPR spin-trapping technique. A similar effect of spontaneous oxidation in liquid media was reported in the EPR study of olive oil autoxidation where radicals were detected by DMPO spin-trap in the oil exposed to air [8]. Analogously, organic hydroperoxides named "initial polymeric hydroperoxides" were detected in intact polymers [15,16], originating possibly from the manufacturing process or the low rate autoxidation under ambient conditions.

We named these species "background" peroxyl radicals, due to their constant presence. Deoxygenation of the oil sample and performing the spin-trapping experiment under an inert atmosphere does not influence the amount of detected DMPO-OOR adduct (peroxyl radical adduct of DMPO) (data not shown). Once this process has begun, the small amount of peroxyl radicals cannot be eliminated by common procedures for peroxide removal like washing the base oil with mineral acids or bases, or even by simple distillation (data not shown). However, ageing does influence it; the increase in the level of "background" peroxyl radical follows the accumulation of hydroperoxides during ageing.

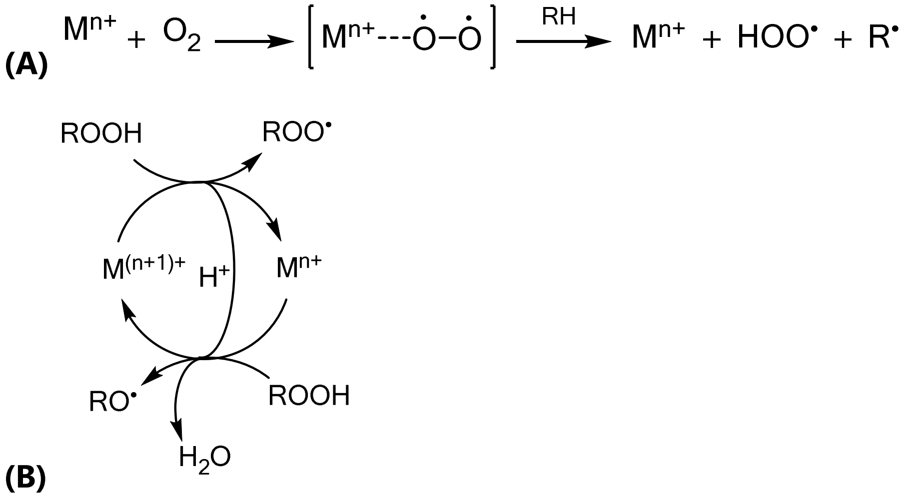
The irregular shape of EPR spectral lines (**Figure 1**) may result from the presence of multiple different species with similar line-shapes that are overlapping. Depending on the structure of the trapped $ROO^{\bullet}$ radical (R is primary, secondary, or tertiary carbon), resulting DMPO-OOR adducts have slightly different coupling constants due to varying steric and electronic effects.

The high field line of the DMPO-OOR spin adduct has an apparent lower intensity than other lines probably due to line broadening, indicating that the adduct has reduced mobility [17]. This effect, however, is not only due to the high viscosity of the medium; when small nitroxide molecule TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) was dissolved in the same sample of base oil, the high field line broadening was not observed (data not shown). This indicates that the trapped radical had a higher molecular mass – it originated from base oil bulk material. Similar effect was observed when lipid oxidation in vegetable oils was followed using PBN (α-phenyl-*N*-*tert*-butylnitrone) spin trap [6].

Metal ion-induced peroxide decomposition

The presence of transition metal ions is one of the determining factors in the ageing of hydrocarbons due to their ability to easily toggle between two oxidation states giving rise to catalytic degradation of hydroperoxides (radical chain branching) and thus increasing concentration of radicals in the medium. This catalytic degradation of hydroperoxides by transition metal ions is a variation of reaction known as the Haber-Weiss cycle (**Scheme 2(B)**) [18]. Transition metal ions can also accelerate ageing by catalyzing the initial step of hydrogen abstraction from the bulk material by activating oxygen through coordination (**Scheme 2(A)**) [19]. In the context of lubricating oils, transition metal ions are present in used engine oils in the form of wear particles and are known to accelerate oil degradation [20].

Scheme 2. Two mechanisms through which transition metal ions accelerate the ageing of hydrocarbons: **(A)** catalyzing hydrogen abstraction by activating oxygen through coordination and **(B)** decomposition of hydroperoxides through redox cycling.



Two transition metals, iron and copper, are particularly relevant due to their presence in steel and brass engine parts and high catalytic activity [21]. In this study we used base oil soluble iron(III) or copper(II) complexes as a simple model of transition-metal autoxidation catalysis. Their effect on radical generation in aged versus non-aged base oil was studied by DMPO spin-trapping technique.

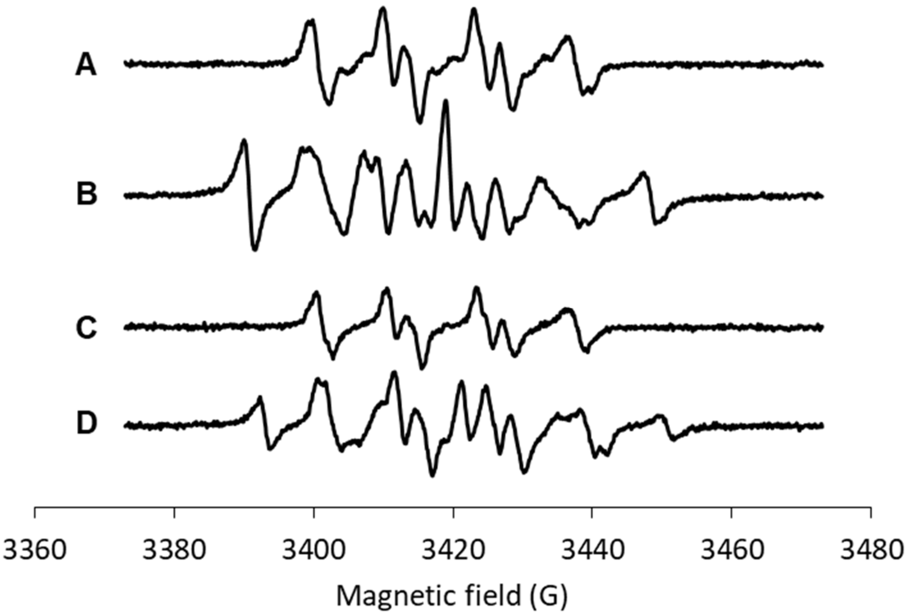


Figure 2. EPR spectra of DMPO (50 mM) adducts of **(A)** non-aged and **(B)** aged samples of base oil immediately after mixing with iron(III) acetylacetonate (5 µM), and spectra of **(C)** non-aged and **(D)** aged samples of base oil after mixing with copper(II) methyl 3-oxoeicosanoate (5 µM). In the case of non-aged oil with both metals (cases A and C), peroxyl radical is dominant, followed by alkoxyl radical (DMPO-OOR; $A_N \approx 13$ G, $A_H \approx 10$ G, $A_H \approx 1$ G; ~90% of the aggregate spectrum; DMPO-OR; $A_N \approx 12.5$ G, $A_H \approx 6$ G, $A_H \approx 2$ G; ~10%). In the case of aged oil with metals (cases B and D), a complex mixture of adducts is obtained. EPR signal intensity obtained by double integration of the spectra (AU): $I_{(A)} = 7.63$, $I_{(B)} = 25.3$, $I_{(C)} = 5.49$, $I_{(D)} = 16.3$.

After the addition of either iron(III) or copper(II) to non-aged oil, peroxyl and alkoxyl radicals were detected (**Figure 2**). These two species are products of the decomposition of hydroperoxides by redox cycling of transition metal ions (**Scheme 2 (B)**) [22]. With both metals, aged oil yielded a complex mixture of DMPO spin adducts with dominant unidentified DMPO spin adduct with a spectral width of 57.5 G. In aged oils, a variety of oxygen-containing autoxidation products is already present and can produce complex chemistry in the presence of transition metal ions and spin-trap.

Deoxygenation of the non-aged base oil samples before the addition of metal ions and DMPO does not influence the nature and the quantity of trapped radicals (data not shown). This confirms that the formation of radicals triggered by metal ions originates from the decomposition of a low amount of hydroperoxides accumulated through the spontaneous autoxidation process at ambient conditions (**Scheme 2 (B)**), and not by *de novo* radical generation (**Scheme 2 (A)**).

The presence of low rate background oxidation of liquid hydrocarbons under ambient conditions was confirmed by studying pure decalin. EPR spin-trapping experiments were performed with a fresh sample of commercially available, antioxidant-free decalin from a newly opened bottle and afterwards with decalin from the same bottle after storage for three months in the dark at room temperature. During that period, decalin was unintentionally exposed to oxygen in the air by occasionally opening the flask.

Only trace amounts of "background" peroxyl radicals were detected in decalin both when it was fresh and three months after opening the flask (**Figure 3 cases A and C respectively)**. However, when decalin samples were supplemented with soluble iron(III) ions before the addition of DMPO, a striking difference was noticed: fresh decalin generated a trace amount of radicals, while in the three months old sample the level of detected radicals increased significantly (**Figure 3 cases B and D respectively)**. The low rate oxidation over three months gave rise to the accumulation of a small amount of hydroperoxides, which upon reaction with soluble iron ions generated peroxyl and alkoxyl radicals.

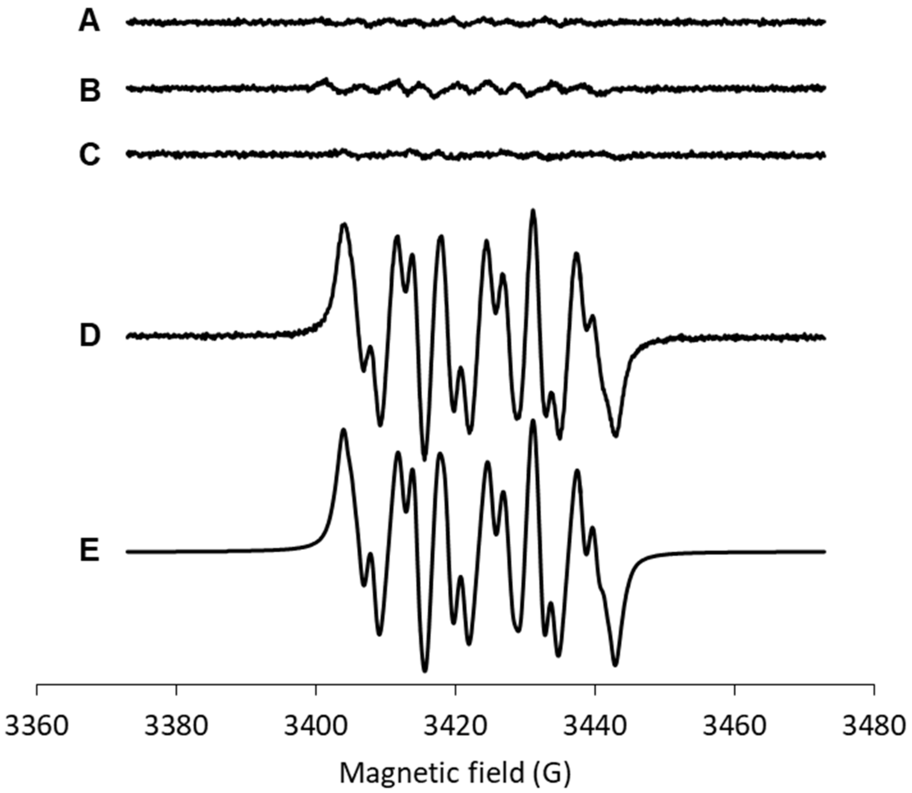


Figure 3. EPR spectra of DMPO (50 mM) adducts in fresh decalin (from freshly opened bottle) **(A)** without or **(B)** with the addition of iron(III) acetylacetonate (5 µM), and decalin from the same bottle after three-month storage in the dark at room temperature **(C)** without or **(D)** with the addition of iron(III) acetylacetonate (5 µM). In samples A, B, and C only traces of DMPO-OOR and DMPO-OR were detected, while in sample D, a significant amount of radicals was detected. **(E)** WinSim simulation of spectrum D (DMPO-OOR; A_N = 13.5 G, A_H = 10.1 G, A_H = 1.0 G; 27 % of the aggregate spectrum; DMPO-OR; A_N = 12.9 G, A_H = 6.1 G, A_H = 2.1 G; 73% of the aggregate spectrum). EPR signal intensity obtained by double integration of the spectra (AU): $I_{(A)}$ = 0.59, $I_{(B)}$ = 1.89, $I_{(C)}$ = 0.79, $I_{(D)}$ = 40.7.

This unexpected finding reveals that the air from the occasional opening of the bottle over the course of three months provided enough oxygen to establish the autoxidation cycle and to result in the accumulation of hydroperoxides. We assume that this phenomenon is ubiquitous in hydrocarbons and should be considered in the storage of base oils as well. However, it should be noted that decalin is very prone to oxidation by oxygen due to the presence of tertiary hydrogen atoms [23].

The ratio of peroxyl versus alkoxyl spin adducts differs in base oil as compared to decalin, alkoxyl adduct being prevalent in decalin. This could be a consequence of the high viscosity of base oil – reactive alkoxyl radicals have a lower probability to collide with DMPO as they get "neutralized" faster by the abstraction of hydrogen from the hydrocarbon medium. Another factor that may compromise the quantitative analysis is that metal compounds rarely achieve true solubility in non-polar organic solvents [24].

Thermal degradation of peroxides

The hydrocarbon autoxidation process is accelerated at high temperatures mainly due to the increased concentration of radical species resulting from the decomposition of hydroperoxides [25]. Thermally-induced homolytic cleavage of hydroperoxides at low concentrations yields alkoxyl and hydroxyl radicals (**Equation 1**) [26].

$$\mathrm{ROOH} \xrightarrow{\Delta} \mathrm{RO^{\bullet}} + {}^{\bullet}\mathrm{OH}$$

Equation 1.

The formation of the alkoxyl and hydroxyl radicals is followed by a fast and non-selective abstraction of hydrogen atoms from the hydrocarbon medium (**Equation 2**). This is especially true for hydroxyl radical due to its very high reactivity with hydrocarbons.

$$\left.\begin{array}{l}\mathrm{RO^{\bullet}} \\ {}^{\bullet}\mathrm{OH}\end{array}\right\} + 2\mathrm{RH} \longrightarrow \left\{\begin{array}{l}\mathrm{ROH} \\ \mathrm{H_2O}\end{array}\right. + 2\mathrm{R^{\bullet}}$$

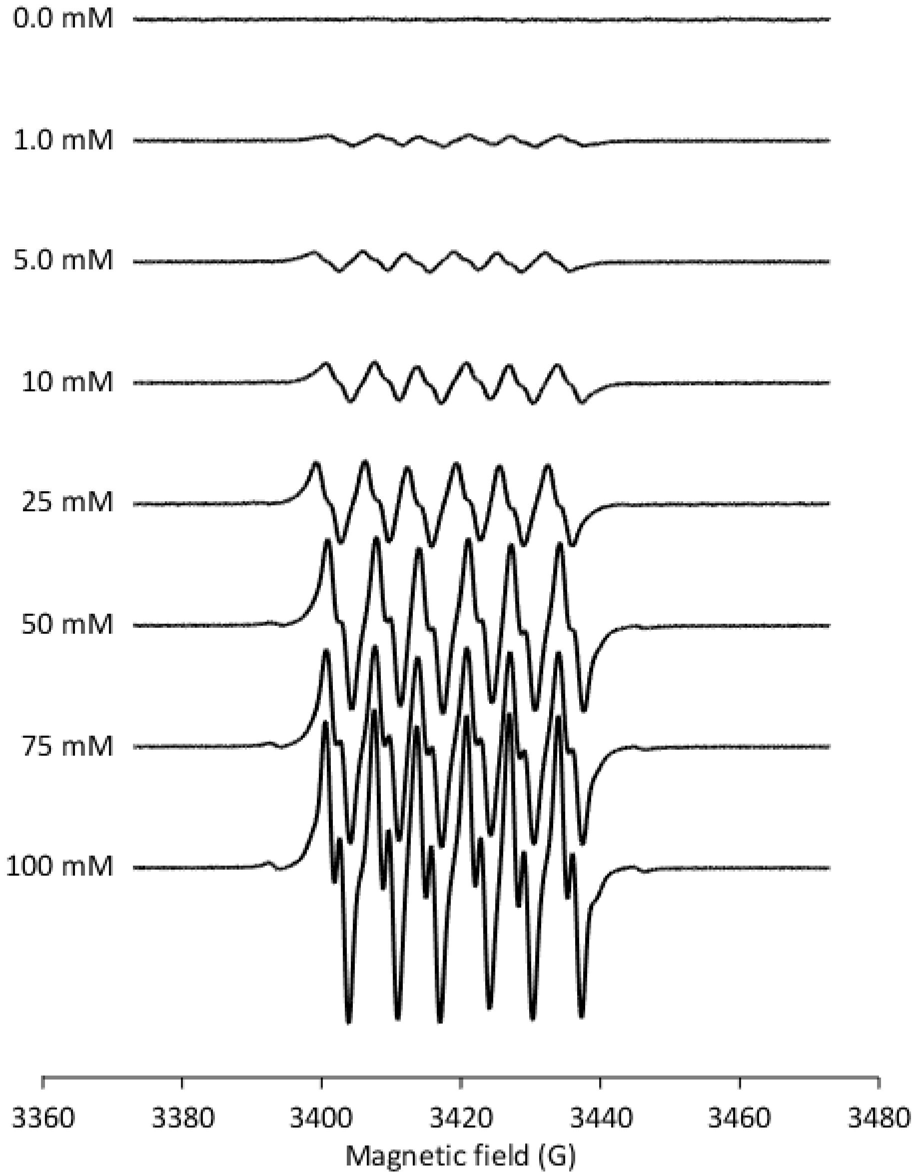
Equation 2.

The resulting carbon-centered radical in turn reacts immediately with dissolved oxygen leading to the formation of peroxyl radical (**Equation 3**).

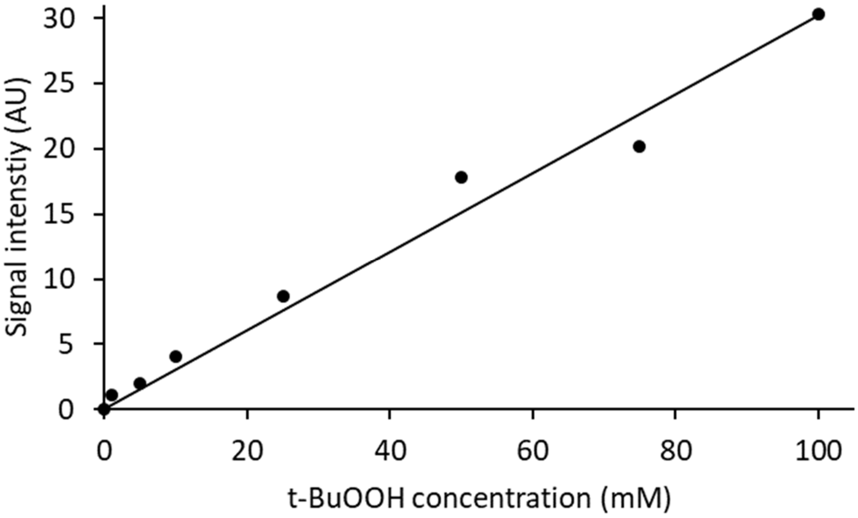
$$\mathrm{R^{\bullet}} + \mathrm{O_2} \longrightarrow \mathrm{ROO^{\bullet}}$$

Equation 3.

First, a protocol for spin-trapping of radicals generated by thermal degradation of peroxides was established using solutions of commercially available tBuOOH (t-butyl hydroperoxide) in base oil. The optimal conditions were found to be thermostating the sample at 90 °C for 5 minutes. Under these conditions mainly alkoxyl radical was trapped. At higher temperatures or with longer exposure times, the degradation of spin adducts results in complex spectra of several overlapping spin adducts and their degradation products (see Supplementary Information).



(A)



(B)

Figure 4. (A) EPR spectra of a series of solutions of tBuOOH (1.0, 5.0, 10, 25, 50, 75, and 100 mM) in base oil containing DMPO (50 mM) after 5 min of in situ heating at 90 °C. Spectra were acquired at 90 °C as well. The major component in all cases is DMPO-OR adduct (A_N = 13.1 G, A_H = 7.0 G, A_H = 1.9 G). **(B)** EPR signal intensity of DMPO-OR adduct (measured as low field line height) plotted against tBuOOH concentration.

Although homolytic cleavage of hydroperoxides produces both alkoxyl radical and hydroxyl radical, only alkoxyl radical is detected by DMPO. Hydroxyl radical is difficult to trap in hydrocarbon media due to its high reactivity [27]. High linearity is observed between the tBuOOH concentration and the signal intensity of DMPO-OR spin adduct (alkoxyl radical adduct of DMPO) measured as low field line height in the range of 1.0 mM to 100 mM tBuOOH (**Figure 4 (B)**).

Base oil testing was then carried out and the samples of aged and non-aged base oils were submitted to in situ heating for 5 minutes at 90 °C in the presence of DMPO.

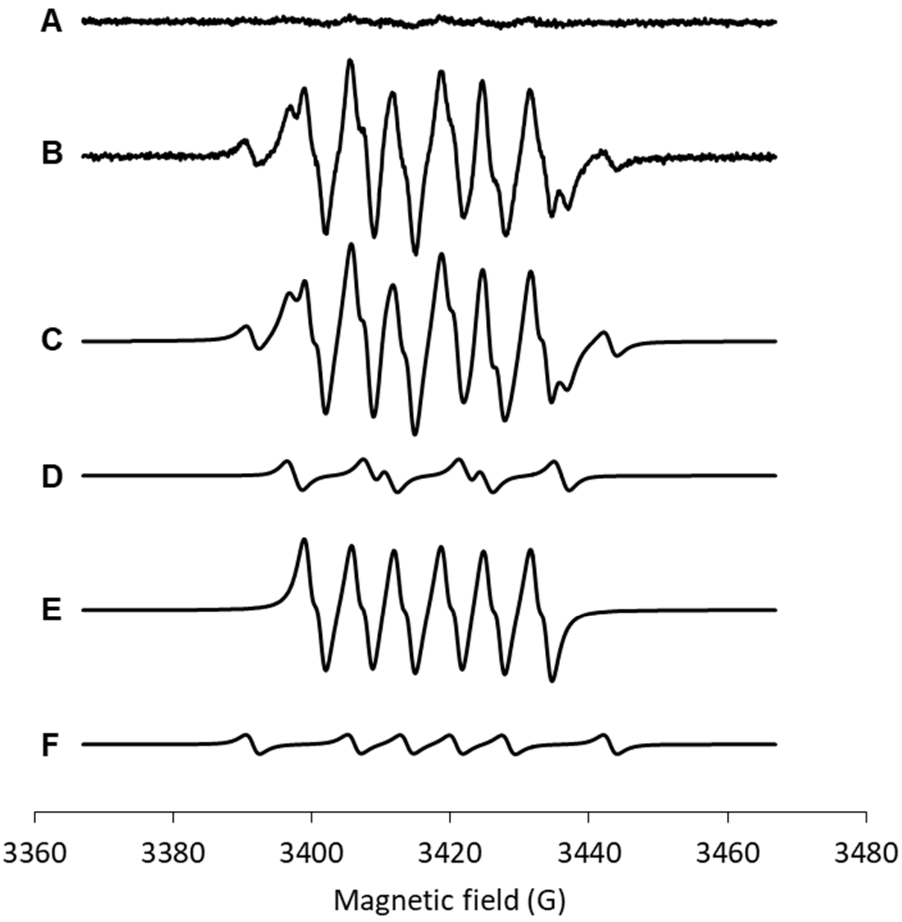


Figure 5. EPR spectra of **(A)** non-aged and **(B)** aged base oil containing DMPO (50 mM) after 5 min of in situ heating at 90 °C. Spectra were acquired at 90 °C as well. **(C)** WinSim simulation of spectrum B. Simulated individual adducts: **(D)** DMPO-OOR (A_N = 13.8 G, A_H = 10.9 G, $A_H \approx$ 0.9 G), 17 % of the aggregate spectrum; **(E)** DMPO-OR (A_N = 12.9 G, A_H = 6.8 G, A_H = 1.7 G), 73%; **(F)** DMPO-R (A_N = 14.7 G, A_H = 22.2 G), 10%. EPR signal intensity obtained by double integration of the spectra (AU): $I_{(A)}$ = 1.81, $I_{(B)}$ = 28.3.

Ageing of base oil strikingly changed its behavior in EPR spin-trapping experiments with thermal treatment. In the non-aged sample, only traces of radicals were trapped, while in the aged sample a mixture of DMPO-OOR, DMPO-OR, and DMPO-R (carbon-centered radical adduct of DMPO) were observed (**Figure 5, A and B respectively**). The array of radical species originates from hydroperoxides accumulated during the ageing treatment. Thermolysis of hydroperoxides generated primarily alkoxyl radical through homolytic cleavage (**Equation 1**), followed by second-generation carbon-centered radical formed through hydrogen abstraction by hydroxyl or alkoxyl radical (**Equation 2**). It is unlikely that carbon-centered radicals originated from direct pyrolysis of alkanes at 90 °C since liquid hydrocarbons are resistant to dissociation of the carbon-carbon bonds up to 200 °C [29].

$$\mathrm{ROOH} + \mathrm{ROOH} \longrightarrow \mathrm{ROO}^{\bullet} + \mathrm{RO}^{\bullet} + \mathrm{H_2O}$$ **Equation 4.**

The peroxyl radical could be a third-generation radical formed after the addition of oxygen to a carbon-centered radical (**Equation 3**), or could be a product of a bimolecular reaction that is important at higher hydroperoxide concentrations (**Equation 4**) [1,28].

UV decomposition

Previous EPR spin-trapping studies showed that the main reaction taking place following UV irradiation of hydroperoxides is their homolytic cleavage (**Equation 5**) [30]. At high concentrations of hydroperoxides (more than 50 mM), a reaction of alkoxyl radical with organic hydroperoxides is observed (**Equation 6**) [30].

$$\mathrm{ROOH} \xrightarrow{h\nu\ (\mathrm{UV})} \mathrm{RO}^{\bullet} + {}^{\bullet}\mathrm{OH}$$ **Equation 5.**

$$\mathrm{ROOH} + \mathrm{RO}^{\bullet} \longrightarrow \mathrm{ROO}^{\bullet} + \mathrm{ROH}$$ **Equation 6.**

Samples of non-aged and aged base oil were deoxygenated and submitted to in situ UV irradiation for 1 min in the presence of DMPO.

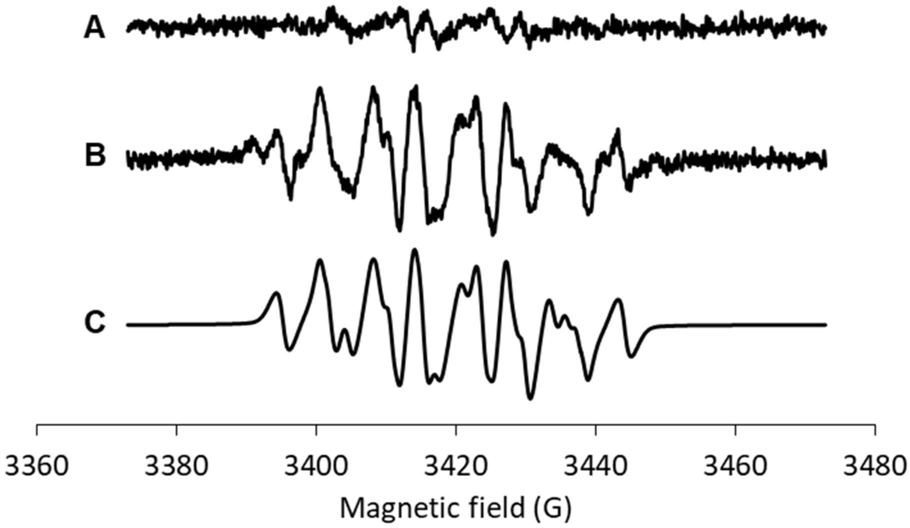


Figure 6. EPR spectra of **(A)** non-aged (DMPO-OOR; $A_N \approx 13$ G, $A_H \approx 10$ G, $A_H \approx 1$ G) and **(B)** aged base oil containing DMPO (50 mM) after 1 min of in situ irradiation by UV light (338-414 nm); **(C)** WinSim simulation of spectrum B (DMPO-OOR ($A_N = 13.3$ G, $A_H = 9.8$ G, $A_H \approx 1.0$ G), 25 % of the aggregate spectrum; DMPO-OR ($A_N = 12.6$ G, $A_H = 6.2$ G, $A_H = 2.1$ G), 58 %; DMPO-R [uncertain assignment] ($A_N = 14.2$ G, $A_H = 20.5$ G), 17 %). EPR signal intensity obtained by double integration of the spectra (AU): $I_{(A)} = 5.43$, $I_{(B)} = 25.9$.

In the non-aged sample, only traces of peroxyl radical were detected (**Figure 6**). On the other hand, in the aged sample mainly alkoxyl radicals were observed, followed by peroxyl radicals and carbon-centered radicals. Carbon-centered radicals are probably second-generation radicals formed through the abstraction of hydrogen from hydrocarbon media by hydroxyl and alkoxyl radicals (**Equation 2**). Carbon-centered radicals were not observed in the non-aged base oil. This observation is confirming that the direct formation of carbon-centered radicals by UV irradiation is not their origin in the aged base oil either.

Samples were deoxygenated before the analysis as, under ambient conditions, enough dissolved oxygen from the air was present in the base oil samples to completely alter the radical chemistry created by UV irradiation.

Discussion

Product sustainability is a growing concern for energy companies. In the lubricant sector, the efforts towards sustainability are reflected in the introduction of recycled and bio-sourced feedstocks in formulations, the building materials that are more prone to oxidation than conventional base oils. Existing methods for analyzing autoxidation rely on studying the accumulation of oxidation endproducts or the evolving physicochemical macroparameters. Such methods often miss the initial phase of the oil degradation where the conversion is low and only traces of oxidation products are present, namely hydroperoxides. Hydroperoxides are the pivotal autoxidation intermediates since all other oxidation products emerge from hydroperoxide cleavage. Hydroperoxide degradation yields free radicals, and a technique of choice for studying free radicals is EPR spin-trapping.

In this work, we used EPR spin-trapping technique to study the degradation of hydroperoxides accumulated in base oil aged in laboratory by heating in the presence of oxygen without catalyst. The degradation of the small amount of accumulated peroxides was triggered by three methods: introduction of transition metal ions, brief heating, and UV irradiation. Besides providing radical detection, EPR spin-trapping using DMPO allows their identification as well. In most samples, a mixture of peroxyl radicals, alkoxyl radicals, and carbon-centered radicals was detected, the prevalence of certain species being influenced by the means of hydroperoxide degradation. Moreover, this method allows quantification of radical generation. It was found that the amount and the variety of radicals detected by EPR spin-trapping was higher in aged as compared to non-aged base oil samples. The precision of radical quantification was emphasized by the experiment presented in **Figure 4** where the amount of trapped alkoxy radical was linearly correlated with the concentration of tBuOOH. This laboratory model is real-world relevant both in terms of base oil ageing (high temperature, oxygen presence), and triggering hydroperoxide degradation (high temperature, presence of transition metal ions, ionizing radiation).

Under ambient conditions (room temperature and presence of oxygen from the air), a low-rate autoxidation process was established in the intact base oil. This was detected by EPR spin-trapping as a constant presence of trace amounts of peroxyl radicals. This result demonstrates the sensitivity of the method as traces of peroxy radicals were detected in base oil that was not aged and in which radical production was not triggered by any means.

Although both autoxidation mechanism and EPR spin-trapping technique have been known for decades, a method developed for studying autoxidation of base oils was never reported. The method developed in this work is a good complementary tool for studying oxidation stability of base oils as it captures initial stages that are missed by conventional techniques. It can be used for other liquid hydrocarbons, and in all materials that undergo autoxidation degradation.

Severe oxidative oil degradation involves significant conversion to oxygenated hydrocarbons. In this second stage of ageing, where degradation products such as alcohols, ketones, and carboxylic acids accumulate and start interacting, the decomposition of hydroperoxides loses its primary role in oil degradation. For studying these processes, the approach developed in this work may not be well suited since it focuses on the chemistry of hydroperoxides.

DMPO spin-trapping experiments with long incubation periods are not advisable for studying autoxidation reactions. Such experiments would emphasize non-innocent probe character of DMPO, since DMPO spin adducts are nitroxides which are known to act as chain-breaking antioxidants [31].

DMPO spin adducts in base oil have lower EPR hyperfine coupling constants than those reported in water. This is explained by the resonance effect of the $NO^{\bullet}$ (aminoxyl) group in media of different polarity [32].

The amount of detected radicals was measured by the double integration of EPR spectra and is noted at the end of the description of each figure. In all tested samples, the same protocol and acquisition parameters were used. Therefore, the quantities of detected radicals are comparable throughout the paper. For spectral simulations, the ratio of individual radical species is presented as a percentage share of the aggregate spectra. One should keep in mind that the presented results are semi-quantitative. The efficiency of radical capture reaction has a specific rate for each radical under given conditions, while the stability of spin-adduct is also dependent on the conditions and the structure of the captured radical.

The role of antioxidant additives in lubricants is to prevent autoxidation reactions which delays base oil degradation and the consequent lubricant performance drop. Understanding base oil oxidation properties on a fundamental level can help in optimizing formulations, especially for base oils that are more prone to oxidation.

Conclusion

With emerging need of more sustainable base oil for lubricant production, recycled and biosourced base oils are becoming a viable option. These products may have compromised oxidation resistance, so there is a need of a method for their evaluation. In this work we established an EPR spin-trapping protocol for studying radical intermediates arising from autoxidation reactions in pure synthetic base oil. This method allows focusing on initial phases of base oil degradation that conventional methods fail to detect, and is therefore capable of predicting oil degradation stability. As we demonstrated that EPR spectroscopy is a sensitive and powerful tool for studying the radical chemistry of autoxidation processes, the impact of selected additives such as antioxidants, metal ion deactivators, and UV stabilizers could also be investigated. Finally, this method also has the potential to be used for routine tests in industrial quality control laboratories.

Experimental

The base oil used in this study was synthetic polyalphaolefin oil constituted of pure saturated hydrocarbon molecules, regularly branched alkanes.

Base oil ageing – accumulation of hydroperoxides

A sample of base oil (30 ml) was placed in a round bottom flask (50 ml) and heated for 1.5 h in an oil bath thermostated at 140 °C with a constant flow of air. The air was introduced through a glass Pasteur pipette connected to a line of compressed air with a 20 ml/min flow. The oxidation was carried out without catalyst.

With this treatment, only the initial products of autoxidation were accumulated, with our goal being to create a pool of hydroperoxides. The protocol was adapted from two sources [1,23] where under given conditions a few mole percent of hydroperoxides were accumulated. In our case, the amount of formed hydroperoxides was roughly estimated to be less than 1 % using NMR by the integration of the signals of hydrogens in α-position to hydroperoxide functional group ($\delta \approx 4$ ppm).

In situ spin-trapping of radicals present in base oil using DMPO

The behavior of non-aged versus aged base oil was investigated in each of the following tests.

No treatment ("background" oxidation). A solution of DMPO (50 mM) was prepared in tested base oil by adding 5 µl of pure distilled DMPO (aliquots can be stored under argon at – 20 °C for months) from a microsyringe to 891 µl of base oil placed in 1.5 ml disposable plastic tubes followed by vigorous stirring on vortex. A fine emulsion was obtained (DMPO has limited solubility in very non-polar media such as pure base oil) and immediately transferred to a 5 mm EPR quartz tube and placed inside the EPR cavity. When using 5 mm EPR sample tubes, the volume we used was sufficient to completely fill the EPR cavity of Bruker EMXnano EPR spectrometer with the sample (in other words, sample height >25 mm).

Soluble metal ions. A 5 µM solution of iron(III) acetylacetonate or copper(II) methyl 3-oxoeicosanoate was prepared in base oil by diluting a 5 mM stock solution of metal ions prepared in the same base oil. Immediately after, DMPO was added as described above to prepare a 50 mM solution. The sample was then placed into a 5 mm EPR tube, inserted in the EPR cavity, and a spectrum was acquired.

Thermal treatment. A sample prepared as explained above was introduced into the EPR cavity equipped with a variable temperature unit thermostated at 90 °C, equilibrated for 5 minutes followed by the acquisition of the EPR spectrum at the same temperature.

UV irradiation. The DMPO solution in base oil prepared as described above was deoxygenated by bubbling with oxygen-free argon for 5 minutes. The sample was then transferred to a 5 mm EPR quartz tube under an inert atmosphere. The sealed tube was placed into the EPR cavity and irradiated in situ for 1 min using a Shimadzu irradiation system with a filter operating in the range of 338-414 nm, followed by immediate subsequent acquisition of the EPR spectrum.

EPR parameters. The EPR spectra were recorded using a Bruker EMXnano EPR spectrometer (Bruker, Wissembourg, France) operating at X-band (9.63 GHz) with the following parameters: modulation frequency, 100 kHz; modulation amplitude 1.0 G; time constant, 5.12 ms; conversion time, 14.65 ms; center field, 3423 G; sweep width, 100 G; sweep time 15.0 s; microwave power, 10 mW; number of scans, 10; Pts / Mod. Amp, 10.240; resolution 1024 points. Data acquisition and processing were performed using Bruker Xenon software. Several different spin adducts were often formed at the same time due to the simultaneous presence of multiple radical species. This resulted in the overlapping of their EPR spectra; the relative content was determined by computer simulation of the spectra of individual species using

WinSIM [33] and fitting the simulated aggregate spectrum to the experimental spectrum.

Acknowledgements

The work presented here was performed at the Analytical Department of Solaize Research Center (CRES) of TotalEnergies. The work of Nikola Babić was funded by TotalEnergies MS through RUC 557.

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