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Amaury Furet, Audrey Sicello, Bruno Guillemat, Christelle Absalon, Emilie Langleron, et al.. Revisiting the mechanism responsible for the light-struck flavor in white wines and Champagnes. Food Chemistry, 2022, 372, pp.131281. 10.1016/j.foodchem.2021.131281 . hal-03411373

**HAL Id: hal-03411373**

**<https://hal.science/hal-03411373>**

Submitted on 2 Nov 2021

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# Revisiting the mechanism responsible for the light-struck flavor in white wines and Champagnes

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## Abstract

The mechanism responsible for the appearance of the light-struck fault upon exposure of white wines and Champagnes to natural or artificial light is examined in light of new experiments involving methionine analogues. The latter show that the formation of volatile sulfur species upon irradiation of riboflavin in the presence of methionine in model wine solutions at pH 3 is not dependent on the existence of neighboring group stabilization of the sulfur-centered cation radical through a 5- or 6-membered cyclic intermediate. Instead, the formation of a dimer radical cation is proposed in agreement with the formation of oxidation products such as dimethyldisulfide at early reaction times and the observed steric effect upon product distribution. The limiting quantum yield for the release of sulfur atoms from a solution of methionine in model wine solutions at pH 3 containing riboflavin was found to be 0.26 (435 nm irradiation). No dependence of the quantum yield or product distribution on the irradiation wavelength was found over the range 365 – 490 nm.

## Keywords

Light-struck fault, riboflavin, methionine, sulfur, photooxidation

## Introduction

The exposure of numerous foods and beverages to artificial or natural light results in undesirable changes in their organoleptic properties. In the case of white wines and Champagnes, this leads to an irreversible degradation commonly known as the light- or sun-struck fault that is characterized by changes in coloration and the smell of rotten eggs and cooked cabbage (Dozon & Noble, 1989). Although the light-struck fault is a complex process whose chemical origins can differ between samples due to variations in grape composition and vinification techniques (Grant-Preece, Barril, Schmidtke, Scollary, & Clark, 2017), the

strongest off-odors such as those of rotten eggs and cooked cabbage are due to the generation of volatile sulfur species. Their formation has been linked to the photoinduced oxidation of sulfur-containing amino acids such as methionine (**Met**) and cysteine (**Cys**) by riboflavin (**Rf**) (Daniela Fracassetti, Limbo, Pellegrino, & Tirelli, 2019; Mattivi, Monetti, Vrhovšek, Tonon, & Andrés-Lacueva, 2000). The photoinduced oxidation of **Met** by **Rf** is quite general, having also been evidenced in milk, dairy products, and beers (De Keukeleire, Heyerick, Huvaere, Skibsted, & Andersen, 2008; Lee & Min, 2009).

Riboflavin is a flavine co-factor and a well-known photocatalyst active the UV-visible region, absorbing light up to ca. 500 nm (Hering, Muhldorf, Wolf, & König, 2016). Excitation of its isoalloxazine core leads to the population of an emissive  $S_1$  excited state ( $\Phi_F = 0.27$ ) which is relatively short-lived due to efficient intersystem crossing to the triplet manifold ( $\tau_S = 5.1$  ns,  $\Phi_{ISC} = 0.70$ ) (Daniel R. Cardoso, Olsen, & Skibsted, 2007). The lifetime of the triplet state is much longer and can reach  $\tau_T = 15$   $\mu$ s in the absence of oxygen and self-quenching (D. R. Cardoso, Libardi, & Skibsted, 2012). The long lifetime and high redox potential of  $^3\text{Rf}^*$  renders it particularly reactive towards food constituents such as phenolic species, peptides, purines, and lipids through either electron transfer or hydrogen abstraction reactions (D. R. Cardoso et al., 2012). In the case of **Met**, Huvaere *et al.* reported that the bimolecular quenching rate of  $^3\text{Rf}^*$  in water is sensitive to the pH, with  $k_q = 4.9 \times 10^7$  s<sup>-1</sup> and  $2.2 \times 10^7$  s<sup>-1</sup> at pH 4.2 and 7, respectively (Huvaere, Andersen, Storme, Van Bocxlaer, Skibsted, & De Keukeleire, 2006). In contrast, **Cys** only quenches  $^3\text{Rf}^*$  efficiently under basic conditions as a result of deprotonation of the thiol group (Daniel R. Cardoso, Franco, Olsen, Andersen, & Skibsted, 2004). The link between  $^3\text{Rf}^*$  and the formation of the light-struck fault is well established: Addition of **Rf** enhances the light-struck fault in wines (Mattivi et al., 2000), whereas quenching of  $^3\text{Rf}^*$  was found to suppress the appearance of the light-struck fault in beers (Goldsmith, Rogers, Cabral, Ghiggino, & Roddick, 2005) and wines (Daniela Fracassetti et al., 2019). Furthermore, the selective removal of **Rf** has been recently proposed to be an effective strategy to improve the light-fastness of white wines (D. Fracassetti, Gabrielli, Encinas, Manara, Pellegrino, & Tirelli, 2017).

Understanding the mechanism responsible for the light-struck fault sensitized by **Rf** is essential in developing strategies for mitigating its effects and also in elucidating the formation of undesirable side-products. Surprisingly, few detailed mechanistic studies of the reaction between  $\text{Rf}^*$  and **Met** or **Cys** have been reported. In the case of wines, the mechanism proposed by Maujean and Seguin in 1983 is widely accepted as accurately describing the formation of volatile sulfur-containing species MeSH and DMDS ( $\text{CH}_3\text{S}-$

SCH<sub>3</sub>) upon irradiation of **Rf** in the presence of **Met** or **Cys** (Maujean & Seguin, 1983). The mechanism proposed bears resemblance to that previously put forth by F. A. Yang et al. in 1967, in which the formation of volatile sulfur products is also accompanied by the production of ethylene as evidenced using <sup>14</sup>C-labelled **Met** (Huvaere et al., 2006; Yang, Ku, & Pratt, 1967). In both mechanisms, the initial step involves oxidative electron transfer quenching of <sup>3</sup>**Rf**\* by **Met** to generate a thiol-centered cation radical that undergoes subsequent decarboxylation and hydrolysis to give methional. The latter is also proposed to be an intermediate in the photooxidation of dairy products, although Silcock and co-workers later showed that it is formed competitively and not sequentially with MeSH (Asaduzzaman, Scampicchio, Biasioli, Bremer, & Silcock, 2020).

Both the proposed intervention of the carboxylate anion and putative hydrogen atom transfer between two radical species suggest that this mechanism may not be able explain the efficient formation of the light-struck fault under the more acidic conditions found in white wines and Champagnes. We report here a detailed photochemical investigation which finds that the quantum yields for the formation of MeSH and DMDS are not dependent on the pH. Furthermore, **Met** analogues in which either the carboxylate or ammonium fragment is removed exhibit identical efficiencies for the formation of MeSH and DMDS. Based on these results, an alternative mechanism involving the formation of a **Met** dimer cation radical is proposed. This mechanism explains the formation of both ethylene and DMDS under anaerobic conditions and is in agreement with the lack of pH dependence.

## Materials and Methods

All commercially-available chemicals and solvents were of analytical or spectroscopic grade and used as received. Water was purified on a Milli-Q system immediately prior to use. Irradiations were carried out on an optical bench composed of a high pressure 200W XeHg lamp coupled to a high-efficiency monochromator. Solutions were placed in a 4-cm pathlength quartz cuvette to ensure complete absorption of light at all wavelengths. Model wine solutions were prepared by combining tartaric acid (3.5 g / L), water and absolute ethanol (88 : 12 v/v) and adjusting the pH to 3.5 with 1M NaOH solution. **Rf** and **Met** were dissolved at the concentrations given below and the solutions deaerated by purging with argon for 20 minutes when required.

Analysis of the irradiated solutions was conducted either by SPME-GC-MS (Thermo-Finnigan Trace Ultra ISQ instrument equipped with an Optimax Wax Plus column) or using a SPME-GC-PFPD (Agilent 7890B instrument equipped with a DAB-WAX column and a

PFPD 5383 detector from OI-Analytics). Sample injection was done using a carboxen-polydimethylsiloxane (Carboxen-PDMS) SPME fiber (Supelco). For the quantitative analysis of methanethiol, DMDS and DMTS, calibration curves were obtained for each species using ethyldithioacetate (**DTA**) in ethanol as an internal standard (see SI). After irradiation, 9 mL of the irradiated solution was transferred to a 12-mL dark glass vial and **DTA** was added ( $[\text{DTA}] = 1 \times 10^{-6} \text{ M}$ ). The sample was then sealed and allowed to rest for 15min under moderate stirring, after which the SPME fiber was introduced into the solution for 15min and then desorbed for 7 minutes into the injector of the GC at 250 °C. The number of molecules of product was directly obtained by the quantitative analysis using the calibration curve for each sulfur species.

The number of photons absorbed was determined from the incident power assuming that all incident photons are absorbed. A mask delimiting the irradiation area was used to ensure that the photon flux remained constant during sample irradiation and measurement of the incident power. The incident power was measured before and after each irradiation using a calibrated powermeter (Thorlabs 100A equipped with a S170C sensor) thanks to the following equation:

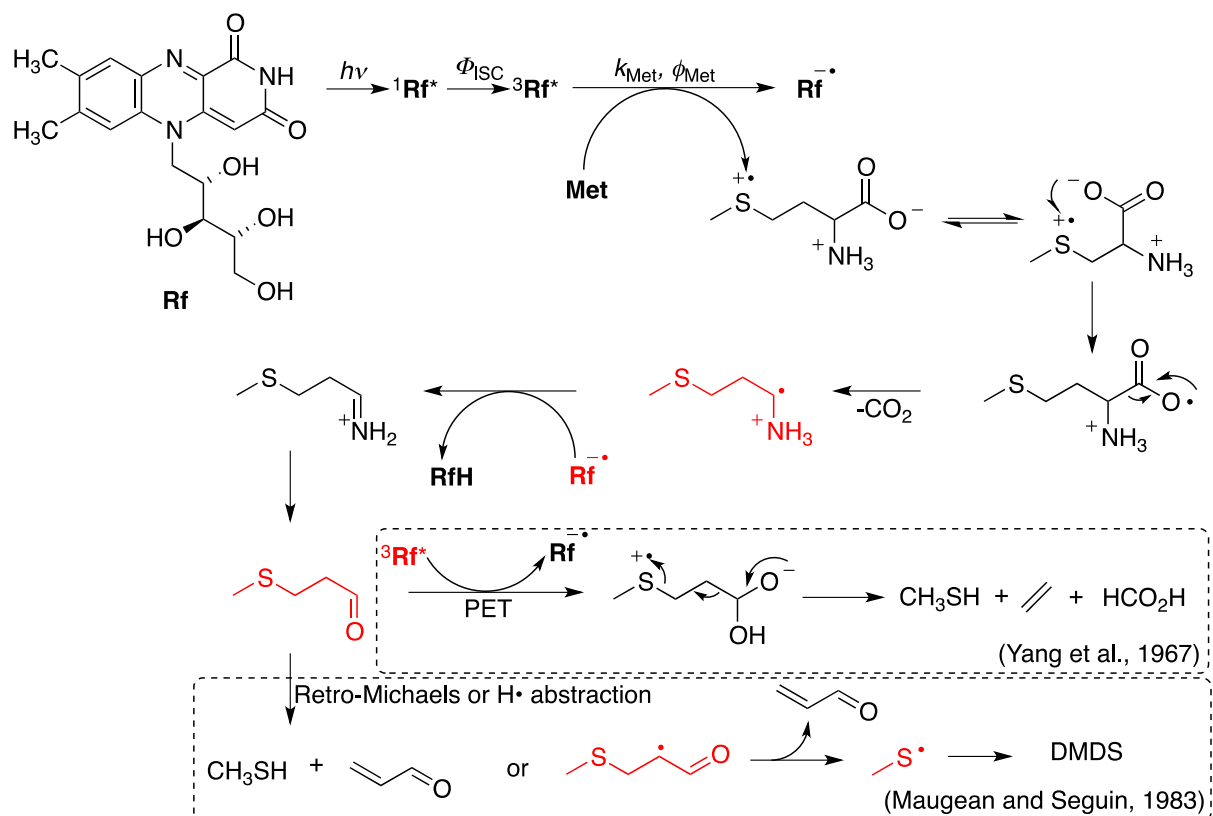
$$I = \frac{Fe \times \lambda}{h \times c}$$

Where  $I$  is the number of incident photons per second,  $Fe$  the incident power (W),  $\lambda$  the irradiation wavelength (m),  $h$  is Planck's constant (Js), and  $c$  the speed of light (m/s). The response of the power meter was checked at 365nm against a ferrioxalate actinometer solution and found to deviate by < 5%.

## Results and discussion

The mechanisms proposed by Maujean and Seguin (Maujean et al., 1983) and by Yang et al. (Yang et al., 1967) share a common pathway leading to the formation of methional even though the latter was not detected by either group, reportedly owing to its instability under the reaction conditions. They then diverge in that Yang et al. propose a second PET reaction between  $^3\text{Rf}^*$  and methional, followed by elimination to form MeSH, ethylene, and formic acid. Formation of latter was confirmed by  $^{14}\text{C}$ -labeled **Met**. Maujean and Seguin instead propose that methional undergoes either a retro-Michael addition reaction or hydrogen abstraction (Scheme 1). In both mechanisms, the MeSH that is produced may undergo autooxidation to form DMDS. In Scheme 1, bimolecular reactions between intermediates

present at very low concentrations are highlighted in red. These include bimolecular reactions between radicals, or between  $^3\text{Rf}^*$  and methional, whose concentration, if formed, was too low to detect directly. Although plausible, mechanisms involving reactions between ephemeral species are expected to be inefficient in fluid solutions. Furthermore, intramolecular electron transfer from the carboxylate anion to the thiol-centered radical cation (pseudo-Kolbe reaction) may be impeded under acidic conditions favoring protonation of the carboxylate anion.



**Scheme 1.** Comparison of the mechanisms proposed by Maujean and Seguin (Maujean et al., 1983) and by Yang et al. (Yang et al., 1967) for the formation of volatile sulfur species upon irradiation of **Rf** solutions containing **Met**. Bimolecular reactions between intermediates present at very low concentrations are highlighted in red.

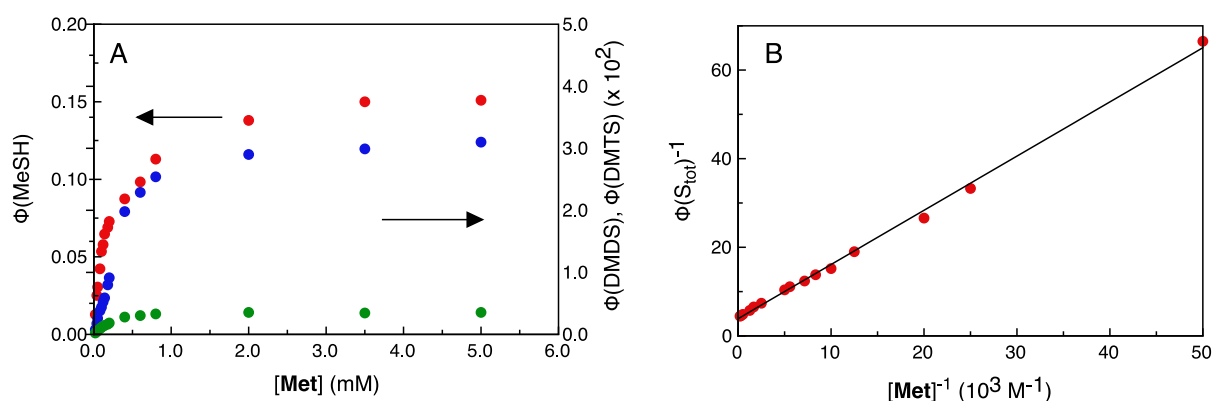
The mechanism in Scheme 1 involves the bimolecular reaction between  $^3\text{Rf}^*$  and **Met**. Because of this, the quantum yield for the formation of volatile sulfur species, and hence the impact of the light-struck flavor, will depend on the concentration of **Met** as has been empirically observed previously. In a photochemical transformation, the quantum yield ( $\Phi$ ) for the formation of a photoproduct is given by eq. 1 (Wagner, 1989):

$$\Phi = \frac{\text{mols of product}}{\text{mols of excited states (photons absorbed)}} \quad \text{eq(1)}$$

where the mols of product and photons are determined by SPME/GC/MS or PFPD and chemical or physical actinometry, respectively. Under our standard conditions (pH 3.5), we found no dependance of the quantum yields upon the irradiation wavelength over the range 365 – 490 nm in agreement with the absence of participation of higher excited states over this wavelength range (see supplementary information). From mass spectral analysis of the irradiated solutions, we identify MeSH as the main photoproduct, accompanied by DMDS and dimethyltrisulfide (DMTS). The latter was also observed by Maujean and Seguin and attributed to subsequent oxidation of the primary photoproducts. (Maujean et al., 1983)

The quantum yield of each species as a function of **Met** concentration is shown in Figure 1A. Over the concentration range explored, MeSH is the major photoproduct formed with a quantum efficiency of 5.5% at 0.1 mM [**Met**] (corresponding to 15 mg / L). The efficiency of MeSH formation is quite significant given the ambient solar flux over the wavelength range that **Rf** absorbs and, combined with the low perception threshold for sulfur-containing volatiles, explains the high sensitivity of Champagnes and white wines rich in **Met** and **Rf** towards the light-struck fault. Clearly, increasing the concentration of **Met** results in greater quantum efficiency for the formation of all three species since a greater proportion of  $^3\text{Rf}^*$  is intercepted by **Met** before deactivating through other channels. It is possible to determine the limiting quantum yield for the oxidation of **Met** by excited **Rf** through a double-reciprocal plot of  $\Phi_{\text{S(Tot)}}^{-1}$  vs.  $[\text{Met}]^{-1}$ , where  $\Phi_{\text{S(Tot)}} = \Phi_{\text{MeSH}} + 2 \cdot \Phi_{\text{DMDS}} + 3 \cdot \Phi_{\text{DMTS}}$  and represents the total atom equiv. of sulfur released from **Met** per photon absorbed. (Wagner, 1989) As shown in Figure 1B, this plot is linear with an intercept of 3.90 corresponding to  $\Phi_{\text{STot}}(\infty) = 0.26$ . Thus, at infinite **Met** concentration, roughly one fourth of all photons absorbed will lead to the liberation of a sulfur atom from **Met**. Correcting for the efficiency of formation of  $^3\text{Rf}^*$ , (70%), one finds that the intrinsic efficiency of the reaction between the excited riboflavin triplet state and  $^3\text{Rf}^*$  can reach  $\phi_{\text{Met}} = 0.37$ . The slope of the double-reciprocal plot gives  $(\phi_{\text{Met}} \cdot k_{\text{Met}} \cdot \tau_{\text{T}})^{-1}$ , from which a value of  $k_{\text{Met}} = 1.5 \times 10^8 \text{ L.mol}^{-1}\text{s}^{-1}$  can be determined. This value is somewhat higher than that determined using laser flash photolysis at a less acidic pH (Draper & Ingraham, 1968).

185



186

187 **Figure 1.** (A) Quantum yields for the formation of MeSH (red circles) DMDS (blue circles,  
 188 and DMTS (green circles) upon irradiation of deaerated solutions of **Rf** at pH 3.5 vs. **Met**  
 189 concentration ( $\lambda_{\text{irr}} = 435 \text{ nm}$ ). (B) Double-reciprocal plot of the total sulfur equiv. from the  
 190 data in (A). Line is best fit according to  $\Phi_{\text{S(Tot)}}^{-1} = 0.0012[\text{Met}]^{-1} + 3.90$  with  $r^2 = 0.998$ .

191

192 To test the mechanism presented in Scheme 1, we proceeded to follow the quantum  
 193 yield for formation of volatile sulfur species as a function of the pH of the solution. We can  
 194 expect that under acidic conditions, when the carboxylate fragment in **Met** is protonated (pH  
 195  $\leq 2.2$ ) (Vcelakova, Zuskova, Kenndler, & Gas, 2004), the pseudo-Kolbe fragmentation will be  
 196 inefficient and formation of the volatile sulfides impeded. Conversely, the fragmentation  
 197 should be facilitated at basic pH. The results obtained at various pH (Table 1), clearly indicate  
 198 that while there is some pH dependence on the relative yields of MeSH, DMDS, and DMTS,  
 199 the yield for that total atom-equivalents of sulfur ( $\Phi_{\text{S(Tot)}}$ ) that is formed remains relatively  
 200 constant. Even at pH  $< 2$ , where **Met** is predominately in its cationic form, there is no  
 201 significant decrease in  $\Phi_{\text{S(Tot)}}$ .

202

203 **Table 1.** Quantum yields<sup>a</sup> for the formation of volatile sulfur species upon irradiation of  
 204 model solutions.<sup>b</sup>

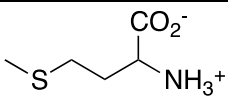
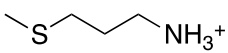
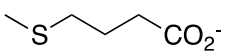
pH	$\Phi_{\text{MeSH}}$	$\Phi_{\text{DMDS}}$	$\Phi_{\text{DMTS}}$	$\Phi_{\text{S(Tot)}}$
1.4	0.025	0.011	0.024	0.119
3.0	0.037	0.025	0.022	0.153
4.0	0.067	0.024	0.020	0.174
5.0	0.062	0.017	0.021	0.160
7.0	0.037	0.011	0.022	0.125
8.9	0.016	0.011	0.023	0.106



<sup>a</sup>±15%. <sup>b</sup>Solutions were purged with Ar and irradiated at 435 nm (15 min), [**Met**]=0.1 mM, [**Rf**]= 50 μM.

The absence of significant pH dependance of the yield of the volatile sulfur species suggests that the intervention of the amino or the carboxylate fragments in the mechanism leading to their formation is not essential. This can be independently verified by comparing the product distribution and quantum yield for **Met** analogues in which either the carboxylate or the ammonium fragment is absent. The results for this study are collected in Table 2 for **Met**, 3-methylthiopropylamine, and 3-thiomethylbutanoic acid. The latter was prepared through the ring-opening reaction of sodium methylthiolate onto  $\gamma$ -butyrolactone as described previously (Zhou, Lu, Wang, Borhan, & Reid, 2010). Within experimental error, we see only small differences in the yield or product distribution of MeSH, DMDS or DMTS, in agreement with the absence of participation by either functional group. This result is in direct contradiction with the radical-fragmentation induced decarboxylation involving a six-membered transition state leading to the formation of  $\alpha$ -aminoalkyl radical. The subsequent formation of an imine intermediate and its hydrolysis to methional also appears unlikely on the basis of the photolysis of solutions containing 3-thiomethylbutyric acid. Furthermore, we observed that DMDS is formed even at short irradiation times in degassed solutions, suggesting that a different reaction pathway other than autooxidation of MeSH exists. Together, these results lead us to believe that an alternative mechanism may contribute to the formation of the light-struck fault.

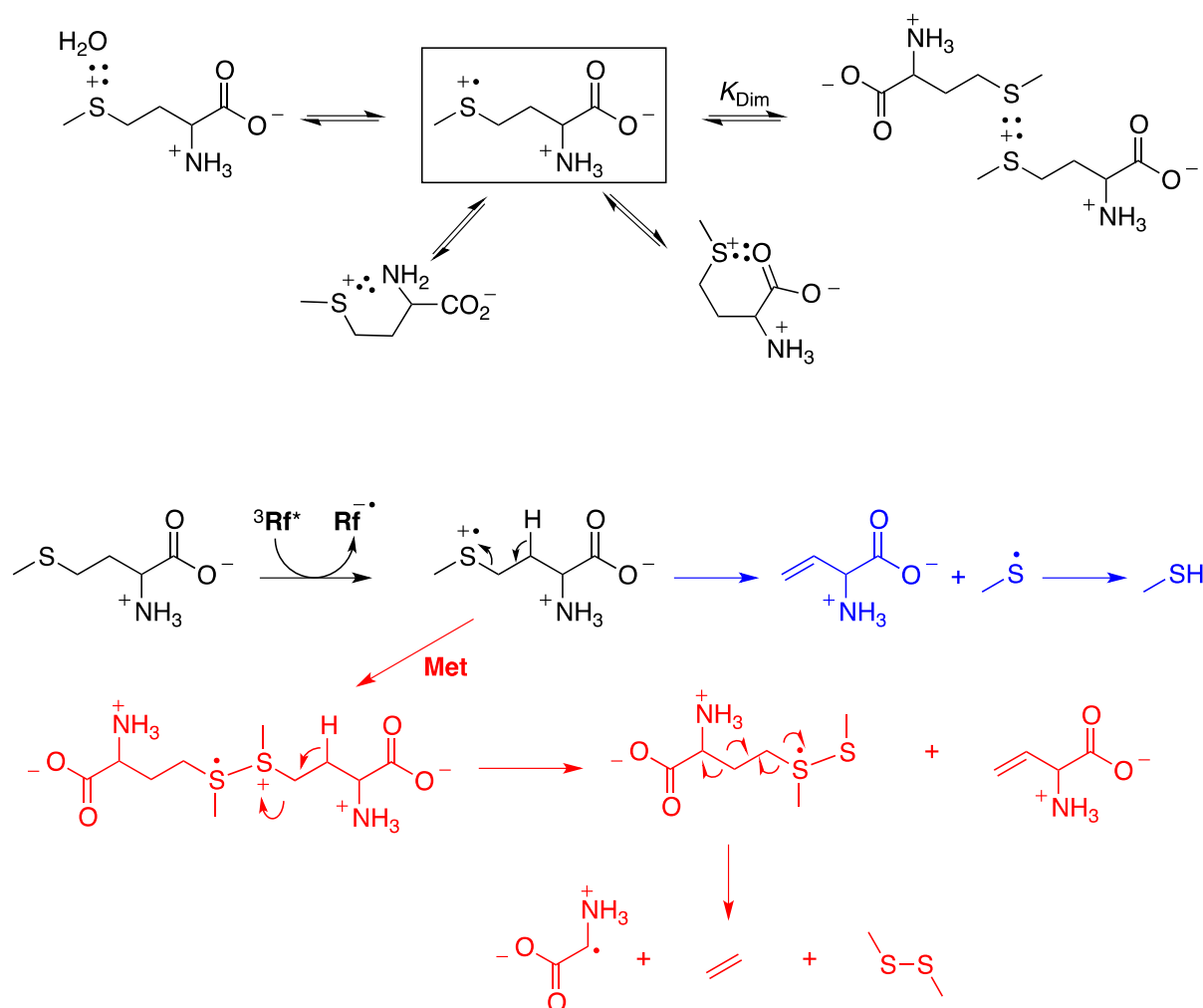
**Table 2.** Structural effects on the formation quantum yield of volatile sulfur species.<sup>a</sup>

Substrate	pH	$\Phi_{\text{MeSH}}$	$\Phi_{\text{DMDS}}$	$\Phi_{\text{DMTS}}$	$\Phi_{\text{S(Tot)}}$
	3.5	0.104	$6.37 \times 10^{-3}$	$1.18 \times 10^{-3}$	0.12
	3.5	0.094	$4.36 \times 10^{-3}$	$1.04 \times 10^{-3}$	0.11
	5.6	0.071	$3.92 \times 10^{-3}$	$0.89 \times 10^{-3}$	0.08

<sup>a</sup>Error = ±15%. Solutions were purged with Ar and irradiated at 435 nm (15 min), Concentrations of substrate = 0.1 mM, [**Rf**] = 250 μM.

The oxidation site in **Met** is understood to be located on the sulfur atom as it possesses the lowest ionization potential (Naito, Kominami, Akasaka, & Hatano, 1977; Reynaud,

Malfoy, & Canesson, 1980). In solution, sulfur-centered cation radicals can be stabilized through formation of a three electron bond with Lewis base sites in the solvent or other solutes, or intramolecularly with neighboring groups (Hendon, Carbery, & Walsh, 2014). In the case of **Met**<sup>•+</sup>, transient absorption spectroscopy identified the formation of a dimer cation radical at low pH, whereas at more basic pH values, a 5-membered cyclic intermediate with an S<sup>•</sup>...N bond was proposed (Scheme 2) (Bobrowski, Hug, Marciniak, & Kozubek, 1994). The formation of other intermediates is nicely reviewed by Forbes and co-workers in their elegant report on the use of time-resolved EPR experiments to elucidate the complex behavior of **Met**<sup>•+</sup> in solution (Yashiro, White, Yurkovskaya, & Forbes, 2005). Under acidic conditions, these authors find that the formation of the dimer cation radical is favored due to protonation of the amino group. Therefore, we may expect that under the more acidic conditions of photolysis present in white wines and Champagnes, the formation of (**Met**)<sub>2</sub><sup>•+</sup> may be plausible. To evaluate this, the equilibrium constant  $K_{\text{Dim}}$  can be estimated from the rates for the formation and the dissociation of the dimer cation radical. These were determined in aqueous solutions for various dialkylsulfides by Asmus and co-workers using pulse-radiolysis, who found them to be very sensitive to steric repulsion (Chaudhri, Mohan, Anklam, & Asmus, 1996). In the case of dimethylsulfide, a value of  $K_{\text{Dim}} = 20$  is calculated at 0.1 mM. For the heterodimer between Me<sub>2</sub>S<sup>•+</sup> and Et<sub>2</sub>S, a value of  $K_{\text{Dim}} = 3.5$  is found instead. We may expect that the dimerization constant for **Met** would lie in-between these two values, indicating that its formation is thermodynamically favored under the experimental conditions found in white wines and Champagnes.

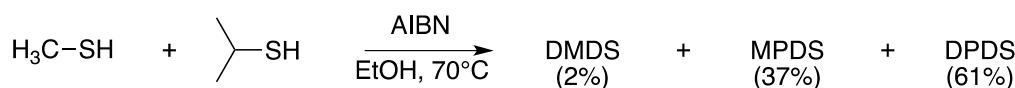
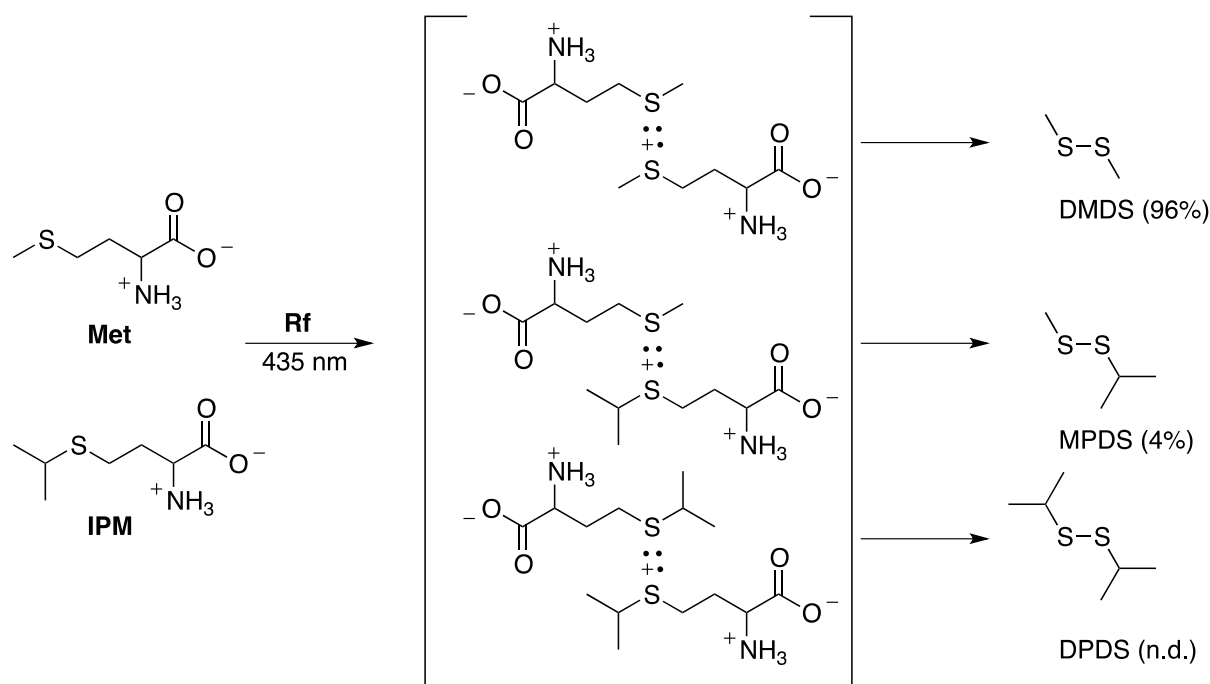


**Scheme 2.** Above: Stabilization of thioether cation radical in solution through a three-electron bond with solvent ( $\text{H}_2\text{O}$ ), neighboring group, or intermolecularly through formation of a dimer cation radical. Below: Proposed mechanistic pathways for the formation of volatile sulfur species upon irradiation of **Rf** in the presence of **Met** through either unimolecular  $\beta$ -deprotonation to yield  $\text{MeSH}$  (in blue) or through a dimer cation radical to give  $\text{DMDS}$ , ethylene, vinylglycine, and a glycine radical (in red).

The formation of a **Met** dimer cation radical may impact the formation of volatile sulfur species by allowing alternative fragmentation pathways. Thus, as shown in Scheme 2, deprotonation at the  $\beta$  position would lead to the elimination of vinylglycine. The ensuing S-centered radical can then undergo  $\beta$ -fragmentation to release  $\text{DMDS}$ , ethylene, and a stable glycine radical. Interestingly, this mechanism leads to the direct formation of  $\text{DMSD}$  without the need for oxidation of  $\text{MeSH}$  and could explain its formation at short irradiation times even in the absence of oxygen as observed above. The formation of ethylene as a by-product of **Met** oxidation was previously observed and provides indirect support for this

mechanism (Lieberman, Kunishi, Mapson, & Wardale, 1965; Yang et al., 1967). Additionally, we have observed the formation of glycine by GC / MS (see supplementary information) during the irradiation of model wine solutions containing **Rf** (250  $\mu$ M) and **Met** (0.1 mM).

To further probe the possible intermediacy of the (**Met**)<sub>2</sub><sup>++</sup> in the direct formation of DMDS, we proceeded to compare the distribution of unsymmetrical disulfides that are formed when **Met** and its isopropyl analogue (**IPM**) are irradiated under identical conditions (Scheme 3). According to the effect of steric encumbrance on the formation of the sulfur-centered dimer cation radical, we would expect the formation of the mixed (**Met**·**IPM**)<sup>++</sup> species to be unfavored. Indeed, the value of  $K_{\text{Dim}}$  estimated from the formation and dissociation kinetics at 0.1 mM is less than unity ( $K_{\text{Dim}} = 0.8$  for Me<sub>2</sub>S and *i*Pr<sub>2</sub>S) (Chaudhri et al., 1996). Because of this, disulfide formation should be biased towards the less sterically-hindered disulfide if it follows from the dimer cation radical. In contrast, free radical recombination is known to be less sensitive to steric hindrance and we may expect a more statistical distribution of disulfides to be formed. The irradiation of **IPM** solutions in the presence of **Rf** under the same conditions as for **Met** results in the sole formation of isopropyl thiol, with diisopropyldisulfide appearing only at high conversions. This is in agreement with the inhibited formation of the dimer cation radical intermediate for **IPM** due to steric interactions. In a competition assay in which equimolar concentrations of **Met** and **IPM** (0.5 mM each) were irradiated in the presence of **Rf**, we only observe the formation of DMDS (96%), with only 4% of mixed disulfide and no diisopropyldisulfide (DPDS) formed (Scheme 3). In fact, even employing a 25-fold excess of **IPM** to over-compensate for its 10-fold lower reactivity towards **Rf**<sup>\*</sup> (see supplementary information), the ratio of DMDS : MPDS : DPDS is only of 71 : 26 : 3. In contrast, a control experiment in which equimolar concentrations of the thiomethyl- and thioisopropyl- radicals were thermally generated in solution through hydrogen abstraction using a radical initiator (AIBN) evidenced the preferential formation of the mixed and diisopropyl disulfides (37% and 61%, respectively). This confirms that free radical dimerization of the alkylsulfur radicals is not overly sensitive to steric hindrance and that disulfide formation during irradiations does not follow this route. The bias towards formation of MPDS and DPDS over DMDS may reflect differences in stability between the radical species.



**Scheme 3.** Competition experiment between **Met** and **IMP** with proposed intermediacy of thioether dimer cation radical formation.

## Conclusion

The mechanism responsible for the light-struck fault in white wines and Champagnes was found to be extremely efficient as determined from the limiting quantum yield for sulfur atom equivalent liberated per photon absorbed (26%), corresponding to 37% from riboflavin triplet excited states. Thus, even at low **Met** concentrations (0.1 mM), the quantum yield for the formation of  $\text{CH}_3\text{SH}$  and **DMDS** are high (5% and 0.4%, respectively). Our results do not evidence a strong dependence of the quantum yields of product formation and their distribution on the pH or excitation wavelength. This suggests that neighboring group effects are small, in agreement with results from mechanistic studies using **Met** analogues. From this, we deduce that the formation of a dimer cation radical species may explain the formation of **DMDS** at short reaction times and in the absence of an oxidizing species such as molecular oxygen. The greater stabilization of a dimer cation radical may offer interesting approaches towards preventing or mitigating the formation of volatile sulfur species responsible for the light-struck fault in Champagnes, white wines, and, potentially, dairy products.

## Acknowledgments

Financial support from the ANR through grant ANR-17-CE07-0043-01, the Conseil Regional Nouvelle Aquitaine (project 2018-1R20305), the Univ. of Bordeaux, and the CNRS is gratefully acknowledged. We are also grateful to the CESAMO analytical facilities of the Univ. of Bordeaux for their assistance.

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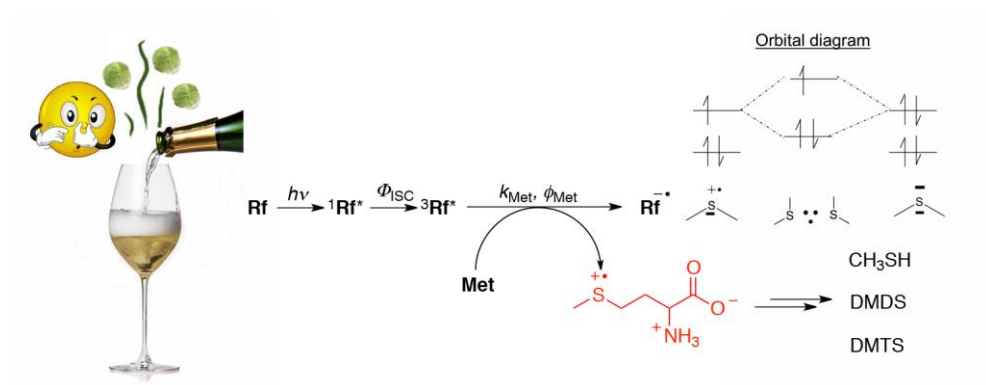
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419 **Graphical abstract**



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