Model Reactions on the Stability of Disulfides in Heated Foods

Helmut Guth, Thomas Hofmann, Peter Schieberle, and Werner Grosch*

Deutsche Forschungsanstalt für Lebensmittelchemie and Institut für Lebensmittelchemie der Technischen Universität München, Lichtenbergstrasse 4, D-85748 Garching, Germany

Bis(2-methyl-3-furyl) disulfide (MFT-MFT) and bis(2-furfuryl) disulfide (FFT-FFT) dissolved either in benzene or in water were heated at 100 °C for 2 h. In benzene, 2-methyl-3-furanthiol and 2-furfurylthiol were formed when the hydrogen donor 1,4-cyclohexadiene or 1,4-hexadiene or the antioxidant BHT was present. In water, MFT-MFT, FFT-FFT, and also cystine were hydrolyzed with formation of the corresponding thiols, which were trapped by the reaction with 4-vinylpyridine. Labeling experiments and the measurement of EPR spectra gave an insight into the mechanism of the disulfide cleavage.

Keywords: *Bis(2-methyl-3-furyl) disulfide; bis(2-furfuryl) disulfide; disulfide cleavage; disulfides; formation from thiols*

INTRODUCTION

Bis(2-methyl-3-furyl) disulfide (MFT-MFT) and bis-(2-furfuryl) disulfide (FFT-FFT) are very strong odorants due to their low odor thresholds (Gasser and Grosch, 1990a). MFT-MFT has been detected in cooked meat (Gasser and Grosch, 1988, 1990b; Farmer and Patterson, 1991; Grosch and Zeiler-Hilgart, 1992) and FFT-FFT in roasted coffee (Tressl, 1981) as well as in wheat bread (Baltes and Song, 1994). The contribution of MFT-MFT to the flavor of roasted coffee (Blank et al., 1992) and black tea (Guth and Grosch, 1993) has been suggested on the basis of aroma extract dilution analyses.

Recently, it has been shown (Hofmann et al., 1995) that these disulfides are easily formed by oxidation of the corresponding thiols even under the condition of cold storage. It has been discussed that this reaction may also take place during enrichment of volatiles for analysis by gas chromatography. For this reason, it is not clear whether MFT-MFT and FFT-FFT belong in fact to the odorants of heated foods, such as cooked meat, or are artifacts formed during sample preparation.

In context with this question, the stability of MFT-MFT and FFT-FFT in heated foods is of interest. To get an insight, the following model reactions with both disulfides in water and also in benzene were performed. The latter solvent was used to mimic apolar conditions, free of compounds from which hydrogen atoms might be abstracted by radicals resulting from the disulfides.

EXPERIMENTAL PROCEDURES

Chemicals. The following compounds were obtained commercially: 2-furfurylthiol (FFT), 2-methyl-3-furanthiol (MFT), 4-vinylpyridine, L-cysteine, 1,4-cyclohexadiene, 1,4-hexadiene, and 2,6-di-*tert*-butyl-*p*-hydroxytoluene (BHT) were from Aldrich, Steinheim, Germany; D_2O and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were gifts of Dr. W. Bors (GSF Research Center, Neuherberg, Germany).

Synthesis of Unlabeled Compounds. *Bis(2-furfuryl) disulfide (FFT-FFT) and bis(2-methyl-3-furyl) disulfide (MFT-MFT)* were prepared according to the procedure of Hofmann et al. (1995).

[β-(4-Pyridyl)ethyl] 2-furfuryl Thioether (PEFTE). A mixture of 2-furfurylthiol (0.46 g, 4.0 mmol) and 4-vinylpyridine (0.5 g, 4.8 mmol), dissolved in diethyl ether (5 mL), was stirred for 2 h at room temperature in the dark. HRGC-MS of PEFTE was performed with an aliquot (0.5 mL) of the reaction mixture: MS-EI, 81 (100%), 32 (85%), 186 (25%), 53 (15%), 39 (10%), 106 (10%), 149 (10%), 173 (10%); MS-CI (isobutane), 220 (100%, $M^+ + 1$).

[β-(4-Pyridyl)ethyl] 2-methyl-3-furyl thioether (PEMFTE) was prepared as reported for PEFTE by using 2-methyl-3-furanthiol instead of 2-furfurylthiol: MS-EI, 106 (100%), 107 (70%), 127 (50%), 45 (40%), 51 (35%), 78 (30%), 219 (M^+, 30%); MS-CI (isobutane), 220 (100%, $M^+ + 1$).

Synthesis of Labeled Compounds. *[$^2H_2$]-2-Furfurylthiol ([$^2H_2$]FFT), [$^2H_3$]-2-methyl-3-furanthiol ([$^2H_3$]MFT), and [$^2H_6$]-bis(2-methyl-3-furyl) disulfide ([$^2H_6$]MFT-MFT)* were prepared and purified according to the methods of Sen and Grosch (1991). [$^2H_4$]Bis(2-furfuryl) disulfide ([$^2H_4$] FFT-FFT) was synthesized as reported for the unlabeled disulfide (Hofmann et al., 1995): MS-EI, 83 (100%), 53 (32%), 230 (4%, M^+); MS-CI (isobutane), 231 (100%, $M^+ + 1$).

[β-(4-Pyridyl)ethyl] [$^2H_2$](2-furfuryl) thioether ([$^2H_2$]PEFTE) and [β-(4-pyridyl)ethyl] [$^2H_3$](2-methyl-3-furyl) thioether ([$^2H_3$]-PEMFTE) were prepared as reported above for the corresponding unlabeled compound.

[$^2H_2$]PEFTE: MS-EI, 83 (100%), 188 (25%), 55 (15%), 175 (10%), 39 (5%), 51 (5%), 84 (5%), 221 (M^+, 5%); MS-CI (isobutane), 222 (100%, $M^+ + 1$).

[$^2H_3$]PEMFTE: MS-EI, 106 (100%), 130 (70%), 46 (55%), 107 (55%), 222 (M^+, 45%), 43 (40%), 108 (40%), 45 (40%); MS-CI (isobutane), 223 (100%, $M^+ + 1$).

Concentrations of Labeled Compounds. The concentrations of the labeled compounds were determined by HRGC with methyl octanoate as the internal standard. The response factors were determined by HRGC of mixtures containing methyl octanoate (100 μg/mL) and the corresponding unlabeled compound (100–150 μg/mL).

High-Resolution Gas Chromatography (HRGC)–Mass Spectrometry (MS) Analysis. HRGC was performed by means of a gas chromatograph, type 4200 (Carlo Erba, Hofheim, Germany) and by using the following thin-film capillaries: CP-Wax 51 for amines (25 m × 0.32 mm i.d., 0.2 μm df, Chrompack, Frankfurt, Germany) and FFAP-CB (25 m × 0.32 mm i.d., 0.2 μm df, Chrompack).

Mass spectrometry was performed by means of the mass spectrometer Incos XL (Finnigan, Bremen, Germany) or an ion trap detector (Sen et al., 1991). The conditions used for the measurement of the mass spectra in the electron impact mode (MS-EI) and in the chemical ionization mode (MS-CI) as well as those used for the registration of the mass chromatograms have been reported earlier (Guth and Grosch, 1990;

* Author to whom correspondence should be addressed.

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Table 1. Thin-Film Capillaries, Selected Ions, and Calibration Factors for Mass Chromatography

analyte	capillary	selected ion (m/z)	IS[a]	selected ion (m/z)	calib factor
2-furfurylthiol (FFT)	FFAP	81	[$^2H_2$]FFT	83	0.83
bis(2-furfuryl) disulfide (FFT-FFT)	FFAP	227	[$^2H_4$]FFT-FFT	231	0.83
[β-(4-pyridyl)ethyl] 2-furfuryl thioether (PEFTE)	FFAP, CP-Wax 51	220	[$^2H_2$]PEFTE	222	0.83
2-methyl-3-furanthiol (MFT)	FFAP	115	[$^2H_3$]MFT	118	0.98
bis(2-methyl-3-furyl) disulfide (MFT-MFT)	FFAP	227	[$^2H_6$]MFT-MFT	233	0.98
[β-(4-pyridyl)ethyl] 2-methyl-3-furyl thioether (PEMFTE)	FFAP, CP-Wax 51	220	[$^2H_3$]PEMFTE	223	0.98

[a] Internal standard.

Table 2. Thermolysis of Mixtures of Disulfides and Their Labeled Analogues

		after a reaction period of 2 h[a]	
no.	reaction system disulfides (μg)	starting disulfides (μg)	product disulfide (μg)
	I. In Benzene (1 mL) at 100 °C		
1	MFT-MFT (100) plus [$^2H_6$]MFT-MFT (100)	MFT-MFT (83) plus [$^2H_6$]MFT-MFT (83)	[$^2H_3$]MFT-MFT (25)
2	FFT-FFT (183) plus [$^2H_4$]FFT-FFT (181)	FFT-FFT (121) plus [$^2H_4$]FFT-FFT (122)	[$^2H_2$]FFT-FFT (73)
	II. In Water (50 mL) at 100 °C		
3	MFT-MFT (100) plus [$^2H_6$]MFT-MFT (100)	MFT-MFT (73) plus [$^2H_6$]MFT-MFT (75)	[$^2H_3$]MFT-MFT (43)
4	FFT-FFT (100) plus [$^2H_4$]FFT-FFT (100)	FFT-FFT (56) plus [$^2H_4$]FFT-FFT (23)	[$^2H_2$]FFT-FFT (11)

[a] At the end of the reaction the disulfides were quantified by mass chromatography.

Table 3. Formation of Thiols by Thermolysis of Disulfides in the Presence of 4-Vinylpyridine

	reaction system		amount (μg) after 2 h[a]	
no.	disulfide (μg)	4-vinylpyridine (μg)	starting disulfide[b,c] (μg)	thiol[c,d] (μg)
		I. In Benzene (1 mL) at 100 °C		
1	FFT-FFT (150)	100	FFT-FFT (132)	FFT (<1)
2	MFT-MFT (150)	100	MFT-MFT (145)	MFT (<1)
		II. In Water (50 mL) at 100 °C		
3	FFT-FFT (56)	500	FFT-FFT (<1)	FFT (52)
4	MFT-MFT (180)	500	MFT-MFT (25)	MFT (112)
5	cystine (4.1)	500	cystine (<0.1)	cysteine (0.74)

[a] Reaction systems 1–4: at the end of the reaction the excess of 4-vinylpyridine was removed by addition of L-cysteine (cf. Experimental Procedures). [b] FFT-FFT and MFT-MFT were quantified by using [$^2H_4$]FFT-FFT and [$^2H_6$]MFT-MFT, respectively, as internal standards (Table 1). [c] Cystine and cysteine, the latter in the form of its [β-(4-pyridyl)ethyl] thioether derivative, were determined by amino acid analysis (Friedman et al., 1970). [d] The thioethers formed by the reaction of FFT and MFT with 4-vinylpyridine were determined by using [$^2H_4$]PEFTE and [$^2H_3$]PEMFTE, respectively, as internal standards (Table 1).

Table 4. Thermolysis of Disulfides Dissolved in Benzene Containing a Hydrogen Donor

	reaction system				at the end of the reaction	
no.	disulfide (μg)	hydrogen donor	vol (mL) of benzene	reaction time/temp	disulfide[a] (μg)	thiol[a] (μg)
1	FFT-FFT (522)	1,4-cyclohexadiene (0.5 mL)	0.5	12 h/100 °C	FFT-FFT (359)	FFT (50)
2	FFT-FFT (522)	BHT (1 mg)	1	12 h/100 °C	FFT-FFT (312)	FFT (58)
3	MFT-MFT (210)	1,4-cyclohexadiene (0.1 mL)	5	2 h/100 °C	MFT-MFT (100)	MFT (30)
4	MFT-MFT (210)	1,4-hexadiene (0.1 mL)	5	2 h/100 °C	MFT-MFT (180)	MFT (30)

[a] The disulfides and thiols were quantified by using the corresponding labeled internal standards listed in Table 1.

Sen et al., 1991). For the isotope dilution assays, either the MS Incos XL or the ion trap detector was coupled with the capillaries indicated in Table 1. Ion abundances were monitored in the ranges given in Table 1. Comparison of the abundance of the selected ion of the analyte to the abundance of the selected ion of the internal standard (see Table 1) provided the data needed to carry out the quantitative calibration of the method. The calibration factors (Table 1) were calculated from the model mixtures as recently described (Guth and Grosch, 1990; Sen et al., 1991).

Electron Paramagnetic Resonance (EPR) Spectroscopy. The EPR spectra were recorded on a Bruker ESP 300 spectrometer (Bruker, Karlsruhe, Germany). The experimental parameters were as follows: modulation amplitude, 0.1 G; sweep rate, 2.8 G^{-1} at a frequency of 9.75 GHz and a gain of 1×10^6.

In a sealed vial (10 mL) a mixture consisting of the disulfide (3.1 μmol) and the spin trap (10 μmol) in either benzene or water (3 mL each) was heated at 100 °C. After 1 h, the mixture was rapidly cooled in an ice bath, and then the EPR spectrum was recorded.

Model Experiments. The composition of the models and the reaction conditions are shown in Tables 2–4.

A solution of the disulfide in diethyl ether was pipetted into a vial. After the solvent was evaporated under a stream of nitrogen, the remaining disulfide was taken up in either water or benzene containing further reactants in some experiments (see Tables 2–4). The vial was sealed and heated. At the end of the reaction time, definite amounts of the labeled internal standards, specified in Tables 2–4, were added to the model. Mixtures dissolved in water were extracted with diethyl ether (3 × 15 mL). After drying over Na_2SO_4, the extract was concentrated to 1 mL by distilling off the solvent. An aliquot (1.0 μL) of the concentrate was then analyzed by HRGC–MS. Aliquots (0.5 μL) of the reaction mixtures in benzene were directly analyzed by HRGC–MS.

RESULTS AND DISCUSSION

A mixture consisting of labeled and unlabeled MFT-MFT (Figure 1), dissolved in either benzene (no. 1 in Table 2) or water (no. 3), was heated to 100 °C. After 2 h, the mixed disulfide [$^2H_3$]MFT-MFT (Figure 1) was formed in yields of 12.5% (benzene) and 21.5% (water), respectively. In a corresponding experiment with the

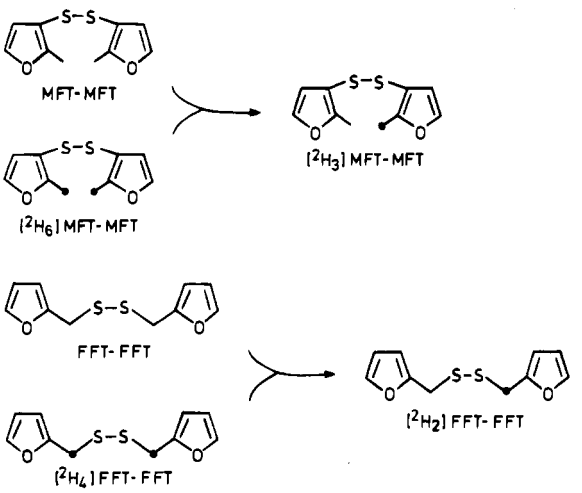

Figure 1. Chemical structures of the disulfides in the model experiments 1–4 (Table 1). (●) position of the deuterium labeling.

disulfide mixture FFT-FFT/[$^2H_4$]FFT-FFT (no. 2 and 4, Table 2), significant amounts of FFT-[$^2H_2$]FFT were detectable. As indicated in Figure 1, these data suggest the cleavage of the disulfides with subsequent combination of the fragments to new disulfides.

In the experiments listed in Table 3, FFT-FFT (no. 1 and 3) as well as MFT-MFT (no. 2 and 4) were heated in the presence of the thiol trapping reagent 4-vinylpyridine. After a reaction time of 2 h, most of the two disulfides was recovered, and no thiol was detectable, when benzene was used as solvent (no. 1 and 2). In contrast to the experiments shown in Table 2, a cleavage of the disulfides could not be detected, as the corresponding labeled disulfides were lacking in the models shown in Table 3. However, in aqueous solution (no. 3 and 4, Table 3) the disulfides were degraded by 100% (FFT-FFT) or 86% (MFT-MFT), respectively, giving rise to significant amounts of the corresponding thiols which were detected after conversion with 4-vinylpyridine into PEFTE and PEMFTE. Also, cystine was cleaved under these conditions (no. 5), forming cysteine in a yield of 18%.

To clarify the source of the hydrogen atoms in the thiols formed, the experiment with MFT-MFT (no. 4) was repeated by using D_2O instead of H_2O as solvent. [β-(4-Pyridyl)[$^2H_1$]ethyl] 2-methyl-3-furylthioether ([$^2H_1$]-PEMFTE) was identified on the basis of its MS-EI spectrum (Figure 2). In comparison to the MS-EI of the unlabeled PEMFTE (see data under Experimental Procedures), the mass of the molecular ion was increased from *m/z* 219 to 220 and that of the base fragment ion from *m/z* 106 to 107 (Figure 2). This indicates the incorporation of one deuterium atom into the thioether derivative formed as the major product (yield 63%) in D_2O.

The formation of [$^2H_1$]PEMFTE can be explained by a reaction sequence that is initiated by the hydrolysis of MFT-MFT yielding [$^2H_1$]MFT and [$^2H_1$]-2-methyl-3-furylsulfenic acid (Figure 3); then [$^2H_1$]MFT is trapped by 4-vinylpyridine. However, as the yield of [$^2H_1$]-PEMFTE was higher than 50% (no. 4, Table 3), we assume that a disproportionation reaction of the sulfenic acid into the corresponding sulfinic acid generates additional amounts of [$^2H_1$]MFT (Figure 3).

As discussed above, MFT-MFT and FFT-FFT, each dissolved in benzene, were split into fragments that recombined to the starting disulfides (no. 1 and 2 in

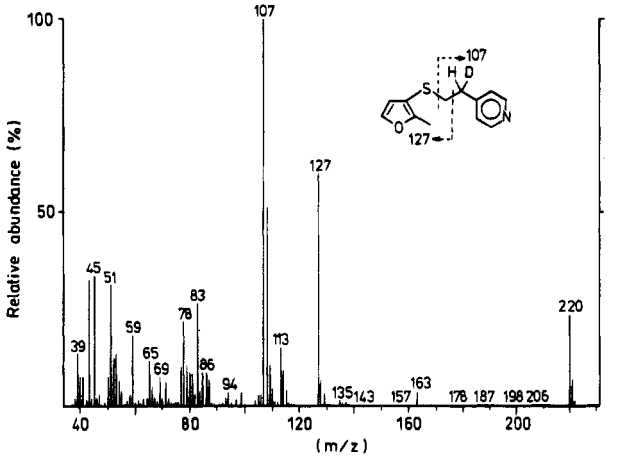

Figure 2. MS-EI of [β-(4-pyridyl)[$^2H_1$]ethyl] 2-methyl-3-furyl thioether ([$^2H_1$]PEMFTE).

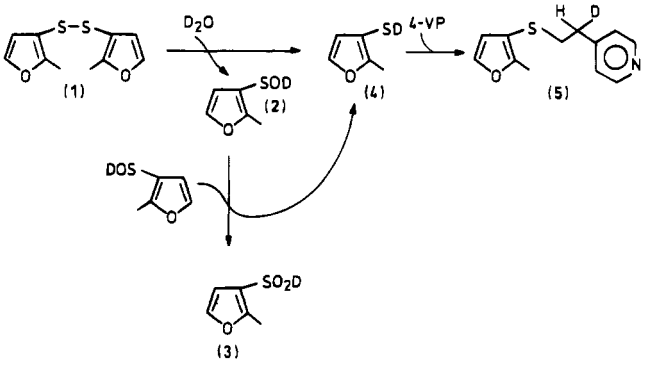

Figure 3. Postulated reaction sequence for the hydrolysis of MFT-MFT in D_2O (1), [$^2H_1$]-2-methyl-3-furylsulfenic acid (2), [$^2H_1$]-2-methyl-3-furylsulfinic acid (3), [$^2H_1$]MFT (4), [$^2H_1$]-PEMFTE (5), and 4-vinylpyridine (VP).

Table 2). Although these disulfides are easily formed by oxidation of the corresponding thiols (Hofmann et al., 1995), this reaction is unlikely here, because no thiols were detectable after thermolysis of the disulfides in the presence of 4-vinylpyridine (no. 1 and 2 in Table 3). An alternative reaction would be a thermolysis of the disulfides into thiyl radicals, which might then combine to the mixed disulfides and to the starting disulfides found in experiments 1 and 2 (Table 2).

To check this hypothesis, FFT-FFT and MFT-MFT, dissolved in benzene, were heated in the presence of different hydrogen donors (no. 1–4 in Table 4). In contrast to the corresponding experiments without a hydrogen donor (no. 1 and 2 in Table 3), the thiols FFT and MFT were formed in the presence of 1,4-cyclohexadiene (no. 1 and 3 in Table 4). FFT was also produced after addition of the antioxidant BHT (no. 2). These results support the suggestion that the thermolysis of the disulfides in benzene yields thiyl radicals which, either, in the absence of hydrogen donors, recombine to disulfides or, in the presence of a hydrogen donor, form thiols by hydrogen abstraction. Thiyl radicals originating from MFT-MFT formed equal amounts of MFT by H abstraction from 1,4-cyclohexadiene (no. 3 in Table 4) as well as 1,4-hexadiene (no. 4). This result suggests that also other food components containing a 1,4-diene structure, e.g. linoleic acid, might act as hydrogen donors for thiyl radicals.

In experiment 1 (Table 4) with 1,4-cyclohexadiene added, the sum of the recovered FFT-FFT plus FFT amounted only to 78% of the amount of the initial FFT-FFT concentration. In the corresponding experiment

Table 5. Mass Spectral Data (MS-EI) of 1-(2-Furfurylthio)cyclohexadiene Isomers

isomer[a]	mol ion m/z	predominant fragment ions (rel abundance in %)
A	192 (28)	80 (100), 79 (80), 81 (32), 114 (31), 53 (20), 112 (19), 193 (18), 67 (16)
B	192 (58)	80 (100), 79 (85), 114 (65), 113 (59),81 (42), 77 (30),112 (20), 53 (12)
C	192 (100)	79 (72), 81 (41), 113 (41), 112 (24), 80 (22), 114 (20), 77 (17), 126 (16)
D	192 (100)	79 (78), 81 (60), 80 (44), 113 (28), 77 (25), 91 (22), 106 (24)

[a] Designation of the isomers refers to the peaks in Figure 5.

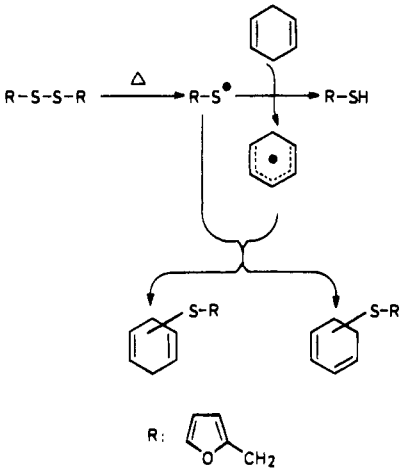

Figure 4. Formation of 1-(2-furfurylthio)cyclohexadiene isomers by the thermolysis of FFT-FFT in the presence of 1,4-cyclohexadiene.

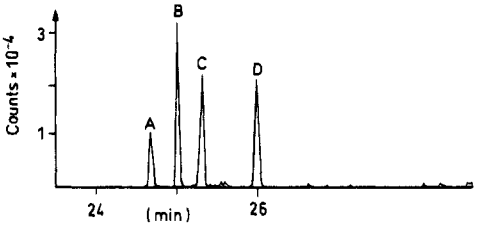

Figure 5. Mass chromatogram (cutting) at m/z 192 after reaction of the model FFT-FFT/1,4-cyclohexadiene (no. 1 in Table 4).

with MFT-MFT (no. 3), the loss (38%) was even greater. Using model 1 (Table 4), it was investigated whether these losses are due to the combination of thiyl radicals, released from FFT-FFT, with the cyclohexadienyl radicals, remaining after the abstraction of a hydrogen atom from 1,4-cyclohexadiene. The possible 1-(2-furfurylthio)cyclohexadiene isomers, formed by this reaction (Figure 4), would have a molecular mass of 192. Therefore, mass chromatograms at m/z 192 were recorded after model 1 had been reacted. Indeed, four peaks appeared in the mass chromatogram (Figure 5) which, on the basis of their MS-EI (Table 5), were identified as 1-(2-furfurylthio)cyclohexadiene isomers.

EPR measurements were performed to detect the postulated thiyl radicals. These studies were started by control experiments in which the spin trap reagent DMPO, dissolved in benzene and water, respectively, was treated in the same way as the models. As in no case was an EPR signal detectable, the following experiments were carried out.

MFT-MFT dissolved in benzene was heated together with DMPO and then rapidly cooled. Six weak signals, which could not be assigned to the expected thiyl radicals, appeared in the EPR spectrum (not shown). However, thermolysis of MFT-MFT in water resulted in a DMPO adduct signal (Figure 6) which, according to Li and Chignell (1991), is characteristic for the DMPO/OH radical adduct (a_N, 14.9 G, a_H, 14.9 G). We

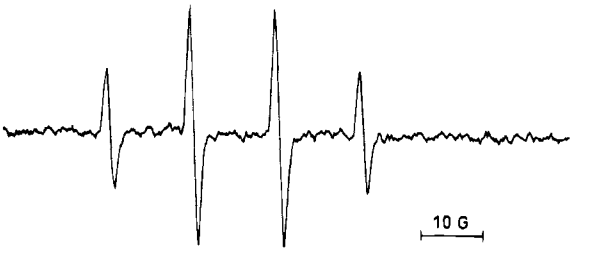

Figure 6. EPR spectrum DMPO/OH radical adducts produced during the thermolysis of MFT-MFT in water.

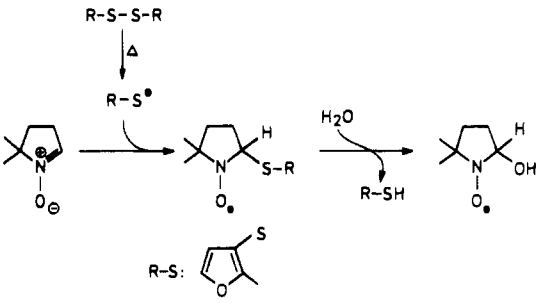

Figure 7. Formation of DMPO/OH radical adducts during thermolysis of MFT-MFT in water (hypothesis).

assume as an explanation that in addition to the hydrolysis of the disulfide (Figure 3), which most likely proceeds via an ionic mechanism (see above), MFT-MFT is also cleaved to some extent into thiyl radicals which combine with DMPO (Figure 7). However, this adduct is probably not stable during heating and is hydrolyzed, generating the DMPO-OH adduct.

CONCLUSION

Disulfides are not stable during heating of foods. They are mainly hydrolyzed with formation of thiols. In the absence of water, they are split into thiyl radicals, which may be transformed into thiols by abstraction of hydrogen atoms, e.g. from antioxidants such as BHT. These results allow the conclusion that thiols might play a greater role in the overall odor of boiled meat and coffee than the corresponding disulfides. For this reason, heated foods and model systems in which MFT-MFT and other disulfides were identified have to be reexamined to clarify whether these compounds contribute in fact to the overall odors (Hofmann et al., 1995).

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