Invited feature article

Gas-phase and matrix-isolation photochemistry of methyl thioglycolate, CH₃OC(O)CH₂SH: Influence of the presence of molecular oxygen in the photochemical mechanisms

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ABSTRACT

The photochemistry of methyl thioglycolate (MTG), $CH_3OC(O)CH_2SH$, in gas phase and in matrix isolation conditions was studied by means of FTIR spectroscopy, and the influence of the presence of molecular oxygen on the photochemical mechanisms was investigated. The UV–vis broad-band photolysis of MTG in gas phase originates $CH_3OC(O)CH_3$ and S_8, while in matrix conditions the photoproducts are CH_3OH, H_2CS, and CO, interacting inside the matrix cage. The photolysis of MTG in the presence of O_2 conducts to the formation of SO_2, independent of the experimental conditions, being CH_3OH, $HC(O)OH$, and CO the other photoproducts for the gas-phase photolysis, and H_2CO, CH_4, and CO_2 for the experiments performed in Ar matrix conditions.

1. Introduction

Thiols are widely used in free-radical photoinitiated polymerization reactions. Several reviews on this subject were published, dedicated to understand the role of the structure of the thiols and the presence of molecular oxygen on the kinetic and mechanistic aspects of the polymerization process [1,2]. In particular, it was reported that the use of methyl thioglycolate (MTG), $CH_3OC(O)CH_2SH$, results in greater photopolymerization reaction rates, attributed to a weakening of the sulfur–hydrogen bond by hydrogen bonding of the thiol group [1]. As far as we know, there are no reports on photochemical studies of MTG, which are of fundamental importance for a complete understanding of the mentioned photoinitiated mechanism.

On the other hand, MTG constitutes the smaller exponent of the series of $CH_3OC(O)(CH_2)_nSH$ compounds, reported as intermediated in the organic sulfur cycle in marine environments, produced by marine phytoplankton [3,4]. Sulfur-containing volatile organic compounds are highly reactive and play an important role in

atmospheric chemistry, particularly in the acid rain production and the formation of secondary aerosols [5,6]. Although the atmospheric reactivity of sulfur-rich species in gaseous phase is well known, their photoreactivity is still sparsely investigated. In this context, the study of the photolysis of MTG, and also its photochemical evolution in the presence of molecular oxygen, becomes significant for a deep comprehension of the atmospheric cycle of sulfur.

In this paper, and as part of a general project dealing with photochemical studies of sulfur-containing compounds with atmospheric interest, we present the gas-phase photolysis of MTG, in absence and in presence of molecular oxygen, followed by FTIR spectroscopy. The gas-phase studies are compared with the photochemistry in matrix-isolation conditions, which allow the detection of reactive intermediates of mainly unimolecular mechanisms, constituting a very useful technique for the complete elucidation of photochemical mechanisms. The photoproducts and intermediate species were detected by their IR spectra, and the photochemical mechanisms were proposed.

In a recent investigation, the IR spectra of gaseous and matrix-isolated MTG were studied [7]. The gas phase IR spectrum was interpreted by the presence of the most stable conformer only, which structure was determined by Fantoni et al. by means of

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microwave spectroscopy [8–10]. On the other hand, the matrix-isolated spectra present evidences of the presence of a high energy conformer. Additionally, the MTG dimer was also isolated by increasing the proportion of MTG in the matrix. According with DFT calculations, $(MTG)_2$ presents two hydrogen-bond interactions, each of them between the oxygen atom of the C—O group of one of the subunit with the hydrogen of the S—H group of the other one [7].

2. Experimental

A commercial sample of methyl thioglycolate (MTG, Aldrich 95%) was purified by repeated trap-to-trap distillation in vacuum. Its purity was checked by means of gas phase FTIR spectrum. The molecular oxygen and Ar (both from AGA) were passed through a trap cooled to $-100\,°C$ to retain possible traces of impurities.

The gaseous samples were prepared by standard manometric methods. The gas phase experiments were performed in a cross-shaped glass cell, equipped with quartz and CsI windows, which allows the measurement of FTIR spectra during the UV–vis irradiation. The IR spectra of the gas phase mixtures were recorded with a resolution of $0.5\,cm^{-1}$ and $1\,cm^{-1}$, with 64 and 4 scans, respectively, on a Nexus Nicolet instrument equipped with either an MCTB or a DTGS detector (for the ranges 4000–400 or 600–$180\,cm^{-1}$, respectively).

The matrices were prepared by pulsed depositions [11,12] of the gaseous mixtures onto a cold CsI window ($\sim10\,K$) of a Displex closed-cycle refrigerator (SHI-APD Cryogenics, model DE-202). In our experimental conditions, the IR spectra of the matrices were measured with a resolution of 0.125 and $0.5\,cm^{-1}$, with 256 and 64 scans, respectively.

The gas phase samples and the matrices were exposed to broad-band UV–vis radiation ($200 \leq \lambda \leq 800\,nm$) from Spectra-Physics Hg-Xe lamp operating at 800 W in order to study the photolysis processes. The output of the lamp was limited by a water filter to absorb infrared radiation for minimizing any heating effect. For the gas phase experiments the FTIR spectra were collected before, during and after the irradiation. For the matrix experiments the FTIR spectra were recorded before and after various times of irradiation.

3. Results and discussion

3.1. Photolysis of MTG in gas phase

A gas phase sample of MTG was exposed to broad-band UV–vis radiation ($200 \leq \lambda \leq 800\,nm$) and FTIR spectra were collected before, during (more than 100 spectra with only 4 scans each were taken in every experiment to closely monitor the changes occurring during the photolysis) and after irradiation. Fig. 1 shows the IR spectra of a vapor sample of MTG before and during the photolysis at different irradiation times. Several changes were observed on IR spectra as a consequence of the photolysis. The intensity of all the absorptions previously assigned to MTG decreases following the same kinetic behavior. Besides of the decay of the IR bands corresponding to MTG, the appearance of new absorptions can be observed in the spectra. To help in the interpretation of the spectra and the assignment of the new signals to the different photoproducts, the IR bands were grouped together, according to their kinetic behavior. Although some of the IR absorptions of MTG and the photoproducts developed on photolysis partially overlap, making difficult the integration of the area of the bands, plots of the IR intensities of the absorptions against the irradiation time are presented in Fig. 2.

An intermediate species, mainly characterized by two broad absorptions, about 2570 and $1738\,cm^{-1}$, first grows on photolysis
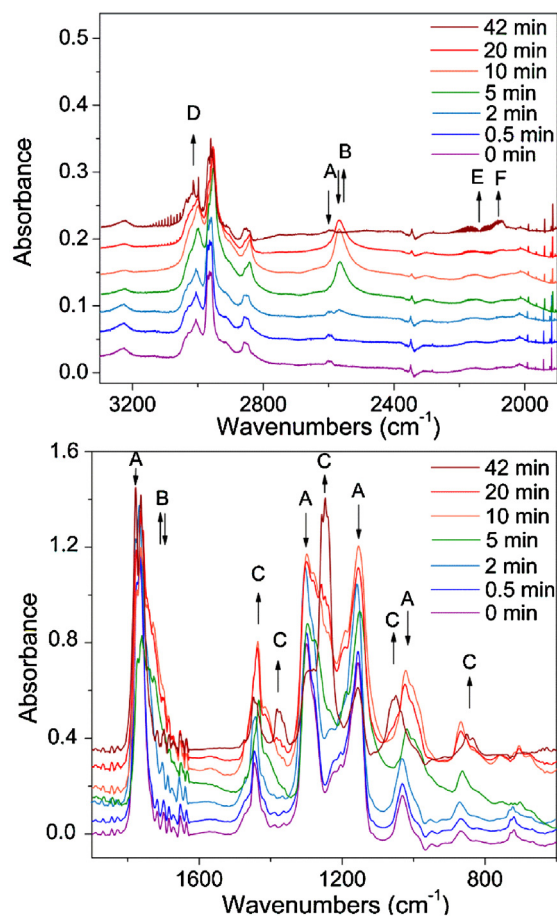

Fig. 1. FTIR spectra of MTG in gas phase before and after 0.5, 2, 5, 10, 20 and 42 min of UV–vis broad-band irradiation in the 1900–3300 (top) and 600–1900 (bottom) cm^{-1} regions. The absorptions assigned to the different species are indicated: A, MTG; B: dimer of MTG; C: $CH_3OC(O)CH_3$; D, CH_4; E, CO and F, OCS.

reaching a maximum at approximately 10 min of irradiation, and then completely disappears at the end of the experiences. Any attempt to associate these signals with a known compound, by comparison with literature values, failed. Considering that the shifts, and also their relative intensities, of these bands with respect to the corresponding absorptions of MTG in gas phase, of $-27\,cm^{-1}$ for $\nu(S—H)$ and $-32\,cm^{-1}$ for $\nu(C=O)$, coincide with the bands observed for the MTG dimer isolated in Ar-matrix [7], the intermediate photoproduct was assigned to a dimer of MTG. Moreover, several bands presented as shoulders of the MTG IR absorptions, that accompanied the kinetic behavior of these two signals, can also be identified as arising from the dimeric form of MTG. Table 1 presents the comparison of the IR bands assigned to $(MTG)_2$ formed by photolysis of gas phase MTG with the ones corresponding to the IR spectrum of the liquid, interpreted by the presence of a dimeric form, and the matrix-isolated MTG dimer [7]. As can be observed in the table, there is a very good agreement of the wavenumbers of the intermediate species formed by gas-phase photolysis of MTG and its dimer. At this point, and trying to understand this unexpected result, it is important to reiterate that the FTIR spectra were taken simultaneously with the irradiation of the sample.

The main photoproduct, that continuously growth on photolysis starting from approximately 5 min of irradiation and remains as a stable species after photolysis, recognized by the IR absorptions centered at 1060, 1248, 1375, 1771 and $2966\,cm^{-1}$, among others,
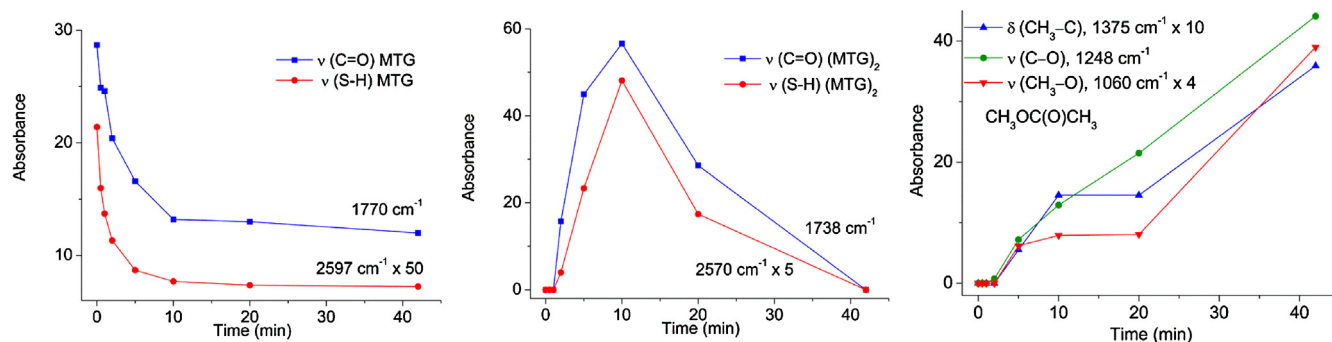
Fig. 2. Plots of the selected IR intensities against the irradiation times assigned to MTG (left), (MTG)$_2$ (middle), and CH$_3$OC(O)CH$_3$ (right) in the photolysis of MTG in gas-phase.
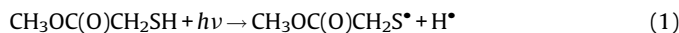
Table 1

Comparison of the vibrational wavenumbers (in cm^{-1}) of the gas phase IR absorptions assigned to methyl thioglycolate dimer, (MTG)$_2$, produced by photolysis of MTG, with (MTG)$_2$ in liquid and isolated in solid Ar.

Gas phase	Liquid phase[a]	Ar-matrix[a]	Tentative assignment[b]
2954	2954	2959	ν_s (CH$_2$)
2570	2570	2566	ν (S—H) $_{o.-p.}$
			ν (S—H) $_{i.-p.}$
1738	1740	1747	ν (C=O) $_{o.-p.}$
			ν (C=O) $_{i.-p.}$
1435	1437	–	δ (CH$_3$); δ (CH$_2$) $_{i.-p.}$
1414	1414	–	δ (CH$_3$); δ (CH$_2$) $_{i.-p.}$
1279	1281	1286	ν_{as} (C—C—O) $_{i.-p.}$
			ν_{as} (C—C—O) $_{o.-p.}$
1197	1192	1198	δ (CH$_2$) $_{i.p.}$
			δ (CH$_2$) $_{o.-p.}$
		1033	δ (C—C—O) $_{i.p.}$
			δ (C—C—O) $_{o.-p.}$
1004	1004	1012	δ (C—S—H); ν (C—C—O)
988	986	992	ν_s (C—C—O); δ (C—S—H)
705	706	709	ν (C—S)
584	585	598	δ (C—C=O); ν_s (C—C—S)
565	564	564	δ (C—C=O); ν_s (C—C—S)
418	419	419	τ (C—C—S—H)

[a] Taken from reference [7].
[b] ν_{as}, antisymmetric stretching; ν_s, symmetric stretching; δ, deformation; τ, torsion; i.-p., in phase; o.-p., out of phase.

with their characteristic band-shapes, was methyl acetate (CH$_3$OC(O)CH$_3$) [13]. The S$_8$ formation was also corroborated by its typical yellowish deposit on the windows of the photochemical cell. The mechanism probably initiates by the formation of free radicals through the rupture of one chemical bond. As it is well known, the photochemistry of thiol compounds, RSH, generally starts trough the breaking of the S—H single bond, forming RS$^\bullet$ radicals and hydrogen atoms [14]. In the present case, the intermediacy of MTG dimer would favor the free radical mechanism, since the S—H bond is weakened in the dimeric structure by the intramolecular hydrogen bond with the carbonylic oxygen. In coincidence with this explanation, it has been previously reported that the photo-initiated thiol-ene polymerization using glycolate esters results in greater reaction rates compared with the reactions performer with other thiols. This difference was attributed to the debilitation of the S—H bond by hydrogen bonding interactions [15]. The formation of methyl acetate can be interpreted as a desulfurization of MTG, probably mediated by (MTG)$_2$, according to Eqs. (1) and (2):

$$CH_3OC(O)CH_2SH + h\nu \rightarrow CH_3OC(O)CH_2S^\bullet + H^\bullet \qquad (1)$$

$$CH_3OC(O)CH_2S^\bullet + H^\bullet \rightarrow \mathbf{CH_3OC(O)CH_3} + 1/8\,S_8 \qquad (2)$$
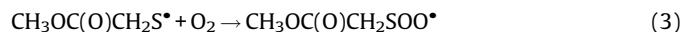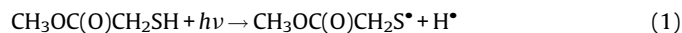
This mechanism constitutes a very interesting result, since desulfurization of thiols is a very important process, particularly

for the petrochemical industry. Several different methods were reported, including for example the oxidation [16], or the reaction with coordination complexes [17]. A photochemical desulfuriza-tion of some thiols using triethylphosphite and triethylborane was also reported [18].

Alternative photochemical channels of gaseous MTG, although in much less extent, produced carbon monoxide, methane and carbonyl sulfide, undoubtedly identified by their characteristic gas-phase IR spectra (see Fig. 1). The low intensity of these absorptions, and also the partial overlapping with other bands in the spectra, prevents a clear determination of their kinetic behavior. However, from a qualitative inspection of the spectra we can conclude that these photoproducts were most probably simultaneously formed in, at least, two or three different photochemical channels.

3.2. Photolysis of MTG in gas phase in presence of O$_2$

The photochemical reaction in gas phase between MTG and molecular oxygen was also studied. Mixtures of MTG:O$_2$ in 1:2 proportion were prepared using standard manometric methods. The fresh mixtures were exposed to broad-band UV–vis radiation. The spectra were collected before, during and after irradiation, as explained previously. No chemical reaction between MTG and molecular oxygen was observed in the time previous to the irradiation. Fig. 3 shows typical IR spectra of a mixture of MTG:O$_2$ in proportion 1:2 before and during the photolysis for various irradiation times. The decay of the IR bands corresponding to MTG can be observed together with the appearance of new absorption in the spectra. After 42 min of irradiation ca. 90% of MTG was consumed. Two main photochannels are discerned, according to the kinetic behavior of the IR new bands. The first one leads to the formation of sulfur dioxide, carbon monoxide, methanol, and formic acid, detected in its dimeric form. The photochemical mechanisms, starting by the formation of the thiyl radical (Eq. (1)), can be tentatively described by Eqs. (3)–(7) (the detected photoproducts are indicated in bold). Eq. (8) represents the whole photochemical process.
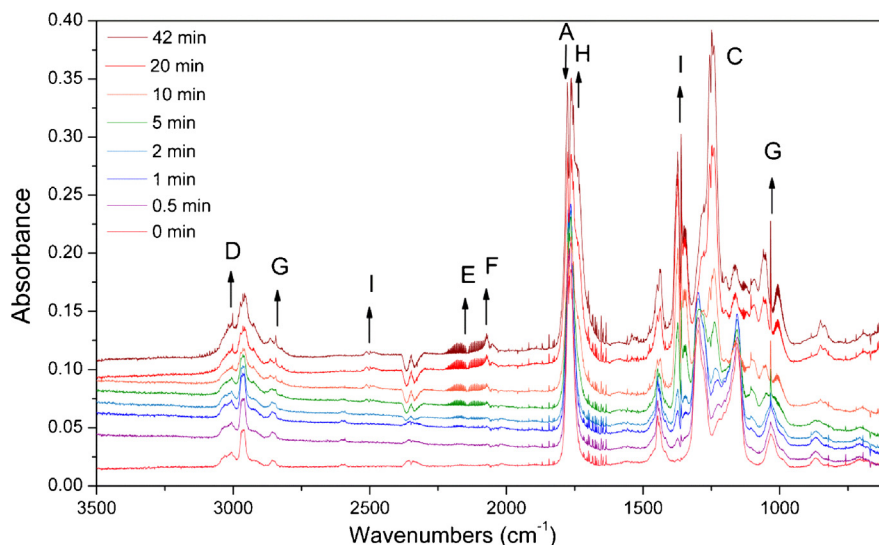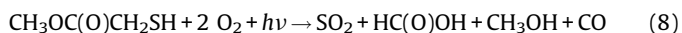
$$CH_3OC(O)CH_2SH + h\nu \rightarrow CH_3OC(O)CH_2S^\bullet + H^\bullet \qquad (1)$$

$$CH_3OC(O)CH_2S^\bullet + O_2 \rightarrow CH_3OC(O)CH_2SOO^\bullet \qquad (3)$$

$$CH_3OC(O)CH_2SOO^\bullet \rightarrow CH_3OC(O)CH_2^\bullet + \mathbf{SO_2} \qquad (4)$$

$$CH_3OC(O)CH_2^\bullet + O_2 \rightarrow CH_3OC(O)CH_2OO^\bullet \qquad (5)$$
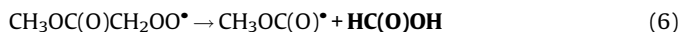
Fig. 3. FTIR spectra of a gaseous mixture of MTG:O_2 in a proportion 1:2 before and after 0.5, 1, 2, 5, 10, 20 and 42 min of UV–vis broad-band irradiation in the 600–3500 cm^{-1} region. The absorptions assigned to the different species are indicated: A, MTG; D, CH_4; E, CO; F, OCS; G, CH_3OH; H, HC(O)OH and I, SO_2.

$$CH_3OC(O)CH_2OO^\bullet \rightarrow CH_3OC(O)^\bullet + \textbf{HC(O)OH} \qquad (6)$$

$$CH_3OC(O)^\bullet + H^\bullet \rightarrow \textbf{CH}_3\textbf{OH} + \textbf{CO} \qquad (7)$$

$$CH_3OC(O)CH_2SH + 2\,O_2 + h\nu \rightarrow SO_2 + HC(O)OH + CH_3OH + CO \qquad (8)$$

The second mechanisms, with a slower kinetic evolution with respect to the first one, conducts to the formation of methyl acetate, and can be attributed to the photolysis of MTG without intervention of molecular oxygen, as previously described by Eq. (1)-(2). Small amount of OCS and CH_4 are also formed by alternative mechanisms or by secondary channels.

3.3. Photolysis of MTG isolated in solid Ar

The matrix isolated MTG (proportion 1:1000, 1:750 and 1:200) was exposed to broad-band UV–vis radiation ($200 \leq \lambda \leq 800$ nm) and IR spectra of the matrix were taken after different irradiation times (see Fig. 4). Several new absorptions, listed in Table 2, appeared in the FTIR spectra after photolysis. To help in the interpretation of the experiments and the identification of the photoproducts, the intensity of the bands were plotted as a function of the irradiation time, and grouped together according with their kinetic behavior. This strategy for the analysis of the results allowed the determination of three different alternative photochemical channels. The plots of the intensities of some of the absorptions against the irradiation times are presents in Fig. 5.
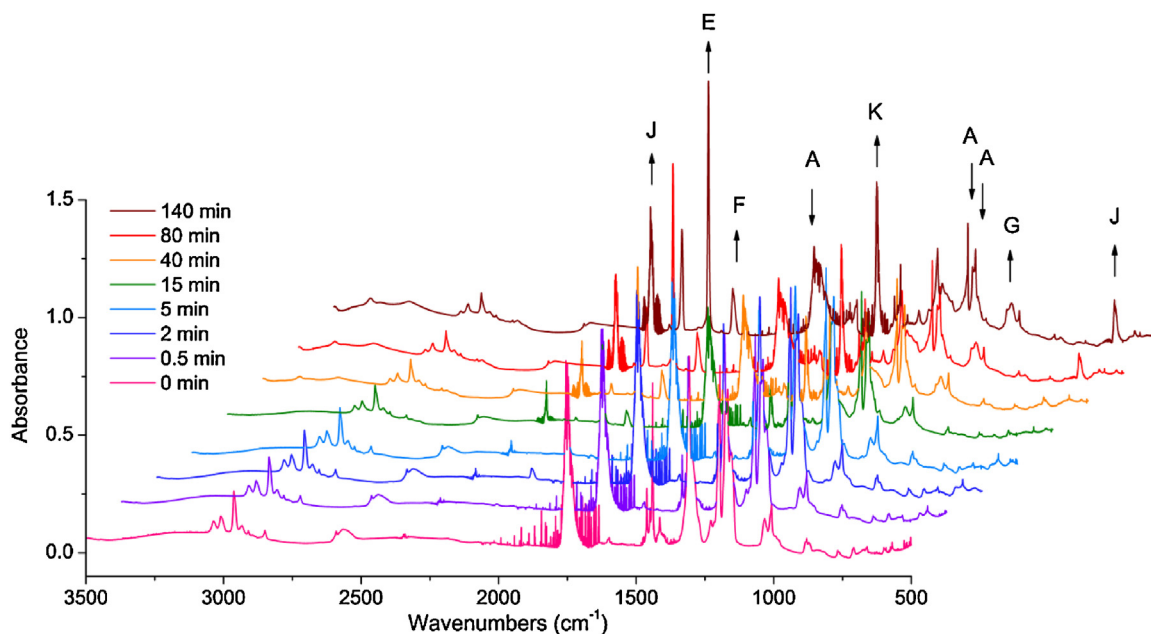

Fig. 4. FTIR spectra of an Ar matrix initially containing MTG in a 1:1000 proportion before and after 0.5, 2, 5, 15, 40, 80 and 140 min of UV–vis broad-band irradiation in the 600–3300 cm^{-1} region. The absorptions assigned to the different species are indicated: A, MTG; G, CH_3OH; E, CO; F, OCS; J, CO_2 and K, CS_2.

Table 2
Wavenumbers and assignments of the IR absorptions appearing after broadband UV–vis photolysis of an Ar matrix containing MTG.

| Wavenumber (cm^{-1})	Vibrational mode[a]	Molecule
3500 3530 }	ν (O—H)	CH$_3$OH
2832	ν (C—H)	CH$_3$OH
2801	ν_{as} (C—H)	CH$_3$OCH$_2$SH
2346		CO$_2$
2343 2340 }	ν (CO)	
2138		CO
2136 2133 }	ν (C=O)	
2130		
2058		OCS
2055		
2053 2051 }		
2049		
2045		
1373	δ (COH)	CH$_3$OH
1252	δ (CH$_2$)	CH$_3$CH$_2$SH
1129	ν (O—CH$_3$)	CH$_3$OCH$_2$SH?
1064	ω (CH$_2$)	CH$_3$OCH$_2$SH?
1053	ν (C—O)	CH$_3$OH
997 992 }	ω (CH$_2$)	H$_2$CS
661 653 }	δ (CO$_2$)	CO$_2$
589	ν (C—S)	CH$_3$CH$_2$SH

[a] ν_s, stretching; ν_{as}, antisymmetric stretching; δ, deformation; ω, wagging.

The main mechanism, described by Eq. (9), conducts to the extrusion of the CO molecule, and the concomitant formation of methanol and thioformaldehyde. A similar mechanism was previously observed after the fragmentation of MTG upon electron impact, investigated by means of mass analyzed ion kinetic energy (MIKE). The initial loss of methanol from MTG$^+$ was followed by the loss of CO and the concomitant formation of SCH$_2^+$ [19].

$$CH_3OC(O)CH_2SH + h\nu \rightarrow CH_3OH + CO + H_2CS \qquad (9)$$
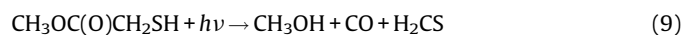
The wavenumbers of the absorptions assigned to CO and CH$_3$OH were compared with the ones of FTIR Ar-matrix spectra of these molecules measured by our research group. H$_2$CS was identified by its most intense absorption on the basis of the monomeric [20] and complexed [21] reported matrix-isolated spectra. The three species, CO, CH$_3$OH and H$_2$CS, were formed inside a matrix cage, without possibility to escape from it. For this reason, and as a consequence of intermolecular interactions, the IR spectra show visible signs of molecular complexation, evidenced by the wavenumber shifts with respect to the pure isolated compounds. The formation of methanol and thioformaldehyde was previously observed after UV light irradiation of dimethyl sulfoxide (DMSO) in low temperature solid argon matrix [22]. In the first step of the photolysis DMSO isomerizes to sulfenic ester, CH$_3$SOCH$_3$, which further dissociates to form both CH$_3$SH···OCH$_2$ and CH$_3$OH···SCH$_2$ complexes. None IR band observed after photolysis of MTG could be identified as belonging either to CH$_3$SOCH$_3$ intermediate or to CH$_3$SH···OCH$_2$ complex. The groups originally present in the MTG molecule, CH$_3$O— and —CH$_2$S—, that clearly favor the formation of CH$_3$OH and H$_2$CS, explain the lack of the CH$_3$SH···OCH$_2$ products in the photolysis of MTG.

A second photochemical mechanism produces carbon dioxide and ethanethiol, according to Eq. (10).

$$CH_3OC(O)CH_2SH + h\nu \rightarrow CO_2 \cdots CH_3CH_2SH \qquad (10)$$
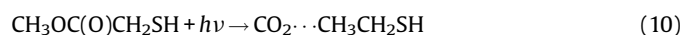
The products were again identified by the comparison with the IR spectra of the pure isolated compounds in Ar matrices (Table 2). The interaction between the two molecules is evidenced not only by the shift of the absorptions, but also by the splitting of the

bending mode of CO$_2$, as a consequence of the loss of degeneration of these fundamentals, typical of CO$_2$ complexation [23]. Small amounts of OCS are also produced in a third mechanism, that presumable leads also to the formation of dimethyl ether (Eq. (11)). Although the bands of CH$_3$OCH$_3$ could not be discarded in the spectra of the irradiated matrices, due to the expected overlapping with the absorptions of other photoproducts produced in greater amount, their presence was not confirmed.

$$CH_3OC(O)CH_2SH + h\nu \rightarrow OCS + CH_3OCH_3(?) \qquad (11)$$
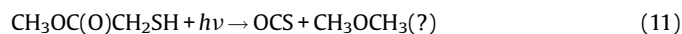
Three other IR absorptions, at 2801, 1129 and 1064 cm^{-1}, present a clear intermediate behavior, as can be observed in Fig. 5.
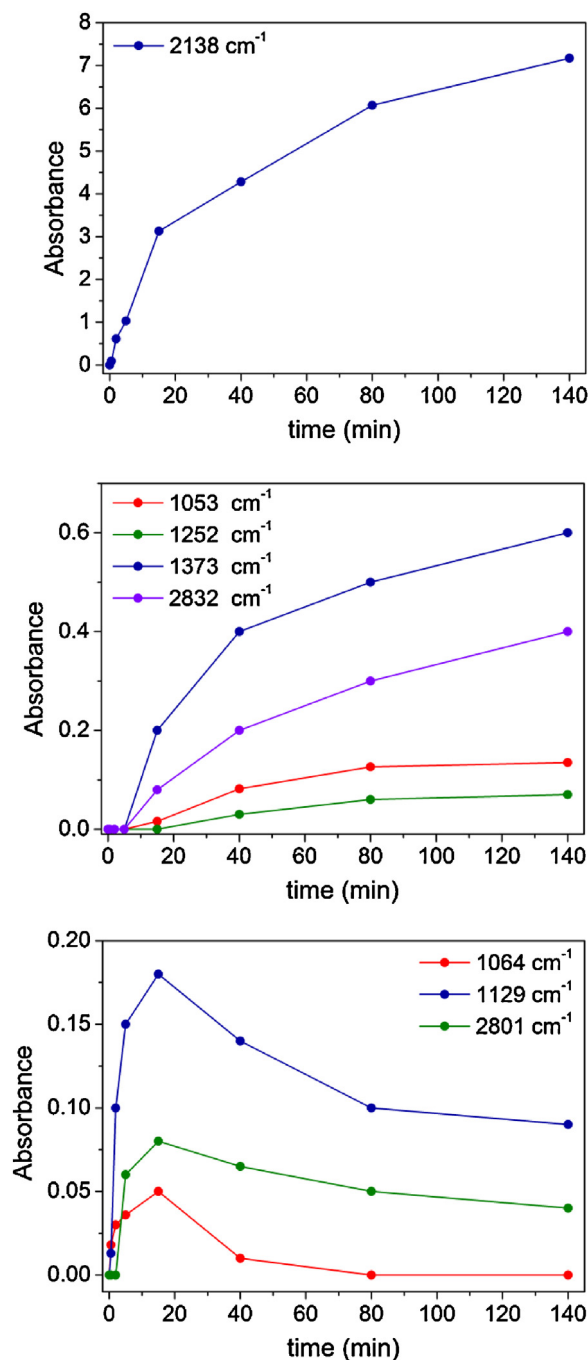

Fig. 5. Plots of the IR intensities against the irradiation times assigned to CO (top), CH$_3$OH (middle) and to an intermediate product (bottom) in the photolysis of an Ar matrix initially containing MTG in a 1:1000 proportion.

Table 3

Wavenumbers and assignment of the IR absorptions appearing after broadband UV–vis photolysis of an Ar matrix containing MTG and O_2.

| Wavenumber (cm^{-1})		Vibrational mode[a]	Molecule
3703		$\nu_s + \nu_{as}$	CO_2
3598		$2\delta + (C_{as}-H)$	CO_2
	3066		CH_4
	3038 }		
	3018		
	2880 }	ν_{as} (CH_2)	H_2CO
	2837 }	ν_s (CH_2)	
	2343 }	ν_{as} (CO_2)	CO_2
	2342 }		
	2278 }	ν_{as} (CO_2)	$^{13}CO_2$
	2277 }	ν (C=O)	
	2157		CO
	2142 }		
	2138 }		
	2130		
2047		ν (C=O)	OCS
1714		ν (C=O)	H_2CO
1500		δ (CH_2)	H_2CO
1340		ν_{as} (SO_2)	SO_2
1265		δ (H—C—O)	H_2CO
1152		ν_s (SO_2)	SO_2
	1096 }	δ_{oop} (CO)	H_2CO
	1085 }		
	662 }	δ (CO_2)	CO_2
	656 }		
525		δ (SO_2)	SO_2

[a] ν_{as}, antisymmetric stretching; ν_s, symmetric stretching; δ, deformation; δ_{oop}, out-of-plane deformation.

The assignment of these bands to one or more species is not trivial, due on one hand for the possible hiding of some of the absorptions by other photoproducts and on the other for the expected shift of the wavenumbers on complexation with the other molecules hosted in the same matrix cage. One plausible explanation is the formation of CH_3OCH_2SH complexed with CO, as an intermediate product of Eq. (9). The synthesis of methoxymethanethiol was performed from the reaction of thioacetic acid S-methoxymethyl ester with NaOH [24]. Although some IR (ATR) absorptions of a benzene solution of the compound were reported, no IR spectrum of the pure sample was found in the literature. A close inspection of the irradiated spectra in the region of the CO molecule seems to support this hypothesis, since initially an absorption centered at 2130 cm^{-1} is formed, while bands at 2133, 2136 and 2138 cm^{-1} are developed as the irradiation times increases. These experimental findings indicate that CO is interacting with different photoproducts, first with the intermediate and at longer times with methanol and thioformaldehyde.

3.4. Photolysis of MTG isolated in solid Ar in presence of O2

Irradiation experiments of MTG with O_2 in solid Ar matrices were conducted with MTG:O_2:Ar proportions of 1:1:200, 1:2:200 and 1:20:200. According to the interpretation of the new IR absorptions appearing after photolysis compiled in Table 3, the main photochemical reaction mechanism of a 1:1:200 MTG:O_2:Ar matrix can be represented by Eq. (12):

$$CH_3OC(O)CH_2SH + O_2 + h\nu \rightarrow CO + SO_2 + H_2CO + CH_4 \qquad (12)$$
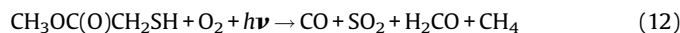
The only effect observed in the irradiated spectra as the proportion of O_2 in the matrix increases was the growth of the production of CO_2, and the concomitant decrease of the signal assigned to CO (see Fig. 6). The IR absorptions are shifted with respect to the values of the isolated compounds, as expected from intermolecular interactions. In this particular case, the final production of four different species in the same matrix cage, SO_2, H_2CO, CH_4 and CO (or CO_2), makes the interpretation of the interactions with a theoretical model very difficult. Additionally, the formation of molecular complexes between the photoproducts and oxygen molecules present in the matrix cannot be ruled out. However, the comparison with related molecular complexes can help in the interpretation of the IR matrix spectra. SO_2 molecule can form molecular complexes acting either as electron density donor or acceptor, giving place to different molecular geometries (see for example reference [25] and references cited therein). In the photolysis of MTG in an Ar matrix doped with O_2, the $\nu_{as}SO_2$ fundamental mode is $-15\,cm^{-1}$ shifted with respect to the same mode in the SO_2 isolated in the stable (S) Ar matrix site [26,27], while the deformation vibrational mode is $+5\,cm^{-1}$ shifted. According to previous studies [25] this trend in the direction of the wavenumber shift might be indicative of a complexation through the lone pair of one of the oxygen atom of the SO_2 molecule, acting as the electron donor. A complex between sulfur dioxide and formaldehyde in O_2 matrices was previously reported [28]. Although the bands of the SO_2 moiety were not informed, the authors observed a red shift in the carbonyl absorption of H_2CO, coincident with our findings.

Other photochemical channels give rise to small amounts of CO and OCS. The wavenumbers of the bands indicate that the other species hosted in the same matrix cage were different than in the
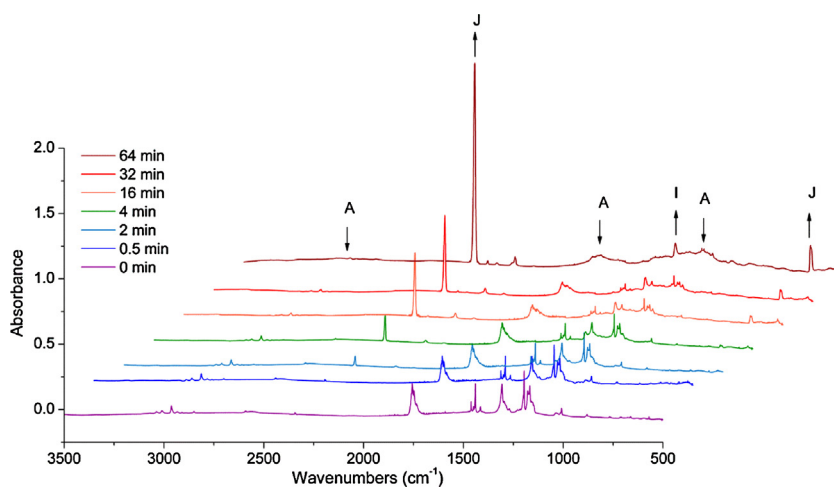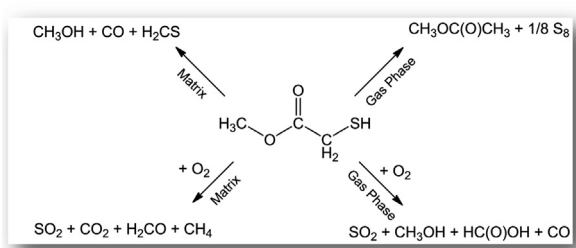

Fig. 6. FTIR spectra of an Ar matrix initially containing MTG and O_2 in a 1:20:200 MTG:O_2:Ar proportion before and after 0.5, 2, 4, 16, 32 and 64 min of UV–vis broad-band irradiation in the 50–3500 cm^{-1} region. The absorptions assigned to the different species are indicated: A, MTG; I, SO_2 and J, CO_2.

Scheme 1. Schematic outline of the MTG photochemistry in gas phase and isolated in solid Ar matrix, alone and in presence of molecular oxygen.

photolysis of an Ar matrix of MTG without molecular oxygen. The absorptions of CO and OCS has been shown to be very sensitive to the complexation, the direction of the shift with respect to free CO depending on the complex geometry (see references [29,30], respectively, and reference cited therein).

4. Conclusions

The photochemical reaction mechanisms of MTG in gas-phase and in matrix conditions, alone and in presence of molecular oxygen, were determined by the FTIR detection of the photo-products. The formation of numerous intermediate species and/or possible molecular complexes transforms the photochemical process description difficult and several photochannels can be considered. Scheme 1 summarizes the main final products identified for each of these experiences.

The photolysis of MTG in gas phase conducts to its desulfuriza-tion, mediated by the dimeric form, and the concomitant formation of methyl acetate ($CH_3OC(O)CH_3$) and sulfur (S_8). On the other hand, the photolysis in matrix conditions, restricted mainly to unimolecular mechanisms and dominated by low temperatures, that allow the isolation of species that are not stable at normal conditions, originates methanol, thioformalde-hyde, and carbon monoxide, interacting inside the matrix cage. If molecular oxygen is present during the photolysis, sulfur dioxide is formed in both conditions. While in gas phase the other products are methanol, formic acid and carbon monoxide, in matrix conditions formaldehyde, methane, and carbon dioxide are the photoproducts formed together with SO_2. It is worthnoting that these photoproducts are of high relevance for chemical processes occurring in the atmosphere.

Acknowledgements

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