

The hydrogen peroxyde radical, HO₂ – a potential tracer of interstellar molecular oxygen

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Abstract. Methane/oxygen ice mixtures are irradiated in an ultra-high vacuum chamber at 10 K with 9.0 MeV α -particles to investigate the role of suprathreshold oxygen atoms in the formation of oxygen-containing hydrocarbon molecules and to elucidate the formation of the hydrogen peroxyde radical, HO₂, as a tracer for hitherto unobserved interstellar molecular oxygen, O₂. Computer simulations calculate the elastic as well as inelastic energy loss of the implant to the irradiated targets. Our experimental data and calculation reveal that the kinetic energy of the implant is transferred almost exclusively via inelastic interactions to the ices yielding methyl radicals, CH₃, and atomic hydrogen, H. These H atoms are mobile even at temperatures as low as 10 K and recombine barrier-less with matrix isolated molecular oxygen to form HO₂ radicals monitored via Fourier transform infrared spectroscopy. In addition, alcohols and carbonic acids with up to 20 carbon atoms are found to be synthesized via O atom insertion, neighboring radical recombination, and/or a multi-center reaction mechanism. Formed on interstellar grains, subsequent grain-grain collisions, cosmic ray particle induced grain mantle evaporation, or explosive grain ejection could release these newly formed molecules into the gas phase of the interstellar medium.

Key words: molecular processes – methods: laboratory – ISM: cosmic rays – ISM: dust, extinction – ISM: molecules

1. Introduction

The very first detection of the interstellar radicals CH⁺, CH and CN initiated the interest in the chemistry of the interstellar medium (ISM) (Verschuur & Kellermann, 1988; Burton et al. 1992). Today, more than half a century later, about 114 molecules, radicals, and ions have been assigned unambiguously in diffuse and molecular clouds, shocked regions, hot cores, as well as outflow of carbon stars (Scheffler & Elsässer 1988). Here, all but six interstellar molecules were detected via rotational lines in the microwave region of the electromagnetic

spectrum in the ISM. The diatomics H₂ and C₂, however, hold no permanent dipole moment and were detected via their electronic transitions (Burton et al. 1992). In addition, C₂H₂, C₂H₄, CH₄, as well as SiH₄ were observed in the outer envelope of the carbon star IRC+10216 through their rovovibrational transitions in the IR region.

The search for interstellar homonuclear oxygen O₂ and nitrogen N₂ molecules presents a particular problem, since both diatomics have no permanent dipole moment and thus show no pure rotational spectrum. In theory, these molecules could be traced through their electronic lines, but exciting these transitions with UV photons seems extremely unlikely, since the interstellar UV radiation field is effectively shielded by grains in dense clouds where significant O₂ column densities are expected (Verschuur & Kellermann, 1988). Likewise, in regions of high shock induced excitation, vibrational emission may occur (Ruffle et al. 1998). Although interstellar N₂ as well as O₂ have not been detected yet, the protonated form of molecular nitrogen, N₂H⁺, was observed via microwave transitions (de Boisanger 1996). But despite identification of other protonated species HCO⁺, HOC⁺, HCS⁺, HN₂⁺, HCNH⁺, HOCO⁺, H₃O⁺, H₃⁺, and H₂D⁺ (Mehring 1996; Turner 1995; Ziurys & Apponi 1995), O₂H⁺ has not been discovered in the ISM yet (Foley et al. 1993).

In this paper, we investigate the formation of an alternative tracer in the search for interstellar O₂ via microwave spectroscopy: the hydrogenated form of molecular oxygen, the hydrogen peroxyde radical HO₂. Although HO₂ has been extensively studied in laboratories (Hougen et al. 1975; Takacs & Howard 1986), no identification have been made in the ISM (Ohishi et al. 1996). Since atomic hydrogen is formed on interstellar grains containing CH₄, NH₃, or H₂O upon galactic cosmic ray MeV ion interaction (Kaiser et al. 1997 and references therein), mobile H atoms could react with cocondensed molecular oxygen via (1) to HO₂:



Tielens et al. suggested a possible HO₂ intermediate as a precursor to form hydrogen peroxyde, H₂O₂, on interstellar ices (Tielens & Hagen 1982). Subsequent grain-grain collisions, cosmic ray particle induced grain mantle evaporation, or explosive grain

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ejection (Schutte & Greenberg 1991; Kaiser et al. 1997) could release these newly formed O₂H radicals into the gas phase.

Besides investigating the HO₂ radical, the present experimental and theoretical studies are aimed to investigate the formation of oxygen containing molecules in interstellar ice mixtures such as detected CO, CO₂, CH₃OH, perhaps H₂CO as well as C₂H₅OH (Charnley 1995; Schutte 1996). Our CH₄/O₂ ices must be regarded as model systems to elucidate elementary processes in the reaction of MeV ion induced oxygen atoms with the simplest saturated hydrocarbon molecule under controlled experimental conditions before extending these investigations to astrophysically realistic ice mixtures.

2. Experimental approach and computational model

The experimental setup is described earlier in detail (Kaiser et al. 1995). Briefly, all experiments are performed in an ultra high vacuum (UHV) chamber at about 4×10^{-10} mbar. The present investigations extend previous studies on neat CH₄ ices (Kaiser & Roessler 1998). Here, CH₄/O₂ (1–2% O₂) ice layers of $4.8 \pm 0.5 \mu\text{m}$ are condensed onto a 10 K silver waver. To generate atomic hydrogen, all targets are irradiated at ion fluxes ϕ with 9.0 MeV α particles of $\phi(\alpha) = 127 \text{ nA cm}^{-2}$. These conditions limit the temperature of the frost surface to $14 \pm 1 \text{ K}$. Here, the choice of MeV particles in our experiments characterizes the flux distribution maximum of galactic cosmic ray particles peaking at about 8–15 MeV, c.f. discussion in Kaiser & Roessler 1998. The solid state is monitored on line and *in situ* with a Fourier transform infrared (FTIR) spectrometer ($4000\text{--}400 \text{ cm}^{-1}$, NICOLET) in absorption-reflection. Further, the ν_2 vibration of HO₂ is integrated between 1409 and 1395.5 cm^{-1} taking the gas phase integral absorption coefficient of $3.3 \pm 0.6 \times 10^{-18} \text{ cm}$ (Lauderdale et al. 1994). After the irradiation exposure, the target is heated to 293 K, and the remaining yellow/red residue solved in dichlormethane. Molecules containing OH-groups were silylated with trimethylsilylchloride (TMSCl) and subsequently analyzed via gas chromatography-mass spectrometry (GC-MS).

Physical processes triggered by the ion implantation into a CH₄ target are simulated with the MARLOWE program extended for quantum mechanical and relativistic treatments of our MeV ions (Kaiser & Roessler 1998). This code calculates elastic and inelastic energy transfers from an impinging particle to the target atom(s) of the condensed hydrocarbon ices.

3. Results

3.1. Computer simulations

The MARLOWE calculations reveal that each 9 MeV α -particle transfers more than 99% of its energy in inelastic encounters to the electronic system of the CH₄ target. This energy transfer leads to a C-H bond cleavage in a single CH₄ molecule forming a methyl radical, CH₃, and atomic hydrogen via reaction (2) (Trakhtenberg & Milikh 1982; Grigor'ev et al. 1988):



Compared to neat CH₄ targets studied earlier (Kaiser & Roessler 1998), the 1–2% O₂ admixture results in generation of one suprathreshold oxygen atom per 100 implanted ions. These suprathreshold species hold kinetic energies up to 10 keV to be transferred in successive collisions to the target atoms of the ice. This process ignites hydrogen, carbon, and oxygen *knock-on particles* in our targets if the transferred energy is larger than the binding energy of the atom. Each knock on particles can transfer their energy in consecutive encounters to the target atoms resulting in a collision cascade of secondary, tertiary, etc., knock-on atoms. Moderated to about 1–10 eV these atoms are not in thermal equilibrium with the surrounding 10 K target. As inferred from bulk experiments, oxygen atoms can react finally with the target molecules via elementary steps of bond insertion, addition to double or triple bonds, or hydrogen abstraction (Stöcklin 1969). These elementary reactions are expected to contribute significantly to oxygen containing hydrocarbon molecules in the solid state as well, c.f. section 3.2.

3.2. Fourier Transform Infrared Spectroscopy (FTIR)

In addition to methyl, carbene, acetylene, ethylene, ethyl, and ethane absorption features, CH₄/O₂ mixtures show prominent ν_2 and ν_3 bands of the O₂H radical, c.f. Table 1. After 60 min α -particle exposure (irradiation dose $D = 30 \text{ eV}$ per molecule), the integrated ν_2 absorption reaches a maximum corresponding to $1.1 \pm 0.2 \times 10^{17}$ O₂H radicals. This data stand in excellent agreement with initially condensed $1.5 \pm 0.5 \times 10^{17}$ O₂ molecules strongly suggesting a hydrogen peroxy radical formation via reaction (1) from molecular oxygen and H atoms. Increasing the irradiation dose results in a further decrease in integral absorption reaching zero intensity after $D = 75 \text{ eV}$ (150 min). These findings and the transition of the OH stretching frequencies from di-, tri-, and tetramers to polymeric water clusters suggest a subsequent reaction of the O₂H radicals via H addition to hydrogen peroxide, H₂O₂, radiation induced bond cleavage to two hydroxy radicals, OH, and a final H addition to water molecules, H₂O as monitored through the $\nu_{\text{deformation}}$ mode. Although the water polymers were identified unambiguously via FTIR spectroscopy, no absorptions of H₂O₂ were identified. The presence of hydroxyperoxide is inferred only indirectly. Further carrier of the -OH groups were identified at 10 K as carboxyl acids as well as primary, secondary, and tertiary alcohols.

In strong contrast to neat CH₄ targets studied earlier in our group (Kaiser & Roessler 1998), irradiation of CH₄/O₂ samples at 10 K and comparable doses yields solid residues after warming the sample to 293 K comprising about 0.5–5% of the condensed target mass (Fig. 2). The FTIR spectra show dominating aliphatic absorptions of methyl and methylene groups as well as torsion-absorptions of up to three linear methylene units, i.e. -(CH₂)₃-CH₃. The presence of oxygen is evident from carbonylic and hydroxylic absorptions. These findings are in strong contrariety to, e.g., Strazzulla et al. (1984) supplying stable residues even after CH₄-target irradiation at lower doses than applied in our experiments. Differences to our results are based predominantly on contamination effects of molecular oxygen in

Table 1. FTIR absorptions of ion irradiated samples at 10 K and 293 K. R indicates an organic group.

assignment	10 K
	frequency, cm ⁻¹
methyl radical CH ₃	629–590
Carbene CH ₂	2790–2795, 1104–1115
Acetylene C ₂ H ₂	3269–3209, 1449–1359, 809–729, 1990–1960
Ethylene C ₂ H ₄	2987–2951, 1023–837
Ethyl radical C ₂ H ₅	2840–2842, 1368–1364
Ethane C ₂ H ₆	1374–1360, 830–817, 1480–1445
Hydrogen peroxy radical O ₂ H	1400, 1102
di-, tri, and tetramers of water, H ₂ O	3724–3708, 3693
polymeric water clusters H ₂ O	3687, 1585, 1593
carboxylic acids RCOOH	1715
primary, secondary and tertiary alcohols ROH	1051–1047, 1110–1115, 1156–1159
	293 K
Methyl group R-CH ₃ cm ⁻¹ .	2961, 2875, 1449, 1378
Methylene group R-CH ₂ -R'	2931, 2852, 1449
up to three linear methylene units, -(CH ₂) ₃ -CH ₃	747, 726

Table 2. Detected molecules in residua of α -particle irradiated CH₄/O₂-targets at 10 K detected as TMS esters. R: OCH-containing organic groups, identification impossible.

	molecule	mass, pg
1	R-O-H	2.1 - 13.6
2	O((CH ₂) ₂₂ -O-H)	14.8–22.4
3	R-O-H	10.7–16.2
4	R-O-H	3.6–4.3
5	C ₁₃ H ₂₇ -COO-H	2.7–3.0
6	R-COO-H	1.7–2.6
7	C ₁₄ H ₂₉ -COO-H	8.5–36.1
8	R-C ₆ H ₁₃	3.0–5.7
9	C ₁₅ H ₃₁ -COO-H	11.3–10.1
10	C ₁₇ H ₃₅ -COO-H	7.8–4.5
11	C ₁₉ H ₂₉ -COO-H (pimar acid)	0.3–2.6
12	C ₁₉ H ₂₇ -COO-H (abietine acid)	1.5–6.5
13	R-C ₄ H ₉	1.1–4.6
14	R-C ₄ H ₉	1.3–3.4

Strazzulla (1984), c.f. Kaiser et al. 1995 for a detailed discussion.

3.3. GC-MS analyses

GC-MS analyses assigned trimethylsilyl (TMS) esters via mass to charge (m/e) data of the parent ion M^+ , the fragment of the methyl group loss $[M-15]^+$, the TMS fragment $[\text{Si}(\text{CH}_3)_3]^+$ at $m/e = 73$, and the carboxylic acid trimethylsilylester fragment $[\text{CO}_2(\text{Si}(\text{CH}_3)_3)]^+$ at $m/e = 117$, c.f. Table 2. Alcohols were identified through their parent ions and the ether fragment at $m/e = 89$ $[\text{O-TMS}]^+$. This procedure identified linear, fully saturated carbonic acid with up to 18 carbon atoms, as well as

partly unsaturated acids with 20 carbon atoms (pimar acid, abietine acid). But despite constant temperatures, pressures, target thickness as well as radiation doses, an oxygen content differing by $\pm 0.5\%$ induces a variation in carbon acid and alcohol yield up to one order of magnitude.

4. Discussion and astrophysical implications

4.1. The hydrogen peroxy radical, HO₂

Our combined experimental and theoretical results strongly indicate formation of HO₂ proceeds through reaction (1), i.e. a simple radical-radical recombination between atomic hydrogen and molecular oxygen at 10–14 K in the CH₄ target. Since this reaction is exothermic by 207.5 kJmol⁻¹, the initially formed HO₂ radical is internally excited, and the excess energy must be released via phonon interaction with the surrounding solid methane matrix to result in a stabilized hydrogen peroxy radical. This concept clearly indicates that HO₂ formation is restricted to interstellar grains, since a potential radiative association in the gas phase cannot get rid of the bond energy via photon emission. In addition, typical number densities of even 10⁶ cm⁻³ in dense molecular clouds cannot stabilize the HO₂ collision complex prior to decomposition to the reactants. Further, reaction (1) holds no entrance barrier (Levine & Bernstein 1987) besides the barrier for H atom diffusion from its formation to the reaction site, and a tunneling effect in the final reaction step does not necessarily have to be involved. Finally, we like to point out that the hydrogen peroxy radical formation does not necessarily have to include MeV particle irradiation of hydrocarbon ices. The only critical limitation is the generation of mobile hydrogen atoms: this can be initiated via MeV particle irradiation and through UV photolyses of H₂O, NH₃, or other hydrogen containing material condensed on interstellar grains as well.

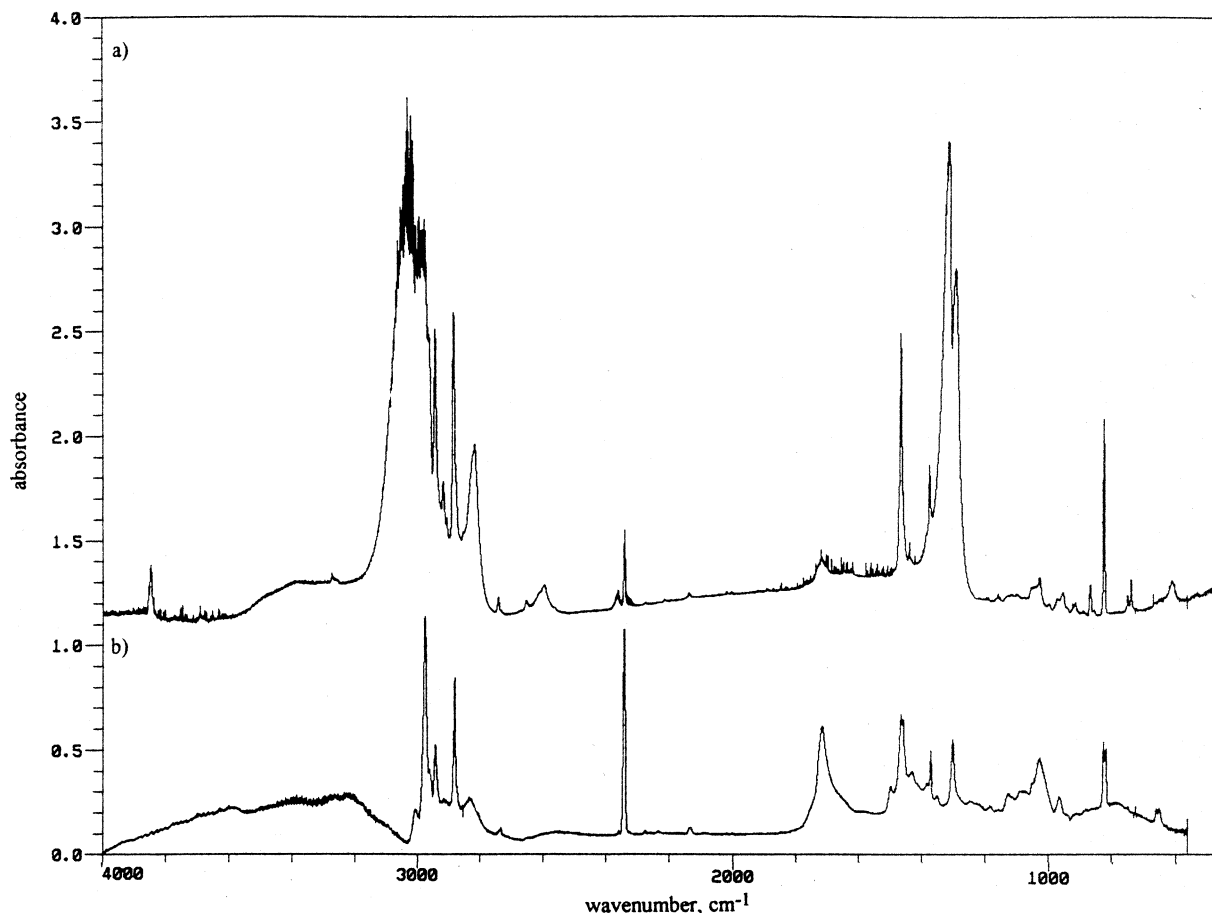
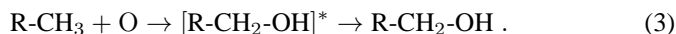


Fig. 1. FTIR spectrum of a 9 MeV α -particle irradiated CH₄/O₂ sample after exposure of a dose of $D = 30 \pm 6$ eV (top) and $D = 136 \pm 25$ eV per target molecule.

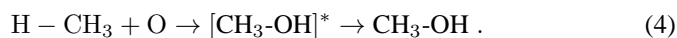
4.2. Alcohols and carbonic acids

Besides the identification of the hydrogen peroxy radical, the 1% O₂ admixture to the neat CH₄ target shows a profound impact on the solid state chemistry. FTIR spectra as well as GC-MS studies clearly demonstrate an incorporation of oxygen atoms to synthesize carboxylic acids as well as alcohols. In addition to the irradiation of neat CH₄ targets which generates suprathermal H and C atoms (Kaiser & Roessler 1998), MARLOWE calculations verify that in the CH₄/O₂ sample energetic O atoms are formed as well. Detailed three dimensional collision cascades suggest that alkanes up to C₁₄H₃₀ are formed within ‘tube-like’ energized zones inside neat CH₄ samples via a multi center mechanism at doses as low as 0.1 eV (Kaiser & Roessler 1998). If suprathermal hetero atoms are present as well, O atoms could react with these newly formed hydrocarbon molecules via classical insertion mechanism:



Here, R represents an aliphatic group, and * the internally excited alcohol intermediate which can divert its internal energy via phonon coupling to the surrounding ice matrix. This mechanism gains support from previous investigation on the O/CH₄ system (Nebeling 1988). These studies validate formation of

the simplest alcohol, methanol (CH₃OH) via the suprathermal reaction (4):



This insertion concept is not limited to our CH₄/O₂ model system alone. This versatile approach can be extended to predict formation of molecules on interstellar grains and solar system ices. Although no laboratory measurements on the O/C₂H₆ system are available, ethanol, C₂H₅OH, for example, might be formed within ices via reaction of suprathermal oxygen atoms with ethane, C₂H₆, reaction (5):



This reaction will be investigated in the near future. Carbonic acids might be formed through a similar mechanism underlying the alkane synthesis. However, further, more detailed studies on this reaction class are necessary.

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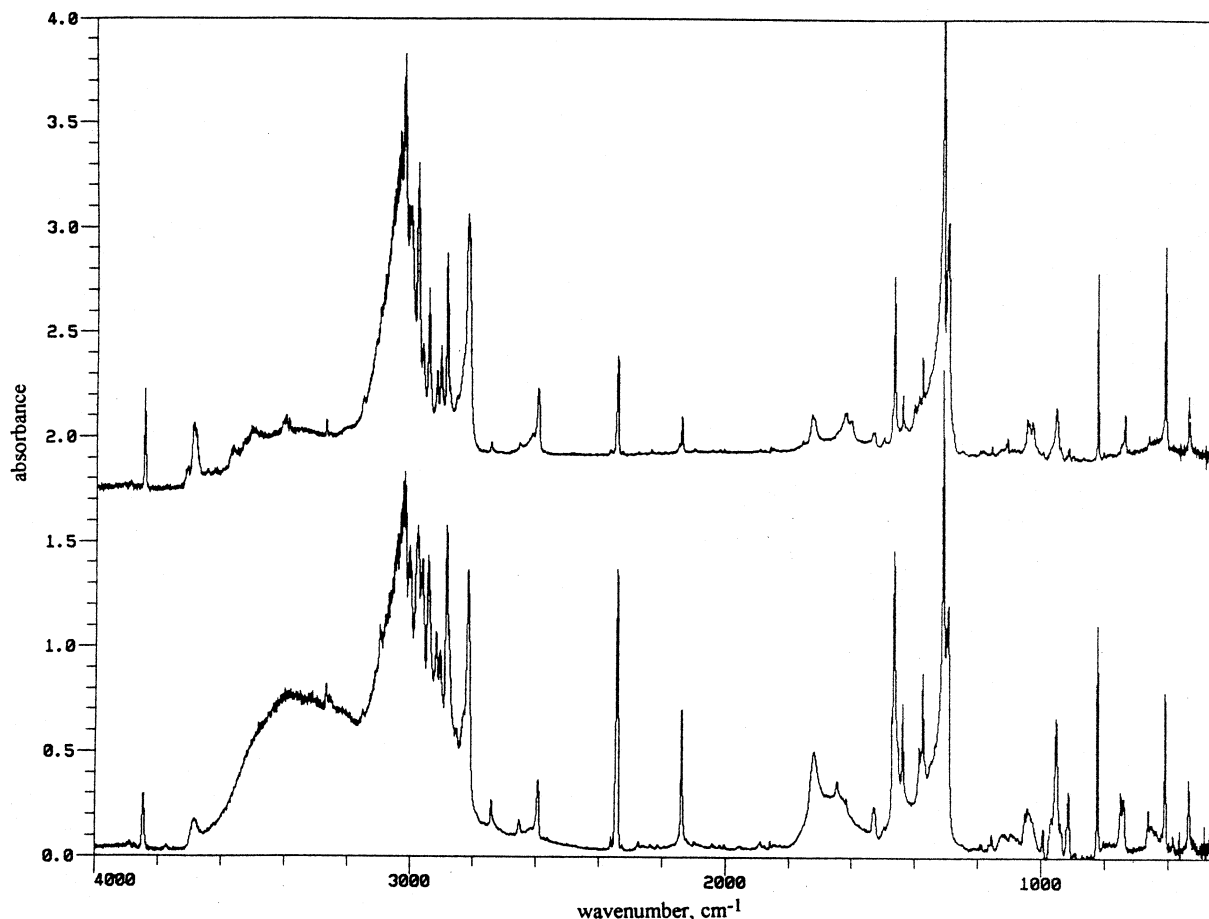


Fig. 2. FTIR spectrum of solid residues in the range of O-H and C-H stretching modes after annealing a 9 MeV α -particle irradiated CH₄/O₂ sample to 293 K.

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